Nanoscale charge heterogeneity and chaotic resistive switching in VO_2-based Mott memristors

Thesis submitted in the partial fulfillment for the Award of Degree

Doctor of Philosophy

By

Pawan Kumar Ojha

SCHOOL OF MATERIALS SCIENCE & TECHNOLOGY
INDIAN INSTITUTE OF TECHNOLOGY
(BANARAS HINDU UNIVERSITY)
VARANASI - 221005
INDIA

Roll No. 18111503

2024

Dedicated to

My Beloved Family

CERTIFICATE

It is certified that the work contained in the thesis titled **"*Nanoscale charge heterogeneity and chaotic resistive switching in VO_2-based Mott memristors*"** by ***"Mr. Pawan Kumar Ojha"*** has been carried out under my supervision and that this work has not been submitted elsewhere for a degree.

It is further certified that the student has fulfilled all the requirements of Comprehensive, Candidacy, and SOTA for the award of Ph.D. Degree.

09/09/2024

Dr. Shrawan Kumar Mishra
(Supervisor)
School of Materials Science & Technology
Indian Institute of Technology
(Banaras Hindu University)
Varanasi - 221005

Assistant Professor
School of Materials Science & Technology/पदार्थ विज्ञान एवं प्रौद्योगिकी स्कूल
Indian Institute of Technology/भारतीय प्रौद्योगिकी संस्थान
(Banaras Hindu University), Varanasi/काशी हिन्दू विश्वविद्यालय, वाराणसी

DECLARATION BY THE CANDIDATE

I, ***"Pawan Kumar Ojha"***, certify that the work embodied in this thesis is my own bona fide work and carried out by me under the supervision of ***"Dr. Shrawan Kumar Mishra"*** from ***"January 2019"*** to ***"April 2024"***, at the ***"School of Materials Science & Technology"***, Indian Institute of Technology (Banaras Hindu University), Varanasi. The matter embodied in this thesis has not been submitted for the award of any other degree/diploma. I declare that I have faithfully acknowledged and given credits to the research workers wherever their works have been cited in my work in this thesis. I further declare that I have not willfully copied any other's work, paragraphs, text, data, results, etc., reported in journals, books, magazines, reports, dissertations, thesis, etc., or available at websites and have not included them in this thesis and have not cited as my own work.

Date: 09/09/2024
Place: Varanasi

Signature of the Student
(Pawan Kumar Ojha)

CERTIFICATE BY THE SUPERVISOR

It is certified that the above statement made by the student is correct to the best of my knowledge.

09/09/2024

Dr. Shrawan Kumar Mishra
School of Materials Science &Technology
IIT (BHU), Varanasi

Associate Professor-सह-आचार्य
School of Materials Science & Technology/पदार्थ विज्ञान एवं प्रौद्योगिकी स्कूल
Indian Institute of Technology/भारतीय प्रौद्योगिकी संस्थान
(Banaras Hindu University), Varanasi/काशी हिन्दू विश्वविद्यालय, वाराणसी

Coordinator
School of Materials Science &Technology
IIT (BHU), Varanasi

Coordinator/समन्वयक
School of Materials Science & Technology/पदार्थ विज्ञान एवं प्रौद्योगिकी स्कूल
Indian Institute of Technology/भारतीय प्रौद्योगिकी संस्थान
(Banaras Hindu University), Varanasi/काशी हिन्दू विश्वविद्यालय, वाराणसी

COPYRIGHT TRANSFER CERTIFICATE

Title of the Thesis: **Nanoscale charge heterogeneity and chaotic resistive switching in VO_2-based Mott memristors**

Name of the Student: **Pawan Kumar Ojha**

Copyright Transfer

The undersigned hereby assigns to the Indian Institute of Technology (Banaras Hindu University) Varanasi all rights under copyright that may exist in and for the above thesis submitted for the award of the ***"Doctor of Philosophy"*** degree.

Date: 09/09/2024
Place: Varanasi

Signature of the Student
(Pawan Kumar Ojha)

Note: However, the author may reproduce or authorize others to reproduce material extracted verbatim from the thesis or derivative of the thesis for author's personal use provided that the source and the Institute's copyright notice are indicated.

Acknowledgements

A research project like this is never the work of anyone alone. The contributions of many different people, in their different ways, have made this possible. I would like to extend my gratitude to the many people who helped to bring this research project to completion. This journey would not have been possible without the support of my family, professors, mentors, and friends.

My first and foremost heartfelt gratitude and indebtedness would be towards Bharat Ratna ***Mahamana Pandit Madan Mohan Malviya Ji****, the founder of Banaras Hindu University, who sacrificed his entire life and efforts in establishing this artistic temple of knowledge and wisdom.*

I would like to express my sincere gratitude to my supervisor, ***Dr. Shrawan Kumar Mishra****, Associate Professor, School of Materials Science & Technology, Indian Institute of Technology (Banaras Hindu University), Varanasi for providing me the opportunity to work in his research group. I am so deeply grateful for his help, professionalism, valuable guidance, everlasting enthusiasm and unstained support throughout my Ph.D. His deep insights helped me at various stages of my research. Finally, I am extremely thankful to him for the freedom he gave me during the course of my research work.*

I cannot find words to express my gratitude to my pedagogue, ***Prof. Shankar Ram****, Retired Professor, Materials Science Centre, IIT Kharagpur. His critical remarks and suggestions have always been very helpful in improving my skills.*

I would also like to express my sincere thanks to RPEC members Dr. Bhola Nath Pal, School of Materials Science & Technology, IIT (BHU), and Dr. Swapnil Patil, Department of Physics, IIT (BHU), for their fascinating advice and criticism, which encouraged me to broaden my research from numerous viewpoints. I would like to thank the coordinator of the School of Materials Science and Technology, IIT (BHU) for providing different instrumental facilities. I would like to express my sincere gratitude to Dr. Nikhil Kumar (DPGC convener) for his valuable inputs, suggestions and affectionate mannerism.

I would also like to acknowledge fruitful support and guidance of all the teacher of the school Prof. D. Pandey, Prof. R. Prakash, Prof. P. Maiti, Dr. (Mrs.) C. Rath, Dr. A. K. Singh, Dr. C. Upadhyay, Dr. B. N. Pal, Dr. S. Singh, Dr. A. K. Mishra, Dr. N. Kumar, Dr. R. Panwar and Dr. A. Kumar for their kind support at all moment during the progress of my research.

I would like to convey my heartfelt gratitude to CIFC, IIT (BHU), Varanasi, Dr. Vasant G. Sathe, UGC-DAE Consortium for Scientific Research, Indore and Dr. Deepash Shekhar Saini, Department of Physics, DDU Gorakhpur University, Gorakhpur and Dr. Bogdan Sava, Engineer at neaspec (attocube systems AG) for their assistance in carrying out the characterization of the synthesized samples. I'm also grateful to the school's staff members and the IIT (BHU) officials for their assistance in completing my thesis during my stay.

With a special thanks to my seniors, lab mates and cheerful group of colleagues Dr. Shyam Babu, Ms. Rajnandini Sharma, Ms. Nitipriya Tripathi, Ms. Simran Sahoo, Mr. Arkaprava Mondal, Mr. D. Rakesh, Mr. Eeshan Ketkar and rest of the energetic youngest group members for their suggestion and healthy discussion of my research issues. I am extremely thankful to my friends Mrs. Kavita Choudhary, Dr. Vishwas Acharya, Mr. Vishal Srivastava, Dr. Rajnikant Upadhyay, Mr. Ashish Kumar Choksey, Mr. Deepak Rathore, Mr. Jaynarayan Mishra, Mr. Taranga Dehury, Mr. Rohit Rodhia, Mr. Shivam Choubey, Mr. Prosun Mondal, Dr. Ravi Patel, Ms. Urvashi Kesarwani, Mrs. Divya Pareek, Dr. Priya Singh, Dr. Ankita Singh and Mr. Prince Mourya for their support, cooperation and sincere help in many ways as well as for making my stay here enjoyable and for their time-to-time encouragement during my bad situations. I would like to thank Department of Science and Technology (DST), New Delhi for financial assistance (Senior Research Fellowship).

I am especially grateful to my parents, ***Mr. Ramdev Ojha*** *and* ***Mrs. Sharda Ojha*** *who supported me emotionally and financially. I always knew that you believed in me and wanted the best for me. Thank you for teaching me that my job in life was to learn, to be happy, to know and understand myself; only then could I know and understand others. I must express my very profound gratitude to my sister Mrs. Rajshree Ojha, Mrs. Kavita Ojha, Ms. Usha Ojha and my brother, C. A. Krishan Kumar Ojha and my nephew Mr. Harshwardhan Saraswat for providing me with unfailing support and continuous*

encouragement throughout my years of study and through the process of researching and writing this thesis. Thank God for the wisdom and perseverance that he has bestowed upon me during this research project and indeed throughout my life to give such a wonderful opportunity and given me the strength to accomplish the assignment.

~ Pawan Kumar Ojha

LIST OF FIGURES

LIST OF TABLES

LIST OF ABBREVIATIONS

VO_2	Vanadium Dioxide
SC	Semiconductor
SMT	Semiconductor → Metal Transition
DFT	Density Functional Theory
VOs	Vanadium Oxides
IR	Infrared
UV	Ultraviolet
MST	Metal → Semiconductor Transition
PF	Poole Frenkel
XRD	X-ray Diffraction
FWHM	Full Width at Half Maximum
NCs	Nanocrystals
NAs	Nano-architects
PLD	Pulse Laser Deposition
ALD	Atomic Layer Deposition
PVP	Poly(vinyl pyrrolidone)
TFMs	Thin Film Memristors
AFM	Atomic Force Microscopy
FESEM	Field-Emission Scanning Electron Microscopy
s-SNOM	Scattering-Type Scanning Near-Field Optical Microscopy
BBAM	Bistable Bi-Local Active Memristor
AM	Active Memristor
SEDs	Single Electric Domains

HRTEM	High-Resolution Transmission Electron Microscopy
SAED	Selected Area Electron Diffraction
VC	Valance Band
CB	Conduction Band
RFs	Radio Frequencies
MIR	Mid-infrared

LIST OF SYMBOLS

T_N	Néel Temperature
T_c	Critical Temperature
$e\text{-}p$	Electron-Phonon
V_{th}	Threshold Voltage
D_e	Crystallite Size
2θ	Diffraction Angle
D	Dimension
V_t	Threshold Field
ρ_e	Effective Resistance
E_1	Anisotropic Electric Field
Z	Impedance Resistance
σ_{ac}	Conductivity
γ_c	Compressive Strain
V_c	Lattice Volume
E_F	Fermi Level
E_g	Bandgap
α_R	Thermal Coefficient
E_b	Binding Energy
I_p	Intensities

ABSTRACT

Vanadium dioxide (VO_2) - a non-stoichiometric oxide semiconductor (SC) offers exotic properties at a self-confined structure of correlated $3d^1$-electrons (spins) useful for non-volatile memory devices, smart switches, and human brain-inspired neuromorphic devices due to correlated phase/charge orders of SC to metallic states. Poor chemical stability and fragile nature limit its technologies of thin films. In view of resolving some of these issues, we developed polymer stabilized VO_2 films (thickness $t \leq 100$ nm), using VO_2 nanocolloids in poly(vinylpyrrolidone) (PVP) (as a VO_2 dispersoid, a molecular template, and a film former) in water, at a (100) Si(p^{++}) substrate. Using a nano SiO_2/TiO_2 gate ($t \leq 10$ nm), VO_2 is grown (011) preferentially in a confined shape of nanoplates (nanocrystals) along the films, mostly of 15 to 40 nm widths at 20–30 nm crystallite size. The results are described with X-ray diffraction (XRD), surface topologies, lattice images, and X-ray photoelectron spectroscopy (XPS) of films in the variable charges order at the itinerant metallic states. A significant V^{5+}-$3d^0$, ≤ 33 at%, is shown in the XPS bands, which induces metallic states at conducting '$V^{4+} \rightarrow V^{5+} + e^{-}$' channels. So, a charge-regulated SC → metal transition incurs via an induced $M_1 \rightarrow$ R-VO_2 metallic state near room temperature.

Employing temperature-controlled Raman spectroscopy, we demonstrate V-V dimers softening in nanostructured VO_2 thin films. Temperature-dependent Raman band shifts and their spectral width (FWHM) suggest an intriguing phonon characteristic that evolves across the semiconductor → metal transition (SMT) during the heating/cooling thermal cycles. The V-V dimers start to collapse above a critical temperature ($T_c > T_{MIT}$) and restoring their initial phase during the cooling process below T_{MIT}. Raman bands suggest an abrupt reversible switching in the optical behaviour at a temperature (T_o = 332 K).

Temperature-dependent sheet resistance variations indicate a smooth reversible resistive switching relatively at a lower temperature (T_e = 340 K). The difference in transition temperatures has been discussed in the framework of light scattering cross-section from the metallic domains that become more extensive at the critical length scale required for percolation conduction in resistive switching. 2D-mean-field approximation associated with Mie scattering are modelled to explain the percolation process during phase transition and to estimate the metallic domain length scale evolved in the semiconducting matrix across the SMT. Our experimental findings explain the occurrence of optical and electrical transitions at the distinct temperature range, suggesting a weak coupling between lattice and optical switching.

A memristor VO_2@TiO_2/Si renders a wide current-voltage (I-V) loop at room temperature, with a leakage current that is well controlled at a high-k TiO_2 gate. It exhibits a reversible switching at a duly small threshold field, $V_t \leq 0.2$ V. This is the smallest V_t tuned reported so far, which is beneficial for the low field, ≤ 1.0 V, devices. The charge models corroborate the effect of field-induced charge order at the interfaces of 'conducting through channels', regulating a reversible I-V hysteresis in an ON/OFF cycle. Thin VO_2 films of unified (011) nanocrystals (NCs) readily metallize at surface charge order on the vibrant NCs (as mini capacitors) in a pool. At the NCs, a nanoscale phase VO_2 can order in a confined domain of temperature (or other stimulus) in a first-order surface phase order, without a phase separation. At a critical charge density, $3d^1$-V^{4+} electrons (e) decouple from the phonons (p) and order in delocalized VO_2 states. Accordingly, it is shown that as the frequency (stimuli) is raised 10^2 to 10^6 Hz, the impendence resistance in thin films VO_2@SiO_2/Si is declined (up to 10^5 times at the room temperature), leading to successive $M_1 \rightarrow M_2/R_1/R_2/R$-$VO_2$ phase orders over the M_1-VO_2 resistive states. The frequency induces, regulates, and monitors exotic charges of

drive the phase order. A metallic R-VO_2 phase thus orders even at 303 K (at 10^5 Hz) that gradually shifts at higher frequencies (up to 10^6 Hz) upon heating to 343 K, i.e. the T_c point at zero frequency. The distinct VO_2 phases are well mapped in the s-SNOM (scattering-type scanning near-field optical microscopy) images at mid-infrared (MIR) bands. A density functional theory is applied to model the phase order at successively decoupled 'e-p' states. The results insight the mechanisms of $3d^1$-V^{4+} electrons decouple and order leading to the metallic VO_2 states.

PREFACE

The swift progression of modern technology necessitates a constant enhancement of electronic device performance. Achieving this improvement requires a comprehensive understanding of the fundamental behavior of materials used in technology. In the post-Moore era, newly introduced materials defy classical solid-state physics theories, displaying unconventional properties that can be harnessed for the development of advanced electronic devices. Transition metal oxides are captivating due to their diverse range of properties, exhibiting both metallic and semiconducting behaviours, along with superconductivity featuring remarkably high critical temperatures. The intricate physical behavior of these compounds arises primarily from the distinctive environment housing electric charges. The chemical bonds between the d-orbitals of multivalent transition metals and the p-orbitals of highly electronegative oxygen anions give rise to energy bands characterized by narrow widths and strong directionality. Consequently, there is a robust coupling between charge, spin, and orbital degrees of freedom. These compounds showcase various electronic configurations, significant electron-electron and electron-phonon interactions, as well as confined electronic systems. The development of thin films of transition metal oxides on a single crystal substrate provides the opportunity to customize material properties by specifying factors such as crystal structure, direction, uniaxial strain, chemical composition, and film thickness. The sol-gel technique proves to be a fitting method for producing crystalline oxide thin films in this context.

The distinctive characteristics of VO_2 position it as one of the most captivating transition metal oxides. VO_2 is a correlated material that undergoes a SMT in the vicinity of room RT. This transition is influenced by the robust correlation among electrons in the d-orbital

of vanadium and is concomitant with a significant structural modification that substantially alters the energy band diagram of the material.

The intricate examination of this transition has been a focal point for numerous researchers over the past fifty years, and it continues to be an unresolved inquiry. The SMT has also been triggered through the application of an electric field in a transistor like device, employing either an oxide layer or an electrolyte as a gate. One explanation for the electric-field-induced transition posits that a Mott transition occurs at the surface of the thin film of VO_2, extending throughout the entire film thickness. This implies that the behavior is highly contingent on the substrate on which the VO_2 thin film is grown, as the film properties and its response to an applied electric field vary based on the substrate's crystal structure and orientation. Clarifying the specific phenomena accountable for the electric-field-induced transition is crucial for a comprehensive understanding.

Simultaneously, we examined the characteristics of VO_2 thin films cultivated on three distinct substrates: Si (100), SiO_2 (100), and anatase TiO_2. These thin films were employed in the creation of memristor devices designed to operate at RT. A comparison of the performance of these devices with those fabricated on various substrates provides valuable insights into the behavior of VO_2 during the SMT.

The thesis is structured into several chapters, each of which is outlined below.

Chapter 1, deals with an introduction to the thesis, delving into the motivation and rationale for selecting vanadium dioxide as a Mott type SC. The chapter explores the theoretical background that underlies the investigation of SMT, emphasizing the unique properties of VO_2 in this context. Additionally, this chapter outlines the potential applications of VO_2 in next-generation memory devices, shedding light on the relevance and significance of studying its behavior during SMT. This comprehensive overview sets

the stage for the subsequent chapters, providing a clear foundation for understanding the research objectives and contributions presented in the thesis.

Chapter 2, presents an intricate exploration of the synthesis methodology (growth processes of VO_2 thin films and SiO_2/TiO_2 nanogate) focusing on the sol-gel based spin coating technique and the subsequent fabrication of devices. The chapter not only outlines the step-by-step process involved in these procedures but also elucidates the underlying working principles. Furthermore, a comprehensive overview is provided for the experimental setup for various characterization methods employed in the present thesis including XRD, TEM, FESEM, AFM, XPS, Raman Spectroscopy, four-probe measurements, semiconductor device analyzer, Impedance Spectroscopy, and s-SNOM.

Chapter 3, offers an in-depth examination is conducted on the temperature-induced phase transition within a nanostructured VO_2 thin film. The chapter provides into the intricacies of the optical phase transition, leveraging insights derived from Raman spectroscopy data.

A key focus is the exploration of variable sizes for charge puddles within the VO_2 samples, providing a comprehensive understanding of their distribution between different phases. This investigation sheds light on the universality of charge puddles in VO_2 samples during the phase transition, offering valuable insights into the nuanced behavior of the material under varying temperature conditions. The detailed analysis and findings presented in this chapter contribute significantly to unravelling the complexities of the temperature-induced phase transition in nanostructured VO_2 thin film.

Chapter 4, presents a comprehensive analysis is provided on the development of prototype low-field memristor devices, constructed from VO_2 films. The chapter delves into the intricacies of the role played by a nanogate composed of SiO_2/TiO_2 in facilitating

charge transfer within the VO_2@(100) Si(p^{++}) films. Specifically, the investigation focuses on the impact of a low-field $0 \leftrightarrow 5$ V swipe on the device's performance.

The experimental results reveal noteworthy outcomes, notably achieving a remarkably small threshold voltage of V_t = 0.12 V during the low-field operation. These finding underscores the effectiveness and significance of the SiO_2/TiO_2 nanogate structures in modulating charge transfer within the VO_2 thin films, particularly in the context of low-field applications.

Chapter 5, systematically investigates a series of $M_1 \rightarrow M_2/R_1/R_2/R\text{-}VO_2$ phases in detail. The s-SNOM images of VO_2 films effectively map all five VO_2 phases in the mid-infrared (MIR) field. These findings suggest a kinetic response of the critical temperature (T_c) point influenced by the decoupled $3d^1$ electrons (orbitals). Consequently, the T_c point consistently shifts from 343 K under terahertz (THz) (5-10 meV) conditions to 353 K under MIR (125 meV) fields employed in the s-SNOM imaging at the nanoscale.

Chapter 6, provides a comprehensive summary of the ultimate experimental findings, results, and conclusions presented in the current thesis. Furthermore, it extends its purview to encompass an insightful exploration of the future trajectory of this work, addressing prospective areas of interest and potential avenues for continued research.

TABLE OF CONTENT

Content *Pages*