Control and investigation of metal-insulator transitions in novel oxides by light and electric field

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2015

Lourembam, J. (2015). Control and investigation of metal-insulator transitions in novel oxides by light and electric field. Doctoral thesis, Nanyang Technological University, Singapore.

<https://hdl.handle.net/10356/65670>

<https://doi.org/10.32657/10356/65670>

**NANYANG
TECHNOLOGICAL
UNIVERSITY**

**CONTROL AND INVESTIGATION OF
METAL-INSULATOR TRANSITIONS IN NOVEL OXIDES
BY LIGHT AND ELECTRIC FIELD**

**JAMES LOUREMBAM
SCHOOL OF PHYSICAL AND MATHEMATICAL SCIENCES
2015**

**CONTROL AND INVESTIGATION OF
METAL-INSULATOR TRANSITIONS IN NOVEL OXIDES
BY LIGHT AND ELECTRIC FIELD**

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School of Physical and Mathematical Sciences

A thesis submitted to the Nanyang Technological University
in fulfillment of the requirement for the degree of
Doctor of Philosophy

2015

Acknowledgements

The successful completion of this PhD thesis has been possible through important contributions from mentors, friends, and family members that have nurtured me scientifically and supported my research ambitions.

First and foremost, I must thank my PhD supervisors Asst. Prof. Elbert Chia, and Assoc. Prof. Tom Wu who provided me an opportunity to explore the wonderful world of condensed matter physics and material science. Their high standards of research excellence starting from the initial process of when a project is conceived to the final product in the form of a publication, have been a great source of education, and I hope to carry this experience and the skills throughout the rest of my career. During the tough process of carrying out challenging research, they have shown tremendous patience and support. Prof. Tom Wu guided me during the difficult process of starting a PhD in Physics, and without the skills in the dark arts of film fabrication, that I learn under his supervision, there wouldn't be many experiments. I owe an immense debt of gratitude to Prof. Chia who welcomed me in his group after Prof. Wu moved to the King Abdullah University of Science and Technology (KAUST), allowing me to continue chasing exciting research themes in condensed matter. Without Prof. Chia's gesture of acceptance and unfailing support, this thesis would not be complete.

I am thankful to Prof. T.Venkatesan, who provided the vanadium dioxide thin films, as well as his scientific insights from his vast experience in oxide materials and the countless brainstorming sessions regarding the project directions. A major portion of this thesis came from the results of this collaboration. I would also like to thank Dr. Jianchun

Wu for his help in contributing to the electric field simulations.

I must mention the good people that taught me so many of my research skills and including how to diagnose and troubleshoot research problems. Dr. Chan La-o-vorakiat was a tremendous help teaching me terahertz spectroscopy and taking time to help whenever I had difficulties with the optical alignment. Dr. Ding Junfeng and Dr. Lin Weinan played no less critical roles in training me in thin film fabrication and electrical characterization techniques. I am also grateful to have fellow co-workers with whom I had wonderful research discussions with. The list includes Dr. Amar Srivastava, Dr. Helene Rotella, Tarapada Sarkar, Dr. He Mi, Dr. Ashok Bera, Cheng Liang, Dr. Peng Hayang, Shen Youde, Xia Huanxin, Dr. Hu Weijin, Sourav Mitra, Dr. Adrian Corentin David, Dr. Tian Yufeng, Zhao Daming. I wish them all a successful future ahead.

Many people at NTU played smaller but no less critical roles in helping me. Assoc. Prof. PHAN Anh Tuấn, head of the PAP division, who has been very generous to me in giving me tremendous moral and financial support after Prof. Wu's departure from NTU. I would also like to thank all my friends at NTU that have brought me tremendous joy, and have made my life outside the lab unforgettable.

Most importantly, special thanks to my family; my father, who as a great teacher in physics nurtured my intellect, my mother, who always supported my career, and my younger sisters Jasmine and Julia. They have been a great source of joy and support, and I will love them always. I would have never made it without their help.

Abstract

Systems with strong interactions such as complex oxides show many emergent properties that are, still to this day, not fully understood. Of particular interest is the metal-insulator transition in complex oxides which arises from the competition between the tendencies of carrier localization and delocalization. To understand and ultimately control metal-insulator transitions in complex oxides, we need to explore the rules governing the interactions in charge, spin and lattice in these systems. To this end, the use of novel techniques in material fabrication, spectroscopy and lithography are invaluable for investigating the metal-insulator transition (MIT). Studies of electronic phases with advanced characterization techniques have revealed new insights into the correlated properties of these oxides. The focus of this dissertation is on understanding and tuning electronic phase transitions in complex oxide thin films and can be broadly divided into two parts.

The first part of this thesis highlights the use of electrostatic modulation using electrolyte gating as a method to tune the electronic functionalities in a strongly phase-separated manganite $\text{Pr}_{0.65}(\text{Ca}_{0.75}\text{Sr}_{0.25})_{0.35}\text{MnO}_3$ and potentially control the emergence of colossal magneto-resistance. The device configuration of this powerful technique, known as the electric double layer technique, provides clean, quasi-continuous and high-density charge accumulation $\sim 10^{15} \text{ cm}^{-2}$ of carrier modulation in the manganite channel. A diverse behavior of transport modulation was observed and the modulation was remarkably enhanced by the application of a magnetic field. The experiments are also supported by the small polaron model, effective medium model and finite element simulation of inhomogeneous local electric field. The first part of the dissertation also

discusses high quality thin film synthesis of manganites using Pulse Laser Deposition. $\text{Pr}_{0.65}(\text{Ca}_{0.75}\text{Sr}_{0.25})_{0.35}\text{MnO}_3$ manganite thin films under biaxial strain displayed presence of magnetic glassy state at low temperatures is accompanied by reemergence of insulating behavior. We discovered that the transport modulation in the channel increased multiple folds in the magnetic glassy state.

The second part of this dissertation probes optical responses in the thin films of vanadium dioxide polymorphs using the techniques of terahertz and time-resolved femtosecond spectroscopy. Vanadium dioxide (VO_2), just like manganites, is a prototypical MIT system. Although, VO_2 exhibits a number of polymorphic forms, a major portion of research on this material has been devoted towards $\text{VO}_2(M1)$ polymorph because of its speedy and abrupt MIT (5–10 K) just above room temperature. $\text{VO}_2(B)$ polymorph, on the other hand, undergoes a broad MIT as wide as 150 K and remained mostly unexplored due to challenges in thin film fabrication. We studied for the first time optical conductivities of $\text{VO}_2(B)$ and construct the electronic phase diagram by indicating the critical temperatures deciding the width and the onset of the MIT in $\text{VO}_2(B)$. We also demonstrate ultrafast optical switching to a metallic state in this system using optical pump-probe technique. Compared to $\text{VO}_2(M1)$ the threshold value of laser fluence is about four times lower, and showed strong temperature dependence. The phase diagram of photoinduced transition in $\text{VO}_2(B)$, remarkably consists of two regions of photoinduced metallicity— one induced by weak pump excitation, and another by strong pump excitation.

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List of Acronymns

AFM: Atomic Force Microscopy

AT: Almeida-Thouless

COI: Charge ordered Insulator

EDLT: Electric Double Layer Transistor

ER: Electroresistance

FC: Field-cooled

FET: Field effect transistor

FFT: Fast Fourier Transform

FMM: Ferromagnetic Metallic

fs: femtoseconds

GEM: General Effective Medium

IL: Ionic Liquid

MIT: Metal-Insulator Transition

MR: Magnetoresistance

OPOP: Optical pump optical probe

PLD: Pulse Laser Deposition

PPMS: Physical Property Measurement System

ps: picoseconds

PS: Phase separation

PT: Phase Transition

RHEED: Reflection High Energy Electron Diffraction

RSM: Reciprocal Space Mapping

SQUID: Superconducting quantum interference device

THz-TDS: Terahertz Time Domain Spectroscopy

UHV: Ultra High Vacuum

XRD: X-ray Diffraction

ZFC: Zero-field-cooled

DEME-TFSI: N,N-diethyl-N-methyl-N-(2-methoxyethyl)ammonium

bis(trifluoromethylsulphonyl)imide

LSAT: $(\text{LaAlO}_3)_{0.3}-(\text{Sr}_2\text{AlTaO}_6)_{0.7}$ (LSAT)

PCSMO: $\text{Pr}_{0.65}(\text{Ca}_{0.75}\text{Sr}_{0.25})_{0.35}\text{MnO}_3$

SiSTO: SrTiO_3 buffer layer on Si

SLAO: SrLaAlO_4

STO: SrTiO_3

List of Publications

1. **J. Lourembam**, A. Srivastava, C. La-o-vorakiat, C. Liang, T. Venkatesan, E. E. M. Chia (2015), "Evidence for Light-Induced Insulator-to-Metal transition in *B*-phase vanadium dioxide" (Under review)
2. J. Ding, **J. Lourembam**, W. Lin, and T. Wu (2015), "Bound magnetic polaron hopping induced giant magnetoresistance in $\text{LaTiO}_3/\text{EuTiO}_3$ superlattices" (In preparation)
3. A. Bera, W. Lin, Y. Yao, J. Ding, **J. Lourembam**, T. Wu (2015), "ZnO/LAO- STO Heterojunctions: Hybrid 1D-2D Diodes with Engineered Insulator-Metal Transition and Interband Tunneling" (Submitted to Small)
4. **J. Lourembam**, A. Srivastava, C. La-o-vorakiat, H. Rotella, T. Venkatesan, E. E. M. Chia (2015), "New Insights into the Diverse Electronic Phases of a Novel Vanadium Dioxide Polymorph: A Terahertz Spectroscopy Study" Sci. Rep. 5, 9182
5. **J. Lourembam**, J. Ding, A. Bera, W. Lin and T. Wu (2014), "Asymmetric electroresistance of cluster glass phase in manganites" Appl. Phys. Lett. 104, 133508
6. **J. Lourembam**, J. Wu, J. Ding, W. Lin, and T. Wu (2014), "Electric field tuning of phase separation in manganite thin films" Phys. Rev. B 89, 014425
7. W. Lin, J. Ding, S. Wu, Y. Li, **J. Lourembam**, S. Shannigrahi, S. Wang, T. Wu (2013), "Electrostatic Modulation of $\text{LaAlO}_3/\text{SrTiO}_3$ Interface Transport in an Electric Double-Layer Transistor" Adv. Mater. Inter. 1, 1300001

8. A. Bera, H. Peng, **J. Lourembam**, Y. Shen, X. Sun, and T. Wu (2013), "A Light Switchable Nanorod Memory: Wurtzite ZnO on Perovskite SrTiO₃" *Adv. Funct. Mater.* 23, 4977
9. L. Mandal, W. Lin, **J. Lourembam**, S. Ogale, and T. Wu (2013), "Electric Field Effects in Functional Metal Oxides" *Functional Metal Oxides: New Science and Novel Applications* (Editor: S. Ogale, Wiley Publications) [Book chapter]

Conferences

1. "Drude conductivity of novel VO₂(B) films as observed by time domain terahertz spectroscopy" **J. Lourembam**, A. Srivastava, C. La-O-Vorakiat, T. Venkatesan and E.E.M. Chia: The OCPA8 International Conference on Physics Education and Frontier Physics, Singapore, June 23–27, 2014. [*OCPA-APS Outstanding Conference Poster Awards: 2nd place in Photonics and Photovoltaics*]
2. "Metal-insulator phase transition in a novel VO₂(B) polymorph observed with terahertz spectroscopy" **J. Lourembam**, A. Srivastava, C. La-O-Vorakiat, H. Rotella, T. Venkatesan and E.E.M. Chia: IPS Meeting 2015, Singapore, March 4–6, 2015
3. "New Insights into the Diverse Electronic Phases of a Novel Vanadium Dioxide Polymorph: A Terahertz Spectroscopy Study" **J. Lourembam**, A. Srivastava, C. La-o-vorakiat, H. Rotella, T. Venkatesan, E. E. M. Chia: APS March Meeting, San Antonio Texas, USA, March 1–6, 2015 [*APS Ovshinsky Travel Award*]
4. "Ultrafast Photoinduced Melting of Insulating State in B-Phase Vanadium Dioxide" **J. Lourembam**, A. Srivastava, C. La-o-vorakiat, C. Liang, T. Venkatesan, E. E. M. Chia: ICMAT 2015 & IUMRS-ICA 2015, Singapore, June 28–July 3, 2015.

5. “Ultrafast Photoinduced Melting of Insulating State in *B*-Phase Vanadium Dioxide”
J. Lourembam, A. Srivastava, C. La-o-vorakiat, C. Liang, T. Venkatesan, E. E. M. Chia: IUMRS-ICAM 2015, Jeju, Korea, October 25–October 29, 2015.

“I was taught that the way of progress was neither swift nor easy.”

-Marie Curie

Introduction and Scope

Motivation

Outline of the thesis

Motivation

Complexity in physical sciences describes phenomena where unexpected properties emerge from strongly interacting collection of constituent parts. While complexity provides opportunities to explore novel and interesting phenomena, they are fundamentally poorly understood. ‘Complexity in material systems’ is one of the recurring themes in the roadmap for grand scientific challenges. Complex oxides are one of the most sought-after classes of materials in condensed matter physics because of their richness in displaying multifaceted electronic properties.^[1] These correlated electronic phases in complex oxides are very sensitive to changes in temperature, carrier doping (chemical and electrostatic) or presence of magnetic field, pressure or light, leading to a host of intricate electronic phase diagrams ranging from superconducting to metallic to insulating phases.^[2, 3] As it turns out, not only the electronic properties but they exhibit a wide range of behaviors that no other class of materials do. For example, their magnetic properties range from ferromagnetic to antiferromagnetic to paramagnetic, the bandgaps span the visible and UV spectrum, dielectric properties ranging from low-k to high-k values, and structure properties display polymorphs ranging from monoclinic to tetragonal with the same chemical stoichiometry.^[4] As such, complex oxides have a proven track record of being reliable bedrock for pursuing fundamental science research. Followed by decades of profound discoveries and emergence of new fabrication and

characterization techniques practical applications, they have emerged to become one of the most sought after materials for current and future technologies.^[5-7]

Key Research Areas

Amongst the vast exotic properties of complex oxides, the metal-insulator transition (MIT) phenomenon is perhaps the most likely candidate for new routes of creating next-generation devices. The primary objective of this thesis is to offer new insights into the physics and possibilities of MIT in complex oxides by revisiting these materials with new characterization techniques using light and electrical probes. This thesis aims to— i) identify key research directions in the physics of metal-insulator transition, ii) provide the necessary guidelines in material selection and techniques for exploring its mechanisms, iii) offer new insights into some of the open questions on the current understanding, and iv) propose ideas of novel devices and future issues based on the experimental and theoretical achievements of this thesis. Some of the unexplored ideas and subjects of contention addressed in this thesis are as follows.

i. Comparison between MIT assisted by structural transition and that without

Metal-insulator transitions in complex oxides are driven by correlation effects which may be electron-electron or electron-phonon interaction in nature. If both phenomena are present, it is extremely hard to disentangle the effects and this has been one of the ongoing core debates that have not been resolved yet. In cases where the electron-phonon interaction is present, MIT is accompanied by a structural phase transition. One of the approaches of understanding the phenomena deeper is to study and compare two very similar systems that show MIT but one is associated with a structural transition while the other is not. We attempt to further this discussion in chapters 5 and 6.

ii. Comparison between the MIT triggered by different mechanisms

The bulk share of the research in MIT has come from temperature-driven MIT. Even with the recent growing interest in understanding and exploring different mechanisms that can trigger MIT, there have been little efforts to distinguish the metallic state induced by different mechanisms. The general assumption is there is no difference in the metallic state regardless of the triggering mechanism. We will show in chapter 6 that the photo-induced metallic state is quite different from temperature driven one.

iii. Multi-tuning vs. single parameter tuning

One of the fresh approaches of studying MIT is to design an experiment under two different external stimuli concurrently. In correlated physics, there are innumerable cases where ‘the sum of the parts is not equal to the whole’. Experiments under multi-tuning may give unexpected responses that cannot be accounted simply by the sum of the responses under single parameter tuning. Multi-tuning approach is properly motivated by this idea that a different physics may be revealed. In this thesis, the multi-tuning approaches of — a) electric field and magnetic field, and b) electric field and strain are adopted.

iv. Bulk transition vs. thin film transition

Thin film oxides may have dimensions ranging from microstructural to unit cell level. While films with large thickness are relaxed from strain, incommensurate, and approach properties of the bulk, ultra-thin films may have large differences with the bulk properties. In fact, one can have MIT in the bulk and a purely insulating phase in the film. Within this discussion, lies the existence of re-emergent insulating phase that appears after the system has transitioned to a metallic state. This little known area is explored in chapter 4. Advancements in fabrication techniques have also made it possible for fabricate novel oxides in thin film forms. Chapters 5 and 6 investigates the physical properties of one

such novel oxide that was earlier difficult to study in thin film form because of its metastable nature.

v. Electrostatic doping at the strongly phase-separated state

Electrostatic doping is becoming a first-choice technique of tuning MIT in oxide films. Most of the MIT systems, however, do not demonstrate phase separation. This thesis covers a comprehensive study on the role of electrostatic doping in modulating phase separation. With this approach, a different perspective was obtained regarding the science of evolution and seeding of phase fractions.

vi. Extreme doping without damage

Finally, a pivotal driving point for this work is what happens to these oxides at extreme doping. Before tackling that question, it is important to find out the techniques that can introduce a large amount of doping without inducing a permanent chemical change in the system. Obviously, chemical doping is out of the question as it already introduces disorder even at small doping concentrations. Electrostatic doping and photo-doping can both offer capabilities of high levels of doping without pushing the system to breaking point. The next big discovery in complex oxides may very well come from the physics at the extreme.

Outline of the thesis

The thesis begins with a background on the oxide materials and the conceptual framework of metal-insulator transition. Two important classes of oxides vis-a-vis manganites and vanadates are taken up for this study and a brief background is discussed in the first chapter. Also included in this chapter are some of the relevant concepts in transport and optical response.

The experimental techniques are discussed in detail in chapter 2 starting from the

fabrication of high quality thin film oxides to electrostatic doping experiments using the electric double layer transistor and branching off towards current optical techniques using terahertz spectroscopy and optical pump-probe experiments. The chapter also covers the basic principle and experimental set-up of these core experiments as well as the benefits and the advances of such techniques.

In chapter 3, investigations on electric field effect on a phase separated manganite $\text{Pr}_{0.65}(\text{Ca}_{0.75}\text{Sr}_{0.25})_{0.35}\text{MnO}_3$, prepared by pulse laser deposition, are discussed. Temperature-dependent non-linear electrostatic modulation on this manganite covers the first portion of this chapter. The second portion illustrates the complementary nature of electric and magnetic field effects in PCSMO and consequence of these findings.

In chapter 4, adequate substrate strain was applied on epitaxially grown PCSMO to engineer a re-entrant insulating phase at low temperatures. Subsequently, such a system was chosen for electrostatic experiments using electrolyte gating and compared with other PCSMO films that did not show this re-entrant phase.

In chapter 5, terahertz conductivity studies on vanadium oxide polymorphs, also grown by pulse laser deposition, are discussed. The analysis of optical spectra was done by fitting various models and the rich electronic phase diagram in vanadium oxide was established.

In chapter 6, ultrafast transient spectroscopy studies on a novel vanadium dioxide polymorph are presented. Besides the relaxation dynamics, the scenario of ultrafast photo-induced phase transition in this system is also described in details.

My thesis closes with a brief epilogue where the summary of the results are discussed in a broad outlook. Furthermore, perspectives towards future challenges and opportunities in complex oxides are given.

Chapter 1 : Materials and Theoretical Background

- 1.1 Materials: Manganites
- 1.2 Materials: Vanadium dioxide
- 1.3 Metal insulator transition in complex oxides
- 1.4 Electrical technique: Electrostatic Carrier Doping
- 1.5 Optical technique: AC conductivity models
- 1.6 Optical technique: Light induced carrier dynamics

1.1 Materials: Manganites

Manganites are complex oxides widely popular amongst condensed matter physicists because of their exotic electronic and magnetic properties.^[1, 8-10] Although the seminal work on manganites was produced by Jonker and van Santen in 1950, most of the ground breaking work on this field came after the discovery of a large magnetoresistance (popularly known as colossal magnetoresistance) in hole-doped manganites in the 1990's.^[8] Hole-doped manganites adopt a chemical formula of the form $R_{1-x}A_xMnO_3$ where R is a rare-earth ion (such as La, Nd, and Pr) and A is an alkaline earth ion (such as Ca, Sr, Be). Manganites typically assume a cubic perovskite structure with each Mn ion resting at the corner of the unit cell, and the oxygen atoms occupy the face-center forming an O_6 octehedra, with the rare-earth/ alkaline ions at the center of the unit cell.^[8]

In such a cubic lattice environment, the degeneracy of 3d-orbitals of an isolated Mn atom split into a lower energy state called ' t_{2g} ' (comprising of d_{xy} , d_{yz} , and d_{zx} levels) and a higher energy state referred to as ' e_g ' (comprising of $d_{x^2-y^2}$ and $d_{3z^2-r^2}$ levels).^[8] Jahn-Teller distortion further reduces the degeneracy in these two states. The degree of divalent alkaline ion doping determines ratio of Mn^{3+} and Mn^{4+} ions.^[8] There is strong

Hund coupling in these systems which favor the spin alignment of electrons. As such in the undoped parent manganite compound RMnO_3 three electrons populate the t_{2g} state and one occupies the e_g orbital, while upon doping some of the Mn ions acquire completely empty e_g orbital. The t_{2g} electrons are generally localized, whereas the e_g electrons are itinerant and hopping through O_p orbitals.^[11] The arrangement and the interplay of Mn^{3+} and Mn^{4+} ions are crucial in understanding many of the electronic properties of manganites.

Figure 1.1: a) Double exchange mechanism in manganites. Electron transfer from Mn^{3+} to Mn^{4+} is mediated by an O^{2-} anion where the transferred electron can replace an electron with identical spin in the O^{2-} anion. In accordance with Hund's principle, the spins of the unpaired electron in the ground state will align parallel to the transferred electron giving rise to ferromagnetism. b) Phase separation scenario of sub-micrometer sized ferromagnetic and antiferromagnetic phases in manganites. [Taken from Dagotto, Science 309, 257 (2005)]

The hopping of e_g electrons can explain for the emergence of ferromagnetic state in manganites as it is energetically favorable for the spins involved to be aligned and this concept was proposed by Zener in 1951.^[12] This mechanism widely known as the double exchange however, cannot justify many of the other exotic phases that develop with subtle changes in temperature such as antiferromagnetic insulating state, charge ordered

insulating state orbital ordering etc.^[13] A schematic picture of the double exchange phenomena is given in fig. 1.1 (a). A comprehensive picture encapsulating the double exchange was required in order to refine the physics of manganites.

The unusual property of competing ground states in manganites is now widely accepted as due to intrinsic phase separation (PS).^[8, 14-16] The groundwork for understanding PS in manganites has been laid by the vast amount of experimental and theoretical works. Several computational works showed that the ground state of manganites can be an inhomogeneous phase separated into two regions with different charge densities, n .^[15] In particular, Yonoki *et al.* used Monte Carlo technique to calculate the density of e_g electrons as a function of the chemical potential μ , very surprisingly some values of carrier densities could not be stabilized, and in fact n was found to be a discontinuous function of μ .^[15, 17] A large volume of experimental work on manganites also confirm the existence of phase separation scenario by identifying intrinsic inhomogeneities risen largely due to the competition between ferromagnetism metallic phase and antiferromagnetic insulating phases although several other phases may also emerge. A magnetic phase separation scenario for manganites is given in fig. 1.1 (b). Some of the excellent experimental works confirming the phase separated state in manganites include Lorentz microscopy, electron Hologram microscopy, scanning tunneling microscopy, neutron scattering, magnetic force microscopy etc.^[18-23]

1.2 Materials: Vanadium dioxide

Vanadium dioxide forms an important class of oxides and there have been extensive theoretical and experimental investigations on VO_2 over half a century ever since Morin reported metal to insulator transition at a critical temperature of 68°C in 1959.^[24] With the discovery of polymorphism in vanadium dioxide, the research has expanded from the well-known polymorphic form $\text{VO}_2(M1)$ to various other metastable forms which

includes $\text{VO}_2(R)$, $\text{VO}_2(A)$, $\text{VO}_2(B)$ and $\text{VO}_2(C)$.^[25] The structural diagram of $\text{VO}_2(A)$ and $\text{VO}_2(B)$ polymorphs is given in fig. 1.2 (c) and (d) respectively. There has been considerable interest in these polymorphic structures both for basic science research and technological applications.

The most popular polymorph of vanadium dioxides, $\text{VO}_2(M1)$ is a strongly correlated oxide that undergoes first order metal to insulator transition which is accompanied by a structural transition from a low temperature monoclinic phase to a high temperature rutile phase.^[26] The physics behind this transition has been a subject of intense debate of whether the structural changes are the sole origin or whether electron correlations also play a role.^[26, 27] The structural phase transition supports the Peierls instability picture where substantial changes in the electronic band structure are associated with the transformation of the tetragonal space group ($P42/mnm$) to monoclinic space group ($P21/c$). This structural phase transition picture is given in fig. 1.2 (a) and (b). The transition to a lower symmetric phase is due to the dimerization of vanadium atoms that twist in V-V cation pairs along the tetragonal c axis along with cell size doubling.^[28] In $\text{VO}_2(M1)$, the crystal field splits the degenerate d orbitals of vanadium into lower lying single electron occupancy t_{2g} levels and empty e_g levels. The t_{2g} bands are further split into a $d_{||}$ (a_{1g}) state and a π^* (e_g^π) doublet. The consequence of V-V dimerization is that the $d_{||}$ state once more splits into lower $d_{||}$ state and the upper $d_{||}$ state leading to opening of a Peierls like energy gap of about 0.7 eV in monoclinic phase.^[28] On the other hand, electron-electron correlations can also account for the metal-insulator transition and was considered to describe MIT in $\text{VO}_2(M1)$ by Mott in 1968.^[29] Even though more elaborate and extensive theoretical and experimental approaches have been attempted, the origin for MIT in $\text{VO}_2(M1)$ is still not resolved. Some recent studies also suggest that the nature of this transition could be understood by considering the contribution of both

electron-electron correlations and dimerization of V ions and have renamed the insulating phase as a Peierls-Mott insulator.^[30]

Figure 1.2: Phase transition at 340 K in VO₂(M1) polymorph from a) monoclinic insulating phase to b) rutile metallic phase. The monoclinic crystal structure is associated with V-V dimerization which resulted in band gap opening of ~0.7 eV at the Fermi level. [Taken from Cocker *et al.* Phys. Rev. B 85, 155120 (2012)]. Crystal structures of various vanadium dioxide polymorphs— c) tetragonal VO₂(A) and d) monoclinic VO₂(B). [Taken from Srivastava *et al.* Appl. Phys. Lett. Mater. 3, 026101 (2015)].

1.3 Metal-Insulator transition in complex oxides

The electronic structure of most solids can be explained from the interpretation of two limits— a wave-like itinerant electrons and a particle-like localized electrons. The first limit is applicable when electron orbitals overlap between electron orbitals and most properties of the solids are described by this band theory but when the electron orbitals are far apart the second limit is relevant and can be accounted by localized atomic wave-functions. However, due to the strong correlations of d and f electrons from the transition metal ions, complex oxides are much harder to describe by these limits.

One of the remarkable consequences of strong correlation in complex oxides is that the phenomena of metal-insulator transitions is pervasive in these systems, and has been a focal point of research in this system.^[29, 31] The long list of complex oxides encompasses VO_2 , V_2O_3 , VO , SmNiO_3 , NdNiO_3 , PrNiO_3 , LaCoO_3 , Ti_2O_3 , Ti_3O_5 , Fe_3O_4 , SrTiO_3 , LaTiO_3 , NbO_2 , iridates, manganites and so on.^[2] Fig 1.3 shows some of the complex oxides that show metal-insulator transition along with their transition temperatures. Several experimental and theoretical studies have been done over the past several decades to understand this spectacular phenomenon and it is widely considered that in these systems there is close relevance of the physical origin of MIT with the strong correlations found in these systems. However, the debate over the mechanisms of MIT in many of these systems hasn't concluded yet. Furthermore, MIT transitions are generally studied as an event driven by temperature and yet in these systems, the phase transitions are extremely sensitive to external stimuli of doping, slight, strain, electric and magnetic fields.^[2, 3, 9, 32-34]

Figure 1.3: a) Select metal oxides that display metal-insulator transition with their transition temperatures, T_{MIT} . [Taken from Yang *et al.* Ann. Rev. Mater. Res. 41, 337, (2011)]

The theory of metal insulator transitions emerged from the pioneering work by N.F. Mott based on a model of electron-electron correlations.^[29] He suggested that this correlation can explain the insulating phase and later came to be termed as the Mott insulator. According to Mott's model, without electron-electron interactions for a single electronic orbital lattice system, there would a singular band formed by the overlapping of individual atomic orbitals. However, when two electrons of opposite spin sit on the same site, a significant Coulomb repulsion comes into play, which according to this model would split the band into in two sub bands resulting in the formation of the insulating state. A simplified theoretical understanding was first achieved by considering the Hubbard model which developed into the Mott-Hubbard model and at the heart of the argument is that there is competition between the kinetic energy and the Coulomb potential energy.^[31, 35] This competition between the tendencies to localize and delocalize drives the metal-insulator transition. While the Mott-Hubbard model can account for the gradual transition, certain features like effective mass enhancement, first order MIT was

not understood. One of the first attempts to understand first-order MIT was done by Brinkmann and Rice (1970) who reexamined the Hubbard approximation was and treated with the Gutzwiller approximation.^[36] Examples of materials exhibiting Mott-Hubbard MIT include transition metal oxides, glasses, amorphous semiconductors etc.^[37]

Another approach to account for MIT phenomena is through the Peierls mechanism without the presence of electron-electron interactions. The Peierls transition is an example of thermodynamic phase transition associated with a change in the crystal structure.^[38] The structural transition results in a drastic change in the lattice periodic potential, and because of strong electron-phonon interactions electron transport also undergo a radical change. The crystal symmetry of the original lattice is lowered in a Peierls insulator. Amongst the several examples of Peierls insulator are NbSe_3 , $(\text{TaSe}_4)_2\text{I}$, $\text{K}_{0.3}\text{MoO}_3$ etc.^[39]

Besides electron-electron correlations and structural transitions, MIT can also be triggered by disorder, which brings us to the Anderson model for the origin of MIT.^[40] The formation of insulators is explained by the phenomena of Anderson localization which is the trapping of electrons at random disorder sites like lattice defects in a sufficiently disordered medium. However, much of Anderson localization driven MIT is restricted to theoretical studies and very little experimental support is available.^[41]

1.4 Electrical technique: Electrostatic Carrier Doping

Modulation of carrier doping in materials is achieved by two approaches— chemical doping and electrostatic doping. Traditionally, carrier doping is introduced into a parent material by chemical doping, where one element in the compound is partially substituted by another element with a different valence electron configuration. Chemical doping is a widely popular method to modulate the carrier concentration in semiconductors.

But unlike chemical doping, electrostatic doping introduces minimum disorder, is reversible, can be continuously tuned, and allows experiments on a single sample getting

rid of sample fabrication variations.^[42] Complex oxides are extremely sensitive to changes in carrier density where even a variation on the order of 0.1 electrons per unit cell can lead to dramatic responses, and as such electrostatic doping is a powerful tool to probe the physical nature of this system.^[31]

Figure 1.4: Illustration of diverse properties of select complex oxides as a function of sheet charge density, n_{2D} at ground state. Silicon is shown as a reference. [Taken from C. H. Ahn Nature 424, 1015 (2003)].

Electrostatic doping is conceptually realized in a field effect transistor (FET). In a FET device, an external electric field creates accumulation or depletion of charge carriers at the surface of the conducting channel between the source (S) and the drain (D). This is achieved by applying voltage across an insulating dielectric (also known as gate dielectric) stacked over the channel. The polarization, σ_P or the areal surface charge density (coulomb cm^{-2}) induced by a gate voltage V_G at the channel and the gate dielectric interface is given by^[43]

$$\sigma_P = \int_0^{V_G} \frac{\epsilon_0 \epsilon_r(V)}{t} dV \quad (1.1)$$

Equation 1.1 is valid on the condition that $V_G < E_b t$ where E_b is the electric breakdown field of the gate dielectric, t is its thickness and ϵ_r the relative dielectric constant.

Alternatively, one can also calculate the sheet charge density (n_s) at the channel interface from the conventional capacitance formula $Q = C_i V_G$ where Q is the accumulated charge and C_i is the capacitance of the device.

The depth of the accumulation or depletion layer in the channel is given by the electrostatic screening length which is generally described in terms of the Thomas–Fermi screening length for Metal–insulator–semiconductor field-effect transistors (MISFETs).^[43, 44] The electric field in the channel is attenuated over a distance that is proportional to the Thomas-Fermi wave vector which is given by^[45]

$$k_{TF} = \sqrt{4\pi e^2 g(\varepsilon_F)} \quad (1.2)$$

where $g(\varepsilon_F)$ is the density of states at the Fermi level of the material in the channel.

From fig. 1.4, we see that many of the exotic physical properties of complex oxides occur at sheet carrier densities of $\sim 10^{14} \text{ cm}^{-2}$ which translates to roughly $10^{19}–10^{22}$ carriers cm^{-3} . There are two approaches to achieve such large carrier modulation. First, the ultrathin channels can be used so that the entire channel thickness is modulated. Second, which is the more powerful method, is to choose a gate dielectric with very large electric breakdown limit which will allow application of larger gate voltage.^[46]

1.5 Optical technique: AC conductivity models

We first describe the frequency dependent conductivity model of a metallic system in the context of the classic Drude-Sommerfield model. This phenomenon describes the electromagnetic response of the diffusion motion of gas of electrons within the metal crystalline structure. The central assumption of this model is that the carriers are considered to be able to move about freely in the lattice, without any restoring force but relaxes subject to a damping force. The equation of motion for a free electron with displacement r , under the application of a time varying electric field $E_0 e^{-i\omega t}$ is given by

$$m \frac{\partial^2 r}{\partial t^2} + m\gamma \frac{\partial r}{\partial t} = -eE_0 e^{-i\omega t} \quad (1.3)$$

where m is the effective mass of the carrier and γ is the damping constant. The solution to this differential equation is given by

$$r = \frac{e E_0 e^{-i\omega t}}{m \omega^2 + i\gamma\omega} \quad (1.4)$$

The total dipole moment per unit volume or polarization density, P is given by

$$P = ner \quad (1.5)$$

where n is the density of free electrons in the system. But, from Maxwell equations,

$$P = \epsilon_0 \epsilon_r E - \epsilon_0 E \quad (1.6)$$

By combining the equations 1.3–1.6, we get the solution of the frequency-dependent dielectric function as

$$\epsilon(\omega) = 1 - \frac{\omega_p^2}{\omega^2 + i\gamma\omega} \quad (1.7)$$

where ω_p is the volume plasma frequency at which the density of the electron gas, n given by $\omega_p^2 = \frac{ne^2}{\epsilon_0 m^*}$. In this expression m^* is the effective mass of the carrier. The scattering rate, (γ) is closely related with the mobility of the carriers, (μ) through the relation $\gamma = e/(m^*\mu)$.

While the Drude model is concise and elegant, it only accounts for the free electrons in the metallic system, but not all electrons in a metal are free and the contribution from bound electrons should also be taken into account esp. in the frequencies close to the interband transitions.^[47] After considering the contribution from the bound electrons represented by $\epsilon_b(\omega)$, the complex dielectric in the Drude model becomes

$$\tilde{\epsilon}(\omega) = \epsilon_b(\omega) + 1 - \frac{\omega_p^2}{\omega^2 + i\gamma\omega} \quad (1.8)$$

When working at frequencies away from the interband resonance of the system

which is particularly valid for terahertz frequencies, the bound electron contribution $\varepsilon_b(\omega)$ is replaced by a constant offset denoted by ε_∞ .^[47] This offset takes into account all pertinent transition, including multiple interband transitions and represents their sum value.

One can also derive the complex conductivity formalism in the Drude model by considering the relationship between the complex dielectric and the complex conductivity which is given by $\tilde{\varepsilon} = \varepsilon_\infty + \frac{i\tilde{\sigma}}{\varepsilon_0\omega}$. The resulting frequency dependent complex optical conductivity is

$$\tilde{\sigma} = \frac{\varepsilon_0\omega_p^2}{\gamma - i\omega} - i\varepsilon_0\omega(\varepsilon_\infty - 1) \quad (1.9)$$

The Drude model is based on the conductivity from a free electron gas and has proven to be the first-choice in modelling for conductivity in most metals and semiconductors. Under this model, the real component of the conductivity is maximum at zero frequency (static) and that the imaginary component is positive reaching its maximum value at carrier scattering rate frequency. However, not all materials follow this conductivity response. In fact, departures from the Drude behaviour have been observed, such as the minimum value of $\sigma_1(\omega)$ at zero frequency and negative values of $\sigma_2(\omega)$. This particular case can be understood by incorporating carrier backscattering effects and phase inhomogeneities. N.V. Smith modified the Drude model by including these parameters to describe the scattering events.^[48] The Drude-Smith model is given by

$$\tilde{\sigma} = \frac{\varepsilon_0\omega_p^2}{\gamma - i\omega} \left[1 + \sum_{j=1}^{\infty} \frac{c_j \gamma}{\gamma - i\omega} \right] - i\varepsilon_0\omega(\varepsilon_\infty - 1) \quad (1.10)$$

where the parameter c_j denotes the fraction of the carrier's original velocity that survived after the j^{th} scattering event.^[48] In practical experimental fittings, the Drude-Smith model is successfully used by considering only the first scattering term (i.e.

$j=1$).^[49-52] A value of c_I equal to zero means no backscattering and ideal Drude conduction whereas $c_I = -1$ will give full backscattering of carriers. Values in the range $-1 \leq c_j < -0.5$ will give negative values of $\sigma_2(\omega)$.

1.6 Optical technique: Light induced carrier dynamics

Non-linear optics

In order to describe more precisely the interaction between light and matter, a detailed discussion on how the dipole moment per unit volume, or polarization $\tilde{P}(t)$ of a material system depends on the electric field $\tilde{E}(t)$ of an incoming light wave. The optical response of the material is often described by the relationship

$$\begin{aligned}\tilde{P}(t) &= \tilde{P}^{(1)}(t) + \tilde{P}^{(2)}(t) + \tilde{P}^{(3)}(t) + \dots \\ &= \varepsilon_0(\chi^{(1)}\tilde{E}^{(1)}(t) + \chi^{(2)}\tilde{E}^{(2)}(t) + \chi^{(3)}\tilde{E}^{(3)}(t) + \dots)\end{aligned}\quad (1.11)$$

where ε_0 is the permittivity of free space and the parameters $\chi^{(1)}$, $\chi^{(2)}$, $\chi^{(3)}$.. are the optical susceptibilities of first, second, third orders and so on.

In conventional optics or weak electric fields, the induced polarization depends linearly on the electric field magnitude in which case only the first term is considered and the other terms are neglected. However, short laser pulses have intense electric fields and in this scenario higher orders must be also considered and such processes are also known as non-linear optics.

Differential Reflectivity

In order to understand the physics of time-resolved differential reflectivity induced by the laser pump, let us first look into the well-known Fresnel reflection equation which describes the relationship between the electric field reflection coefficient r of the material (determined by the input polarization state) its complex refractive index ($\tilde{n}_2$) and the complex refractive index of the surrounding medium ($\tilde{n}_1$). The Fresnel formula is

$$r = \frac{\tilde{n}_2 - \tilde{n}_1}{\tilde{n}_1 + \tilde{n}_2} \quad (1.12)$$

The material reflection coefficient or reflectivity R is obtained by squaring the modulus of the electric field reflection coefficient i.e $R = |r|^2$. Also the complex refractive index of the material can be expressed as $\tilde{n}_2 = n_{2r} + in_{2i}$ where n_{2r} and n_{2i} are the real and imaginary parts. The new reflectivity becomes $R + \Delta R$ due to laser pump induced change in the refractive index of the sample which becomes $\tilde{n}_2 + \Delta\tilde{n}_2$. In most pump-probe experiments, the differential real refractive index is very small i. e. $|\Delta n_{2r}| \ll |n_{2r}|$. In this limit the differential reflectivity is given by

$$\frac{\Delta R}{R}(\hbar\omega_{probe}, t) \cong \frac{4\Delta n_{2r}(\hbar\omega_{probe}, t)}{n_{2r}^2(\hbar\omega_{probe}, t) - 1} \quad (1.13)$$

Typical timescales

In order to understand the underlying carrier dynamics in a system, the most important requirement is to probe the system with a technique that can resolve time scale shorter than the carrier dynamics. The various physical phenomena involving electronic and lattice motion in matter occur in sub picosecond to nanoseconds range, and as such the dynamics were very hard to study until the arrival of ultra-short laser technology. These lasers have extremely short temporal width (in femtoseconds) and are much faster

compared to the carrier dynamics. As a result, these laser pulses are capable of taking “snapshots” of electronic and atomic processes thereby building temporally resolved observations of these systems. In short, ultrafast spectroscopy has become an important tool to study carrier dynamics in many condensed matter systems. An overview of some of the important mechanisms in carrier dynamics and their relevant temporal regimes are discussed in the following paragraphs, however, the time scales are not rigid and may vary with the material under study.

Optical excitation or Non-thermal regime— the arrival and the subsequent absorption of high intensity femtosecond pump beams on the material sample creates a highly excited electron-hole non-equilibrium population. This process falls within 10-100 fs of the temporal regime assuming time = 0 as when the pump beam arrives on the sample.^[53, 54] Within this same timescale, an induced coherent electron polarization is also observed. In this regime, carrier distribution cannot be defined by a bath temperature.

Thermalized or hot-carrier regime— next, the highly excited electron-hole plasma dissipates energy through inelastic electron-electron scattering leading to carrier redistribution. This process is known as electron thermalization, and takes place in the timescale ranging from sub-picoseconds to a few picoseconds.^[53, 54] The electrons and the holes equilibrate and the carrier distribution can be defined by a bath temperature which may or may not be equal for electrons and holes.

Recombination or isothermal regime— even after the electron thermalization process, there is still thermal non-equilibrium between the carriers and the lattice. The equilibrium is reached in the temporal regime of picoseconds to microseconds by the processes of electron-phonon scattering where the electron loses its energy to the lattice bath and carrier trapping.^[53, 54] Both the carrier distribution and the lattice can be defined by the same temperature in this regime.

Carrier Relaxation Models

The various lifetimes present in a system can be accurately resolved given that the temporal resolution of the pump-probe spectroscopy set-up is significantly larger than the underlying electronic and atomic processes of the system. The transient reflectivity (transitivity) signal is traditionally modelled by based on exponential decay curve. For example for a system with two- decay characteristic times, say τ_1 and τ_2 the temporally resolved signal, $g(t)$ is given by

$$g(t) = u(t)(A \exp \frac{-t}{\tau_1} + B \exp \frac{-t}{\tau_2}) \quad (1.14)$$

where $u(t)=0$ for $t<0$ and $u(t)=1$ for $t>0$, A and B are amplitudes corresponding to the decay times. This double exponential decay time expression can model the thermalization and recombination carrier dynamics of a typical semiconductor material excited by a femtosecond pulse laser.^[55, 56] In this case, the faster lifetime component τ_1 represents the thermalization process which is in the range of one ps. On the other hand, the longer lifetime component may survive up to nanoseconds and describes the recombination process.

We have discussed how the different fundamental relaxation processes are disentangled by the generation of non-equilibrium carriers. To summarize this, we can take the example of different processes and their corresponding characteristic time in semiconductors as shown in Table 1.1. In this table, auger recombination is a process where the energy released by the recombination of two carriers is transferred to a third carrier which then undergoes thermalization. The other processes have already been discussed. We should point out that the characteristic time may be different for different materials.

<i>Fundamental process</i>	<i>Characteristic time(s)</i>
Carrier–carrier scattering	10^{-15} – 10^{-12}
Carrier–optical phonon thermalization	$\geq 10^{-12}$
Optical phonon–acoustic phonon interaction	$\sim 10^{-11}$
Carrier diffusion ($\sim 0.1 \mu\text{m}$)	$\sim 10^{-11}$
Auger recombination ($\sim$ carrier density 10^{20} cm^{-3})	$\sim 10^{-10}$
Radiative recombination	$\sim 10^{-9}$
Lattice heat diffusion($\sim 1 \mu\text{m}$)	$\sim 10^{-8}$

Table 1-1: Different relaxation process in photoexcited semiconductor. Compiled from Othonos, J. Appl. Phys, 83, 1789 (1998)

Chapter 2 : Experimental Concept, Techniques and Setup

2.1 Pulse Laser Deposition

2.2 Film characterization

2.2.1. X-Ray Diffraction

2.2.2 Atomic force Microscopy

2.2.3 Superconducting Quantum Interferometer Device

2.3 Electric Double Layer Transistor

2.4 Terahertz spectroscopy

2.5 Optical pump-probe experiments

2.5.1 The Laser System: Generation of ultra-short lasers and Amplification

2.5.2 The pump-probe configuration

This chapter discusses the main experimental techniques used in this dissertation and includes fabrication and characterization of structure, electrical transport, and optical properties of epitaxial complex oxide thin films. The experimental workflow of the thesis is given by Fig 2.1. The leftmost side covers experimental techniques for electrical probe, while the right side covers optical characterization techniques.

Figure 2.1: Experimental techniques workflow of the projects. The main techniques are shown in blue while the green colored ones are the complimentary techniques.

2.1 Pulsed Laser Deposition

Pulsed Laser Deposition is a popular approach for thin film growth of oxides, metals, organic substances and even topological insulators and two dimensional materials.^[57-59] Ever since the invention of high-powered laser light with pulses in the nanosecond regime in the 1970s, researchers have been experimenting with the pulsed laser for fabricating materials but the success of pulsed laser deposition (PLD) only arrived in the late 1980s with the successful growth of cuprate superconductors using this technique.^[57] Now, it is widely used particularly for fabricating oxides as it extremely versatile to be used for growing almost any oxide thin films and provides advantages over other growth techniques such as the thermal deposition.^[60, 61] Some of the leverages provided by this technique in oxide growth are— 1) atomic layer by layer growth deposition, 2) access to growth of metastable phases far-from-the-equilibrium growth conditions, 3)

stoichiometric transfer of target materials to the substrate, 4) film thickness can be monitored and calibrated with high accuracy, and 5) offers possibility of growing artificial heterostructures and superlattices by combining different target materials.^[62]

The schematic of a standard PLD is illustrated in Fig. 2.2 along with the main components. The essential physical processes of a PLD in step by step description is as follows— i) ablation of the target material by high energy laser radiation, ii) creation of energetic plasma which propagates towards the substrate in the form of a plume and finally, iii) re-condensation onto the substrate. The detailed narrative on these processes is given in the following paragraphs. The oxide PLD system in our laboratory uses KrF excimer laser with a wavelength 248 nm, pulse duration 20 ns (FWHM), and maximum pulse energy of 150 mJ, as the source of pulse laser. The intense pulsed- laser passes through an optical window of the ultra-high vacuum (UHV) chamber which can reach pressures as low as 10^{-8} torr. As many as 6 target materials can be loaded inside the UHV chamber at a time and can reach temperatures as high as 900°C. The system also comes with a differentially pumped reflection high-energy electron diffraction (RHEED) system which provides real time analysis of surface morphology and film thickness during the growth process. The RHEED houses an independent vacuum system and can be operated at oxygen pressure of 10 mTorr or lower.

Figure 2.2: Schematic diagram of a PLD-RHEED set-up which can load upto 3 targets at a time.

When the laser-pulses reach the target, there is strong light-material interaction and the adsorbed energy from the photons is immediately converted into electronic excitation and later to thermal, chemical, and mechanical energy.^[57] It has been already mentioned that one of the attractive features of PLD is that it allows stoichiometric transfer of target materials which is possible because the ablation process is not an equilibrium thermal evaporation process and hence there is no preferential ablation of any cationic species.^[57] The plasma is then formed near the surface of the target and expands forwards. The choice of laser wavelength, pulse duration and fluence is critical for this non-equilibrium material transfer.^[61]

2.2 Film characterization

2.2.1. X-Ray Diffraction

Electromagnetic radiation with photon energies between 100 eV to 100 keV are classified as X-rays. The De-Broglie wavelength of this energy range corresponds to 0.01 to 10 nm. The interatomic distances in crystals fall in the 0.15 –0. 4 nm range and when X-rays with wavelengths in that range falls on a periodic crystalline structure fraction, X-ray diffraction is observed. Making use of this diffraction effects, one can investigate the structural properties of a crystal using X-rays.

The crystallographic investigations of the thin films were performed on D8 Advance XRD, Bruker, Germany (powder diffractometer) first and then on SmartLab High Resolution XRD, Rigaku, Japan (thin film diffractometer) which utilizes Cu K α radiation. The structure qualities of the thin films were analysed using line θ - 2θ scan, rocking curves and reciprocal space mapping. With these analyses, we were able to determine the crystal structure, the crystallinity, the orientation, phase information and substrate strain and also detect the presence of any impurity phase.

θ - 2θ line scans employed in Bragg-Brentano geometry provided the hkl Miller indices where x-rays interfere and thus the crystal structure of the films. The out of plane lattice parameter of the films can also be calculated from this measurement. The lattice interplanar distance d_{hkl} , is related to the X-ray wavelength λ as

$$n\lambda = 2d_{hkl}\sin\theta \quad (2.1)$$

In a cubic system, $d_{hkl} = c/\sqrt{h^2 + k^2 + l^2}$, where c is the lattice parameter. For c-oriented (00 l) thin films, c becomes the out of plane lattice parameter.

However, in plane misfit strain cannot be determined from the θ - 2θ scan and only reciprocal space mapping (RSM) can provide quantitative information in this aspect. Rigaku's SmartLab Ge(220)x2 analyzer was used for high-resolution RSM images of the

films. RSM gives an X-ray scattering intensity distribution as a function of reciprocal area Q_x , Q_z compared to the θ - 2θ scan which gives intensity distribution along the Q_z line. The differences in the in-plane lattice parameter, a and the out-plane lattice parameter, c between the film and the substrate can be determined from the separation of the intensity peak positions along the Q_x , Q_z axes. The lattice mismatch between the film and the substrate in the in-plane (δ_a) and out-plane direction (δ_b) can be determined from the following relations

$$\delta_a = \frac{a_f - a_s}{a_s} \text{ and } \delta_c = \frac{c_f - a_s}{a_s} \quad (2.2)$$

where a_f , c_f are the lattice parameters of the film in-plane and out-plane and a_s is the lattice parameter of the pseudo-cubic substrate.

2.2.2 Atomic Force Microscope

Atomic force microscopy (AFM) is based on the principle of measuring the interaction force between the tip and the sample surface. This interatomic interaction is repulsive and extremely short-range in nature which is why this technique can image surface morphology with less than one nanometer roughness. AFM measurements were carried out in Dimension V, Veeco operated in tapping mode to determine the thickness and the surface quality of the oxide thin films. All measurements were done ex situ directly after film deposition to minimize surface contamination. The force constant of the tip used was 42 N/m. Dimension V also have the capabilities of advanced scanning modes to measure different physical interactions such as magnetic force, conductive atomic force etc.

2.2.3 Electrical transport

The basic transport characterizations of the films were done by measuring the resistance as a function of temperature with a two-point or four point geometry. For highly resistive

films, the two-point geometry was preferred, while for films with smaller resistivity, four-point Van-der-Pauw geometry was adopted. The electric field experiments were performed by adopting Hall-bar geometry. In this geometry, four side contacts are positioned on the side of the current path allowing detection of the Hall voltage. DC transport measurements of the films were performed inside a Physical Property Measurement System (PPMS, Quantum Design, USA). In general, temperature range of 2–400 K was used. Magnetoresistance resistance measurements were also done in the same setup by varying the magnetic field from 0 to 9 T.

2.2.4 Superconducting Quantum Interferometer Device

Superconducting quantum interference device (SQUID) is a highly sensitive magnetometer based on the principle of superconducting device known as the Josephson junction. It can measure changes in magnetic field approaching 10^{-18} tesla. The working principle is this— the sample moves in a vertical direction resulting in a change in magnetic flux. This results in an induced current from which the magnetization values are determined.

The magnetization measurements were performed by SQUID Quantum Design, MPMS XL. The measurements can be done in three modes— i) DC magnetization, ii) AC magnetization, and ii) Reciprocation Sample Option (RSO). With the RSO option, magnetization sensitivities in the order of 10^{-8} emu are possible.

2.3 Electric Double Layer Transistor

Electrostatic doping is achieved by selecting the material as the channel in a field-effect transistor configuration, which is at the heart of most electronic devices. A conventional field effect transistor has three main components— the source, the drain and the gate. The source and the drain are the two electrode terminals connected to the

channel. The carrier density in the channel is modulated by applying voltage across the gate electrode which is insulated by the channel by a thin layer of oxide known as the gate dielectric. A schematic side view of a field transistor is shown in Fig. 2.3(a). The choice of the gate dielectric is important to produce large carrier modulation.^[63] While SiO_2 is the most common gate dielectric, recently by replacing it with ionic electrolytes, scientists have been able to achieve unmatched levels of carrier doping concentrations, and in some cases, discovery of new exotic phases.^[64-74] These ionic electrolytes have cationic and anionic parts and when a positive gate voltage is applied the cationic parts travel towards the interface of the channel and the dielectric and vice versa for the negative gate voltage. This self-organization of ions leads to the formation of an electric double layer across the interface separated by less than one nm of thickness. Such field effect devices are appropriately labeled as electric double layer transistor. Fig. 2.3 (b) shows one such EDLT device. The Helmholtz electric double layer can be thought of as a capacitor composed two sheets of ions— one on the electrolyte and another on the channel surface.^[75, 76] EDLT can achieve unprecedented levels of charge modulation because the ionic liquids can sustain very high electric fields before breaking down.^[64, 77]

Figure 2.3: a) Side view of a FET transistor shown along with the electrical connections with the source, drain, and gate electrodes. In an EDLT device, the insulator which acts as a gate dielectric is chosen to be an ionic liquid. (b) Three-dimensional view of an EDLT

device where the gate is chosen to be one of the isolated electrodes.

The EDLT device is engineered by means of a systematic four step process— i) thin film deposition, ii) patterning the film, iii) electrode deposition, and iv) ionic liquid confinement. Figure 2.4 shows the EDLT device fabrication steps. After the film has been deposited, device patterns based on Hall bar geometry are developed using photolithography and wet etching. A positive photoresist (AZ 400) and gold etchant (KCl + HCl) were the chemicals used. The basic procedure of this process involves applying the photoresist, aligning the photomask, exposure to intense light, removal of the photoresist exposed to light by using developer, etching the exposed part of the film and then finally removing all photoresist by using acetone. Electrode deposition was made using the sputtering process after aligning the shadow mask with the patterned area under the microscope. A diamond knife with very fine tip was used to isolate the channel from the gate electrode. As a final step silicone gel was applied around the channel area to confine the ionic liquid and to avoid any unwanted connections. Care was taken so as to make sure that a reasonably large portion of the gate area was covered to obtain high modulation capability.

Figure 2.4: Step by step EDLT device fabrication process. The four primary steps are i) thin film fabrication, ii) patterning using photolithography and wet etching, iii) electrode thin films deposition on the electrodes, and iv) ionic liquid confinement on the channel.

2.4 Terahertz spectroscopy

The development of terahertz spectroscopy has been hailed as one of the greatest milestones of spectroscopy and has been made possible by the continued advancement of femtosecond lasers over the last two decades. Typically, the THz region of the electromagnetic spectrum corresponds to the frequency range from 0.1 THz to 10 THz which corresponds to the wavelength range of 3 mm and 30 μm ($1 \text{ THz} = 10^{12} \text{ Hz} = 33.3 \text{ cm}^{-1} = 4.1 \text{ meV}$). Terahertz time-domain spectroscopy (THz-TDS) has been applied to explore physical nature of materials and has been quite successful particularly in condensed matter systems.^[53, 78] The ability to detect both the amplitude and phase of the THz pulse is a crucial factor contributing to popularity of THz-TDS.^[79]

The general optical arrangement for a typical THz-TDS is described as follows. The output beam of an ultrafast laser is initially split into two arms. One arm is employed as a

THz pulse generating beam and emits cycles of coherent THz pulses which can interact with the sample and is further tightly refocused on a detector. The other arm is employed as a gating beam and is temporally coincident with the THz in the detection medium. Using a variable optical time delay system, the amplitude and phase properties of the THz electric field is directly resolved in the time domain.

There are two main approaches of generating and detecting THz radiation—photoconductive switching and optical rectification. We will discuss only the first approach which is relevant in this thesis. A more detailed description of THz detection and generation can be found in several reviews.^[78, 80] Photoconductive switching uses a photoconductive material, typically a semiconductor like GaAs whose conductivity is significantly different in dark and light conditions. The semiconductor is connected to the external circuit through electrodes. Figure 2.5 shows the schematic of how THz emission by photoconductive switching works. When the laser pump arrives at the semiconductor charge carriers are created in ultrashort time. The voltage applied across the electrodes forces the created carriers to accelerate in the direction of the electric field causing radiation of electromagnetic waves in the THz range. In order to emit THz radiation the charge carriers have to move at a rapid pace as described by the equation

$$E_{THz} = \frac{\partial J}{\partial t} \quad (2.3)$$

Although the THz radiation is given off in several directions, it is preferentially coupled out through a high-index photoconductor. The excited carriers recombine within a short duration of time and the device returns to its initial ‘dark’ conditions.

Figure 2.5: Generation of terahertz by photoconductive antenna. (a) Geometry of photoconductive emitter (b) A voltage bias is applied before excitation. (c) Charge carriers created by the pump pulse accelerate in the static field. (d) An induced polarization is created in the photoconductive material. (e) The creation of transient current $\vec{J}(t)$ is responsible for terahertz radiation. (f) After recombination it returns back to steady state.

A commercially available THz-TDS equipment TeraView's TPS spectra 3000 is employed in our experiments. The instrument can generate a wide range of terahertz radiation ranging from 60 GHz to 3 THz. Fig. 2.6 shows the schematic diagram of the optical components arrangement inside the instrument. It uses resonant photoconductive switching approach to generate and detect THz waves and photoconductive emitter and receiver were fabricated on low-temperature-grown GaAs. The optical delay stage to map

the THz signal in the time domain comes in two modes— rapid scan and step scan. The entire system is purged with dry air to minimize THz absorption by water vapor. To characterize the sample optical response, the THz electric field transmitted through the sample is compared with a reference with the sample. The sample stage comes with two equally sized holes in the copper plate and is attached to a vertical motorized linear stage which allows collection of the transmitted spectra of the sample and the reference in turns. The whole sample holder is a part of a continuous flow Helium-4 cryostat (or a closed cycle cryocooler), that comes with a temperature controller allowing measurements ranging from 10 K to 400 K.

Figure 2.6: Schematic diagram of THz-TDS setup using photoconductive antenna to generate and detect terahertz pulses adopted by Teraview 3000.

2.5 Optical pump-probe experiments

Ultrafast optical spectroscopy is a powerful method to study physical phenomena and manipulate material properties at femtosecond time scales that may not be accessible under equilibrium conditions.^[55] The development of ultrafast optical spectroscopy was

possible due to the astonishing progress in the laser technology such as generation of stable very short sub-100 fs optical pulses and chirped pulse amplification.^[56] In condensed matter systems, manipulation of any macroscopic property or even driving a phase transition is strongly associated with rearrangement of structural, magnetic, and electronic orders.^[81] To investigate this underlying association, ultrafast spectroscopy gives access to the relevant timescales providing us with understanding of fundamental physics as well as their importance for potential applications.

2.5.1 The Laser System: Generation of ultra-short lasers and Amplification

Micra Oscillator: The Ti:Sapphire laser is an optical oscillator comprising of four important components namely an optical pump, a gain medium, a high reflector and a partial reflector (also known as output coupler). Light intensification is achieved when it passes through the gain medium. In order to gain further amplification, light passes through the gain medium multiple times inside the laser cavity which is the region between the high and the partial reflector. The laser output is realized when a fraction of light transmits through the output coupler.

In a Ti:Sapphire oscillator the gain medium is comprised of sapphire as the common host media doped with Ti^{3+} ions. This particular configuration of the gain medium provides a large gain bandwidth. The Micra-10 oscillator can give an average modelocked power >750 mW at the central wavelength of 800 nm. The typical pulse bandwidth falls between 30 to 75 nm.

Amplifier RegA 9000:

Amplification of the femtosecond pulses is an integral of ultrafast laser systems. Amplification of pulsed lasers can be achieved by passing them through another optically pumped Ti:sapphire crystal.

However, there is a serious issue of pulse broadening during the laser amplification.

Femtosecond pulses have somewhat wide spread of spectra and become broader during propagation inside the optical crystals of the amplifier due to group dispersion effects.^[82] In order to reacquire the same short time duration of the pulses before amplification, the pulses are stretched before amplification and later compressed back after amplification.^[82]

In a regenerative amplifier, CW lasers can be used to pump the gain medium. The trapping of pulses and the eventual release of amplified pulses are achieved with the help of a Pockels cell and a polarizer. In our laboratory setup we use RegA 9000 regenerative amplifier from Coherent Inc. to realize amplification of ultrashort lasers. This amplifier can operate at a very high repetition rate of 250 kHz delivering a power up to 6 μ J. The RegA 9000 comes with an included packages of pulse stretching and compression and its pump laser is the Verdi CW green DPSS laser. The output pulse width from the amplifier is < 50 fs.

2.5.2 The pump-probe configuration

In a typical optical pump-probe configuration, an ultrafast laser beam is separated into two beams, the pump, and the probe, with a variable time delay achieved by varying the optical paths of the two beams. The pump beam is much intense and excites the sample. The change in properties initiated by the pump beam is monitored by the weaker probe beam. Such a configuration allows the user to investigate time-resolved optical responses such as reflectivity, transmission etc. Our set up adopts transient reflectivity measurement configuration as shown in the Fig. 2.7.

Figure 2.7: Schematic sketch of the ultrafast pump-probe setup for transient reflectivity mode measurements. Sketch was drawn by Dr. Chan La-o-vorakiat.

Our laser source has a repetition rate of 250 kHz and a central wavelength of 800 nm. The 800 nm RegA output from the oscillator is compressed at the grating compressor and then tubed and sent to the experiment and from where we can control the pulse duration of the laser. In our time-resolved reflectivity measurements, a beam splitter divides the ultrashort laser pulses into pump and probe beams. The two beams are then made to spatially overlap on the sample with the help of lenses and lenses and XYZ positioners. The probe beam can navigate the arrival of the pump beam as close as 10 fs and as far as 1.4 ns with the help of the delay stage. Both beams pass through neutral density filters which will allow the user to choose a suitable attenuation for the probe and pump

power(usually probe is 10 times weaker than the pump). Also, with the help of polarizer, the polarizations of pump and probe are made orthogonal to each other to minimize the detection of the pump signal and thereby improving the signal-to-noise ratio of our measurement. The reflected probe signal is then sent to a mirror and then focused on an avalanche photodetector (APD) for detection. The signal from the photodiode is then detected with the assistance by a lock-in amplifier and therefore the laser reaching the sample has to be modulated. A rotating optical chopper placed on the path of the probe beam provides this modulation. Generally, the chopping frequency is set at 3000 Hz and the lock-in amplifier is set to detect this frequency. The transient reflectivities measured are then recorded in the computer.

Chapter 3 : Electrically tunable percolative phase separation in manganites

3.1 Introduction

3.2 Experiments

3.3 Results and Discussion

3.3.1 Electric field modulated insulator-metal transitions of the PCSMO film

3.3.2 Electric field effect on the small polaron transport

3.3.3 Electric field effect on the phase separation

3.3.4 Complementary electric field and magnetic field effects

3.4 Summary

3.1 Introduction

Colossal magnetoresistance materials (CMR) and cuprate superconductors are the most popular oxide channel materials in FET configurations.^[43] Attempts to modulate a cuprate superconducting channel were first made by Mannhart and his co-workers, while for CMR it was first studied by Ogale *et al.*^[83-85] Since then a large body of work has been done, and is motivated by the fact that these systems have properties that may give gigantic response to small changes in carrier concentration.^[43, 86] In manganites particularly electrostatic tuning is an effective tool to explore its rich phase diagram; phases such as ferromagnetic metallic, charge-ordered antiferromagnetic insulating and paramagnetic semiconducting may exist in sub-micrometer and micrometer scales.^[1, 8, 9, 13, 16] The prospect of achieving the electric control of magnetization in manganites has attracted a lot of researchers, with the hope reading and writing magnetic information

using a ferromagnetic manganite device.^[87-89]

Historically, three types of FET configurations have been used in the electrostatic modulation of manganites (a) conventional FET using a high-K dielectric material like SrTiO_3 ^[90, 91] (b) ferroelectric FET (FeFET) where the gate dielectric is a ferroelectric material like $(\text{Pb,Zr})\text{TiO}_3$ and BiFeO_3 ^[92, 93] (c) Electric double layer transistor (EDLT) where an ionic liquid replaces the traditional oxide dielectric.^[94, 95]

Figure 3.1: a) Electrostatic modulation of 5 nm thick $\text{La}_{0.8}\text{Ca}_{0.2}\text{MnO}_3$ channel gated with the ionic liquid EMIM:TFSI for gate voltages $V_G = 0$ V (black line), +1 V (blue line), -1 V (red line). b) Schematic side-view of the EDLT device with Helmholtz double layer forming at the LCMO/ionic liquid interface for a positive applied V_G . [Taken from Dhoot *et al.* Phys. Rev. Lett 102, 136402 (2009)].

Capable of tuning sheet charge densities on the order of $10^{14} - 10^{15} \text{ cm}^{-2}$ is one to two orders of magnitude larger than that in conventional FETs, electric double-layer transistor (EDLT) is powerful technique to gain easy electrical access to the exotic electronic and magnetic phases of manganite.^[94-97] Dhoot *et al.* were the first to conduct EDLT experiments on manganites.^[94] They chose $\text{La}_{0.8}\text{Ca}_{0.2}\text{MnO}_3$ as the channel and carried out thickness dependent study and found that the electrostatically doped layer can extend up to 5 nm. Xiang *et al.* and co-workers were able to tune the conductivity of

electron-doped $\text{Ca}_{1-x}\text{Ce}_x\text{MnO}_3$ thin films by as large as 120,000% using ionic gating showing the extremely efficient control of metal-insulator transition in this manganite.^[95] Mentioned may be made for other works using EDLT on manganite systems that includes $\text{Pr}_{1-x}\text{Sr}_x\text{MnO}_3$, $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ etc.^[96-98]

Figure 3.2: Phase diagram of strongly correlated $\text{Pr}_{0.65}(\text{Ca}_y\text{Sr}_{1-y})_{0.35}\text{MnO}_3$ manganite. The blue and the red colored region represent the charge ordered and ferromagnetic regions respectively. The blended colored region indicates the phase-separated state. The various temperature points represented in the phase diagram are — T_C , T_N , T_{CO} , and, T_{SR} are the ferromagnetic transition, antiferromagnetic transition, onset of charge ordering and spin-reorientation temperatures respectively. Redrawn from Blake et al. Phys. Rev. B 66, 144412 (2002)

We chose a strongly correlated manganite system, $\text{Pr}_{0.65}(\text{Ca}_{0.75}\text{Sr}_{0.25})_{0.35}\text{MnO}_3$ (PCSMO) which has many competing ground states.^[99-101] In the manganite family, $\text{Pr}_{0.65}(\text{Ca}_y\text{Sr}_{1-y})_{0.35}\text{MnO}_3$, as one can introduce isoelectronic doping (replacing the element with similar valence numbers) by varying y to tune from one ground state to another.^[102, 103] In fact as y goes from 0.8 to a mere change of 0.6, it dramatically transforms from a charge ordered insulator (COI) to a ferromagnetic metal (FMM).^[102] This phase transition

is also closely connected to mesoscopic phase separation in PCSMO where (sub) micrometer-sized domains of different phases co-exist over a wide range of temperature.^[104, 105] PCSMO in its bulk form adopts an orthorhombic crystal structure belonging to the *Pnma* space group with lattice parameters $a = 5.445$ (or $3.851 \times \sqrt{2}$) Å, $b = 7.680$ (or 3.840×2) Å, and $c = 5.441$ (or $3.848 \times \sqrt{2}$) Å.^[102, 106]

The competition between the various degrees of freedom in PCSMO, renders the system extremely sensitive to external stimuli particularly to changes in doping concentration x and bandwidth W . Traditionally, x is modulated by chemical doping while W is tuned by either pressure or chemical substitution.^[31, 96] However, these techniques are not suitable for continuous tuning. We will explore the possibility of electrostatically tuning the various phases of PCSMO by adopting the EDLT configuration. This is a powerful method to achieve quasi-continuous modulation of doping. Also, the double-exchange mechanism in manganites allows control of the bandwidth, W by using an external magnetic field.^[107, 108] By adopting a multi-tuning approach of both x and W by electrostatic doping and magnetic field respectively, we investigate the underlying physics of phase separation in this manganite. The experimental results of this work have been published in Phys. Rev. B 89, 014425(2014).

3.2 Experiments

PCSMO films of various thickness ranging from 10 nm to 100 nm were grown on commercially available (001) $(\text{LaAlO}_3)_{0.3}-(\text{Sr}_2\text{AlTaO}_6)_{0.7}$ (LSAT), cubic structure with $a = 3.87$ Å) substrates using pulsed laser deposition (PLD) at a growth temperature of 770 °C and a growth oxygen pressure environment of 40 Pa. The PCSMO target was prepared by solid-state reaction method. After the deposition, oxygen pressure inside the chamber was increased up to 1000 Pa, the films were annealed in this high oxygen environment for at least 20 minutes at the growth temperature followed by slowly cooling to room

temperature. LSAT has cubic structure with lattice parameter $a = 3.87 \text{ \AA}$, and the PCSMO films grown on LSAT adopts a pseudo cubic structure.

The structures of the PCSMO films were characterized using X-ray diffractometer (SmartLab, Rigaku) which showed that the films were epitaxially oriented in the c-direction with no impurity phases. An atomic force microscope (AFM, Dimension V, Veeco) was used to determine the thickness and the surface quality of our PCSMO films. All the electrical transport measurements were measured by externally connected meters in a Physical Property Measurement System (PPMS-14T, Quantum Design) using a traditional hall bar and two-point geometries. All magnetic measurements of the PCSMO films were done in a superconducting quantum interference device magnetometer (SQUID, MPMS XL-5, Quantum Design).

We chose 30-nm PCSMO films on LSAT as the optimal thickness for our EDLT experiments considering the two factors that thinner films are more suitable for electrostatic experiments and films with less than 30-nm thickness were insulating which were harder to modulate. In order to fabricate the EDLT device, the PCSMO films were first patterned into a Hall bar configuration of dimension $900 \text{ \mu m} \times 300 \text{ \mu m}$ using photolithography and wet etching methods. It was followed by sputtering of 70-nm Au through a shadow mask on the patterned PCSMO film. The Au electrodes were found to have good Ohmic contact and hence can serve as excellent electrodes. We chose the ionic liquid (IL) N,N-diethyl-N-methyl-N-(2-methoxyethyl)ammonium bis(trifluoromethylsulphonyl)imide (DEME-TFSI) to be the gate dielectric in our EDLT device. Special care was taken to make sure that the ionic liquid covered the entire channel area and a sizeable portion of the gate electrode by confining the IL with commercially bought silicone paste. Electrical connections with the electrodes were taken out through Au wires but precautions were taken not to position Au wires in the IL

confined area.

The PCSMO EDLT device is then transferred to the PPMS chamber which was kept at a pressure of about 7 torr during all the measurement cycle. This relatively low pressure environment ensures minimum measurement artifacts due to the sensitivity of the ionic liquid on humidity conditions.^[95] The ionic liquid, DEME-TFSI, transitions to a frozen state at 180 K, where the ionic parts become immobile.^[65] Before the ions are completely frozen, the IL goes through a rubber state at intermediate temperatures where their mobility is significantly slowed but not stopped.^[77] We chose a temperature of 230 K, in the rubber state of the IL, to apply the gate bias as this is a safe way to avoid any electrochemical reaction due to the application of the gate voltage. At 230 K, the gate bias was applied for about half an hour which will allow enough time for the rearrangement of cations and the anions to form a Helmholtz double layer. The gate voltage of $[-3\text{ V}, +3\text{ V}]$ was chosen to avoid any irreversible electrochemical damage to the device.^[77, 109] For a chosen gate voltage, the connections to the gate electrodes were not removed until the temperature-dependent transport measurements for that gate voltage was complete. After the completion of transport measurements for one gate bias the EDLT device was warmed up to 300 K in order to unfreeze the ionic liquid before proceeding with the next gate bias. A tiny gate leakage current 0.1–5 nA was detected at 230 K which significantly reduced as the temperature was lowered. During all the temperature-dependent measurements a cooling/warming rate of 3 K/min was maintained. We chose to systematically apply the gate voltages in the following sequence: -3 V , -2 V , -1 V , 0 V , $+1\text{ V}$, $+2\text{ V}$ and $+3\text{ V}$.

Figure 3.3: a) θ -2 θ XRD scan of 30-nm thick PCSMO film grown on LSAT(001) substrate. (b) Schematic side view of the PCSMO channel EDLT in the accumulation state of the device along with the ionic liquid DEME-TFSI which serves as the gate dielectric. The cationic and the anionic parts of the ionic liquid are also shown. (c) Schematic view of EDLT under the measurement conditions. The direction of the electric field in the channel is indicated by the blue colored down arrows. AFM topography map of the PCSMO film (d) after deposition but before introducing the ionic liquid and (e) immediately after the gating measurements. Both surface profiles have a scan size of $1 \times 1 \mu\text{m}^2$. Images (d) and (e) have a RMS surface roughness of 0.908 and 1.04 nm, respectively.

We also carried out in-depth surface quality analysis of the EDLT channel before and after the gating experiments using AFM to investigate the possibilities of electrochemical damage. After the gating experiments, the channel was cleaned with isopropanol before doing AFM surface analysis. We found that there was no noticeable difference in the surface quality of these two measurements and the root-mean-square roughness of these

two surfaces were very similar. Moreover, the transport measurements were repeated in zero gate bias after the gating measurement sequences. A significant deviation in the transport data under zero gate bias before and after the gating cycle would indicate irreversible damage to the channel.

3.3 Results and Discussion

3.3.1 Electric field modulated insulator-metal transitions of the PCSMO film

Temperature vs. resistance (R - T) curves for 30-nm PCSMO film grown on LSAT at different applied gate voltages during both cooling and warming cycles are shown in Figure 3.4. The strong thermal hysteresis in the R - T curve for a particular gate voltage is a manifestation first-order phase transition in PCSMO with phase separation existing over a wide temperature range.^[20] It is also quite evident that PCSMO shows a marked metal-insulator transition and thermal hysteresis. At the ferromagnetic transition temperature, metallic puddles start developing in PCSMO and as the temperature is further lowered, the metallic phases grow and eventually form a percolating path which occurs around 50 K for our 30-nm PCSMO grown on LSAT.^[18] In a simple double exchange manganite such as bulk LSMO the resistance peak temperature, T_P is same as the ferromagnetic transition temperature T_C but in our strongly phase separated system, PCSMO, these temperature points are different but are closely related.^[18, 110] At zero gate bias, the values of T_P for the cooling and warming cycles are 85 K and 98 K, respectively. PCSMO is a hole-doped manganite so a $-ve$ V_G leads to hole accumulation in the channel while $+ve$ V_g leads to hole depletion in the channel. On increasing the gate voltage from -3 V to $+3$ V, the T_P gradually shifts to lower temperature values with a corresponding increase in the absolute value of resistance at T_P . We observe a 4 K shift of T_P on cooling and a 2 K shift on warming across our chosen gating range. For our measurement set, we

did not observe any 'aging' effect of resistance due to repeated thermal cycles.

Figure 3.4: a) Resistance vs. temperature curves for the device with 30-nm PCSMO channel during both warming and cooling cycles (indicated by the arrows) under various applied gate voltages V_G . (b) $\Delta R/R(0)$ or $[(R(V_g)-R(0))/R(0)]$ as a function of temperature. The measured data for the warming cycle are represented by the open symbols while the cooling cycles are represented by the closed symbols.

The nature of electrostatic modulation can be better understood in terms of electroresistance (ER) which we define as the resistance modulation with respect to the zero gate, i.e., $\frac{\Delta R}{R(0)} = \frac{R(V_g) - R(0)}{R(0)}$. During the cooling cycle, for +3 V gate bias a maximum value of ER (39%) was observed at ~ 50 K, whereas for -3 V gate bias ER peaked at ~ 57 K with a value of $\sim 29\%$ was found at 57 K for $V_G = -3$ V. Also, during the warming cycle, the maximum value of ER is $\sim 42\%$ at 69 K and $\sim 23\%$ at 72 K for +3 V

and -3 V gate biases respectively. The modulation in sheet carrier density, n_s , induced by the applied gate bias can be calculated from a simple capacitance formulation from electrostatics. The areal capacitance of the EDLT device is typically around a value of $10 \mu\text{F}/\text{cm}^2$ and is equal to the ratio of areal charge to the gate voltage.^[65] This capacitance value is also adopted by other published EDLT works using DEME-TFSI.^[65, 67] Following this, the calculated values of n_s corresponding to applied V_G of 1 V, 2 V and 3 V are 6.25×10^{13} , 1.25×10^{14} and $1.88 \times 10^{14} \text{ cm}^{-2}$ respectively.

3.3.2 Electric field effect on the small polaron transport

High-temperature transport behavior in manganites generally follows a hopping model.^[111] This behavior covers those temperatures well above T_P . For high quality manganite films, the small polaron hopping model gives a better description of the transport behavior in the high temperature regime while other models like thermally activated hopping and variable range hopping are ascribed for manganite films of lower crystallinity.^[112] We find that the small polaron model provides the best fits to our films. The conductivity described by this model is given by the equation^[16]

$$\sigma = \frac{\sigma_0 T_0}{T} \exp\left(-\frac{E_{hop}}{k_B T}\right) \quad (3.1)$$

where T_0 is optical phonon energy in temperature units; E_{hop} is the polaron activation energy and σ_0 is proportional to the product of the fractional density of hopping states and carrier doping per unit cell.^[16, 113]

Systems described by a polaron model display strong electron and lattice correlation.^[114] In general, the value of E_{hop} approximately equal to half of the polaron binding energy.^[16] It has been suggested that because of Jahn-Teller distortion the charge carriers are confined as small polarons. In this scenario, one can estimate that the E_{hop} is an indirect indicator of the degree of Jahn-Teller distortion in the manganite system.^[115]

As expected, the $\text{Pr}_{0.65}(\text{Ca}_y\text{Sr}_{1-y})_{0.35}\text{MnO}_3$ family show by a big polaron coupling constant ($\gamma_p > 4$) and a huge polaron mass (m_p) to lattice effective mass (m^*) ratio as a result of strong electron-phonon interaction.^[111]

The E_{hop} values are modulated by about 3 meV ($\sim 2.5\%$) under our gating experiments. If we look into the ER data, we observed that in this temperature range, ER is changed only a few percent (max value 7%). These two observations are coherent and conclusively point that the electrostatic gating small modulation in the polaron transport regime. The variation of E_{hop} under different gating voltages is illustrated in Figure 3.5(b).

Figure 3.5: a) High-temperature resistance curve fitted with the small polaron model for both the warming and cooling cycles at zero gate bias. (b) Activation energy E_{hop} vs. temperature data plots determined from the small polaron fitting.

3.3.3 Electric field effect on the phase separation

When the temperature is low enough for PCSMO to enter the phase separated state, our gating experiments may have two important fallouts— i) inhomogeneity in electric field distribution, and ii) modulation of the constituent phases at a constant temperature. Let us discuss the former case first. The ionic liquid DEME-TFSI can sustain very large electric fields and an applied gate bias of one volt can give electric field as large as 10 MVcm^{-1} .^[77] Given that we know the value of electric field inside the ionic liquid, E_{IL} , it is possible to determine the strength of the electric field in the manganite channel, E_M by taking into account the interface conditions for electric field vectors. According to Maxwell's equations, at the interface the displacement electric field, D remains continuous at the electrolyte/manganite interface assuming linear dielectric materials. This means

$$\varepsilon_{IL} E_{IL} = \varepsilon_M E_M \quad (3.2)$$

where ε_M is the effective static dielectric constant of the manganite and ε_{IL} the static dielectric constant of the ionic liquid.

The static dielectric constant of ionic liquids is determined to be in the range 10–15.^[116, 117] However, in a phase-separated manganite the static dielectric constant is the average response of the individual dielectric responses the COI (ε_i) and FMM (ε_m) phases.^[118, 119] The permittivity values have been reported to be $\varepsilon_i = 35$ and $\varepsilon_m = 55000$.^[119] Assuming ε_{IL} as 10 and E_{IL} as 10^7 V/cm , then E_M in a purely insulating PCSMO is $\sim 3 \times 10^6 \text{ V/cm}$ while in a pure metallic PCSMO, it is $\sim 2 \times 10^3 \text{ V/cm}$. In a phase separated scenario, the electric field inside the manganite channel is expected to exhibit inhomogeneous distribution with values falling between these two extreme ends. As one changes the relative fraction of the COI and the FMM phases either by temperature or magnetic field, the effective ε_M would change and so also the nature of electric field

distribution in the channel.

The inhomogeneity in the electric field distribution is clearly illustrated in our model simulation using finite element method as shown in Figure 3.6. In this model four metallic discs of 5 nm radii are placed in an insulating matrix which acts as the mother host. It is evident from the color map that the electric field in the insulating region is significantly enhanced whereas it is screened and trivial in the metallic phase. The input electric field applied across the electrodes chosen for this simulation is 10^6 V/cm. In reality, the metallic phases in PCSMO are not exactly spherical or static. They can be dynamic and may possess sharp geometric features. At such sharp projections, the local electric field can be enhanced and it is quite likely that it will reach strengths large enough to produce local effects in the insulating phase and may even cause dielectric breakdown forming a local conducting network. Also, the morphology of the manganite phases is dynamic in nature and therefore warrants a dynamic distribution of the local electric field.^[120]

Figure 3.6: Schematic electric field distribution inside a toy model consisting of metallic and insulating phases. The electric field is screened in the metallic bubbles as shown by the small values of electric field.

Electric field effects on the modulation of co-existing manganite phases can be

understood by modelling the transport behavior using the general effective medium (GEM) theory.^[121, 122] This model describes the effective conductivity (σ_E) of a binary composite mixture as a function of the conductivities of the individual components (σ_H for the high conductivity component and σ_L for the low conductivity component), the volume fraction of the components (f is the fraction of the metallic component present), the geometrical dimensions and distributions (t), and a critical volume fraction that determines percolating network (f_c). The effective conductivity σ_E is thus given by

$$(1 - f) \left(\frac{\sigma_L^{1/t} - \sigma_E^{1/t}}{\sigma_L^{1/t} + A\sigma_E^{1/t}} \right) + f \left(\frac{\sigma_H^{1/t} - \sigma_E^{1/t}}{\sigma_H^{1/t} + A\sigma_E^{1/t}} \right) = 0 \quad (3.3)$$

where the parameter $A = (1 - f_c)/f_c$ and for three dimensional systems t is closer to 2.^[122]

The GEM model has been used by various researchers to describe phase separation in manganites.^[123-125] The end members of the PCSMO family of compounds are $\text{Pr}_{0.65}\text{Sr}_{0.35}\text{MnO}_3$ (PSMO) and $\text{Pr}_{0.65}\text{Ca}_{0.35}\text{MnO}_3$ (PCMO). Here, the ground state of PSMO is FMM phase while that of the PCMO phase is COI. So in our GEM model, we can assume that the conductivity values of the FMM phase in PCSMO as equivalent to that of PSMO and similar argument for connecting the COI phase with PCMO. For the PCSMO manganite, equation 3.3 now reduces to

$$A\sigma_E + \{\sigma_H^{1/2} + f(\sigma_L^{1/2} - \sigma_H^{1/2}) - A\sigma_L^{1/2}\}\sigma_E^{1/2} - \sigma_L^{1/2}\sigma_H^{1/2} = 0 \quad (3.4)$$

The FMM volume fraction, $f(T)$ which is a function of temperature, can be estimated from the ratio of measured magnetic moment to saturation magnetic moment i.e. $\frac{M(T)}{M_s}$.

The values of $M(T)$ and M_s for the PCSMO film was experimentally determined from a series of magnetization vs. temperature (M vs. T) and magnetization vs. magnetic field (M vs. H) experiments using the SQUID as shown in Figure 3.7. The M vs. T curve show a clear paramagnetic to ferromagnetic transition around 130 K. The value of M_s was

determined as $2.6 \mu_B/\text{Mn}$ from the M - H curve measurement at 10 K. Using the FMM volume fraction obtained from magnetization measurements labelled as f_{exp} , we then proceeded to calculate f_c using eqn (3.4), the effective conductivity σ_E of PCSMO predicted by the GEM theory near the percolation transition. The values of f_c were chosen in a range of 0.17–0.25 as guided by previous GEM studies on other manganite systems. We found that the simulated effective conductivity was closest to the experimental conductivity values of PCSMO at $f_c = 0.24$, which is consistent with previous reports.^[123, 125] The effective PCSMO conductivity cannot be simulated for the entire temperature range because of the extremely large resistances of the PCMO below 75 K which falls beyond the capabilities of the meter. All in all, the simulated conductivity values of PCSMO from the GEM model matches well with the experimental data. The small deviation that we observed may be attributed to the simplification of the actual manganite phase separation by the considerations in the GEM model.^[123]

One implication of the GEM theory is that any modulation in the values of effective conductivity, σ_E originates from changes in the volume fraction of the constituent components. We can thus calculate the electric modulation of the FMM fraction, f_{calc} , in the PCSMO channel from the experimentally determined values of electric field induced conductivity modulation. Following equation 3.4, the FMM volume fraction, f_{calc} , for $f_c = 0.24$ and $t = 2$ can thus be expressed as

$$f_{\text{calc}} = \frac{(\sigma_L^{1/2} - \sigma_E^{1/2})(\sigma_H^{1/2} + 3.167\sigma_E^{1/2})}{\sigma_E^{1/2}(\sigma_L^{1/2} - \sigma_H^{1/2}) + 3.167\sigma_E^{1/2}(\sigma_L^{1/2} - \sigma_H^{1/2})} \quad (3.5)$$

Fig 3.7(c) shows the modulation of ferromagnetic fraction, f_{calc} , of the PCSMO channel at $T = 80$ K using the eqn above. As expected, the application of –ve gate voltages leads to growth of FMM domains inferred from the data that at 80 K as V_G is changed from +3 V to –3 V, and Δf increased by about 0.15% .

Figure 3.7: (a) Ratio of magnetization to saturation magnetization, $\frac{M}{M_s}$ of the PCSMO film as function of temperature under field-cooled 0.1 kOe magnetic field. Magnetization vs. magnetic field plot at 10 K is shown in the inset. (b) Plots of conductivity values of PCSMO. The green solid circles represents the experimental values while the green open symbols are values calculated based on the GEM model with $f_c = 0.24$. The blue symbols and the red symbols represent the values of insulating and metallic phases in our model and are taken from Blake *et al.* Phys. Rev. B 66, 144412 (2002) (c) Modulation of ferromagnetic fraction by an applied gate voltage at 80 K calculated from the GEM theory.

3.3.4 Complementary electric field and magnetic field effects

PCSMO belongs to the ‘low’ or ‘intermediate’ bandwidth manganites.^[8] The bandwidth, W is related to the hopping amplitude of the electrons via the double exchange mechanism in the e_g band. An external magnetic field can not only modulate W but also reduce the spin scattering in carrier conduction.^[126, 127] Multi-tuning by both electric, E and magnetic field, H allows one to scan the x - W 2D phase space in PCSMO. In the context of phase separation scenario, magnetic field favors FMM domains and at a substantially large magnetic field, it can induce long range FMM ground state. The role of electrostatic doping in the presence of the magnetic field is unclear in PCSMO and can be

better understood by studying the electric field modulation of magnetoresistance, $MR = \left(\frac{R(H)-R(0)}{R(0)}\right)$.

MR was measured for the PCSMO channel devices at several temperature points under gate biases of +3 V and -3 V were taken as illustrated in the fig. 3.8(a). The multi-tuning response of PCSMO can be better understood from the plot of electroresistance (ER) vs. magnetic field (H) as shown in fig. 3.8(b). Here electroresistance is defined with respect to $V_G = -3$ V i.e. $\frac{\Delta R}{R(-3V)} = \frac{R(+3V)-R(-3V)}{R(-3V)}$.

Remarkably, ER(-3V) attains a peak value of ~250% at 80 K under a biased magnetic field of 1.38 T (0.52 T) during the increasing (decreasing) H cycle. On the other hand, the peak value of $\frac{\Delta R}{R(-3V)}$ is a mere ~90% observed at 50 K. Let us define H_{peak} as the

value of the magnetic field where ER is largest for a particular temperature. The relation of H_{peak} with temperature is shown in Fig. 3.8(c). H_{peak} increases gradually with temperature and we could imagine that H_{peak} as a point in the phase diagram where it is most sensitive to external stimuli of E and H . By increasing the temperature, we move away from the sensitive phase-separated point. To maintain this sensitive phase-separated point an increasing magnetic field can serve as a counteracting force. The complementary behavior of E and H is also demonstrated by Fig. 3.8(d) which shows the modulation of ER as a function of temperature at select magnetic fields. ER at non-zero magnetic fields is clearly enhanced when compared to the ER curve at zero magnetic fields.

Figure 3.8: (a) Magnetoresistance (MR) vs temperature for the PCSMO device under -3 V (open circles) and +3 V (filled circles) gate biases shown for increasing magnetic field. (b) ER as a function of applied magnetic field. ER is defined as $\Delta R/R(-3V) = ((R(+3V) - R(-3V))/R(-3V))$. The filled and open symbols represent the processes of increasing and decreasing magnetic field respectively. (c) Magnetic field at the peak ER plot against temperature. (d) ER vs. temperature curves at different magnetic fields.

Noticeably, the complementary behavior of E and H is not a straight-forward relationship and it is strongest at 80 K from our temperature set. This corresponds to a sensitive phase-separated regime where phases of degenerate energies strongly compete. The case of the enhanced ER in the presence of a magnetic field can be quantitatively understood in the context of the GEM model. As described in details in the previous sections, the FMM volume fraction, f_{calc} can be calculated by using the conductivity data to solve eqn. The curve of f_{calc} vs. applied magnetic field for $V_G = +3$ V and -3 V at 80 K

is shown in fig 3.9. We recall that at this temperature the ER attains a peak value ($\sim 250\%$) under a biased magnetic field of 1.38 T. From the GEM calculations we find that the calculated FMM volume fraction changed by about 0.51% when a positive +3 V is reversed to -3 V. However, without any magnetic field, the gate polarity reversal could change only a mere $\sim 0.15\%$.

Figure 3.9: Plot of ferromagnetic phase fraction, f_{calc} as a function of the magnetic field at 80 K under +3 and -3 V gate biases.

While both the effects of both E and H get stronger in the phase-separated regime, one can try to weigh the strengths of these two effects by comparing the ER measured without any magnetic field with the MR measured at a fixed V_G . We also define H_{equi} as the magnetic field that can modulate the resistance of the PCSMO channel by the same value as a gate voltage of -3 V. H_{equi} vs. temperature curve is in Fig. 3.10. If we look at the temperature regime $60 \text{ K} \leq T \leq 120 \text{ K}$ which corresponds to the phase separated regime, H_{equi} values are smaller. While for lower ($< 60 \text{ K}$) and higher temperatures ($> 120 \text{ K}$), H_{equi} attains larger values. This means that the gate voltage of -3 V, in the context of channel resistance modulation, can substitute much larger magnetic fields at regimes away from the phase separation state. This is an illustration of subtle differences between E and H in the PCSMO channel. While both E and H have common features and

complementary effects, it is important to differentiate them. We expect the distribution of local electric field to be inhomogeneous and highly directional inside the PCSMO channel, the magnetic field is regarded to be of isotropic nature.

Figure 3.10: Equivalent magnetic field, H_{equi} versus temperature. H_{equi} is defined as the magnetic field that produces equivalent resistance modulation in the PCSMO channel as that by an electric field as the gate bias is reversed from +3 V to −3 V.

3.4 Summary

In summary, the electric field induced conductivity modulation in a phase-separated channel can be understood only by considering the effects of strong correlation present in the system. On the other hand, in a simpler system like a semiconductor, the relative change in conductivity is proportional to the relative change in sheet carrier density. The gating experiments on PCSMO reveal dissimilar transport modulation at high and low temperature regimes. At high temperatures where the small polaron hopping is relevant, the effect of the electric field is somewhat weak whereas at lower temperature, in the phase-separated state, the electric field effect is greatly enhanced. Furthermore, the electric field is complemented by the magnetic field in the context of transport modulation in a phase separated channel. Multi-tuning by both electric and magnetic field

is strongest at 80 K where maximum ER value of 250% was observed and this would correspond to a point in the phase diagram where it is most sensitive to external stimuli. This complementary effect can be understood in the framework of the general effective medium model. Using this model we estimated that the electric field induced change in FMM volume fraction in the PCSMO channel is boosted by 0.51% in the presence of an applied magnetic field. These observations can serve as guidelines to conduct interesting microscopy experiments like Lorentz transmission electron microscopy to map the spatial evolution of FMM and COI domains under simultaneous electric and magnetic stimuli.

Chapter 4 : Gate control of re-entrant insulating phase in the cluster glass regime of manganite thin films

4.1 Introduction

4.2 Experiments

4.3 Results and Discussions

4.3.1 Thickness dependent insulator-metal transitions of strained PCSMO films

4.3.2 Cluster glass phase in PCSMO film

4.3.3 Electric field effect on cluster glass phase

4.3.4 Issues of electric field induced strain and oxygen migration

4.4 Summary

4.1 Introduction

Traditionally, magnetic phase control in complex oxides is achieved by the introduction of an applied magnetic field. In a vast number of these oxides the electronic and the magnetic orders are coupled very strongly and as it turns out, an applied magnetic field could modulate the electronic properties in these systems.^[128, 129] Eventually, electric control of magnetism was a vision many researchers in academia and industry were really excited about.^[130, 131] While magnetic control of multi-functionalities in complex oxides was a major breakthrough, it is clunky and unpractical from a viewpoint of building a device as it more often than not the required magnetic field was in the order of a few tesla. On the other hand, the ability to externally control the functionalities of magnetic materials by the application of a few volts would be highly desirable from technological as well as fundamental research perspectives, and would supplement the recent developments in the

field of magnetoelectronics and spintronics. In complex oxides, research efforts in this direction has been mostly towards electric field control of ferromagnetism onset or switching of magnetization and little attention has been given to electrically tuning the magnetic phase separation or the spin-glass state.^[88, 92]

Manganites displaying phase separation (PS) are also considered part of the family of disordered magnetic systems.^[132] A common feature in such systems is the emergence of a magnetic glassy behavior also known as the spin glass state.^[132-134] Spin glasses originate from disorder and frustration in spin interactions leading to new magnetic ‘orders’ from unusual symmetry breaking.^[132] Bifurcation in susceptibility, χ vs. temperature curves for the zero-field-cooled (ZFC) and the field-cooled (FC) plot is a strong signature of the spin-glass transition.^[135] The spin-glass transition in manganites is an intriguing case. For example, the glassy state in the archetypal PS manganites $\text{La}_{5/8-y}\text{Pr}_y\text{Ca}_{3/8}\text{MnO}_3$ (LPCMO) have been labelled as ‘cluster glass’ where the spin orientations of local ferromagnetic clusters are "frozen" resulting in the absence of true long-range conventional magnetic order.^[133, 136] It is believed that each magnetic cluster acts like an individual spin.^[132] Above the ‘cluster-glass’ transition, the spins of the magnetic clusters are free to rotate and below this transition they froze in random directions.^[132] Interestingly, the onset of FM transition temperature is much higher than the onset of cluster glass transition temperatures in this system. Fundamentally, ‘cluster-glass’ can be considered as a form of spin-glass with some additional features that will be discussed in the following sections.

Figure 4.1: Magnetic phase diagram showing the glassy state developing at low temperatures and low magnetic field for select manganites— a) $\text{La}_{1/4}\text{Pr}_{3/8}\text{Ca}_{3/8}\text{MnO}_3$ (Glass) b) $\text{La}_{0.215}\text{Pr}_{0.41}\text{Ca}_{3/8}\text{MnO}_3$ (G) and c) $\text{La}_{0.225}\text{Pr}_{0.40}\text{Ca}_{0.375}\text{MnO}_3$ (PS frozen). The glassy states are mentioned in the parenthesis. [Taken from Wu *et al.* Nature Mater. 5,881 (2006), Sharma *et al.* Phys. Rev. B 78, 134205 (2008), Ghivelder *et al.* Phys Rev. B 71, 184425 (2005)]

Phase-separation in manganites can manifest either as glassy PS state or as a dynamic fluid-like PS states.^[120, 132, 137] It is well known that the electronic and magnetic properties are strongly correlated, and as a result the magnetic glassy behavior is expected to bear implications in the macroscopic conductivity pathways of these manganites. One can also expect that this glassy nature to be strongly sensitive to external stimuli like magnetic field, temperature, substrate-strain and electric field. Furthermore, by selecting an appropriate substrate, one can impose quasi-control of the mis-fit strain on the epitaxial manganite film.^[138, 139] Using substrate strain as a control parameter, it is possible to tune the competing energetic phases in manganites and even possibly even the magnetic glassy state. Additionally, it is unclear how the magnetic glassy state stabilized by substrate strain in manganite thin films will respond to electrical stimuli. In fact by modulating the carrier density in glassy cobaltates by chemical doping, it was found that the glassy magnetic order in this system has a strong response to hole-doping levels.^[140] Manganite channel field effect devices thus provide a much bigger platform to study the physics of

magnetic glassy states that is not available in bulk counterparts.

We have already discussed that PCSMO display many exotic phases with phase separation over a broad temperature range. This makes PCSMO a good candidate to study the possibility of a glassy magnetic state and its ramifications on transport data. Also, by choosing SrTiO_3 (STO) as the substrate, one can introduce long range tensile strain in the PCSMO films since the bulk lattice parameters of PCSMO are smaller than that of STO (cubic with a lattice constant of $a=3.905 \text{ \AA}$) which results in a lattice mismatch of 1.48%. In the previous chapter, we discussed the physics of electric field tuning the phase separation in PCSMO. Here we will build on that work to look into the possibilities of electrostatically tuning the cluster glass phase in PCSMO by using the EDLT configuration. A major portion of this work has been covered in our publication Appl. Phys. Lett. 104, 133508 (2014).

4.1 Experiments

Epitaxial PCSMO films were grown on (001)-oriented STO substrates using pulsed laser deposition as reported in the previous chapter. The EDLT devices were also fabricated by repeating the steps used for the PCSMO grown on LSAT. For this device also we chose commercially bought ionic liquid DEME-TFSI as gate dielectric. Hi-resolution XRD measurements of the PCSMO films were performed using X-ray diffractometer (SmartLab, Rigaku). Electrical transport measurements of all films and devices were also carried out in a physical property measurement system (PPMS-14T, Quantum Design) with the help of externally connected meters. Magnetic characterizations of the films were conducted using a superconducting quantum interference device SQUID magnetometer (MPMS XL-5, Quantum Design).

4.3 Results and Discussions

4.3.1 Thickness dependent insulator-metal transitions of strained PCSMO films

Manganite thin films can display electronic and magnetic properties quite different from their bulk counterparts. In general, thin films exhibit reduced Curie temperature T_C leading to reduced T_P and are more likely to show stronger phase separation.^[141-143] These features become more dramatic with reduction in the film thickness. Mills *et al.* made theoretical arguments that biaxial strain introduced in epitaxial thin films with lattice mis-match substrates strengthens the Jahn-Teller distortions which subsequently increase e_g electron band splitting favoring electron localization.^[144] They described the relation between T_C and biaxial strain by the following equation^[138]

$$T_C(\epsilon) = T_C(\epsilon = 0)(1 - \alpha\epsilon_B - \frac{1}{2}\beta\epsilon_{bi}^2) \quad (4.1)$$

where $T_C(\epsilon)$ and $T_C(\epsilon = 0)$ are the curie temperatures with strain and without strain. ϵ_B and ϵ_{bi} are bulk and biaxial strain respectively. The parameters α and β are associated with the unit cell volume variations under strain and the Jahn-Teller splitting energies respectively. One can clearly see from the equation that biaxial strain always decreases the ferromagnetic onset and has a quadratic difference. Experimentally, however, the substrate can induce a variety of effects and not just biaxial strain for eg. oxygen deficiency, dimensional effects, interfacial effects.^[138, 145, 146]

Let us first look into quality of PCSMO films as a function of thickness before discussing the thickness-dependent transport. The structural variations of PCSMO films deposited on STO substrates are studied from XRD measurement as shown in Figure 4.2 (a). The XRD θ - 2θ scans show that all the PCSMO films of various thicknesses are c -oriented. Fig 4.2(b) shows the out-of-plane lattice parameter as a function of film thickness. As expected, the out-of-plane lattice parameters goes to lower values as the

film thickness reduces indicating thinner films are under stronger tensile strain from substrate. FWHM parameters of the diffraction peaks increases with decreasing film thickness as shown in Fig 4.3(c), which indicates the thinner films have relatively less crystalline quality.

Figure 4.2: a) X-ray diffraction data for PCSMO films of various thicknesses. b) Out of plane unit cell lattice parameter as a function of thickness. Thinner films have lower out-of-plane lattice parameter values and hence under larger tensile strain from substrate. c) The corresponding FWHM data of the films at (002) peaks. FWHM parameters of the diffraction peaks increases with decreasing film thickness, which indicates the thinner films for relatively less crystalline quality.

In phase separated manganites, biaxial strain promotes long-range charge ordering.^[138, 142] As a result, if the thickness of the film was too small then it will stabilize the insulating state making it hard to measure its electrical transport properties. The thickness dependent transport properties of PCSMO films are shown in Fig. 4.3(a). For films thinner than 30 nm, there was no metal-insulator transition, and as we grew thicker

films the temperatures of peak resistance, T_P gradually increased. Interestingly, the height of the resistance-drop, below T_P was modest strongly indicating that in the low-temperature region, the presence of competing PS states has not been washed out. Hence, we focused on the PCSMO films of this thickness as it is good candidate for magnetic glassy behavior and for electric field experiments. The reciprocal space map of the 40-nm thick PCSMO film on STO was taken around the (022) peak, and reveal that the film had the same in-plane lattice parameters as the substrate.

Figure 4.3: a) Thickness dependent resistivity curves of PCSMO films grown on STO substrate. The values of T_P are indicated by the down arrows. b) Reciprocal space map of the 40-nm thick PCSMO film grown on STO around the (022) peak.

4.3.2 Cluster glass phase in PCSMO film

A closer inspection of the low-temperature behavior of the 40-nm thick PCSMO film can be made from the magnetic measurements. Zero-field cooled (ZFC) and field cooled (FC) magnetic measurements were performed on this sample at applied perpendicular magnetic fields of 100, 200, 1000, 5000 Oe. The magnetization vs. temperature plots show a bifurcation of ZFC and the FC curves generating a lambda (λ) shaped feature present a typical shape as shown in Fig. 4.4 (a). The bifurcation of the ZFC and FC curves

is observed at temperature, T_m , and the maximum magnetization of the ZFC curves is at temperature T_f . T_f is also the glass transition temperature or the spin freezing temperature. Such features are attributed to magnetic inhomogeneity and spin-glass state.^[132] We have mentioned that cluster glass is a type of spin-glass system but a canonical SG system is reported to hold the following additional characteristics: (i) The values of T_m and T_f are much closer (ii) T_m is unchanged for varying applied magnetic fields, and (iii) the FC magnetization remains almost constant at temperatures below T_f .^[135] The magnetization measurements on the 40-nm thick PCSMO show that T_f is much lower than T_m , T_m is a function of temperature, and $M_{FC}(T)$ continues to increase below T_f . Hence, the low temperature magnetic order in PCSMO should be classified as CG rather than a canonical SG. This conclusion is also consistent with other PS manganites where FMM domains exist as clusters in the AFM matrix.^[132]

We also performed magnetization (M) vs. applied magnetic field (H) measurements on the 40-nm thick PCSMO on STO at select temperatures of 10 K, 50 K, and 100 K as shown in Figure 4.4(b). From the M vs. H data at 10 K, the saturation magnetization, M_S of the film was estimated to $2.71 \mu_B/\text{Mn}$. Theoretically, the saturation magnetization in manganites is estimated by accounting for the spin only values of manganese $3d$ electrons:

$$M_S = x \times Mn^{3+} \left(S = \frac{4}{2} \right) + (1 - x) \times Mn^{4+} \left(S = \frac{3}{2} \right) = 4x\mu_B + 3(1 - x)\mu_B$$

(4.2)

where x is the fraction of hole doping concentration.^[16] For the amount of hole concentrations in our PCSMO film, the estimated value of M_S is $3.35 \mu_B$. The smaller experimental value of M_S may be due to spin-freezing nature in this system.^[147] The M vs. H curves exhibit hysteresis which indicates that it has ferromagnetic signature even at 100 K [inset of Figure 4.4(b)]. Also, with increasing temperature the coercive field decreases.

One of the characteristics of cluster-glass systems is the field dependence of the

freezing temperature, T_f . Mean-field theory predicts the existence of critical lines in the magnetic field vs. temperature phase diagram of such glassy systems. The so-called “Almeida-Thouless (AT) line” is the first of these lines which occurs in Ising spin systems and its behavior near the freezing temperature follows the equation^[148]

$$H(T) = H_0 \left(1 - \frac{T_f}{T_{f0}}\right)^p \quad (4.3)$$

where T_{f0} is the zero-field spin freezing temperature. By plotting H v T_f and fitting it to equation 4.3, we get the following parameters: $p = (1.12 \pm 0.28)$, $T_{f0} = (99 \pm 6)$ K, and $H_0 = (2044 \pm 313)$ Oe. This result suggests the existence of AT critical line in our system which also point towards a magnetic glassy state with disordered spin.^[149, 150] The magnetic phase diagram is constructed from the experimentally determined values of T_f and T_m from the ZFC and FC curves [Figure 4.4(d)].

Figure 4.4: (a) M-T curves of the PCSMO film on STO at various magnetic fields ($H = 0.1, 0.2, 0.5, 1$ and 5 kOe). The solid and the open symbols represent the FC and the ZFC curves respectively. The glass transition temperature T_f , where the ZFC curve reaches the maximum and the merging temperature, T_m for the 100 Oe curve are indicated

by arrows. (b) M-H loop for the PCSMO film on STO measured at temperatures— 10 K, 50 K and 100 K. Inset shows the hysteresis loop zoomed in the low-field regime highlighting the coercive fields. (c) Field dependence of T_f fitted by Almeida-Thouless equation 4.3. (d) Magnetic phase diagram of PCSMO on STO. The phase boundaries are determined from the values of T_f and T_m . The blue and the red solid lines are guide to the eye.

4.3.3 Electric field effect on cluster glass phase

Clearly, we have established that our 40-nm thick PCSMO on STO is a cluster-glass at low temperatures. We now look into the effects of electrostatic doping on this system by using an EDLT configuration as shown in Figure 4.5(a). As a reminder, negative gate voltage will lead to accumulation of holes while positive gate voltage depletes hole density at the interface. Also, at low temperatures our PCSMO channel exhibits coexisting FMM and COI phases as shown in Figure 4.5(b). It is expected that electrostatic doping can modulate the FMM fraction or the size of the hole-rich clusters in the phase-separated region.

The resistances versus temperature curves for the 40-nm thick PCSMO on STO under different gate biases are shown in Figure 4.5(c). As we have seen, PCSMO undergoes a percolative metal-insulator transition which is closely associated with the characteristic temperature of peak resistance T_P . However, unlike the PCSMO films with small biaxial strain, the 40-nm thick PCSMO on STO has a fragile metal-like state and as the temperature is further reduced (< 30 K), the resistance slope changes sign again and a reentrant insulating behavior is observed at T_R . The percolation path is broken at T_R . In manganites, one of the factors attributed to the cause of this anomalous reentrant insulating behavior was the magnetic glassy state.^[91, 136, 146, 151-155] At temperatures lower

than T_R the magnetization values are strongly suppressed. This hints that the freezing of FMM spin clusters are closely related to the reentrant insulating behavior.

One of the most telling results about the electric field effect experiments on this system is that the strongest resistance modulation due to gating occurs in the low-temperature cluster glass state whereas in the high-temperature region ($> T_P$), the resistance modulation was quite weak. When the device is operated in the depletion mode as shown in Figure 4.5(d), the electroresistance, $\Delta R/R = ((R(V_G) - R(0V))/R(0V))$ is significantly enhanced reaching values upto 200% for $V_G = +3$ V at $\sim T_R$. In comparison, the electroresistance in the hole accumulation mode can only reach a maximum about 43 % at $V_G = -3$ V, leading to an asymmetric nature of gate modulation. Here in this device, the electric field also modulates the values of T_P just like our previous PCSMO on LSAT device. During the cooling cycle the gating modulates T_P by 11 K, while during the warming cycle T_P is modulated by a value of 3 K. Interestingly, the point of reentrant insulating state, T_R can be electrostatically tuned by 5 K during the cooling cycle.

These field effect results are quite different from our previous findings reported in the previous chapter where the PCSMO films were relaxed indicating the importance of biaxial strain in understanding low-temperature cluster glass phase in manganites.

Figure 4.5: (a) Schematic circuit diagram of the EDLT device fabricated on PCSMO on STO. (b) Illustration of co-existing FMM and COI phases in the cluster glass state of PCSMO and the role of electric field. (c) Resistance vs temperature curves for the 40-nm thick PCSMO on STO under various applied gate voltages (-3 V, -2 V, 0 V, $+1$ V and $+3$ V). During the cooling cycle, for $V_G = +3$ V and -3 V, the temperature of peak resistance are represented by T_{P1} and T_{P2} , while the temperature onset of reentrant insulating state are represented by T_{R1} and T_{R2} , respectively. (d) Electroresistance, $\Delta R/R = ((R(V_G) - R(0V))/R(0V))$ plotted as a function of temperature. The plot includes only the cooling cycle data for clarity. To ascertain the close association between the cluster glass state and the reentrant insulating state the glass transition temperature, T_f and the merging temperature, T_m from the 100 Oe magnetization measurements are shown as dotted lines on the graph. Also shown are the onset temperature T_R and T_P from the cooling data under gate bias of $+3$ V.

The insulating behavior in the cluster glass state of PCSMO is quite robust under the

gating experiments. We observe that the reentrant insulating behavior persists at gate voltages as large as -3 V and the modulation for negative gate voltages are not as large as the positive gate. This also means that even $V_G = -3$ V cannot electrostatically induce a percolating conducting network of FMM domains. One of the possible reasons for this asymmetric electroresistance may be because the ground state of 40 nm-thick PCSMO film on STO is closer to a robust COI phase than a pure FMM phase.^[101-103] The accumulated holes at negative bias may not drive the system towards a phase transition as the ground state is far away from the FMM phase. The enhanced positive electroresistance supports this scenario because when the device is operated in depletion mode, the system navigates towards a more stable COI state with smaller FMM fraction. Furthermore, there is strong of carrier localization in the reentrant insulating state which means the accumulated holes has weak effects on the insulating ground state of the PCSMO on STO film.

As we increase the temperature of the system, we move from a magnetic glassy state to a fluid phase separated at intermediate temperatures. Recent electric field study on these systems showed that an electric field can align the spin states of fluid like FMM regions in manganites.^[156, 157] As a consequence the conductivity of the system increase due to applied electric field. Detailed comparison between the electric field effects on the fluid like state and the glassy state was done by Guo *et al.*, where they showed that electric field induces electrophoretic-like FMM domain motion at intermediate temperatures while at lower temperatures identified with the glassy state, the domain motion is constrained and electrical switching cannot be achieved.^[157] However, unlike the devices used in these reports, EDLT can also introduce carrier doping by electrostatic means allowing it modulate the glassy state inaccessible by the earlier devices. This is because in principle, carrier doping can control the seeding of FMM phases in these

manganites.

4.3.4 Issues of electric field induced strain and oxygen migration

Introduction of strain and oxygen migration are conceivable scenarios in field effect experiments in oxides esp. when dealing with a strong electric field.^[158, 159] While electric field induced strain effects are significant in ferroelectric field effect transistors, in EDLT configuration the strain induced by electric field can be omitted because the mechanical interaction between the oxide channel, and the ionic liquid is expected to be rather weak. In addition, in ferroelectric field effect transistors, the electric field induced strain resulted in ambipolar mode of the device i.e. the channel resistance increased for both positive and negative gate polarities. Considering that our EDLT device using the PCSMO on STO structure produced bipolar effects, we can regard that strain is not a dominating factor.

The role of electric field induced oxygen migration in the manganite channel is not so straightforward to rule out. A key point in this context is that introduction of oxygen vacancies result in higher resistances in manganites.^[160] If electric field drives oxygen migration in the manganite channel then, in principle, a positive gate bias will remove negatively charged oxygen ions from the manganite channel consequently increasing the channel resistance. In order to study the role of oxygen migration, we designed the gating experiments taking an ordered sequence of gate biases. Figure 4.6 shows temperature-dependent resistance curves for the PCSMO on STO channel at three gate biases— 0 V, +3 V, and 0 V repeated again after the completion of one full gating cycle (+3 V, +1 V, 0 V, -2 V and -3 V). The second zero gate measurement was taken after a time elapsed of about 15 hours during which the device was still kept inside the PPMS chamber maintained at a pressure of ~7 torr. We observe the two zero gate biases curves do not strictly lie on top of each other and there is a noticeable difference at low temperatures. This indicates of a possibility of electric field driven electrochemical

process involving oxygen ions at the surface of the manganite channel. However, the memory effect in our device is not enormous and is restricted to the low temperature regime. The intermediate and the high temperature regions have more or less good reproducibility. We can infer from this that compared to the electrostatic doping effects the electrochemical effects are smaller otherwise a stronger dependence on the gating history would have been observed.

Figure 4.6: Resistance vs. temperature curves for the PCSMO on STO channel EDLT under gate voltages of 0 V and +3 V. The zero-gate bias transport was remeasured after one complete gating cycle.

EDLT devices were also fabricated for the 30-nm thick PCSMO film on STO. At this thickness the transport behavior is completely insulating in our temperature range of measurement. Very different from the 40-nm device, the temperature dependent electroresistance curves follow parallel paths at different gate voltages for the 30 nm PCSMO on STO. Larger electroresistance was expected for this device because thinner films lead to larger contribution of the modulating channel to the device transport properties but quite contrary it was significantly reduced. It is important to note that the 30 nm PCSMO film showed no evidence of intrinsic phase separation. Our experiments

seems to suggest that it is much harder to electrostatically seed the FMM domains and modulate their growth in homogeneous insulating phase. In such systems the scale of electrostatic control of the various phases particularly in the glassy state depends on the intrinsic volume fraction of FMM phase and electrostatic doping works like a feedback mechanism.

Figure 4.7: Temperature dependent resistance measurements under various applied gate voltages -3 V, 0 V +3 V on 30- nm thick PCSMO film on STO. Only the measurements during the cooling cycle are plotted as there was no thermal hysteresis at this thickness for the temperature range of our experiment. Inset shows electroresistance as a function of temperature and gate voltage.

The thickness dependent gating measurements also showed us that the asymmetrical nature of electroresistance could be possible for other glassy states in strongly correlated oxide systems like cobaltates.

4.4 Summary

The transport behaviors of a strongly phase-separated manganite PCSMO under substrate strain were studied and a unique electrostatic modulation enhancement at the glassy state was found. Moreover, we observed that in this system the emergence of the magnetic glassy state at low temperatures is accompanied by reemergence of insulating behaviour.

Understanding the response due to external electrical stimuli on the magnetic glassy state should be taken in account while developing strategies toward future oxide based device applications. Our results also provide a guideline for exploring the magnetic glassy state in correlated electron oxides by means of electrostatic doping.

Chapter 5 : Terahertz conductivity across the phase transition in vanadium dioxide polymorphs

5.1 Introduction

5.2 Experiments

5.3 Results and Discussion

5.3.1 THz transmission of VO₂ polymorphs

5.3.2 Optical complex conductivity of VO₂(B) polymorph

5.3.3 Optical complex conductivity of VO₂(M1) polymorph

5.3.4 Construction of electronic phase diagram

5.4 Summary

5.1 Introduction

Vanadium dioxide can assume a number of polymorph variants exhibiting interesting physical phenomena such as metal-insulator transitions.^[26, 161-164] The diversity of polymorphism in this system offers a broad application in many technological fields such as optical switches, cathode material in batteries, high speed electronics, electro-chromic and thermo-chromic applications memory devices, solar cells, field emission displays etc.^[165-167] VO₂(M1) and VO₂(B) polymorphs are particularly attractive systems to study for the purposes of generating applications in technology due to two main reasons. First, they exhibit metal-insulator transition near room temperature and second accompanied with this electronic transition is a strong optical response esp. in the infrared region.

The structure of VO₂(M1) and VO₂(B) polymorphs are derived from an oxygen bcc lattice along with vanadium in the octahedral sites.^[25] In VO₂(M1), the oxygen octahedra

are aligned along two perpendicular axis while the in VO₂(B), the oxygen octahedra is primarily aligned in one direction.^[25] While VO₂(M1) and VO₂(B) are both monoclinic structures, there are subtle differences. The space group of VO₂(M1) is $P2_1/c$ (14) and the parameters of the monoclinic cell are $a = 5.75 \text{ \AA}$, $b = 5.42 \text{ \AA}$, $c = 5.38 \text{ \AA}$, $\beta = 122.6^\circ$, $Z = 4$.^[25] On the other hand, the space group of VO₂(B) $C2/m$ (12) with the cell parameters $a = 12.03 \text{ \AA}$, $b = 3.693 \text{ \AA}$, $c = 6.42 \text{ \AA}$, and $\beta = 106.6^\circ$, $Z = 8$.^[25, 168] The VO₂(M1) polymorph when heated up to 68°C undergoes a structural phase transition into rutile VO₂(R) phase. The parameters of the rutile cell are $a = b = 4.55 \text{ \AA}$, $c = 2.88 \text{ \AA}$, $Z = 2$; the space group is $P4_2/mmm$ (136).^[25] It is expected that the small value of β would lead to lower defects and grain boundaries. Also, it is important to note that there is no structural phase transition in VO₂(B) in the temperature range 10 K to 400 K.^[168] We will discuss the implications of these structure differences in the following paragraphs.

The structural phase transition in VO₂(M1) is intimately associated with a sharp electronic phase transition.^[26] Remarkably, VO₂(B), where there is no structural phase transition, also undergoes several orders of magnitude change in the conductivity.^[164] It is sufficed to say that a comparative study between these polymorphs may reveal new insights into the role and correlation between electronic and structural phase transition. The V-V dimerization plays a crucial role in understanding the nature of conductivity, and it is also relevant to compare these polymorphs in this context too. In the monoclinic insulating phase of VO₂(M1), V-V dimer pairs (of bond distances $\sim 2.65 \text{ \AA}$) are formed along the c-axis of the rutile lattice and consequently creating a large dimer-to-dimer distance ($\sim 3.12 \text{ \AA}$) along the V chain.^[169] This large dimer distance inhibits conductivity. However, in the rutile metallic state, VO₂(R) all the vanadium chains are straight with periodic V-V bond distances ($\sim 2.87 \text{ \AA}$).^[169] VO₂(B) on the other hand, does not show a significant variation of V-V distance as a function of temperature.^[168]

Understanding the electronic and optical response of $\text{VO}_2(B)$ is appealing on its own due to the novelty of the subject notwithstanding the intriguing comparisons with $\text{VO}_2(M1)$. Moreover, $\text{VO}_2(B)$ being metallic in room temperature is advantageous over $\text{VO}_2(M1)$ for certain industrial applications like materials for electrode design. While a lot of research work has been done to understand the origin of the metal-insulator transition in $\text{VO}_2(M1)$ by several optical techniques,^[170–181] there has been no previous study made on characterizing the metal-insulator transition in $\text{VO}_2(B)$. Let us discuss some of the important works done on $\text{VO}_2(M1)$ using THz-TDS first.

Figure 5.1: (a) Normalized THz transmission and phase shift curves averaged over the range 0.3–1.2 THz across the metal-insulator transition in the 160 nm thick $\text{VO}_2(M1)$ film grown on glass substrate. The transmission curves show significant thermal hysteresis. The dashed lines indicate sigmoidal fits to the observed data and the turning point of the sigmoidal fits are indicated by the arrow along with the temperature point. . [Taken from Jepsen *et al.* Phys. Rev. B. 74, 205103 (2006)] (b) Temperature dependence of THz conductivity in 100 nm thick $\text{VO}_2(M1)$ deposited on (100) rutile TiO_2 substrate. The green and the red lines are conductivities during the cooling and the warming cycle with the THz polarization is oriented parallel to the c_R -axis of the crystal. The blue and the brown curves represent the data taken when the THz polarization is oriented parallel to the b_R -axis of the crystal. [Taken from Abreu *et al.* New J. Phys. 14 083026 (2012)]

THz-TDS is a convenient method to investigate the electronic phases of these VO₂ polymorphs because the electronic phase transition is complemented by a parallel change in the optical response. THz -TDS was first used to study the metal-insulator transition in VO₂(M1) thin films by Jepsen *et al.* (Figure 5.1) and several THz-TDS on VO₂(M1) reports followed this work.^[182] THz conductivity study of VO₂(M1) revealed more information about the nature of phase transition over a traditional four-point DC conductivity measurement. The first order phase transition in VO₂(M1) was confirmed to be of percolating nature characterized by a phase separation scenario between sub-micrometre sized metallic and insulating phases. THz spectroscopy is capable of detecting conducting phases of nanometer length scales which remains undetectable by long-range transport measurements due to macroscopic spacing between the electrodes.^[182] By including several phase-separated conductivity models such as the effective medium theory (EMT) and the Drude-Smith scenario in the THz- TDS analysis, the knowledge of phase transition in VO₂(M1) has expanded.^[49] The popular EMT models used in analysis of VO₂ systems are Bruggeman EMT and the Maxwell-Garnett EMT.^[49, 182, 183] Another important finding was using THz-TDS to study the origin of conductivity anisotropy in strain engineered VO₂(M1) thin films by Abreu *et al.*^[184] In their report, they found that the MIT transition temperature along the c_R-axis of the crystal was at 365 K rather than 340 K, which is the structural transition temperature. They proposed Mott driven MIT along the along the c_R-axis of the crystal to explain the disagreements in the MIT values.

In our experiments, we make a systematic study of THz conductivities across the metal-insulator transition of 60-nm VO₂(B) thin films deposited on (001) SrLaAlO₄ (SLAO) substrate. There has been no previous report of THz study on this polymorph. The THz conductivity response are then compared with that of VO₂(M1) thin films also

deposited on SLAO substrate with similar thickness of 60-nm. By studying these measurements against standard frequency-dependent conductivity models, detailed nature of electronic phase transition can be known. The different electronic orders in these two vanadium dioxide can be distinctly separated from this study. The experimental results of this study have been published in Sci. Rep. 5, 9182 (2015).

5.2 Experiments

Single phase VO₂(*B*) and VO₂(*M1*) thin films were deposited on the SLAO (001) substrate using Pulsed Laser Deposition. A commercial Vanadium single crystal (100) orientated target for 5N purity from Goodfellow was used for ablation. The optimization conditions for the film growth were achieved by fixing the laser energy density at $\sim 2 \text{ J cm}^{-2}$ and the substrate temperature at 500 °C. Lower oxygen pressures $\sim 1 \times 10^{-4}$ Torr gave rise to single phase *M1* phase while higher oxygen pressures $\sim 7 \times 10^{-3}$ Torr stabilized the *B* phase. The oxygen background pressure influences the oxidation of vanadium both in the laser plume and on the substrate. Controlling the background oxygen pressure allows us to realize the thin films of the various vanadium dioxide polymorphs. Both films were prepared at a thickness of $\sim 60 \text{ nm}$ as determined from the Rutherford Backscattering spectra.

The 1D XRD spectra of VO₂(*B*) and VO₂(*M1*) thin films as grown on SLAO are shown in Figure 5.2(c) and (d) respectively. We observe that the XRD reflections of VO₂(*B*) are aligned in χ with the substrate (azimuthal angle, $\chi = 0$) whereas the VO₂(*M1*) phase reflections are not. This means that VO₂(*B*) thin film is highly oriented in *c* direction. For the VO₂(*M1*) films off-chi peaks at $2\theta = 27.89^\circ$ was assigned to (011) crystallographic plane and for the VO₂(*B*) film the peak at $2\theta = 29.05^\circ$ is assigned to (002) plane.

Figure 5.2: XRD patterns for (a) $\text{VO}_2(\text{B})$ and (b) $\text{VO}_2(\text{M1})$ thin films. Phase reflections of $\text{VO}_2(\text{M1})$ are not aligned in χ with SLAO substrate and there are no peaks at $\chi = 0$. Temperature-dependent resistivity curves for (c) $\text{VO}_2(\text{B})$ and (d) $\text{VO}_2(\text{M1})$ thin films. AFM images of (e) $\text{VO}_2(\text{B})$ and (f) $\text{VO}_2(\text{M1})$ in a scan area of $5 \times 5\ \mu\text{m}^2$.

Temperature-dependent electrical transport measurements of both films were done in four point geometry inside Physical Property Measurement system (Quantum Design). As

shown in Figure 5.2(d), the temperature-dependent resistivity of VO₂(M1) show an abrupt MIT at 340 K with four orders of magnitude change. In comparison, the VO₂(B) show a broad MIT manifested in four orders of resistivity change as the temperature varies from 400 K to 160 K (Figure 5.2(c)). These results are consistent with previous reports on these VO₂ polymorphs.^[26, 164] For the VO₂(B) film there is a weak thermal hysteresis at low temperatures below 240 K while for the VO₂(M1) the hysteresis is notable around 340 K.

The morphology at the surfaces of the VO₂(B) and the VO₂(M1) films were characterized using an atomic force microscope (AFM, Dimension V, Veeco). The VO₂(M1) have larger surface roughness with the RMS value of ~2.61 nm, while for VO₂(B) the RMS roughness value falls to ~0.98 nm.

The complex refractive indices of SLAO substrate in our operational THz range are determined by performing the THz-TDS experiments with reference to the vacuum. This step is necessary in order to determine the THz conductivities of the film. Figure 5.3 shows the complex refractive index, $\tilde{n}_{sub}$ of SLAO substrate in the THz frequency range at select temperature points. The values are found to vary little with temperature and frequency. The data for $\tilde{n}_{sub}$ at a particular temperature was used to determine the optical conductivity at that temperature.

Figure 5.3: (a) Real and (b) imaginary parts of the complex refractive index of SLAO in the THz range.

The THz-TDS measurements for the VO_2 thin films were then performed using SLAO substrate as the reference. Figure 5.4(a) shows electric field signal of $\text{VO}_2(B)$ and $\text{VO}_2(M)$ films deposited on SLAO in the time-domain. Only the main THz pulse was considered for subsequent analysis and the weaker etalon pulse appearing due to multiple reflections inside the substrate was truncated. For the 1 mm thick SLAO substrate, the main pulse and the etalon pulse are well separated in time domain and this allows for easy truncation of the etalon pulse without loss of relevant information. The amplitude and the phase of the THz transmission of the VO_2 polymorphs were determined by performing Fast Fourier Transform (FFT) on the time domain THz signals.

Figure 5.4: (a) Raw THz electric field waveform transmitted through (a) VO₂(B) at 295 K (b) VO₂(M1) at 297 K and (c) VO₂(R) at 352 K. The bottom panels in (a), (b) and (c) show the corresponding difference subtracted from the substrate.

5.3 Results and Discussions

5.3.1 THz transmission of VO₂ polymorphs

The THz transmittance, $T(\omega)$ is the ratio of the THz electric field waveform of the sample (film+substrate), $\tilde{E}_s(\omega)$ to the reference (bare substrate), $\tilde{E}_r(\omega)$. Figure 5.5(a) and (b) shows the transmittance amplitudes of VO₂(B) and VO₂(M1) films respectively as a function of frequency and temperature. The transmittance amplitude of the VO₂ films in the insulating state is close to unity. After VO₂(M1) film undergoes phase transition to the R phase there is significant absorption in the transmittance as shown in Figure 5.4(c). The bottom panels of Figure 5.4 represent the corresponding difference in the THz waveform $\Delta E(t)$ between the sample and the reference. For VO₂(B) film, as the temperature is steadily increased, there is more and more THz absorption, the absorption onset is ~ 240 K. However, for VO₂(M1) film there is a sharp THz absorption around ~ 340 K which is quite distinct from the steady THz absorption in VO₂(B) as a function of temperature. Within our THz frequency range, there are no observable phonons in both VO₂ polymorphs. The frequency-dependent complex refractive indices ($\tilde{n} = n + i\kappa$) of the films are determined from the experimental transmittance $T(\omega)$ by fitting to the

formula^[185, 186]

$$T(\omega) = \frac{2\tilde{n}(\tilde{n}_{sub}+1)\exp[\frac{i\omega d(\tilde{n}-1)}{c}]\exp[-\frac{i\omega\Delta L(\tilde{n}_{sub}-1)}{c}]}{(1+\tilde{n})(\tilde{n}+\tilde{n}_{sub})+(\tilde{n}-1)(\tilde{n}_{sub}-\tilde{n})\exp[\frac{2i\omega d\tilde{n}}{c}]} \quad (5.1)$$

where ΔL is the difference in the thickness of the sample and reference substrates, d is thickness of the film, $\tilde{n}$ and $\tilde{n}_{sub}$ are the complex refractive indices of film and substrate, respectively, and c is the speed of light in vacuum. Multiple internal reflections inside the film are accounted for in this equation.

Figure 5.5: Frequency and temperature-dependent transmittance of (a) VO₂(B) and (b) VO₂(M1) thin films grown on SLAO.

The complex conductivity $\tilde{\sigma} = \sigma_1 + i\sigma_2$ of the films can be calculated by using the complex refractive indices in the following relations—

$$\sigma_1(\omega) = 2n\kappa\omega\epsilon_0 \quad (5.2)$$

$$\sigma_2(\omega) = (\epsilon_\infty - n^2 + \kappa^2)\omega\epsilon_0 \quad (5.3)$$

where ϵ_0 is the permittivity of free space and ϵ_∞ is the high frequency dielectric constant. For VO₂(B), ϵ_∞ is initialized to 1 as it was an unknown quantity while for VO₂(M1) it was initially set to 9 based on previous reports.^[187, 188] After determining the complex conductivities of the films, ϵ_∞ is used as a temperature-dependent parameter in fitting the conductivity data.

5.3.2. Optical complex conductivity of VO₂(B) polymorph

We will discuss the temperature dependent THz conductivity of VO₂(B) first and followed by that of VO₂(M1). The temperature-dependent complex conductivities in the THz frequency range of VO₂(B) films are shown in Figures 5.6 (a) and (b). $\sigma_1(\omega)$ is undetectable below 240 K because the transmission is $\sim 100\%$, which means that the system is a purely insulating state. 240 K marks the onset of positive $\sigma_1(\omega)$ indicating the transition from an insulating state towards a conducting one. As the temperature in the system is gradually increased, $\sigma_1(\omega)$ also increases. The temperature dependent $\sigma_1(\omega)$ of VO₂(B) has a maximum at the lowest THz frequency which gradually decreases with increasing frequency. On the other hand, $\sigma_2(\omega)$ is zero at the lowest frequency and grows with increasing frequency. This trend is a clear signature of a Drude response in the system.

As discussed in Chapter 1, equation 1.9 is our Drude equation which we restate here and is given by

$$\tilde{\sigma} = \frac{\epsilon_0 \omega_p^2}{\gamma - i\omega} - i\epsilon_0 \omega (\epsilon_\infty - 1)$$

where ω_p is the plasma frequency, γ is the free carrier scattering rate. $\sigma_1(\omega)$ and $\sigma_2(\omega)$ curves for each temperature point are simultaneously fitted to the above equation as shown in in Figures 5.6(a) and (b). The fitted curves are shown by the dash red lines and are reasonably good. Although $\sigma_1(\omega)$ is relatively featureless as a function of frequency, simultaneously fitting both $\sigma_1(\omega)$ and $\sigma_2(\omega)$ to the complex Drude equation significantly reduces the range of the error bars in the fitting parameters, γ and ω_p .

Figure 5.6: Temperature-dependent (a) real and (b) imaginary conductivities of VO₂(B) thin films grown on SLAO. The red dash lines indicated the Drude fit lines.

Both ω_p and γ show similar temperature dependence. The plots of temperature-dependent Drude parameters are shown in Figure 5.7(a) and (b). As the temperature is gradually increased these fitting parameters also increase but only up to ~ 280 K. Beyond this temperature their values approach saturation. We can see that temperature regions $240 \text{ K} \leq T \leq 280 \text{ K}$, and $280 \text{ K} < T \leq 400 \text{ K}$ have quite different conductivity behaviours. We label these temperature intervals as conductivity regimes I and II respectively.

The relationship of ω_p and γ with carrier density and mobility has been discussed in chapter 1. The dc conductivity σ_0 can also be obtained from these parameters and is given by the expression $\sigma_0 = \frac{\epsilon_0 \omega_p^2}{\gamma}$. The temperature dependence nature of σ_0 is illustrated by

Figure 5.7(c). In regime I, all three parameters: $\omega_p/2\pi$, γ and σ_0 show positive slope w.r.t. temperature variation, while in regime II these parameters are almost temperature independent.

Figure 5.7: Temperature-dependent (a) plasma frequency, (b) scattering rate, and (c) calculated dc conductivity of VO₂(B) thin films grown on SLAO. (d) Logarithmic plot of dc conductivity determined from (c) vs reciprocal temperature along with the linear fittings. The dashed lines separates conductivity regimes I and II.

The dc conductivity is useful in calculating the thermal activation energy, E_a and which is related to temperature by the following expression

$$\ln \sigma_0 = A - \frac{E_a}{k_B T} \quad (5.4)$$

where k_B is the Boltzmann constant. By fitting σ_0 to the above equation we get the values of activation energies in regime I and II as E_a (regime I) = (260 ± 30) meV, and E_a

(regime II) = (47 ± 3) meV respectively where k_B is the Boltzmann constant. Figure 5.7(d) shows the plot of $\ln \sigma$ vs $1000/T$ along with the linear fits. The presence of small activation energy in regime II indicates that even at high temperatures VO₂(B) is not purely metallic. The large difference between the activation energies of regimes I and II is consistent with our claim that the conductivity mechanisms of VO₂(B) in these temperature regimes are quite different. Even though fitting in regime I is not as perfect as that of II, it does not counter the observation that there are two different conductivity regimes. It merely means there is carrier conduction cannot be fully described by simple thermal activation. The different temperature-dependent electronic states of VO₂(B) can be understood as follows— (i) below 200 K, VO₂(B) is completely insulating showing 100% transmission, (ii) conductivity regime I ($240 \text{ K} \leq T \leq 280 \text{ K}$) is an intermediate state in the electronic phase transition with poor conductivity, larger activation energy and temperature-dependent Drude parameters, (iii) conductivity regime II ($280 \text{ K} < T \leq 400 \text{ K}$) is the highly conducting state of VO₂(B) after the transition is completed with much smaller activation energy. Thus we can see that the electronic phase boundaries in VO₂(B) can be more clearly understood using THz-TDS compared to tradition dc transport measurements where the phase boundary is not that apparent.

5.3.3 Optical complex conductivity of VO₂(M1) polymorph

The temperature-dependent complex conductivities of 60 nm thick VO₂(M1) film grown on SLAO in the THz frequency range are shown in Figure 5.8. The onset temperature of positive $\sigma_1(\omega)$ for VO₂(M1) is 343 K and it increases with temperature. Previous THz conductivity reports on VO₂(M1) films have revealed that the conductivity follows a Drude-Smith model.^[49] As expected $\sigma_1(\omega)$ of VO₂(M1) is larger at higher frequencies, while $\sigma_2(\omega)$ is zero at the lowest frequencies and with increasing THz frequency becomes negative first and then crosses over to positive values. This behavior

is consistent with a Drude-Smith model.

As discussed in Chapter 1, the Drude-Smith model can describe percolating transport and hence can describe the conductivity nature of VO₂(M1) phase separation and percolating network determine electronic pathways. The Drude-Smith model is described by equation (1.9) and is given by

$$\tilde{\sigma} = \frac{\epsilon_0 \omega_p^2}{\gamma - i\omega} \left[1 + \sum_j \frac{c_1 \gamma_j}{\gamma - i\omega} \right] - i\epsilon_0 \omega (\epsilon_\infty - 1)$$

where c_1 represents the backscattering events. The physical interpretation of c_1 have already been discussed in detail in Chapter 1. Besides the Drude-Smith model, it is important to discuss the effective medium theory (EMT) models which have also been used to describe THz conductivities of VO₂(M1) with relative success.^[49, 182, 183] As we have mentioned in the preceding paragraphs, there are two popular models with the EMT framework that has been used to describe the conductivity behaviour of VO₂(M1). These are Bruggeman effective medium theory (BG-EMT) and Maxwell Garnett effective medium theory (MG-EMT).^[182, 183] However, these models were not able to give accurate description of the experimentally observed values. The conductivity behaviour of VO₂(M1) can only be described properly by the Drude-Smith formalism. Cocker *et al.* also found that Drude-Smith is a more suitable model over EMT in systems where the grain boundaries of the film persist even when the system has a significantly large conducting fraction.^[49] Figures 5.8 (a) and (b) show real and imaginary conductivities for VO₂(M1) film grown on SLAO respectively along with Drude-Smith fittings (red solid lines) for warming cycle. Figures 5.8(c) and (d) show $\sigma_1(\omega)$ and $\sigma_2(\omega)$ of VO₂(M1) for the cooling cycle. The Drude-Smith model gave excellent fits to the experimental conductivities of $\sigma_1(\omega)$ and $\sigma_2(\omega)$ of VO₂(M1).

Figure 5.8: Complex conductivities of VO₂(M1) thin film grown on SLAO during the cooling cycle (a),(b) and during the warming cycle (c),(d). The red solid lines are the simultaneous complex fitting using the Drude-Smith model at each temperature.

While at temperatures far above 340 K, VO₂(M1) is expected to be metallic the frequency-dependent conductivities do not follow an ideal Drude behaviour as evidenced by the non-zero value of c_1 . The VO₂(M1) thin film is highly granular and its quite likely that the nanogranular boundaries persist even after the transition which may give rise to non-ideal Drude behaviour even at high temperatures. In scenarios where grain boundaries persist even at significant conducting fractions, it has been argued that the Drude-Smith provides a better description than the EMT models.^[49, 189]

We observe thermal hysteresis in the optical conductivities of VO₂(M1). We will describe the conductivity in the warming cycle unless otherwise stated. Figure 5.9 shows

temperature-dependent plots of ω_p , γ , σ_0 and c parameters obtained from the Drude-Smith fittings of complex conductivities of VO₂(M1). The dc conductivity σ_0 , in this case, is given by the modified equation, $\sigma_0 = \frac{\epsilon_0 \omega_p^2 (1+c)}{\gamma}$. Analogous to our earlier analysis of VO₂(B), we can define conductivity regime I as the temperature range of 343 K–349 K and conductivity regime II as 352 K–400 K based on the temperature dependence nature of ω_p , γ and σ_0 . The plasma frequency, the scattering rate, the fitting parameter c and the dc conductivity increase with increasing temperatures in conductivity regime I; while in regime II they remain largely temperature-independent. The large negative values of c are due to substantial carrier backscattering which results in suppression of low-frequency conductivities.^[50, 52, 190] The temperature-dependent nature of fitting parameter c in conductivity regime I supports the percolation scenario in VO₂(M1).^[189] Inset of figure 5.9 (c) is the plot of logarithmic dc conductivity, $\ln(\sigma_0)$ versus reciprocal temperature, $1000/T$. The activation energies of VO₂(M1) in the two temperature regimes can be determined from the slope of the linear fitting. In the low-temperature conductivity regime I, the activation energy E_a of VO₂(M1) is (2200 ± 500) meV while in the high-temperature conductivity regime II, E_a is (20 ± 8) meV. The energy difference between E_a (regime I) and E_a (regime II) is much larger in VO₂(M1) compared to that in VO₂(B). This is consistent with the observations in the Drude parameters where the temperature dependence slope of ω_p and γ is steeper in VO₂(M1) compared to VO₂(B).

Figure 5.9: Temperature-dependent (a) the plasma frequency (b) the scattering rate and (c) calculated dc conductivity and (d) back scattering parameter for VO₂(M1) films grown on SLAO during the warming cycle. The inset of (c) shows the logarithmic plot of σ_0 vs reciprocal temperature. The dashed lines separates the conductivity regimes I and II of VO₂(M1)

Conductivity regime I, which is the intermediate state in the phase transition of VO₂(M1) is quite rich in physics showing a substantial enhancement of the carrier effective mass, m^* (as large as $5m_e$.) in this region from the interpretation of the infrared conductivity spectra.^[175, 191] In the metallic (R) state (at $T \sim 350$ K), m^* is reported to be close to $2m_e$.^[188] Assuming $m^* = 2m_e$, in the metallic (R) phase, we obtain the carrier density of our VO₂(M1) thin film to be $\sim 3.6 \times 10^{20} \text{ cm}^{-3}$. We can also determine the carrier mobility from the relation $\gamma = \frac{(1+c)e}{m^*\mu}$ which is the modified in order to take into account the carrier backscattering parameter. The carrier mobility μ is determined to be $11.35 \text{ cm}^2/(\text{V}\cdot\text{s})$ at $T = 352$ K for VO₂(M1). Our values of carrier density

and mobility are quite close to the previous THz-TDs reports on this material.^[49, 183] On the other hand, Hall Effect measurements, at this temperature, reported lower values of mobility although the values of carrier density are quite similar.^[192] This disagreement is not unexpected because Hall measurement is a DC measurement method while THz-TDS is an AC method. Also, Hall measurements unlike THz spectroscopy may give unreliable results at low-mobilities.^[193] In a contact technique like Hall Effect charge carriers to traverse long distances (in the order of μm or more) across the biased electrodes. In contrast, THz-TDS technique gives conductivity information of carriers traversing in sub-pico second timescales and can be considered as ‘conductivity snap-shots’.^[193] As such carrier trapping scenario is far less likely in THz-TDS and the mobility determined from this technique represents the upper limit of the system under consideration. Carrier density and the mobility parameters of VO₂(*B*) can also be compared with that of VO₂(*M1*) by assuming $m^* = 2m_e$. For VO₂(*B*), at $T = 295$ K, the calculated values are $N \approx 6.4 \times 10^{19} \text{ cm}^{-3}$ and $\mu \approx 21.9 \text{ cm}^2/(\text{V}\cdot\text{s})$.

The contributions from granular origin of phase transition and intrinsic inhomogeneities in VO₂(*M1*) give rise to its non-ideal Drude conductivity. But, there is no evidence of phase separation or inhomogeneities in VO₂(*B*) from the THz measurements which explains why it has excellent Drude fittings. The conductivity of VO₂(*B*) which can be described by a simple Drude model, is surprisingly lower than that of VO₂(*R*) which does not have an ideal Drude conductivity behaviour. This uncommon difference in the electronic nature can be explained in two-fold — first, VO₂(*B*) is an epitaxial grown films with negligible grain boundaries resulting in no carrier backscattering. The surface of VO₂(*M1*) on the other hand, is much rougher as seen from the AFM images in Figure 5.2(e) and(f) due to the presence of grain boundaries. The large roughness can be attributed to the larger β inter-axial angle which impedes epitaxial growth. Second, VO₂(*B*) has larger

activation energy compared to VO₂(R) which means that the barrier of thermal activation of carriers in VO₂(B) is higher. When VO₂(M1) undergoes transition to VO₂(R) the contribution from the backscattering parameter c is reduced indicating the role of grain boundaries in carrier transport is lessened.

5.3.4 Construction of electronic phase diagram

We have already discussed that the narrow intermediate conductivity regime I in VO₂(M1), is a strongly correlated phase and it displays unique properties such as mass enhancement and an optical pseudo-gap in the infrared range.^[175, 176, 191, 194] It is quite likely that the intermediate state of VO₂(B), may also be described by strong electronic correlations. We also performed THz-TDS experiments on another VO₂ polymorph, VO₂(A) and found it to be completely insulating in the THz frequency range and in the operational temperature regime. Single phase tetragonal epitaxial VO₂(A) thin film on SLAO was prepared using PLD. The thickness was kept the same at 60-nm for this film too. The main findings of THz spectroscopy study on these various VO₂ polymorphs can be summarized by plotting their electronic phase diagrams as shown in Figure 5.10.

Figure 5.10: Electronic phase diagram of (a)VO₂(B), (b) VO₂(M1), and (c) VO₂(A) thin films fabricated on SLAO. The blue colored regions represent the insulating phases, while the orange colored regions represent the highly conducting phase. The intermediate phase is represented by the blue and orange gradient region. The conductivity regimes I and II

are also indicated in the phase diagram.

5.4 Summary

One of the key results in our THz-TDS is the characterization of the MIT in VO₂(M1) and VO₂(B). The central results in the comparison of these polymorphs can be summarized by the following table.

	<i>VO₂ (B)</i>	<i>VO₂ (M)</i>
Conductivity model	Drude	Drude-Smith
MIT- Transition gap	50 K	6 K
Height of MIT	4 orders of conductivity change	5 orders of conductivity change
THz modulation	Analog-like	Digital like
Phonon resonance modes	None (0 to 2.5 THz)	None (0 to 2.5 THz)
Percolating behavior	No evidence	Strong evidence

Table 5-1: Summary of the comparative THz study between the polymorphs VO₂(B) and VO₂(M1)

VO₂(B) undergoes a broad MIT with the onset of conducting behaviour much closer to room temperature and hence it may be more suitable for optoelectronic devices at *room temperature operation* than the well-known VO₂(M1). These VO₂ polymorphs can also be used as THz modulators tuned by temperature. VO₂(M1) which undergoes a sharp phase transition is more desirable for digital-like THz modulation^[195], while VO₂(B) with its the broad phase transition is more suitable for analog-like THz modulation. THz spectroscopy is a viable technique for studying phase transitions and polymorphism in materials.

Chapter 6 : Ultrafast control of phase transition in vanadium dioxide

6.1 Introduction

6.2 Experiments

6.3 Results and Discussion

6.3.1 Temperature and fluence dependent studies of transient reflectivities of $\text{VO}_2(B)$ polymorph

6.3.2 Transient reflectivities of $\text{VO}_2(B)$ at temperatures above 300 K

6.3.3 Photoinduced phase diagram of $\text{VO}_2(B)$

6.4 Summary

6.1 Introduction

Traditionally, femtosecond optical spectroscopy is widely used in condensed matter physics because of its ability to probe at the fundamental timescales of electronic motion and to disentangle electronic and structural phenomena.^[56, 196-198] Investigating the dynamics of carriers in several material systems such as semiconductors, metals and strongly correlated systems, has led to dramatic increase of our scientific understanding on electronic transport, electron–electron and electron–phonon scattering processes, dynamics of quasiparticles and Cooper pairs, precessional magnetization dynamics, and the role of charge, spin, and lattice degrees of freedom.^[54, 56, 199-201]

This chapter discusses time-resolved studies of carrier dynamics in VO_2 with particular relevance to metal-insulator transitions (MIT). In MIT systems such as VO_2 , there are two important issues in the research community. First, it's to determine the

speed of MIT and second the ability to tune the transition. To address these issues, ultrafast pump-probe technique has been the first choice for researchers ever since light induced insulator-to-metal phase transition has been observed in VO_2 .^[177, 202] Some of the reasons that study of light induced phase transition (PT) is very attractive are— i) its reversible, ii) non-destructive, iii) non-contact method and iv) can create transient states of matter. Some of the select examples of phase transitions induced by light irradiation include systems such as, KMnO_3 , NdNiO_3 , magnetites, etc.^[203-208] It has been proven that light can change not only the electronic order but can also modify/destroy charge and orbital orders.^[196, 200, 209, 210]

Figure 6.1: (a) Pump-probe reflectivity experiments on $\text{VO}_2(\text{M1})$ using variable pulse compressions. (b) Photoinduced phase transition as a function on pulse width. [Taken from Cavalleri *et al.*, Phys. Rev. B 70, 161102(R) (2004)] (c) Transient reflectivity at pump wavelength 800 nm with variable fluence. Transient reflectivity below 7 mJ cm^{-2} pump threshold are represented by the blue lines while, those above by the red lines. (d) Fourier transforms of the transient reflectivity curve (d) at 1.7 mJ cm^{-2} (below threshold) and (e)

24 mJ cm⁻² (above threshold). Solid lines indicates fitting to Lorentz oscillators. [Taken from Wall *et al.* Nature Comm. 3, 721 (2012)]

There have been quite a handful of experimental reports using ultrafast pump-probe spectroscopy to study the physics of phase transition in the well-known VO₂(*M1*).^[81, 176-179, 202, 211-213] Table 6.1 describes some of these results along with the differences in the sample quality and phase transition time. While these reports undeniably indicate that the pump laser can act a driving force to induce non-thermal phase transition, the timescales and the origin of the transition is disputed. The first femtosecond dynamics study on this VO₂ polymorph was done by Cavalleri *et al.* where they reported structural phase transition due to photoexcitation.^[202] In this report as well as other follow-up ones, it was claimed that a simultaneous photoinduced structural phase transition is essential for photoinduced insulator to metal transition in VO₂. In this case, above certain laser fluence, photoexcitation disturbs the lattice potential of the monoclinic (*M1*) crystal structure and initiates a non-thermally structural transition into the tetragonal rutile phase on an ultrafast timescale. The crucial arguments in this line of reasoning were— i) observation of a minimum rise-time of 80 fs as the ‘structural bottleneck’ and ii) the loss of the equilibrium-phase phonon.^[177] Cavalleri *et al.* observed that the phase transition rate become progressively faster by compressing the pulse durations but below 80 fs, the transition rate saturated.^[177] By taking Fourier transform of the transient reflectivity of VO₂(*M1*) at various fluences, Wall *et al.* found that below the fluence threshold, there are four Raman active modes corresponding to V-V dimerization while above the fluence threshold, these phonons are lost leading to a broad feature.^[81]

VO ₂ (M1) sample details	Laser pump source for triggering MIT	Phase transition time	Reference
32 nm thick films grown by sputtering	780-nm Ti: sapphire laser	~5 ps	[214]
200 nm thick films on glass substrate	800-nm 50-fs Ti: sapphire laser	100 fs to 50 ps	[202]
50 nm thick films on Si with Si ₃ N ₄ buffer layer	790 nm (15-100) fs Ti: sapphire laser	75 fs to 454 fs	[177]
Grown on sapphire, MgO and glass substrates by PLD with thicknesses 20 to 500 nm	400-nm 130-fs 50-Hz Ti: sapphire laser	1 ps to 1 ns	[215]

Table 6-1: Ultrafast switching of MIT in VO₂(M1) from various OPOP experimental results.

However, in a recent report, Wegkamp *et al.* argued using time-resolve photoelectron spectroscopy that photo-excitation of the insulating state can lead quasi-instantaneously to a metal followed by structural transformation.^[216] This excludes the aforementioned 80 fs structural bottleneck of VO₂(M1) as they reported that the quasi metallic state does not require initiation by a structural phase transition. Further, Hsieh *et al.* 's work on ultrafast excitation under high pressure reported that the lattice symmetry remains robust while the system undergoes photoinduced IMT and attributed it to a collapse of Mott gap due to photo-excitation of carriers.^[213] As strong electron-electron interactions of Mott behaviour and the structurally driven phase transition representing Peierls instability are closely

connected in vanadium dioxide, it is possible that both mechanisms of photo induced phase transitions are coupled together. At the current stage, a complete theoretical explanation of the photoinduced phase transition in vanadium dioxide is lacking. Other techniques used in understanding photoinduced phase transition in $\text{VO}_2(M1)$ include terahertz pump-probe, time-resolved X-ray diffraction and four dimensional ultrafast electron microscopy.^[178, 217, 218]

Figure 6.2: (a) Change of photoemission of $\text{VO}_2(M1)$ as a function of pump delay close to Fermi energy. In this experiment, photoelectrons are detected immediately in the band gap, indicating quasi-instantaneous metallic phase. (b) Temporal evolution of integrated photoemission intensity below (green) and above (purple) Fermi level. [Taken from Wegkamp *et al.* Phys. Rev. Lett. 113, 216401 (2014)]. (c) Transient reflectivity of $\text{VO}_2(M1)$ as a function of applied pressure. A 400 nm pump of fluence $\sim 3.6 \text{ mJ cm}^{-2}$ was used in this case. (d) Fourier transforms of the transient reflectivity curves of (c). The two A_g phonon modes at ~ 5.8 and ~ 6.8 THz which corresponds to the $M1$ phase was consistently observed. [Taken from Hsieh *et al.* Appl. Phys. Lett. 104, 021917 (2014)]

We have discussed the large volume of reports available on the ultrafast non-thermal phase transition in $\text{VO}_2(M1)$. However, there is no ultrafast pump-probe study done on $\text{VO}_2(B)$ so far. In this chapter, we will discuss the ultrafast dynamics on this polymorph and compare the similarities and the differences with the literature reported on the

VO₂(M1) polymorph. Clearly, on the main motivation of this study is the charm of controlling of MIT transition by light which is an appealing quality for both pure scientific pursuit of understanding MIT and technological applications demanding high speed switching. The OPOP results on VO₂(B) is being under consideration for being published in a journal.

6.2 Experiments

60-nm thick VO₂(B) thin films were fabricated by Pulsed Laser Deposition under optimal growth conditions as described in the previous chapter. For the pump-probe measurements, the films were grown on specially fabricated Si substrate that comes with 20-nm buffer layer of SrTiO₃ (SiSTO).

The detailed set-up of the optical pump-probe experiments has been described in Chapter 2. The source of both pump and probe beams was a sub-50 fs pulse beam with a center wavelength of 800 nm. To improve the signal to noise, the pump and probe pulses were cross polarized. The beam diameter of the probe beam was set to ~25 μm while the pump beam was focused to a much larger area with diameter of ~50 μm . This configuration ensures a good pump-probe overlap. We systematically designed temperature and fluence dependent transient reflectivity measurements on VO₂(B) thin film. The sample was mounted on a continuous flow cryostat which can go down up to 4 K. During the fluence dependent measurements, care was taken that only the probe power was steadily increased and no other parameters in the experiment was changed including the the probe power. All sets of transient reflectivity measurements were made up for a pump-probe delay up to 1400 picoseconds (ps).

We also performed absorbance spectrum measurements in the range 220–900 nm with the help of commercial UV-Vis spectrophotometer (Jasco, Model V-650).

6.3 Results and Discussion

6.3.1 Temperature and fluence dependent studies of transient reflectivities of VO₂(B) polymorph

Figure 6.3: Transient differential reflectivity $\Delta R/R$ spectra for VO₂(B) films on SiSTO as a function of temperature. A pump pulse of fluence of $\sim 1.15 \text{ mJ/cm}^2$ at 800 nm was used. Log plot of $\Delta R/R$ vs. time at the same fluence for temperatures— (b) 100 K and (c) 300 K shown along with the bi-exponential fitting. The black arrows pointing down indicates, t_p the delay time at the maximum value of $\Delta R/R$.

We will first discuss the temperature-dependent pump-probe measurements on VO₂(B) thin films fabricated on SiSTO for the pump fluence of $\sim 1.15 \text{ mJ/cm}^2$. The transient reflectivity for a pump-probe delay up to 25 ps in the temperature range 100 K – 300 K is shown in Fig 6.3(a). We clearly observe two different dynamics as a function of temperature. In the temperatures range 100 K – 160 K, there is a sharp initial positive peak followed by decay dynamics. At temperatures above 160 K, after the rising edge in $\Delta R/R$ brought by the pump pulse, the differential reflectivity increases (may last up to several ps) instead of decreasing. The differential reflectivity eventually goes through a slow decay. This dissimilar dynamics for $T < 160 \text{ K}$ and $T \geq 220 \text{ K}$ can only be explained by the different electronic phase of VO₂(B) at low temperature (insulating) and at high temperature (metallic). Detailed electrical and optical characterization of metal-insulator

transition in $\text{VO}_2(B)$ was already described in Chapter 5. We will try to understand these dynamics by fitting to a two-temperature exponential model.

For a particular temperature and fluence, the carrier dynamics of $\text{VO}_2(B)$ on SiSTO can be described by fitting the transient reflectivity to the following exponential equation

$$\frac{\Delta R}{R} = Ae^{-t/\tau_1} + Be^{-t/\tau_2} + C \quad (6.1)$$

where τ_1 and τ_2 are respectively the fast and slow characteristic time in the carrier dynamics. The constant C represents the long-lived dynamics in the experiment. Figs 6.3(b) and (c) show the fitting results at 100 K and 300 K respectively using the equation described above. At 100 K $\text{VO}_2(B)$ is insulating, while at 300 K, it is metallic and we can clearly observe two different dynamics at these temperatures. Similar fitting analyses were also done at other temperature points. The following paragraphs are on the discussion of the fitting results.

The nature of the coefficient, A in the insulating and the metallic phase is clearly distinguishable. At high temperature metallic state ($T \geq 220$ K), A assumes negative values, while at lower temperature insulating state ($T < 160$ K), it is positive. Moreover, the fast characteristic time τ_1 signifies decay dynamics in the insulating state, while in the metallic state, it represents growth dynamics. It is important to mention here that this growth in the transient reflectivity has been previously reported in $\text{VO}_2(M1)$ and has been described as a well-known feature for photoinduced metallic state.^[179, 219] The insulating state of $\text{VO}_2(M1)$, on the other hand, has a sharp peak followed a rapid decay in the transient reflectivity signal when excited by pump-fluence lower than the threshold.^[212, 219] This feature bears a close resemblance with our transient reflectivity observations for $T < 160$ K at pump fluence $\sim 1.15 \text{ mJ/cm}^2$. However, the slow characteristic time τ_2 exists for all temperatures in our operational range. The values of τ_2 range from 300 to 4000 ps. In order to highlight the nature of the growth dynamics we have defined a parameter t_p , as

the optical delay where $\Delta R/R$ is maximum and are shown in Figs. 6.3 (b) and (c) by the black down arrows. In the insulating state of $\text{VO}_2(B)$, t_p has values in the sub-ps, while in the metallic state, it is in the order of a few ps can be as large as ~ 30 ps. More discussion on the fitting parameters and t_p will be done in the subsequent sections.

Figure 6.4: Transient differential reflectivity $\Delta R/R$ spectra for $\text{VO}_2(B)$ at pump fluences (a) $\sim 1.8 \text{ mJ/cm}^2$ and (b) $\sim 3.45 \text{ mJ/cm}^2$ with variable temperature. Fluence-dependent, $\Delta R/R$ at fixed temperatures— (c) 150 K and (d) 300 K.

The pump-probe reflectivity experiments were repeated at other excitation fluences— 1.8 mJ/cm^2 and 3.45 mJ/cm^2 . Figs. 6.4 (a) and (b) show the transient reflectivity, $\Delta R/R$ for 1.8 mJ/cm^2 and 3.45 mJ/cm^2 respectively in the temperature range 100 K–300 K. At 1.8 mJ/cm^2 fluence, the sharp decay dynamics is observed for $T < 140 \text{ K}$, while at higher temperatures it showed growth dynamics. At 3.45 mJ/cm^2 fluence, the sharp decay dynamics cease to exist and only the growth dynamics was observable within the 25 ps delay.

Next, we will discuss the fluence-dependent transient reflectivity results of $\text{VO}_2(\text{B})$ at a fixed temperature. Fig. 6.4 (c) shows $\Delta R/R$ for $\text{VO}_2(\text{B})$ obtained by varying the pump fluences from 0.46 to 4.6 mJ/cm^2 at 150 K. At this temperature, the sharp positive peak of $\Delta R/R$ was observable only for fluences 0.46 mJ/cm^2 and 1.15 mJ/cm^2 , but for higher fluences, the growth dynamics appeared. Fluence-dependent $\Delta R/R$ at 300 K was also performed as shown in Fig. 6.4(d). At 300 K, $\text{VO}_2(\text{B})$ is already in the metallic state and as expected for all pump fluences at this temperature, the growth dynamics was apparent.

Figure 6.5: Temperature-dependent values of (a) A , (b) t_p , (c) τ_1 and (d) τ_2 for $\text{VO}_2(\text{B})$ at three different fluences— 1.15, 1.8 and 3.45 mJ/cm^2 . The bi-exponential fitting of the transient reflectivity curves in Fig 6.3, 6.4 gave the values of A , τ_1 while t_p is the pump-probe delay at the largest value of $\Delta R/R$. The line, $A=0$ is also shown in (a).

Fig. 6.5 shows (a) A , (b) t_p , (c) τ_1 , and (d) τ_2 as a function of temperature determined from the transient reflectivity measurements. While the nature of τ_2 as a function of temperature is ambiguous and seems largely temperature independent, the

other three parameters, support a consistent scenario. The coefficient A changes from positive to negative for pump fluences 1.15 and 1.8 mJ/cm². The negative onset of A for 1.15 mJ/cm² is 180 K, while for 1.8 mJ/cm² it is 140 K. For 1.15 mJ/cm² fluence, at $T \geq 180$ K, τ_1 represents growth characteristic time, while for 1.8 mJ/cm², the growth dynamics starts from 140 K. On the other hand, for the fluence of 3.45 mJ/cm², the coefficient A is negative at all temperatures in our operational range and growth characteristic time exist even at 100 K for this fluence. The change in the values of A from the positive to the negative is a signature of VO₂(B) undergoing transition from an insulator to a photoinduced metal. The fast characteristic time, τ_1 falls in the range of 1–3 ps when VO₂(B) is in the insulating state, while it has much more interesting temperature dependence in the photo-induced metallic state. We can see that there is evidence that the pump threshold required to melt the insulating state is strongly dependent on temperature and the dynamics for fluences near to the threshold requires deeper analysis. We define (i) “weak photoexcitation” for a fluence near the threshold and (ii) “strong photo-excitation” for a fluence much greater than the threshold value. Under “weak photoexcitation” τ_1 manages to reach a large value (~ 30 ps). However, under “strong photoexcitation”, τ_1 reduces to smaller values (< 5 ps). This lengthening of τ_1 might be a signature of competing dynamics and a possible role of co-existing insulating and photometallic phases. We should keep in mind that at both weak and strong excitations τ_1 represents growth dynamics. The peak of $\Delta R/R$, t_p occurs at pump-probe delays of less than 0.3 ps when VO₂(B) is in the insulating state. Meanwhile, in the photoinduced metallic state, t_p occurs in time-delays of tens of ps after the arrival of the pump pulse.

Figure 6.6: Fluence-dependent values of (a) A , (b) t_p , (c) τ_1 and (d) τ_2 for $\text{VO}_2(B)$ at two different temperatures— 150 and 300 K. The line, $A=0$ is also shown in (a).

We will now discuss how the parameters t_p , A , τ_1 , and τ_2 changes as a function of fluence by keeping the temperature fixed. The plots are shown in Fig 6.6. Remarkably, these parameters follow similar features as a function of temperature or fluence. At 150 K, as the pump fluence is gradually increased, the transient differential reflectivity of $\text{VO}_2(B)$ changes from fast decay dynamics to growth dynamics and is supported by positive to negative sign conversion of A . We have already established that sign conversion of A is a signature of an electronic phase transition. Furthermore, when the pump fluence is near the threshold limit there is lengthening of fast characteristic time, τ_1 . Also like previous observations, τ_1 decreases to smaller values (<5 ps) at “strong photoexcitation”. From the temperature and fluence-dependent experiments, we find that the fluence threshold, F_{th} increases as the temperature is lowered, which is expected because lower temperature stabilizes the insulating phase. The critical fluence, F_{th} of $\text{VO}_2(B)$ for e.g. at 150 K is

1.49 mJ/cm². In previous pump-probe experiments on VO₂(M1), this strong temperature dependence of F_{th} was interpreted as photoinduced softening of the insulating state followed by complete melting at higher fluences.^[179]

Previous transient spectroscopy experiments have reported that the value of the fast characteristic time, τ_1 of VO₂(M1) may vary from sub 100 fs to 1.7 ps.^[177, 220] On the other hand, the insulating state of VO₂(B), τ_1 falls in the range (1.1–2.8) ps which is quite comparable. The origin of τ_1 in VO₂(M1) has been suggested to be self-trapping of photo-excited carriers and it's possible that in the insulating state of VO₂(B), this process contributes to τ_1 .^[178, 219, 221] As VO₂(B) transitions to a photoinduced metallic state, τ_1 represents growth dynamics instead of decay dynamics and may be caused by long-range co-operative effects that destroy the relaxation pathways.^[210, 221] The growth dynamics in VO₂(M1) is attributed to the expansion of the initial seeding of metallic phase by photoexcitation. This nucleation event happens on a timescale of several picoseconds. It is possible that the growth dynamics in VO₂(B) is a representation of the processes of nucleation and growth of metallic phases. We also observe persistence of transient differential reflectivity which is a consequence of destruction of trapping or relaxation mechanisms. The slow characteristic time, τ_2 is present in all our pump-probe measurements. The timescale range of τ_2 suggest recovery dynamics from the transfer of lattice energy of the film to the substrate is the relevant process. The photoexcited system returns to its equilibrium state eventually. Carrier recombination may occur through — i) radiative recombination ii) non-radiative recombination or iii) auger recombination. In this context, the diffusion of hot carriers out of the excitation volume should also be considered. Previous time-resolved experiments on VO₂(M1) did not report τ_1 lengthening from "weak photoexcitation". In VO₂(B), τ_1 lengthening is observed in a temperature regime 50 K wide (Fig 6.5 (b)) which is roughly one-third of

its MIT transition width (~ 150 K). In contrast $\text{VO}_2(M1)$ has a sharp MIT width in the range 5–10 K.^[222] Since the lengthening of τ_1 is observed in the intermediate phase within the transition width, it is much more probable to notice this change in $\text{VO}_2(B)$ rather than in $\text{VO}_2(M1)$. We can expect that τ_1 lengthening would experimentally be observable in $\text{VO}_2(M1)$ in very narrow temperature regime (2–3 K) within the transition width. The other main difference between the photoinduced metallic state in $\text{VO}_2(B)$ and $\text{VO}_2(M1)$ is the strength of F_{th} . The fluence threshold of $\text{VO}_2(B)$ is only one-fourth of that $\text{VO}_2(M1)$, which is about $6\text{--}7 \text{ mJ/cm}^2$.^[81]

6.3.2 Transient reflectivities of $\text{VO}_2(B)$ at temperatures above 300 K

At temperatures above 300 K, $\text{VO}_2(B)$ is already deep into the metallic phase. Hence, in this temperature regime ($T \geq 300$ K) we expect the transient reflectivities to be quite similar. This agrees with experimentally observed results as shown in Fig 6.7.

Figure 6.7: Plot $\Delta R/R$ vs. time curves in the temperature range 300 K–370 K for $\text{VO}_2(B)$ taken at a fluence of 1.15 mJ/cm^2

Since in the 300 K–370 K temperature regime, $\text{VO}_2(B)$ is metallic, the fast characteristic time, τ_1 represents the growth characteristic time and values $\sim(2\text{--}3)$ ps. In this regime, there is no evidence of lengthening of τ_1 , because it is far away from the insulating phase. The coefficient, A is negative and the peak of reflectivity is around 10 ps. The slow characteristic time τ_2 may last up to 1 ns. The detailed analyses of these parameters are illustrated in Fig 6.8.

Figure 6.8: Plot of (a) A , (b) τ_p , (c) τ_1 and (d) τ_2 as a function of temperature in the temperature range 300 K–370 K for $\text{VO}_2(B)$ taken at a fluence of 1.15 mJ/cm^2 .

6.3.3 Photoinduced phase diagram $\text{VO}_2(B)$

As we have discussed, one of the possible origins of MIT in $\text{VO}_2(M1)$ is due to electron-electron interactions which is explained in the Mott transition theory. In this model, there is a certain critical electron density, n_c beyond which the system exists as a

metal. The value of n_C is given by^[37, 223]

$$n_C = (0.25/\alpha_H)^3 \approx 3 \times 10^{18} \text{ cm}^{-3} \text{ for VO}_2(M1) \quad (6.2)$$

where $\alpha_H = \frac{\hbar^2 \varepsilon}{m^* e^2}$, ε is the dielectric constant and $\hbar$ is the planck's constant. Since the carrier density is very important in the context of understanding MIT in VO₂ systems, we will try to calculate an approximate value in the photoinduced metallic state and compare it with the thermal activated carrier density of VO₂(B). We can assume one pump photon produces one charge carrier and there are no multiphoton absorption processes, the density of the photo-generated carriers, Δn can be estimated from the equation

$$\Delta n = \alpha \frac{(1 - R)}{h\nu} F_{th}$$

where R is the reflectivity, α is the absorption factor, and ν is the frequency. At 150 K, the values of the parameters for VO₂(B) are $R = 0.11$, $\alpha = 5.5 \times 10^4 \text{ cm}^{-1}$ and $\nu = 3.75 \times 10^{14} \text{ Hz}$. The reflectivity was calculated from the ratio of the power of the reflected and the incident beam and α from the UV-Vis absorbance spectrum (Fig 6.9(a)). When the pump fluence is 3.45 mJ/cm^2 , Δn is determined to be $\sim 3.1 \times 10^{21} \text{ cm}^{-3}$. At this fluence even the pure insulating state of VO₂(B) melts because of the extremely large carrier concentration. The number of photo-generated carriers is comparable to the intrinsic carrier density metallic VO₂(B) at room temperature.^[222] Hall experiments show that at 300 K carrier density of VO₂(B) is about $\sim 10^{22} \text{ cm}^{-3}$ and is six orders of magnitude greater than the low temperature insulating phase of VO₂(B).^[222] The comparison between the photo generated carrier density and the temperature dependent intrinsic carrier density is given in Fig. 6.9(b).

Figure 6.9: (a) Absorbance spectrum of VO₂(B) film. The absorption contribution from the substrate is subtracted from the sample response. (b) Carrier density vs. temperature plot of VO₂(B). The red symbol denotes the photo generated carrier. The intrinsic carrier density data points are taken from Srivastava *et al.* APL Mater. 3, 026101 (2015).

The fluence-temperature threshold values determined from the pump-probe reflectivity dynamics were used to populate the non-equilibrium phase diagram of the photoinduced MIT in the VO₂(B), as shown in Fig. 6.10 (a). The phase boundaries are estimated from the two-dimensional set of points and it divides the fluence-temperature phase into three regions of unique dynamics. First, the blue colored phase boundary separates the insulating and metallic regions and F_{th} values were used as the data points (eg. F_{th} at 150 K is 1.5 mJ/cm²). As mentioned earlier, F_{th} is the fluence value where the coefficient A changes sign from positive to negative. We can further divide the photoinduced metallic state into two regions— I and II to represent the dynamics from “weak photoexcitation” and “strong photoexcitation” respectively and is demarcated by the red lines. In the “weak photoexcitation” regime I, $\tau_1 > 5$ ps with a characteristic τ_1 lengthening feature while in the “strong photoexcitation” regime II, $\tau_1 \leq 5$ ps.

Figure 6.10: (a) Phase diagram of ultrafast MIT in $\text{VO}_2(B)$. The blue and the red colored regions represent the insulating and the metallic phases respectively. The metallic phase is further partitioned into two regions — I) weak photoexcitation (blue and red streaks) and II) strong photoexcitation (single red). (b) Schematic free energy diagram of the MIT transition in $\text{VO}_2(B)$. The diagram is constructed in terms of free energy and electronic configuration. The difference between photoinduced MIT and thermally activated one is also illustrated.

One can estimate the upper limit of increase in lattice temperature by considering that the entire pump energy has been converted to absorbed heat. The temperature increase in the photoexcited volume of the film due to the pump excitation is calculated from the formula, $\Delta T = \Delta Q / c_p m$, where ΔQ is the heat absorbed, c_p is the specific heat, and m is the mass of the excited volume. The low temperature specific heat of $\text{VO}_2(B)$ was assumed to be the same as that of low temperature $\text{VO}_2(M1)$ which is given by $0.068 \times 10^{-4} T^3 \text{ cal K}^{-1} \text{ mol}^{-1}$ for $T \leq 25 \text{ K}$.^[224] The density of $\text{VO}_2(B)$ is 4.031 g cm^{-3} .^[25] The amount of heat absorbed per volume is the product of fluence and optical penetration depth. The corresponding temperature change for fluence as large as 3.45 mJ/cm^2 is only 32.5 K compared to the large transition width of 150 K . This means that the pure lattice heating effects can drive the insulating state of $\text{VO}_2(B)$ to regime I in the phase diagram

but not into regime II.

One of the possible explanations for photoinduced phase transitions is generation of non-equilibrium phases from an equilibrium phase by external stimulation.^[209] In the free energy phase diagram, the equilibrium state is represented by a global minima and the system resides in this state if unperturbed. The transient states can be represented by free energy local minima having energies higher than the equilibrium one.^[178, 209, 221] Depending on the excitation, it's possible to get a variety of transient states even with a single original equilibrium state. If the local minima are separated by significant energy barriers, there would be slow relaxation towards the equilibrium state.^[209] In our case, the global free energy minima of low temperature $\text{VO}_2(B)$ can be considered as an insulating state while the photoinduced metallic state can be considered as a local minima. The difference between photoinduced metallic phase and thermally activated metallic phase is also illustrated in Fig. 6.10 (b). This justification of photoinduced phase transitions was initially proposed for the organic salts such as $(\text{EDO-TTF})_2\text{PF}_6$ where photoinduced MIT was observed.^[210] Currently, this argument has been applied to many other materials such as manganites, CuO etc.^[225, 226] An exciting frontier in this topic is the use of laser pump, X-ray probe techniques that promises to record direct observation of the structural transformation initiated by a light pulse.

6.3 Summary

Optical pump-probe experiments on epitaxial films of $\text{VO}_2(B)$ were performed for the first time and the ultrafast optical switching to a metallic state in this system was achieved. Compared to $\text{VO}_2(M1)$ the threshold value of laser fluence is about four times lower and with strong temperature dependence. The phase diagram of photoinduced transition in $\text{VO}_2(B)$, remarkably consists of two regions of photoinduced metallicity— one induced

by weak excitation, and another by strong excitation. This is the first detailed analysis on photoinduced metallic phase introduced by weak excitation in vanadium dioxide system. Our experimental results not only demonstrate photo-switching from an insulator to a metal at the ultrafast timescale, but also predicts that systems with a broad MIT transition are favourable candidates to access both the two regimes of photoinduced metallic state. This study progresses one of the major goals in optical switching research which is manipulating phase transitions on a sub-picosecond timescale by ultrashort laser pulses. Our study will also give guidance to the material selection and optoelectronic device designs.

Chapter 7 : Conclusions and future directions

In this thesis, we studied oxide thin films that show metal-insulator transitions and explored the modulation of their electronic properties by light and electric field effect. We started our studies with a strongly phase-separated manganite, $\text{Pr}_{0.65}(\text{Ca}_{0.75}\text{Sr}_{0.25})_{0.35}\text{MnO}_3$ (PCSMO). The EDLT technique was used to investigate the electric field effect on epitaxial PCSMO thin films and new insights into the effect of external electric field stimuli on phase separation were made. It was found that both electric and magnetic field effects are strongest in the phase separated regime and are complementary to each other. In the next project, substrate strain was introduced into PCSMO which revealed existence of cluster glass phase in low temperatures. Glassy phase separation and fluid-like phase separation have different responses in the presence of electric field. Adopting a multi-tuning approach such as electric and magnetic field or electric field and strain provides a new platform for understanding the correlated phases. After the electric field effect studies on PCSMO, the next material of our choice was VO_2 with main focus towards the B phase polymorph. Optical characterization and tuning of MIT in this system was successfully performed. THz modulation in $\text{VO}_2(B)$ is analog-like revealing a broad temperature width (50 K) in MIT transition while $\text{VO}_2(M1)$ shows digital-like THz modulation of narrow transition width (6 K). MIT in $\text{VO}_2(B)$ can be optically tuned and the pump threshold required is four times smaller than that of $\text{VO}_2(M1)$. The photoinduced metallic phase can be subdivided into two regions— one from weak photoexcitation, and another from strong photoexcitation introduces two different dynamics. These discoveries using the light and electrical probes not only open up new

avenues for technological applications but also provide new experimental framework to investigate many other interesting classes of condensed matter systems. The comprehensive optical and electronic study covered in this thesis, is particularly relevant to research efforts on achieving advanced phase transition devices.

Merging light and electric field techniques

There are still several attractive research directions offered by these two complex oxide systems which can be initiated based on the background built by this thesis. Amongst the several directions, integration of the light and electric field techniques to study complex oxides is an important one. This can be achieved by fabricating a gated structure and tuning the THz/optical response. This is possible because in complex oxides, changes in conductivity and changes in optical response are closely associated with one another. THz spectroscopy will offer unique experimental access to electronic effects under electrostatic modulation. It can probe the dynamic characteristics of the carrier under gating effects providing a means to build a comprehensive static and dynamical conductivity library. One important difference in such photonic FET device is that there is no need to apply source-drain current to monitor the tuning of transmission or reflection. Figure 7.1(a) shows the schematic of THz –TDS experiment on VO₂ FET configuration.

Active photonic devices

The FET configuration can also be used to build photonic devices such as THz/Optical modulators using these complex oxides as the channel. Briggs *et al.* fabricated one of such attractive device — a photonic waveguide modulator based on the temperature-controlled MIT transition in VO₂(M1).^[227] A voltage controlled waveguide modulator device would be more promising for telecommunications purposes. A different

but an impressive modulator based on these phase change material would be based on the Mach-Zehnder configuration. In a Mach-Zehnder interferometer, FET structures can be integrated in both waveguide arms. By using the gating voltage to control the phase in the waveguide, interference can go from constructive to destructive. In this way a Mach Zehnder interferometer can convert phase modulation into intensity modulation. Fig. 7(b) illustrates a VO₂ based Mach-Zehnder interferometer with voltage tuning capabilities. Another approach of incorporating voltage gated electric field in photonic structures is designing an active metamaterial structure.^[228] In an active metamaterial device, the metamaterial array electrode can function as a voltage gate. In the design of such a structure, the electrodes are deposited on top of the complex oxide thin film. These materials esp. manganites and vanadium dioxides being highly sensitive to biased electric field may undergo phase transitions, thereby allowing tuning of THz transmission through voltage control of electronic phases at the split gaps. For real world applications, most electronic devices require room temperature operation so we have to bear in mind that achieving multifunctional devices based on these materials require control of phase transitions in room temperature. Traditionally, manganites have been proven to be quite stubborn in manipulating at room temperature, whereas, in vanadium dioxide, room temperature control of electronic phase transition by gating voltage has been already shown.^[159]

Figure 7.1: Proof-of-concept devices based on complex oxides. a) THz transmission of VO₂ based back gate geometry field effect device. A thin dielectric (SiO₂) is grown on top of the substrate (Si). The channel and the electrode layer complete the multi-layer stack. b) Mach Zehnder interferometer based on VO₂ waveguide. Electric field is applied in one of the arms which can introduce modulation in intensity and/or phase in that arm.

Advanced techniques to probe metal-insulator transition

In order to realise the technological possibilities of these materials, it is crucial to understand the physics governing the phase transitions in these systems better. An approach that has emerged as tremendously exciting that promises to play an important role in gaining insight into the phase transitions in complex oxides and that has not been addressed in this thesis is spatially resolved characterization techniques. Co-existence of competing phases is not an uncommon phenomenon in correlated oxides and when macroscopic probes are adopted, the underlying physics under external stimuli such as electric field or light may be washed out by spatial averaging. However, by combining nanoscale probing techniques with biased electric field or laser pump, these phenomena can be studied from a new perspective far inaccessible by macroscopic approaches. Nanoscale scanning SQUIDs, scanning kelvin probe microscopy, and magnetic force microscopes can resolve the physics of electric field seeding and growth of magnetic phases in manganites. Optical nanoscale probes such as scanning near-field optical

microscopy has proven to be useful in obtaining topographic and spectroscopic information simultaneously at the surfaces of complex oxides.

Designing artificial metal-insulator transition materials

Complex oxides, fabricated in the form of thin films, have been proven to be a fertile ground for the discovery and investigation of many interesting of electronic p and phase transitions. With continuous advancements in thin film technology, it has been recently possible to create atomically sharp interfaces in an oxide heterostructure composed of two different compounds. This development has given rise to new opportunities study novel physics at the oxide interface. Some of the new discoveries at the oxide interface include charge transfer, polar catastrophe, structural coupling, and orbital and electronic reconstructions.^[87, 229] A golden opportunity to follow-up this research direction is to search for artificial metal-insulator transition materials based on oxide heterostructure. One could start with a parent compound which is insulating but on chemical doping becomes metallic. For example, EuTiO_3 is an insulator but doping with La makes it metallic. By creating EuTiO_3 and LaTiO_3 , one might be observe new electronic properties perhaps even a correlated metallic phase. The field of oxide thin films is ripe for such research directions.

Research in complex oxides is experiencing tremendous growth, and has benefited from rapid developments over the last two decades in thin film fabrication, lithography, and temporally resolved characterization techniques. Because of its interdisciplinary nature of research it offers substantial intellectual and technical challenges for scientists in the field of condensed matter, materials science, and device design equally.

Appendix

A1. Extraction of refractive indices

The extraction of complex refractive index of a thin film $\tilde{n} = n + i\kappa$ from transmittance first requires extracting the complex refractive index of the substrate for the given THz frequency range. Let's define these two configurations as— i) substrate–vacuum and ii) sample–substrate respectively. The sample should be homogeneous with flat and parallel surfaces. We will look into the sample-substrate configuration first and then simplify the model for the substrate-vacuum case.

Figure A1.1: Optical path of the THz beam for the sample-substrate configuration.

Transmission through (a) substrate and (b) sample

In the sample-substrate configuration, the THz transmittance across the substrate is first observed and followed the THz transmittance across the sample as shown in Fig A.1 (a) and (b) respectively. Here, medium 1, 2, and 3 represents vacuum, film, and substrate respectively. The thickness of the film is d , while the thicknesses of the substrates are $L1$

and L2 respectively for (a) and (b) cases as shown. The thickness difference between the substrates is ΔL . The electric field component of the THz pulse transmitted for only the substrate, $\tilde{E}_{ref}(\omega)$ [Fig A1.(a)] is given by

$$\tilde{E}_{ref}(\omega) = T_{13}(\omega) \times P_1(\omega, d) \times T_{31}(\omega) \times P_3(\omega, L1) \times E(\omega) \quad (A1)$$

The frequency-dependent electric field of the THz transmission through the film, $\tilde{E}_s(\omega)$ [Fig A1.(b)] is given by

$$\tilde{E}_s(\omega) = T_{12}(\omega) \times P_2(\omega, d) \times T_{23}(\omega) \times P_3(\omega, L2) \times T_{31}(\omega) \times P_1(\omega, \Delta L) \times FP(\omega) \times E(\omega) \quad (A2)$$

In the above equations the different parameters are described below

$$T_{ab}(\omega) = \frac{2\tilde{n}_a}{\tilde{n}_a + \tilde{n}_b} \text{ (transmission coefficient from medium } a \text{ to medium } b, \text{ and } a, b = 1, 2, 3)$$

$$P_a(\omega, x) = \exp\left[-\frac{\tilde{n}_a \omega x}{c}\right] \text{ (propagation coefficient in medium } a \text{ over a distance } x, a=1, 2, 3)$$

and $x = L1, L2, \Delta L, d$)

$E(\omega)$ is the electric field of the incident THz pulse

$FP(\omega)$ is the Fabry–Pérot term which takes into account multiple forward and backward reflections inside the medium

In the sample-substrate configuration, $\tilde{n}_1 = 1$, $\tilde{n}_2 = \tilde{n}$ and $\tilde{n}_3 = \tilde{n}_{sub}$. The complex transmission coefficient is given by the ratio of $\tilde{E}_s(\omega)$ to $\tilde{E}_{ref}(\omega)$ which is

$$T(\omega) = \frac{\tilde{E}_s(\omega)}{\tilde{E}_{ref}(\omega)} = \frac{2\tilde{n}(1+\tilde{n}_{sub})}{(1+\tilde{n})(\tilde{n}+\tilde{n}_{sub})} \times \exp\left[\frac{i\omega d(\tilde{n}-1)}{c}\right] \times \exp\left[-\frac{i\omega \Delta L(\tilde{n}_{sub}-1)}{c}\right] \times FP(\omega) \quad (A3)$$

$$\text{with } FP(\omega) = \frac{1}{1 - \frac{(\tilde{n}-1)(\tilde{n}-\tilde{n}_{sub})}{(\tilde{n}+1)(\tilde{n}+\tilde{n}_{sub})} \exp\left[\frac{2i\omega d\tilde{n}}{c}\right]}$$

The transmittance formula for a thin film reduces to

$$T(\omega) = \frac{2\tilde{n}(\tilde{n}_{sub}+1) \exp\left[\frac{i\omega d(\tilde{n}-1)}{c}\right] \exp\left[-\frac{i\omega \Delta L(\tilde{n}_{sub}-1)}{c}\right]}{(1+\tilde{n})(\tilde{n}+\tilde{n}_{sub})+(\tilde{n}-1)(\tilde{n}_{sub}-\tilde{n}) \exp\left[\frac{2i\omega d\tilde{n}}{c}\right]} \quad (A4)$$

For the substrate-vacuum configuration, we simply have to substitute $L1, L3 = 0$ and $\tilde{n}_3 = \tilde{n}_1$ in equation A3. The transmittance for the substrate will be

$$T(\omega) = \frac{4\tilde{n}_{sub}}{(1+\tilde{n}_{sub})^2} \times \exp\left[\frac{i\omega d(\tilde{n}_{sub}-1)}{c}\right] \times FP(\omega) \quad (A5)$$

where $\frac{1}{1 - \left(\frac{\tilde{n}_{sub}-1}{\tilde{n}_{sub}+1}\right)^2 \exp\left[\frac{2i\omega d\tilde{n}_{sub}}{c}\right]}$ and d here represents the thickness of the substrate

Figure A1.2: Optical path of the THz beam for the substrate-vacuum configuration.

Transmission through (a) vacuum and (b) substrate

A2. Electric field distribution in inhomogeneous media

In our model simulation of electric field inside a phase-separated system, we assume that the embedded metallic phases are spherical and their distribution is symmetric. However, a model closer to a real phase-separation in a manganite system would require considering metallic phases of different shapes and distributions.

Figure A2.1: Electric field distribution inside an insulating matrix embedded with metallic structures. (a) Each metallic inclusion is symmetric in shape while (b) the shape and the distributions of the metallic inclusions are asymmetric. The applied electric field across the system was 10^6 V/cm.

Finite element simulations using the DC module in COMSOL was used to simulate electric field simulations of other possible scenarios in phase separation. Fig. A2.1(a) shows electric field distributions by including triangular metallic shapes also. In these simulations the values of static dielectric constants of metallic and insulating phases are the same as in our previous simulation i.e. 55000 and 35 respectively. The applied voltage was also kept the same but in the horizontal direction. We observed that the electric field enhancement is larger for the triangular metallic shapes than the circular shapes. It is also enhanced if the distances are closer. Clearly, vicinity to sharp projections should be a non-trivial issue. Fig. A2.1(b) shows a random distribution of various metallic phases of different shapes. In this scenario also we realized that whenever the sharp protrusions from the metallic phase are quite close, the electric field enhancement was may be as large as four orders of magnitude higher than the value inside the metallic structure.

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