Filamentary physics and modelling in redox-based resistive devices

Loy, Desmond Jia Jun

2020

Loy, D. J. J. (2020). Filamentary physics and modelling in redox-based resistive devices.
Doctoral thesis, Nanyang Technological University, Singapore.
<https://hdl.handle.net/10356/147065>

<https://hdl.handle.net/10356/147065>

<https://doi.org/10.32657/10356/147065>

This work is licensed under a Creative Commons Attribution-NonCommercial 4.0
International License (CC BY-NC 4.0).

Downloaded on 26 Apr 2023 20:25:44 SGT

**NANYANG
TECHNOLOGICAL
UNIVERSITY**

SINGAPORE

**Filamentary Physics and Modelling in Redox-Based Resistive
Devices**

DESMOND LOY JIA JUN

SCHOOL OF PHYSICAL AND MATHEMATICAL SCIENCES

2020

Filamentary Physics and Modelling in Redox-Based Resistive Devices

DESMOND LOY JIA JUN

SCHOOL OF PHYSICAL AND MATHEMATICAL SCIENCES

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

2020

Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research done by me except where otherwise stated in this thesis. The thesis work has not been submitted for a degree or professional qualification to any other university or institution. I declare that this thesis is written by myself and is free of plagiarism and of sufficient grammatical clarity to be examined. I confirm that the investigations were conducted in accord with the ethics policies and integrity standards of Nanyang Technological University and that the research data are presented honestly and without prejudice.

13th Aug 2020

.....
Date

.....
Desmond Loy Jia Jun

Supervisor Declaration Statement

I have reviewed the content and presentation style of this thesis and declare it of sufficient grammatical clarity to be examined. To the best of my knowledge, the thesis is free of plagiarism and the research and writing are those of the candidate's except as acknowledged in the Author Attribution Statement. I confirm that the investigations were conducted in accord with the ethics policies and integrity standards of Nanyang Technological University and that the research data are presented honestly and without prejudice.

13th Aug 2020

.....
Date

.....
Lew Wen Siang

Authorship Attribution Statement

This thesis contains material from 3 papers published / accepted in the following peer-reviewed journals and conferences in which I am listed as an author.

Chapter 3 is partly published as a peer reviewed journal as Desmond Jia Jun Loy, Putu Andhita Dananjaya, Xiao Liang Hong, Danny Pak-Chum Shum and Wen Siang Lew, "Conduction Mechanisms on High Retention Annealed MgO-based Resistive Switching Memory Devices" – Scientific Reports, 8, 14774 (2018).
<https://doi.org/10.1038/s41598-018-33198-0>.

Part of this chapter has been reproduced from Scientific Reports Springer Nature under the Creative Commons Attribution 4.0 International License:
<https://creativecommons.org/licenses/by/4.0/>.

The contributions of the co-authors are as follows:

- Andhita and I came up with the initial project direction and edited the manuscript drafts.
- I prepared the manuscript drafts. The manuscript was revised by Andhita, Dr. Hong and myself.
- I designed the study and performed all the laboratory work at the School of Physical and Mathematical Sciences, Nanyang Technological University. I also analyzed the data.
- All sample preparation was conducted by me at the School of Physical and Mathematical Sciences, Nanyang Technological University.
- Dr. Shum & Prof. Lew provided guidance in the interpretation of the conduction mechanism and retention measurement data.

Chapter 3 is partly published as a conference proceeding as Desmond Jia Jun Loy, Putu Andhita Dananjaya, Wai Cheung Law, Gerard Joseph Lim, Funan Tan, Xiao Liang Hong, Samuel Chen Wai Chow, Eng Huat Toh and Wen Siang Lew, "Hopping Conduction Temperature Investigations on High Retention Electrochemical Metallization MgO-based Resistive Switching Devices in the Low Resistance State" –

Conference Proceedings in Electron Devices Technology and Manufacturing Conference, IEEE (2019). DOI: [10.1109/EDTM.2019.8731244](https://doi.org/10.1109/EDTM.2019.8731244)

The contributions of the co-authors are as follows:

- Andhita and I came up with the initial project direction and edited the manuscript drafts.
- I prepared the manuscript drafts. The manuscript was revised by Andhita and myself.
- I designed the study and performed all the laboratory work at the School of Physical and Mathematical Sciences, Nanyang Technological University. I also analyzed the data.
- All sample preparation was conducted by me at the School of Physical and Mathematical Sciences, Nanyang Technological University.
- Wai Cheung, Gerard, Funan, Xiao Liang and Samuel assisted in experimental data collection.
- Dr. Toh & Prof. Lew provided guidance in the interpretation of the conduction mechanism and measurement data.

Chapter 4 is partly published as a conference proceeding as Desmond Jia Jun Loy, Putu Andhita Dananjaya, Somsubhra Chakrabarti, Kuan Hong Tan, Samuel Chen Wai Chow, Mun Yin Chee, Jia Rui Thong, Kun Qi Hou, Jia Min Ang, Gerard Joseph Lim, Yong Chiang Ee, Eng Huat Toh, Wen Siang Lew, “Impact of Stopping Voltage and Hopping Conduction on the Oxygen Vacancy Concentration of Multi-Level HfO₂-Based Resistive Switching Devices” – Conference Proceedings in IEEE Silicon Nanoelectronics Workshop (2020). DOI: [10.1109/SNW50361.2020.9131623](https://doi.org/10.1109/SNW50361.2020.9131623).

- Andhita and I came up with the initial project direction and edited the manuscript drafts.
- I prepared the manuscript drafts. The manuscript was revised by Andhita, Dr. Chakrabarti and myself.
- I designed the study and performed all the laboratory work at the School of Physical and Mathematical Sciences, Nanyang Technological University and GlobalFoundries Singapore. I also analyzed the data.

- All sample preparation was conducted by me at the School of Physical and Mathematical Sciences, Nanyang Technological University
- Kuan Hong, Samuel, Mun Yin, Jia Rui, Kun Qi, Jia Min and Gerard assisted in experimental data collection.
- Dr. Ee, Dr. Toh & Prof. Lew provided guidance in the interpretation of the switching mechanism and measurement data.

Chapter 4 is partly published as a peer reviewed journal as Desmond Jia Jun Loy, Putu Andhita Dananjaya, Somsubhra Chakrabarti, Kuan Hong Tan, Samuel Chen Wai Chow, Eng Huat Toh and Wen Siang Lew, “Oxygen Vacancy Density Dependence with Hopping Conduction Mechanism in Multi-Level Switching Behavior of HfO₂-Based RRAM Devices” – ACS Applied Electronic Materials 2(10), 3160-3170 (2020). <https://doi.org/10.1021/acsaelm.0c00515>.

Part of this chapter has been adapted with permission from Desmond Jia Jun Loy, Putu Andhita Dananjaya, Somsubhra Chakrabarti, Kuan Hong Tan, Samuel Chen Wai Chow, Eng Huat Toh and Wen Siang Lew, “Oxygen Vacancy Density Dependence with Hopping Conduction Mechanism in Multi-Level Switching Behavior of HfO₂-Based RRAM Devices” ACS Applied Electronic Materials 2(10), 3160-3170 (2020). Copyright 2021 American Chemical Society.

- Andhita and I came up with the initial project direction and edited the manuscript drafts.
- I prepared the manuscript drafts. The manuscript was revised by Andhita, Dr. Chakrabarti and myself.
- I designed the study and performed all the laboratory work at the School of Physical and Mathematical Sciences, Nanyang Technological University and GlobalFoundries Singapore. I also analyzed most of the data.
- All sample preparation was conducted by me at the School of Physical and Mathematical Sciences, Nanyang Technological University and GlobalFoundries Singapore.
- Kuan Hong and Samuel assisted in experimental data collection.

- Dr. Toh & Prof. Lew provided guidance in the interpretation of the switching mechanism and measurement data.

Chapter 5 is under revision as a peer reviewed journal as Desmond Jia Jun Loy, Kunqi Hou, Mun Yin Chee, Samuel Chen Wai Chow, Putu Andhita Dananjaya, Somsubhra Chakrabarti, Eng Huat Toh, Wen Siang Lew, “Filament Evolution and Compact Modelling of Multi-level Resistance HfO₂-based RRAM Devices” – Under revision in IEEE Transactions on Electron Devices.

- Kun Qi and I came up with the initial project direction and edited the manuscript drafts.
- I prepared the manuscript drafts. The manuscript was revised by Andhita, Dr. Chakrabarti and myself.
- Kun Qi assisted in the compact modelling and analysis.
- I designed the study and performed all the laboratory work at the School of Physical and Mathematical Sciences, Nanyang Technological University. I also analyzed most of the data.
- All sample preparation was conducted by me at the School of Physical and Mathematical Sciences, Nanyang Technological University.
- Mun Yin and Samuel assisted in simulation data collection.
- Dr. Toh & Prof. Lew provided guidance in the interpretation of the switching mechanism, modelling and measurement data.

Other peer-reviewed journals and conference papers published that are not included in this thesis include the following:

Xiao Liang Hong, Desmond Jia Jun Loy, Putu Andhita Dananjaya, Funan Tan, Chee Mang Ng & Wen Siang Lew, "Oxide-based RRAM materials for neuromorphic computing" – Journal of Materials Science, 53, 8720 (2018).
<https://doi.org/10.1007/s10853-018-2134-6>.

Nagaraj Lakshmana Prabhu, Desmond Jia Jun Loy, Putu Andhita Dananjaya, Eng Huat Toh, Wen Siang Lew, Nagarajan Raghavan, “Exploring the Power – Prediction

Accuracy Trade-Off in a Deep Learning Neural Network using Wide Compliance RRAM Device” – Conference Proceedings in International Symposium on Next-Generation Electronics, IEEE (2019). DOI: [10.1109/ISNE.2019.8896449](https://doi.org/10.1109/ISNE.2019.8896449)

Putu Andhita Dananjaya, Desmond Jia Jun Loy, Samuel Chen Wai Chow, Wen Siang Lew, "Unidirectional threshold switching induced by Cu migration with high selectivity and ultralow OFF current under gradual electroforming treatment" – ACS Applied Electronic Materials, 1, 2076 (2019). <https://doi.org/10.1021/acsaelm.9b00446>.

Nagaraj Lakshmana Prabhu, Desmond Jia Jun Loy, Putu Andhita Dananjaya, Eng Huat Toh, Wen Siang Lew, Nagarajan Raghavan, “Exploring the Impact of Variability in Resistance Distributions of RRAM on the Prediction Accuracy of Deep Learning Neural Networks” – Electronics, 9(3), 414 (2020). <https://doi.org/10.3390/electronics9030414>.

Putu Andhita Dananjaya, Desmond Jia Jun Loy, Mun Yin Chee, Samuel Chen Wai Chow, Jia Min Ang, Kun Qi Hou, Jia Rui Thong, Somsubhra Chakrabarti, Yong Chiang Ee, Wen Siang Lew, “Bulk-limited Effect in Gradual Conductance Switching Behaviour of HfOx-based Memristive Devices for Analog Synaptic Device Applications” – Conference Proceedings in Silicon Nanoelectronics Workshop, IEEE (2020). DOI: [10.1109/SNW50361.2020.9131609](https://doi.org/10.1109/SNW50361.2020.9131609).

Somsubhra Chakrabarti, Jia Min Ang, Jia Rui Thong, Kun Qi Hou, Mun Yin Chee, Putu Andhita Dananjaya, Desmond Jia Jun Loy, Yong Chiang Ee, Wen Siang Lew, “Effects of Thermal Annealing on Ta₂O₅ based CMOS compatible RRAM” – Conference Proceedings in Silicon Nanoelectronics Workshop, IEEE (2020). DOI: [10.1109/SNW50361.2020.9131617](https://doi.org/10.1109/SNW50361.2020.9131617).

13th Aug 2020

.....
Date

.....

Desmond Loy Jia Jun

Abstract

As we are moving towards a more data-centric and energy-consuming world, there is an increasingly strong need to search for more efficient alternatives in computing memory. Resistive random access memory (RRAM) has been one of the most promising alternatives to existing memories due to its simple metal-insulator-metal structure, high scalability, low power, multi-bit characteristics and compatibility to complementary metal oxide semiconductor. An RRAM is made up of two metal electrodes sandwiching a dielectric layer and its switching mechanism is based on redox reactions of oxidation and reduction. Recently, there have been dielectric studies ranging from the high-k materials such as HfO_x to the lesser known lower-k materials such as MgO .

In this thesis, the focus is on the conduction mechanisms, switching dynamics and modelling of HfO_x and MgO -based RRAMs. While conduction mechanisms such as Schottky emission and hopping conduction were shown to be the dominant mechanisms, the novelty of the ion conduction comes from the cationic-filament switching in MgO -based RRAM with Cu as the top electrode. Electrical and material characterizations suggest the presence of a Cu filament. Multi-level switching is also found in both HfO_x and MgO -based RRAMs, which would provide a good platform for neuromorphic computing. In the investigation of multi-level states, the gradual RESET slope angle was revealed to have a direct relation with the number and controllability of multi-level states. Thereafter, a proposed HfO_2 switching model shows that the activation energy obtained from a wide range of temperatures is directly related to the reset stop voltage but inversely related to the oxygen vacancy density.

A comprehensive hierarchical modelling study of HfO_x -based RRAMs is also performed, covering the aspects of kinetic Monte Carlo (kMC) and Simulation Program with Integrated Circuit Emphasis (SPICE) compact modelling. In the kMC filament evolution study, the number of defects were computed at different regions and it was found that all parts of the filament are affected during the rupture process. The ruptured gap length was also estimated through the analysis of oxygen vacancy behavior at different RESET stopping voltages. The kMC and SPICE HfO_x -based models also agrees with the experimental findings in this work. Hence, this work comprises of conduction mechanism physics and switching dynamics coupled with modelling for a better understanding and prediction analysis studies for future integration with transistors and for different applications.

Acknowledgements

First, I would like to thank my supervisors, Dr. Danny Shum, Dr. Toh Eng Huat, Elgin Quek and Prof. Lew Wen Siang for constantly guiding and supporting me throughout my Industrial-PhD journey. Dr. Danny Shum, Dr. Toh Eng Huat and Elgin Quek provided technical insights and advice from the industrial perspective while Prof. Lew provided guidance and support from the research point of view since I was an undergraduate student.

Next, I would like to express gratitude to my senior PhD course mates who guided and paved the way for me in this journey, Dr. Gerard Lim, Dr. Funan Tan, Dr. Wai Cheung, Dr. Eugene Tay along with other group members whom I had the opportunity to work with. Special gratitude to Dr. Andhita Dananjaya for being such a patient mentor and guide throughout my entire PhD journey.

I would like to thank my device team members in GlobalFoundries, especially to Dr. Chang Wei, Dr. Sun Yongshun, Zheng Ping, Pu Jinfei and Myo Aung for being very patient in guiding me and constantly helping me with my work and providing me insights from the industry perspective even though I did not have any prior industrial background or knowledge.

I would also like to thank my SUTD collaborators Prof. Pey Kin Leong, Prof. Nagarajan Raghavan and Dr. Alok Ranjan for their constant guide and support and for allowing me to use their facilities throughout my Industrial-PhD journey.

I would like to express my gratefulness to my business associates, Dato' Dr. Ng Jet Wei and Datin Ho Li Peng for taking me under their wings and sharing your decades of finance knowledge and business experiences with me, and who have been a tremendous guidance and encouragement whenever I needed a break from my Industrial-PhD.

I would also like to give special thanks to my Northbrooks Secondary School Mathematics teacher Mr. Benjamin Yong Yik Yen, for being my mentor and great role model in shaping a large part of my adolescence; and to my Pioneer JC Physics Teacher Mdm Ong Lay Yean, who spent a lot of time guiding me and never giving up on me when I was struggling in grasping Physics concepts, and even helping me until my 2nd 'A' Levels. Without them, I would not have made it this far in education.

And finally, I would like to thank my dearest parents, Loy Teck Sang and Cheong May Leng, and my brother Loy Jia Le for all your never-ending support and love. I will not be where I am without any of you.

This thesis is dedicated to my beloved parents, Loy Teck Sang and Cheong May Leng.

This 4-year journey has been filled with numerous challenges. First is the nature of my work as a GlobalFoundries-NTU Industrial-PhD student where I had to juggle with demands from my company, PhD projects and collaborations. As the only Industrial-PhD student who started the GlobalFoundries-NTU project, and as the main Industrial-PhD student of this project since the beginning, I had a huge responsibility in ensuring that things go smoothly between the two parties, from planning to execution. Secondly, coming from a family that struggled financially in the past, I was at a point of my life where I started receiving income and needed to plan for my family's and my future finances. And whenever I had a break from my Industrial-PhD studies, I will spend my free-time in some finance and business ventures on the sidelines, which also served as a challenge by itself. Lastly, COVID-19 has also proved to be extremely challenging as it occurred during my final semester of PhD where I could not spend the remaining critical months in the research facilities due to the lock-down of schools. The post lock-down period was not easy as I often had to work through tight schedules due to time restrictions imposed on the facilities. With a little time left after the lock-down, I had to constantly come up with a Plan B after Plan B due to the delay of my experiments and projects, resulting in several incomplete projects planned for my Industrial-PhD. Towards the final month of my industrial-PhD, my project deadlines caught up with me from all sides and I was struggling to keep up with all of them. However, some way, somehow, I garnered the strength and support from those who constantly guided and helped me through this Industrial-PhD journey to complete this thesis. With that many responsibilities, tasks, and contingencies throughout my Industrial-PhD journey, how I managed to get through this industrial-PhD journey is a miracle.

However, this is not the first time that a miracle has happened to me. Constant struggles in Junior College followed by 2 years as an 'A' level drop-out and a University reject, I know all about uncertainties and missed opportunities. I never thought any of these was possible as I was wondering what to do next in life aimlessly a decade ago. I kept reflecting at the times

where I topped my class in secondary school, yet I was at the rock bottom in Junior College. With some newfound motivation after my 2 years of national service, I spent a whole year studying and I retook my 'A' levels as a private candidate but most of the subjects fared worse than the first time. Devastated, I thought that this was over, but I still applied for some university courses without putting much hope because I have learnt numerous times that hope can easily become hopeless. I was working part-time, and every day was a mental torture, and just when I was about to give up, I received a late June call from NTU Physics, Bachelor of Science and the rest is history, a miracle.

Certainly, my undergraduate journey was not easy, I struggled a lot with my basics. And the decision to put me in the learning group of students with poorer physics basics background was not an encouraging label either. However, I was determined to prove everyone wrong. With determination and to make up for lost time, I emerged in the dean's list for 2 consecutive years. The last decade has taught me a lot about cherishing opportunities when they came, along with hard work, resilience, determination, persistence, preparedness, adaptability and boldness which allowed me to reap the fruits of my labour. From an NTU President's research scholar, 1st Class Honours and a dean lister to having the opportunity to present my work at international conferences in the U.S. and culminating in encouraging remarks from Singapore's next prime minister, Heng Swee Keat – "I hope Desmond can go on to catalyse other new R&D collaborations between GlobalFoundries and NTU in the future.", I am certainly humbled by the opportunities and rewards I was given.

This is my life story so far, but this is just the beginning and I will carry on these attributes and lessons into my future endeavors. I am where I am today because of the people who have helped me along this journey, those whom I have acknowledged and more. I hope that my story inspires many not to give up but to persevere on, and with determination and luck, you will see the light at the end of the tunnel. This past decade has been an eye-opener for me, and I have certainly learnt more from my failures than from my successes. Now, I live everyday as if it is my last, and live life to its fullest. I will end with a quote adapted from one of the world's most famous musical, Les Misérables, which has been with me since the start and got me through all my struggles over the past decade.

"Even the darkest night will end and the sun will rise." – Victor Hugo, Les Misérables.

Table of Contents

Filamentary Physics and Modelling in Redox-Based Resistive Devices	1
Statement of Originality	3
Supervisor Declaration Statement	4
Authorship Attribution Statement	5
Abstract	10
Acknowledgements.....	11
Table of Contents	14
Chapter 1 Introduction.....	18
1.1 Resistive Random Access Memory (RRAM) as an Emerging Memory	19
1.2 RRAM Dielectric Switching Materials	22
1.2.1. Hafnium Oxide	24
1.2.2. Tantalum Oxide	25
1.2.3. Magnesium Oxide.....	25
1.3 Conduction Mechanisms of Oxide-based RRAMs	26
1.3.1 Bulk-limited & Electrode-limited Conduction Mechanisms	27
1.4 Switching Dynamics of Oxide-based RRAMs.....	29
1.4.1 Electrochemical Metallization Memory (ECM) & Valence Change Memory (VCM) 30	
1.4.2 Multi-Level States of RRAMs	32
1.4.3 Filament Formation, Rupture and Gap Dynamics	33
1.5 Modelling of Oxide-based RRAMs	34
1.5.1 Kinetic Monte Carlo (kMC) Modelling	35
1.5.2 Compact Modelling	36
1.6 Research Objectives	36
1.7 Thesis Organization.....	37
Chapter 2 Experimental Techniques	39

2.1	Device Fabrications.....	40
2.1.1	Ultraviolet (UV) Photolithography	41
2.1.2	Etching	43
2.1.3	Sputter Deposition	44
2.2	Electrical Characterizations.....	46
2.2.1	Direct Current (DC) Measurements.....	47
2.2.2	Alternating Current (AC) / Pulsed Measurements	48
2.2.3	Endurance using DC & Pulsed Measurements	50
2.2.4	Retention Measurements using Voltage-stress and Temperature-stress.....	50
2.3	Material Characterizations	51
2.3.1	Atomic Force Microscopy (AFM).....	51
2.3.2	Transmission Electron Microscopy (TEM) & Scanning Electron Microscopy (SEM)	52
2.3.3	X-ray Photoelectron Spectroscopy (XPS)	55
Chapter 3 Conduction Mechanisms of MgO and HfO₂-based RRAMs		57
3.1	Ru/MgO/Ta and Ru/MgO/Cu RRAM Devices.....	58
3.1.1	Electrical Characteristics of Ru/MgO/Ta and Ru/MgO/Cu RRAM Devices.....	58
3.1.2	Schottky Emission of Ru/MgO/Ta and Ru/MgO/Cu RRAM Devices.....	60
3.1.3	Retention of Ru/MgO/Cu and Ru/MgO/Ta RRAM Devices	64
3.1.4	TEM Ru/MgO/Cu RRAM Devices showing Cu atoms inside MgO	66
3.2	Pt/MgO/Cu RRAM Devices.....	67
3.2.1	Electrical Characteristics of Pt/MgO/Cu RRAM Devices	67
3.2.2	Hopping Conduction of Pt/MgO/Cu RRAM Devices.....	68
3.2.3	Endurance and Retention of Pt/MgO/Cu RRAM Devices	69
3.2.4	TEM & EDX of Pt/MgO/Cu RRAM Devices.....	70
3.3	Hopping Conduction of Pt/HfO ₂ /Ti RRAM Devices.....	71
3.4	Chapter Summary.....	73

Chapter 4 Switching Dynamics in MgO and HfO₂-based RRAMs	74
4.1 Multi-level states in MgO-based RRAM Devices	75
4.1.1 Absence of Multi-level states in Pt/MgO/Cu RRAM Devices	75
4.1.2 Multi-level states in Pt/MgO/Ta RRAM Devices	76
4.1.3 Multi-level states in Pt/MgO/Ti RRAM Devices	78
4.2 Multi-level states of Pt/HfO ₂ /Ti RRAM Devices	80
4.2.1 Current-Voltage, XPS & TEM Characterizations of Pt/HfO ₂ /Ti RRAM Devices	83
4.2.2 Temperature Characterization & Arrhenius Equation Relation between High Resistance State and Temperature	86
4.2.3 Switching Model Between Activation Energy, Reset Stopping Voltage and Reset Multi-Level Resistance States	89
4.3 Chapter Summary	92
Chapter 5 Area Independent Filamentary RRAM and HfO₂-based RRAM Modelling	93
5.1 Filamentary RRAM in MgO & HfO ₂ -based RRAM Devices	94
5.1.1 Area Dependence of Pt/MgO/Cu RRAM Devices	94
5.1.2 Area Dependence of Pt/MgO/Ta RRAM Devices	95
5.1.3 Area Dependence of Pt/HfO ₂ /Ti RRAM Devices	96
5.2 Pt/HfO _x /Ti as a 3D Kinetic Monte Carlo (KMC) RRAM Model	99
5.2.1 kMC Model Fitting and Verification with Experimental Results	100
5.2.2 Filament Evolution Analysis at Different Regions of the Filament	102
5.2.3 Investigation of Ruptured Gap at different RESET Stopping Voltages	108
5.3 Pt/HfO _x /Ti as a SPICE Compact RRAM Model	110
5.3.1 Compact Model Fitting and Verification with Experimental Results	110
5.3.2 Prediction Analysis Studies of RRAM integrated with GlobalFoundries 40 nm transistor model	114
5.4 Chapter Summary	117
Chapter 6 Conclusions and Future Works	118
6.1 Conclusions	119

6.2	Future Works.....	121
6.2.1	Integration of Pt/HfO ₂ /Ti with GlobalFoundries 40 nm transistors	121
6.2.2	Finite Element Model for RRAM & Transistor devices.....	124
Appendix.....		132
A1	FN-Tunneling Investigations Pt/MgO/Ta and Pt/MgO/Cu RRAM Devices	132
A2	FN-Tunneling & Trap-Assisted Tunneling Investigations of Pt/HfO ₂ /Ti RRAM Devices 133	
A3	kMC Model Parameter Investigations.....	135
A4	SPICE Model Parameter Investigations	136
A5	SPICE Model Prediction Analysis	139
A6	Numerical Model Parameter Investigations	141
Publications List.....		145
References.....		150

Chapter 1

Introduction

This chapter presents resistive random-access memory (RRAM) in comparison with other memories, followed by the dielectric materials explored in literature. Conduction mechanisms of RRAMs such as bulk-limited and electrode-limited conduction mechanisms were discussed. Switching mechanisms such as valence change memory (VCM) and electrochemical metallization memory (ECM) were also discussed. Multi-level states, switching dynamics, filament evolution and different types of RRAM modelling such as kinetic Monte Carlo (kMC), and compact modelling were also discussed. This chapter will end off by discussing the research objectives and thesis organization in detail.

1.1 Resistive Random Access Memory (RRAM) as an Emerging Memory

The advent of the 21st century has seen an ever-increasing population and a rapid advancement of technology in the world. These factors result in an increasing demand of memory usage in the memory market. The first digital revolution occurred from the early 90's to mid-00's where personal computers, handphones and the internet first dominated the world of technology. Thereafter, it started from the mid-00's till the present where mobile devices such as laptops, tablet PCs and smartphones took over and brought computer memory demand to the next level. As the demand for memory devices increases, the need for faster and more efficient memory devices increases as well.[1] However, we are facing the limits of data transfer speed due to the latency gap between the various types of memories found in our computers and memory devices as shown in Figure 1.1.

Figure 1.1 Computer memory hierarchy [2, 3]

Figure 1.1 exhibits a memory hierarchy which can be found inside a modern-day computer. The core of any computer begins with a central processing unit (CPU), where the fastest operations take place. The speed at which operations take place is known as the access latency, and it can be seen from the memory hierarchy that the CPU has the highest access latency. As we move down the memory hierarchy, caches such as SRAMs take over the data processing and DRAM is where the main memory is stored. So far, these are the volatile memories where the data is lost when the power is turned off. Heading down to the secondary and tertiary memory

are non-volatile memories such as FLASH, solid-state drives (SSDs) and hard disk drives (HDDs). These non-volatile memories retain data when the power is turned off, and have the lowest access latency but highest storage space.[2]

However, there is a major issue occurring between the relative access latencies of DRAM and Flash memory. While the access latency of DRAMs is of the order of 100 nanoseconds, the access latency of Flash memories is of the order of milliseconds. This large difference in access latency is known as the latency gap, which results in a bottleneck in data transfer and processing speeds. The latency gap slows down the speed at which data is being transferred from the main memory to the secondary memory, thus causing the memory hierarchy to be inefficient. With an increasing demand for faster and more efficient computing devices, the latency gap issue serves as a major problem in the world of computing and technology. Since then, industries and institutions from all over the world have begun on a quest to find a replacement for memories which has the capability to overcome the latency gap issue. This issue could be mitigated in the new memory hierarchy replaced by emerging memories as shown in Figure 1.2. The potential candidates of emerging memories are resistive random access memory (RRAM), spin-transfer torque (STT)-magnetic random access memory (MRAM) and phase change random access memory (PCRAM).[4, 5]

Figure 1.2 A novel computer memory hierarchy replaced by emerging memories

Furthermore, in comparison with non-volatile memories, it can be seen from Table I that these emerging memories have the capability to exhibit a 10-nanosecond order access latency, which mitigates the issue of latency gap. In addition, when compared to conventional memories such as SRAM, DRAM and Flash, these emerging memories are superior in performances such as cell size, retention and energy per bit. These parameters make emerging memories ideal candidates to replace conventional memories in the computer memory hierarchy.

Table I Memory comparison between existing memories and emerging memories.[6]

Parameters	Current Memories				Emerging Memories			
<div><div></div>Efficient</div> <div><div></div>Acceptable</div> <div><div></div>Needs Improvement</div> <div><div></div>Not efficient</div>	SRAM	DRAM	FLASH		STT-MRAM	PCRAM	RRAM	
			NOR	NAND				
	Common Materials	Polysilicon or Metal Gate with gate oxide		Oxide/Nitride/Oxide (ONO)		Ta/CoFeB/MgO/CoFeB/W/Ru	SiO ₂ /GeSbTe/SiO ₂	TiN/HfO ₂ /Ti/TiN
	Cell area	~150F ²	6F ²	10F ²	≤4F ²	6F ² -20F ²	4F ² -20F ²	≤4F ² if 3D
Multi-bit	1	1	1	3	1	>2	>2	
Voltage	<1V	<1V	>12V	>20V	<2V	<3V	<3V	
Read time	<1ns	~10ns	~50ns	~10μs	<10ns	~10ns	<10ns	
P/E time	<1ns	~10ns	10μs/ 100ms	100μs/ 1ms	<10ns	~50ns	<10ns	
Retention	N/A	~64ms	>10y	>10y	>10y	>10y	>10y	
Endurance	>10 ¹⁶	>10 ¹⁶	>10 ⁵	>10 ⁴	>10 ¹⁵	>10 ⁸ ~ 10 ¹⁰	>10 ⁶ ~ 10 ¹²	
Write Energy (per bit)	<1fJ	~10fJ	~10pJ	<10fJ	~0.1pJ	~10pJ	~0.1pJ	

In comparison to all the emerging memories, RRAM stands out due to its smaller cell size, multi-bit capability and energy per bit. Smaller cell size and multi-bit capability gives RRAM an edge over the other emerging memories in terms of higher memory density. In addition, a lower energy per bit decreases the power consumption of the memory device, making RRAM a perfect candidate as a replacement for conventional memories.[7] Random access memories (RAMs) prove to be more superior as compared to direct access memories such as that used in compact disks (CDs). While RAMs allow data information to be retrieved in any random order, direct access memories only allow data to be retrieved in an orderly fashion. This means that a shorter time is required for RAMs to retrieve data as compared to direct access memories. Therefore, most modern memories use RAMs, which are much faster in data retrieval as compared to direct access or read-only memories (ROMs).

Over the past decade, non-volatile memories research has been on the surge in institutions and industries to improve the endurance and reliability of flash memories. These limitations have become more significant as memory devices scale down in sizes to keep up with the rising demands of the digital world.[8] In recent years, alternative NVMs[9] such as resistive random access memories (RRAMs) have emerged as one of the potential candidates,[10-12] owing to its simple metal-insulator-metal (MIM) structure, high speed, low power, high scalability, and complementary metal oxide semiconductor (CMOS) compatibility.[7, 13-21] RRAMs consist of three layers of materials, namely metal-insulator-metal (MIM) structures. The top electrode of an RRAM is usually an active electrode while the bottom electrode is usually an inert electrode. The working principle of RRAMs are based on chemical redox reactions, *i.e.* oxidation and reduction reactions. Redox reactions form a filament or bridge across the two metal layers within the insulator. When a filament is created, a connection is formed between the two metal layers. Considering a filament to be a wire connecting between two metal plates, a low resistance state (LRS) or SET occurs when a filament is formed while a high resistance state (HRS) or RESET occurs when a filament is ruptured. When a filament is formed, it would be a “1” state and when a filament is ruptured, it would be a “0” state.[22] Further details of the working principle of RRAMs will be discussed in Section 1.4 later.

1.2 RRAM Dielectric Switching Materials

Recently, numerous RRAM insulator materials such as binary metal oxides[23, 24], chalcogenides[25, 26] and perovskite oxides[27, 28] have been studied. However, among these materials, binary metal oxides were the most extensively studied due to their resistance to thermal stress and compatibility with CMOS.[23, 24, 29] Oxide-based RRAM are the most widely studied due to their dielectric properties in the formation and rupture of metallic or oxygen vacancy-driven conductive filaments (V_o^+) in MIM structures.[30-38] Out of all the binary oxides, hafnium oxide (HfO_x) and tantalum oxide (TaO_x) are the materials that have been explored quite extensively and are rather mature materials.[39] Density functional theory (DFT) revealed that the V_o^+ formation energy of HfO_2 varies from 0.95 eV to 1.4 eV, while that of Ta_2O_5 varies between 0.52 eV to 0.6 eV. While the higher formation energy of the HfO_2 favors the V_o^+ formation during cycling and thus improves the endurance, the lower formation energy of Ta_2O_5 makes the V_o^+ formation more stable, resulting in a higher retention.[40] Both HfO_x and TaO_x have also shown to exhibit multi-level state properties.[41, 42]

In general, current memory technologies exhibit binary states of “1” and “0” but there is a transition towards multi-level states to increase memory density for storage applications. This transition is useful for neuromorphic applications where RRAMs can be used as basic building blocks of neural networks and neuromorphic computing in place of Von Neumann computing. This is to keep up with the ever-increasing demand in consumption in today’s data-centric world.[41, 43-50] MgO is a less explored material but has great potential as they exhibit high retention and multi-level states as well, as reported in this work. Definitely, the list of oxides is non-exhaustive as there are a lot of different oxides reported such as AlO_x , [51] TiO_x , [52] CuO_x , [53] and many others. [1, 54]

Performances such as cell area, multi-bit, switching speed, switching voltage, switching current, endurance, retention, ON/OFF ratio and thermal stability of HfO_x , TaO_x and MgO-based RRAMs were compared in Table II. The best reported performances were obtained from HfO_x and TaO_x RRAM devices. Furthermore, in comparison to RRAM industry benchmark based on FLASH memory, only HfO_x and TaO_x -based RRAM devices have the potential to meet and exceed those industry specifications due to their low switching voltage, fast speed, high endurance, and high retention. However, as HfO_x -based RRAMs exhibited a slightly better performance than TaO_x -based RRAM devices, a lot of focus has been placed on investigating HfO_x -based RRAMs in this work. On the other hand, as little studies were performed on MgO-based RRAMs, it is worth to investigate to confirm and compare the performances with its HfO_x and TaO_x -based counterparts. These RRAM performances are further elaborated in Sections 1.2.1, 1.2.2 and 1.2.3 In these Sections, the structure begins with an overview of the oxide material, followed by their electrical performances as an elaboration of Table II from literatures, and ending off with any interesting findings from the material-based RRAM stack. While these materials exhibit stellar electrical properties, the high variability of RRAMs remains a topic of concern as it could adversely impact the differentiation of binary states of “1” and “0”.

Table II RRAM stack performances (further elaborations in Sections 1.2.1, 1.2.2. and 1.2.3.)

Reported Parameters	RRAM Main Stack Performances			Industry Goto Specs (FLASH)
<div>Efficient</div> <div>Acceptable</div> <div>Needs Improvement</div> <div>Not efficient</div>	HfO _x	TaO _x	MgO	Selected Material
Cell area	10 × 10 nm ²	50 × 50 nm ²	10 × 10 μm ² (This Work)	100 × 100 nm ²
Multi-bit	Yes	Yes	No	Not required
Switching Speed	10 ns	sub-ns	20 ns	200 ns
Switching Voltage	~1 V	~1 V	~2 V	1.2 V
Switching Current	~10 μA	~10 μA	~100 μA	100 μA
ON/OFF Ratio	100x	100x	50x	100x
Endurance	10 ⁸ cycles	10 ¹² cycles	10 ³ cycles (This Work)	10 ⁵ cycles
Data Retention	>10 years at 125°C (This Work)	3000 hours of baking at 150°C	>10 years at 85°C (This Work)	>10 years at 125°C
Thermal Stability	1200 K	900 K	700 K	1000 K

1.2.1. Hafnium Oxide

HfO_x is one of the most commonly studied oxides due to its high dielectric constant in the gate dielectric of metal oxide semiconductor field effect transistors (MOSFETs), good thermal stability and its multi-level state properties.[41, 44, 55-58]

While there is a trade-off between endurance and retention due to the degradation of the high resistance state caused by the irreversible growth of the V_O⁺ filaments, [40, 59] HfO_x-based RRAM have shown to exhibit fast speed, high endurance and high retention. Yuan *et al.* has shown that endurance can be improved in HfO_x-based RRAM by 3 orders upon nitridation treatment. [60] It has also been reported by Lee *et al.* that operation power and ON/OFF ratio can be improved by inserting an oxygen getter layer to scavenge oxygen from HfO_x layer. [61, 62]

10 × 10 nm² and even smaller HfO_x-based RRAM devices have also been demonstrated by Govoreanu *et al.* and Zhang *et al.*, respectively for scalability optimization.[63, 64] More recently, Pi *et al.* has demonstrated HfO_x-based crossbar array capabilities with a 2 nm critical

dimension.[65] With all these industry-standard performances, HfO_x is definitely an oxide material that has high potential in delivering best-performing RRAMs.

1.2.2. Tantalum Oxide

Similarly, TaO_x is also a high dielectric constant material which exists two stable phases, *i.e.* conducting TaO_2 and insulating Ta_2O_5 , which allows TaO_x to be engineered for an optimized performance.

TaO_x -based RRAMs are known to exhibit high endurance and multi-level state properties. M.-J. Lee *et al.* reported an endurance of 10^{12} cycles, exhibiting robustness in the TaO_x dielectric material.[66] TaO_x -based RRAM also demonstrated a high retention as reported by Zhang *et al.* where both LRS and HRS maintained their resistances after 3000 hours of baking at 150°C .[67]

Prakash *et al.* also demonstrated 3-bit multi-level characteristics in TaO_x -based RRAM,[68] while Yu *et al.* reported a 3D TaO_x -based RRAM vertical structure for improved scalability.[69] Hence similar to HfO_x , the exceptional performances makes TaO_x a great candidate for an RRAM dielectric material.

1.2.3. Magnesium Oxide

MgO on the other hand is a lower dielectric constant material, and it is less-known and less-explored as compared to its HfO_x and TaO_x counterparts. MgO -based RRAMs were inspired by spin transfer torque-magnetoresistive random-access memory (STT-MRAM) where MgO was used as a tunnel barrier for the magnetic tunnel junction (MTJ), critical in determining the performance of the MTJ. MgO was used as a tunnel barrier and is suitable to be an RRAM switching layer due to its intrinsic properties such as large bandgap and high thermal conductivity.[70, 71]

However, MgO -based RRAMs have also shown to exhibit high retention and multi-level states in this work. According to the MgO -based RRAM works published in literature, inert electrodes Ru [72] and Pt [70, 73, 74] and active electrodes Ti,[72] ITO, [75] Ta[73] have been

explored. Recently, this work have also reported a retention of >10 years at 85°C in Ru/MgO/Ta, Ru/MgO/Cu and Pt/MgO/Cu devices.[20, 21]

1.3 Conduction Mechanisms of Oxide-based RRAMs

The physics of ion and electron migration across different interfaces of the RRAM can be understood from conduction mechanisms. The conduction mechanisms can be investigated from the pre-switching part of direct current (DC) current-voltage (I - V) curve fittings, which were elaborated in Section 2.2.1. There are many types of conduction mechanisms as exhibited in Figure 1.3 and they can be categorized into two main groups, electrode-limited and bulk-limited conduction mechanisms. While electrode-limited conduction mechanisms mainly occur at the electrodes, bulk-limited conduction mechanisms mainly occur within the dielectric. Figure 1.3 shows the different conduction mechanisms occurring between the various electrode and dielectric interfaces of an RRAM device corresponding to Table III, which will be elaborated further in Section 1.3.1.[76]

Figure 1.3 Conduction mechanisms in MIM structures as indicated by (1) Schottky emission (S-E), (2) Fowler-Nordheim (F-N) tunneling, (3) direct tunneling, (4) tunneling from cathode to traps, (5) Poole-Frenkel (P-F) emission, (6) F-N-like tunneling from trap to conduction band, (7) Trap-to-trap hopping, (8) Tunneling from traps to anode. The conduction mechanism equations can be found in Table III.

1.3.1 Bulk-limited & Electrode-limited Conduction Mechanisms

There are many types of conduction mechanisms in dielectric films, *i.e.* electrode-limited and bulk-limited conduction mechanisms. While Schottky emission,[77-79] Fowler-Nordheim tunneling,[80, 81] direct tunneling,[82, 83] and thermionic-field emission[84, 85] are electrode-limited conduction mechanisms, Poole-Frenkel (P-F) emission,[86, 87] hopping conduction, [88, 89] Ohmic conduction,[70, 90] space-charge-limited-conduction (SCLC),[91, 92] ionic conduction,[35, 93] and trap-assisted tunneling (TAT) [94, 95] are bulk-limited conduction mechanisms.[83] Table III shows ten types of conduction mechanisms and their respective equations, but this list is non-exhaustive as there are many variations of conduction mechanisms reported. As different interfaces give rise to different conduction mechanisms, there are numerous dominant conduction mechanisms to be investigated. As observed from Table III, the conduction mechanism equations are expressed in terms of the current density as a function of electric field, where most of the conduction mechanisms have electric field and temperature dependences.

Table III. Different types of conduction mechanisms in RRAM devices as per Figure 1.3.

	Conduction Mechanism	Current Density Expression	Electric Field and Temperature Dependency
(1)	Schottky Emission	$J_{SE} = \frac{4\pi q m^* (kT)^2}{h^3} \exp \left[\frac{-q(\phi_B - \sqrt{qE/4\pi\epsilon})}{kT} \right]$	$J_{SE} \propto T^2 \exp \left(A \frac{\sqrt{E}}{T} - B \right)$
(2)	Fowler-Norheim (F-N) Tunneling	$J_{FN} = \frac{q^2}{8\pi h \phi_B} E^2 \exp \left(\frac{-8\pi\sqrt{2qm^*}}{3hE} \phi_B^{3/2} \right)$	$J_{FN} \propto E^2 \exp \left(\frac{-A}{E} \right)$
(3)	Direct Tunnelling	$J_{DT} \approx \exp \left\{ \frac{-8\pi\sqrt{2q}}{3h} (m^* \phi_B)^{1/2} \kappa \cdot t_{ox,eq} \right\}$	$J_{DT} \propto \exp(-A \cdot \kappa t_{ox,eq})$
(4)	Tunnelling from cathode to traps	$J_{TAT} = A \exp \left(\frac{-8\pi\sqrt{2qm^*}}{3hE} \phi_T^{3/2} \right)$	$J_{TAT} \propto \exp \left(\frac{-A}{E} \right)$
(5)	Poole-Frenkel emission	$J_{PF} = q\mu N_C E \exp \left[\frac{-q(\phi_T - \sqrt{qE/\pi\epsilon})}{kT} \right]$	$J_{PF} \propto E \cdot \exp \left(A \frac{\sqrt{E}}{T} - B \right)$
(6)	F-N-like tunnelling from trap to conduction band	$J_{FN} = \frac{q^2}{8\pi h \phi_B} E^2 \exp \left(\frac{-8\pi\sqrt{2qm^*}}{3hE} \phi_B^{3/2} \right)$	$J_{FN} \propto E^2 \exp \left(\frac{-A}{E} \right)$
(7)	Trap-to-trap hopping (Mott hopping)	$J_{VRH} = \sigma_0 \exp \left(\frac{-T_0}{T} \right)^{\frac{1}{4}} \cdot E$	$J_{VRH} \propto E \cdot \exp \left(\frac{-A}{T} \right)^{\frac{1}{4}}$
(8)	Tunnelling from traps to anode	$J_{TAT} = A \exp \left(\frac{-8\pi\sqrt{2qm^*}}{3hE} \phi_T^{3/2} \right)$	$J_{TAT} \propto \exp \left(\frac{-A}{E} \right)$
(9)	Ohmic conduction	$J_{ohmic} = \sigma E = q\mu N_C E \exp \left[\frac{-(E_C - E_F)}{kT} \right]$	$J_{ohmic} \propto E \cdot \exp \left(\frac{-A}{T} \right)$
(10)	Ionic conduction	$J_{ionic} \propto \frac{E}{T} \exp \left\{ \frac{-\Delta G^\ddagger}{kT} \right\}$	$J_{ionic} \propto \frac{E}{T} \exp \left(\frac{-A}{T} \right)$

In determining the dominant conduction mechanisms, the RRAMs were first screened into electrode-limited or bulk-limited conduction mechanisms. Band-alignment diagrams were used in the screening process as bands shift based on an applied external electric field, resulting in electrons to favor one direction over another. Figure 1.4(a) shows the initial state where the bands are flat, and when a positive voltage is applied to the anode as shown in Figure 1.4 (b), the bands were shifted in a manner where electrons need to overcome a lower energy barrier to reach the anode, producing a SET state. On the contrary, when a positive voltage is applied to the cathode as shown in Figure 1.4 (c), the bands were shifted in a manner where electrons need to overcome a lower energy barrier to reach the cathode, producing a RESET state.

Figure 1.4 Band alignment diagrams from (a) initial state where the bands are flat, (b) SET state where the bands are shifted for electrons to move towards the anode, and (c) RESET state where the bands are shifted for electrons to move towards the cathode.

Thereafter, the band alignment energies were obtained by taking reference to the band alignment of Silicon as shown in Figure 1.5(a) and (b), given by Ru/MgO/Ta and Pt/HfO₂/Ti RRAMs respectively. The conduction band offset (ΔE_c) of Ru/MgO and Pt/HfO₂ RRAMs were calculated to be 2.15 eV and 3.05 eV respectively. In comparing to the electron affinities of MgO and HfO₂, i.e. 2.55 eV ($> 2.15 \text{ eV } \Delta E_c$) and 2.65 eV ($< 3.05 \text{ eV } \Delta E_c$), a larger energy is required for electrons to overcome the ΔE_c of Pt/HfO₂ than for Ru/MgO. As a larger energy is required to overcome the bulk processes, Ru/MgO/Ta and Pt/HfO₂/Ti RRAMs are electrode limited and bulk limited conduction mechanisms respectively.[70] Thereafter, fitting analysis

on I-V curves were used to further identify the dominant conduction mechanisms. These procedures were later used to identify the conduction mechanisms in Sections 3.1.2, 3.2.2 & 3.3 for different MgO-based and HfO_x-based RRAMs.

Figure 1.5 Band alignment diagrams to determine electrode-limited and bulk-limited conduction mechanisms using examples from (a) Ru/MgO/Ta and (b) Pt/HfO₂/Ti RRAMs.

1.4 Switching Dynamics of Oxide-based RRAMs

The most common switching mechanisms in RRAMs are known to be electrochemical metallization (ECM) memory and valence change memory (VCM). The switching mechanisms of RRAMs are usually determined by the tendency of active electrode atoms to form either a cationic metallic filament or an anionic V_o^+ filament for ECM and VCM, respectively.[96] Other than material characterizations such as *in-situ* transmission electron microscopy (TEM) and scanning transmission electron microscopy (STEM), an abrupt or gradual reset could also reveal the respective ECM or VCM switching. The multi-level switching property is also another important switching dynamics aspect of RRAM as the individual margin states needs to be controlled well to prevent excessive overlapping between states. Multi-level states are very useful for storage and for neuromorphic applications. The gap dynamics is another area of interest in studying the formation and rupture of the filament, *i.e.* the behavior of atoms

under the influence of different voltage and temperatures. Typically, physics-based models such as kMC models are used to explain the gap dynamics and filament evolution, which will be discussed in the next Section.

1.4.1 Electrochemical Metallization Memory (ECM) & Valence Change Memory (VCM)

While filaments in ECM are formed by cationic metallic species generated from the active electrode, VCM are formed by anionic V_o^+ . For simplicity, the schematic of filament evolution in Ru/MgO/Cu ECM devices was exhibited in Figure 1.6(a). The rupture and formation of filament give rise to binary memory states of RRAM devices determined by its HRS and low LRS, respectively.[7] A SET state occurs when HRS becomes LRS while a RESET state occurs when LRS becomes HRS.[97] Further elaboration of a typical RRAM I – V curve indicating the SET/RESET and LRS/HRS states can be found in Section 2.2.1 later. In the SET process, a compliance current limit is imposed to protect the RRAM devices from high current damages.[29] As exhibited in Figure 1.6(a) during the SET process, a positive voltage was applied to the top electrode to oxidize Cu into Cu^+ ions at the Cu/MgO interface [O]. Thereafter, Cu^+ ions were reduced at the Ru/MgO interface to form back Cu atoms [R]. This process continues until the entire filament is formed. Similarly, the RESET process would require a negative voltage applied to the top electrode to oxidize Cu atoms into Cu^+ ions at the Ru/MgO interface [O]. Cu^+ ions were reduced at the Cu/MgO interface to form back Cu atoms, thereby rupturing the filament [R].[35, 98] The same process can be said about VCM except that the filament is formed by the migration of V_o^+ . V_o^+ are formed when anion migrate from the top electrode into the insulator. Ta metal atoms and MgO insulator atoms are used in this illustration as shown in Figure 1.6(b). Similarly, positive voltage is supplied to the top electrode, but reduction occurs this time at the top electrode/insulator interface [R]. This results in the formation of V_o^+ and metal oxide which again follow the direction of the current and accumulate at the bottom electrode/insulator interface. This process again occurs when the filament is formed. In the rupture of the filament, reverse redox reaction, *i.e.* oxidation occurs where V_o^+ and metal oxide are formed back to the original state of metal oxide [O].[76]

Figure 1.6 Redox reactions defining the forming, SET and RESET processes of (a) Electrochemical metallization (ECM) in Ru/MgO/Cu devices, (b) Valence change memory (VCM) in Ru/MgO/Ta devices.

However, while the definitions of ECM and VCM are as such, there are also some exceptions to the rule. For instance, Wedig *et al.*[99] mentioned that TaO_x, HfO_x and TiO_x are typical VCM materials,[100] but specific conditions were performed to the RRAM stacks to exhibit ECM properties, which was also supported by first principles of density functional theory. These special conditions include using a 2 nm thin TaO_x, using vacuum annealing to increase the conductivity in the oxide layer. However, the filament breaks after the voltage is removed, indicating a volatile switching. In addition, the RRAM interfaces discussed were Ta/TaO_x, Hf/HfO_x, Ti/TiO_x and Ta/C/Ta₂O₅ where the electrodes or carbon materials were added to modify or decrease interface dynamics and to suppress oxygen reaction. Furthermore, the authors mentioned the uncertainty of the Ta, Hf and Ti metallic filaments on whether they remain metallic or partially oxidizes, suggesting another volatile switching case. Privitera *et al.* also reported Hf and Ti metal gettering layers and oxygen exchange layers (OEL), which are known to be very thin, having a role to play in the metallic filament formation in TiN/OEL/HfO₂/TiN RRAM devices.[101] Furthermore, there have been experimental evidence that ECM devices exhibited abrupt reset due to a large-scale filament rupture.

Chandrasekaran *et al.* shown this by observing a gradual reset in a thicker TiW barrier layer between the electrode and oxide interface but observed an abrupt reset in a thinner TiW barrier layer, which was attributed to VCM and ECM, respectively.[102] Experimental and theoretical studies performed on the Ti/HfO₂ interface engineering for RRAM also exhibited a relationship between V_o^+ formation energy and V_o^+ charge.[103] Finally, it has been reported that Pt/HfO₂/Ti RRAM devices exhibited VCM,[104, 105] as the capacitance of the filamentary RRAM is independent of the resistance state. This is consistent with the very thin V_o^+ filaments of VCM. Therefore, it is possible that ECM switching could be obtained from VCM devices, and vice versa, by a specific layer, thickness, and/or stack engineering.

1.4.2 Multi-Level States of RRAMs

Currently, there are a lot of research in the aspect of scaling down RRAM dimensions to improve the memory scalability.[106] There are also other reports of three-dimensional (3D) crossbar architectures such as vertical and crossbar structures to improve the storage density.[107, 108] However, these methods are often complex and require additional fabrication processes which increase the cost per bit of the RRAM. Recently, there is a strong interest towards multi-level states to increase the memory density as a more feasible solution for storage applications. For instance, Prakash *et al.* and Kim *et al.* have demonstrated a 3-bit multi-level cell in TaO_x-based RRAM devices.[68, 109, 110] Different methods of controlling the multi-level states include varying the compliance current, varying the reset stop voltage (V_{stop}) and by varying pulse height and widths.[111] An illustration of multi-level state characteristics is shown in Figure 1.7 by varying the V_{stop} of Pt/HfO₂/Ti devices, which will be explained in greater detail in Section 4.7 later. Other than storage applications, the transition to multi-level states can also provide a solid platform for neuromorphic applications due to the increasing interconnectedness and data consumption in today's world.[41, 43-50]

Figure 1.7 An illustration of multi-level state characteristics exhibiting over 8 states by varying V_{stop} .

1.4.3 Filament Formation, Rupture and Gap Dynamics

While there were many proposed RRAM models to provide better physics understanding, the filament evolution and behavior has been one of the highly debated topics in RRAM today, specifically between ECM and VCM cells where the filaments are composed of cations and anions, respectively. And while some suggested the complementing presence of both cations and anions in filament formation, others claimed that VCM cells can exhibit ECM switching mechanism and vice versa.[99, 101, 102, 112, 113] More specifically, a chalcogenide electrode-based hybrid RRAM with a mixed ECM-VCM filament has also been reported, depending on whether copper or oxygen diffusion is dominant at a particular electric field.[112] Another area of debate is the filament behavior at electrode/oxide interfaces where the rupture and formation takes place.[106, 114, 115] While it has been reported that switching mostly occurs at a small gap located at the Schottky electrode/oxide interface during rupture,[55, 116-119] there have also been literatures showing that switching occurs throughout the entire filament, not just at a small gap at the electrode/oxide interface.[120-124] Wu *et al.* observed disconnected Ni fragments remaining in the SiO_x dielectric of $\text{Ni}/\text{HfO}_2/\text{SiO}_x/\text{n}^+\text{Si}$ RRAM devices after the reset process using *in-situ* TEM, which acted as preferred pathways for filament to form during the subsequent set process.[120] Shin *et al.* also reported V_o^+ remaining in the dielectric after the reset process of $\text{Mo}/\text{SiO}_x/\text{Pt}$ and suggested a gap to represent regions of the filament where there was lower V_o^+ density.[121] Bai *et al.* reported a model in $\text{W}/\text{WO}_x/\text{TiN}$ devices where the oxygen ions recombine with WO_x to form a continuous WO_3

layer during reset, resulting in a high resistance state. The set process was further explained by the oxygen ions moving out of the WO_3 layer, resulting in a conductive filament.[122] Li *et al.* reported a shrinking conductive filament in a HfO_2 -based RRAM from an electron hologram data plot but still observed distinct V_o^+ channels at the oxide/electrode interface after the reset process.[123] Arita. *et al.* also shown another example of Cu residual remaining after the RESET of Cu/MoOx/TiN RRAM devices and attributed it to the surface oxidation of TiN.[124] Hence, the gap dynamics of the RRAM filament would provide new insights to the switching phenomena.

1.5 Modelling of Oxide-based RRAMs

Over the past few decades, there has been a surge in proposed RRAM switching models, *i.e.* kMC and compact models to explain and model the physics observed from experimental results. These physics-based models utilize physical mechanisms to simulate the switching process. While kMC models use Monte Carlo statistics to simulate the movement of the individual atoms and ions during generation and recombination, compact models present a more simplistic approach by considering a changing height of a block of conductor to represent the filament evolution.

A physical model and a thermally activated hopping model were proposed by Ielmini for multi-level state filament growth and ion migration.[125] Similarly, a physical model was applied by Bousoulas *et al.* to highlight the local electric field and temperature profiles of SET/RESET transitions.[126] Numerical models were also proposed by Larentis *et al.* and S. Kim *et al.* to explore temperature and field-accelerated migration of V_o^+ .[127, 128]. Arrhenius equation models were also investigated by Chiu *et al.* and Khurana *et al.*[129, 130] Furthermore, a negative voltage modulated multi-level resistive switching during reset was observed and explained using conduction mechanisms by Chakrabarti *et al* and Samanta *et al.*[131, 132] On a similar note, temperature dependent conduction mechanisms were used by Bai *et al.* to explain the V_o^+ evolution at different multi-level states.[133] A V_o^+ evolution model was also proposed by Qi *et al.* to explain the dendritic filament under different negative electric fields.[134] While these literatures exhibit various methods of explaining filament evolution in multi-level states, there have been limited physics understanding on the behavior and density of oxygen vacancies (n_D) at different V_{stop} . In this Section, kMC and compact modelling will be thoroughly discussed.

1.5.1 Kinetic Monte Carlo (kMC) Modelling

Physics-based models consist of physical mechanisms that drives switching such as diffusion, generation/recombination, and conduction mechanisms such as Schottky emission, hopping and trap-assisted tunneling (TAT) mechanisms. As resistive switching is influenced mainly by electric field and temperature, physics-based models employ Poisson's equation and Fourier's equation to calculate electric potential and temperature, respectively.[135] Hatem *et al.* presented a Schottky model based on quantum mechanics and electron band theory to simulate the bipolar resistive switching of Pt/Ta₂O₅/TaO_x/Pt RRAM.[136] Jagath *et al.* explored the conduction mechanisms of RRAMs more thoroughly by incorporating the TAT model with the Schottky model to simulate the current–voltage (I – V) characteristics.[137] Another TAT approach was investigated and exploited by Guan *et al.* in using the kMC method to simulate the generation and recombination of atomistic processes of V_o^+ and considered Mott hopping for trap-to-trap hopping.[138, 139] Abbaspour *et al.* integrated the TAT approach from a two-dimensional (2D) to a three-dimensional (3D) structure and incorporated the Fourier's heat equation to account for temperature effects during resistive switching.[140] Additionally, Padovani *et al.* has demonstrated a multi-phonon TAT approach which accounted for power dissipation through phonon exchange in their kMC model.[141]

In the kMC modelling, material and transport properties of a particular RRAM stack such as the behavior of V_o^+ in the oxide layer were thoroughly considered. The model begins with only a handful of V_o^+ defects in the oxide as per as-fabricated RRAM devices. As a positive voltage is applied to the RRAM in the simulation, the increase in energy causes the generation of V_o^+ defects in an almost linearly increasing fashion at random locations of the oxide. This eventually forms a V_o^+ filament bridge, connecting the two electrodes of the RRAM device, producing a SET state. Conversely, as a negative voltage is applied, the increase in energy causes the number of V_o^+ defects to recombine with oxygen ions (O^{2-}) in an almost linearly increasing fashion, breaking off the filament bridge and producing a RESET state. A more detailed explanation of the filament evolution can be found later in Section 5.2.2 later.

1.5.2 Compact Modelling

While kMC models have been shown to accurately represent the experimental physics in the atomic scale, compact models complement Physics-based models by considering conceptual simplifications and physical assumptions of experimental processes.[142] Notably, SPICE software such as Cadence has been built for Very Large-Scale Integrated Circuit (VLSIC) designs to simplify computations and save simulation time. As it was commonly known that switching is based on the filament behavior during generation and recombination processes, compact models are built to account for the switching dynamics of a single dominant filament.[30, 143-147] Due to the metallic-like filament conduction, most compact models defined an ohmic LRS and non-ohmic HRS, which uses TAT.[30, 143-147] The HfO_x-based compact model by Puglisi *et al.* and the Stanford compact model by Guan *et al.* considers the dynamics of the filament gap with respect to time and voltage,[143, 144] while the compact model by Bocquet *et al.* considers the dynamics of filament size with respect to time and voltage.[145] An improved model was created by Huang *et al.* to include both gap and size dynamics of the filament.[146, 147] Thereafter, the model created by Puglisi *et al.* included random telegraph noise (RTN) to exhibit random noise during RRAM characterizations.[148] These RRAM compact models take temperature and filament variation into account to better represent the physics and dynamics.

1.6 Research Objectives

This work aims to fill the research gap of conduction and switching mechanisms of MgO and HfO₂-based RRAM devices in the HRS, while modelling HfO₂-based RRAM devices for the industry. The change in filament gap during the RESET process were explained by electron/ion conduction and multi-level state switching dynamics, which were later modelled using kMC and SPICE to further bridge physics to the industry. While the existing experimental and modelling works on MgO and HfO₂-based RRAM devices introduced in previous Sections show some conduction and switching dynamics investigations, there seemed to be a lack of understanding of the behavior of ions/electrons during filament rupture. Therefore, this work bridges this gap by extending the existing works to investigate more conduction mechanisms, further exploring switching dynamics using multi-level states, and finally modelling these RRAM characteristics for prediction analysis for industry.

The main motivation of this research work is to address “How can the filamentary physics and modelling of RRAM be integrated to industry?” Figure 1.8 shows a flow of the three main chapters of this thesis, which eventually achieves the goal of prediction analysis for industry. The research objectives are broken up into two main wings, the first being experimental where stack development and optimization were performed with material and electrical characterizations. Dominant conduction mechanisms were explored using band alignment and fittings, while switching dynamics were investigated using multi-level states and fittings. Thereafter, area studies were also performed, and all these findings were implemented into the second wing, the physical modelling. KMC and SPICE were used in modelling the switching characteristics of the HfO₂-based RRAM devices, which aims to achieve prediction analysis for the industry.

Figure 1.8 Objectives and scope of research, exhibiting the 3 main chapters of this thesis.

1.7 Thesis Organization

This thesis consists of 6 chapters as follows: introduction, experimental techniques, conduction mechanisms of MgO and HfO₂-based RRAM devices, switching dynamics of MgO and HfO₂-based RRAM devices, modelling physics of Pt/HfO₂/Ti RRAM devices and ending with conclusion and future works. **Chapter 1** discusses the recent advances in RRAM, the underlying physics of RRAM from mechanisms to modelling and the motivations of this work. **Chapter 2** describes the fabrication and characterization techniques used in the making and testing of RRAM devices. **Chapter 3** focuses on the conduction mechanisms of various MgO and HfO₂-based RRAM devices to investigate the behavior and movement of ions and electrons

at low voltages without the influence of the higher voltage switching process. **Chapter 4** is a continuation of Chapter 3 where the switching dynamics of various HfO_2 and MgO -based RRAM devices were investigated. It also includes the multi-level state switching processes that have proven useful in transitioning from a traditional 2-state memory into a multi-state memory, useful for neuromorphic computing. **Chapter 5** extended the physics mechanisms of Chapter 3 & Chapter 4 into filamentary investigations and filamentary-based modelling of $\text{Pt/HfO}_2/\text{Ti}$ devices. The filamentary RRAM models not only provided more physics explanations on the mechanisms, but also created a platform for future integration with the 40 nm transistor. **Chapter 6** builds up on Chapters 3, 4 & 5 where it utilizes the physics mechanisms and models of $\text{Pt/HfO}_2/\text{Ti}$ devices for future industrial 40 nm or smaller 1T1R integration and neuromorphic applications.

Chapter 2

Experimental Techniques

This chapter discusses the experimental techniques used in the fabrication and characterization of RRAM devices. The fabrication of RRAM devices includes a two-step lithography, deposition, and etching processes while the characterization of the RRAM devices can either be in the form of electrical or material characterizations. Electrical characterization techniques include both direct current (DC) and alternating current (AC) or pulse measurements. Advanced characterizations techniques such as device retention and endurance measurements were also performed on the RRAM devices and discussed in this chapter. Material characterizations such as Atomic Force Microscopy (AFM), Transmission Electron Microscopy (TEM), Scanning Electron Microscopy (SEM) and X-ray Photoelectron Spectroscopy (XPS) were also performed on the RRAM devices and discussed in this chapter.

2.1 Device Fabrications

The RRAM device fabrication includes the standard processes of 2-step lithography, etching, deposition and lift off where the process flow is shown in Figure 2.1. In step ①, Si/SiO₂(300 nm) wafers are cut into small 1.5 cm × 1.5 cm square pieces and soaked in Acetone followed by Isopropyl Alcohol (IPA) baths in ultrasonic for 10 minutes. These samples are dried using nitrogen N₂ and heated at 100°C for 2 minutes for the removal of residual IPA. This cleaning process ensured that the samples are free from wafer shards and organic contaminants that might adversely affect the uniformity of the spin-coating process or the subsequent sample performance. Step ② is where the samples were spin-coated by photoresist and soft-baked while step ③ is the UV exposure process. This is followed by step ④ where the samples are developed to remove the exposed areas. An etching using ion milling was followed in step ⑤ to remove a depth of Si/SiO₂, leaving behind a cavity in the Si/SiO₂ sample. The cavity was filled with 10nm of bottom electrode of the RRAM as shown in step ⑥ using a magnetron sputtering process. The photoresist was then lifted off in step ⑦ and the remaining structure is the bottom electrode embedded in the Si/SiO₂ sample. Steps ⑧ to steps ⑬ mirrors steps ② to steps ⑦, respectively except that the lithography patterns were perpendicular to the bottom electrode, creating a cross-point structure when 10nm of insulator and 30nm of top electrode were deposited and lifted off from steps ⑪ to ⑬. In the following Sections 2.1.1 to 2.1.3, this full fabrication process flow will be thoroughly discussed and explained.

Figure 2.1 Fabrication process of RRAM devices consisting of a 2-step lithography process, etching and deposition processes

2.1.1 Ultraviolet (UV) Photolithography

After cleaning the samples with Acetone and IPA as per step ① of Figure 2.1, the spin-coating process follows with AZ5214E positive photoresist spin-coated onto the samples surface at 6000 rpm for about 60 seconds as per step ② of Figure 2.1. The spin-coated samples are baked using a heater at 110°C for 2 minutes to harden the photoresist as a soft baking process and cooled to room temperature. The spin-coater and heater on the wet bench is shown in Figure 2.2(a). After the soft-baking process, the soda-line glass mask as shown in Figure 2.2(b) was hooked up to the UV mask aligner stage where the spin-coated samples are placed directly and brought to the correct height below the soda-line mask. The soda-line mask and the UV mask aligner were exhibited in Figures 2.2(b) and (c), respectively. The UV exposure was followed as per step ③ of Figure 2.1 for 16 seconds. The developing process was continued where AZ531 developer was used to develop the UV exposed samples after about 15 seconds. The AZ531 developer was mixed with de-ionized water at the concentration of 1:4 and the developing process was stopped by deionized water. As AZ5214E is a positive photoresist, the regions that are exposed to UV light were weakened and the developing process would remove those weak regions, thus producing RRAM device patterns on the photoresist

as shown in step ④ of Figure 2.1. The device patterns fabricated using UV lithography range from $5 \times 5 \mu\text{m}^2$ to $50 \times 50 \mu\text{m}^2$.

(a)

(b)

(c)

Figure 2.2(a) Heater (left) at a temperature of 110°C for 2 minutes & spin-coater (right) at 6000 rpm for 60 s, (b) soda-line glass mask with different patterns (c) UV mask aligner

2.1.2 Etching

After the developing process where the RRAM device photoresist patterns are formed on the samples, the etching process is used to etch directly into regions that are not covered by photoresist, *i.e.* the Si/SiO₂ regions. The photoresist needs to be sufficiently thick and have a slow etch rate to prevent any depletion during the etching process, and in this case the spin-coated photoresist thickness is $\sim 2\ \mu\text{m}$. The etching process employed is an ion milling process where ion bombardment is used to remove any surface material, forming an cavity region as described in step ⑤ of Figure 2.1. This was also shown in Figure 2.3(a) where Argon ions were ejected from the ion gun and bombarded onto the specimen, forming a cavity in the ion beam irradiating area. A rotation was also required to ensure a uniform etching process. The etch rate for Si/SiO₂ wafers were pre-calibrated prior to the ion milling process, which was followed by atomic force microscopy (AFM) to measure the etch depth accurately before the deposition process. AFM techniques and deposition processes will be discussed in greater detail in Sections 2.3.1 and 2.1.3 respectively. If the thickness of the etched material is important, secondary ion mass spectrometry-end-point detection (SIMS-EPD) will be utilized. As shown in Figure 2.3(b), the SIMS-EPD is a detection of the number of elemental ion mass at each interval of time during the milling process. When a particular material has been etched, the SIMS-EPD will detect a high number of these elemental ions as indicated by a peak. When a material has been etched completely, it forms a flat line close to zero, indicating little amount of material ions remaining. This process continues until a desired thickness or type of material has been reached.

(b)

Figure 2.3(a) Ion milling system exhibiting the working processes, (b) secondary ion mass spectrometry-end-point detection (SIMS-EPD) showing different element profile peaks, indicating the presence of a particular material.

2.1.3 Sputter Deposition

Following the etching process in step ⑤ of Figure 2.1, all layers of the RRAM device is deposited via magnetron sputtering process as shown in steps ⑥, ⑪ and ⑫ of Figure 2.1. The working principle of magnetron sputtering is where negatively charged material targets are bombarded by positively charged argon plasma ions, causing the target material ions to detach from the material surface and deposited onto the samples as shown in Figure 2.4(a).[149] In the fabrication of the RRAM devices, metals such as Ta, Ti, Cu, Pt and Ru are deposited via direct current (DC) sputtering while oxides such as MgO and HfO₂ are deposited via radio frequency (RF) sputtering. Due to the low conductivity of oxides, using DC sputtering will result in excessive positive charge build up on the oxide targets, resulting in little to no deposition. Therefore, RF sputtering is necessary as the 2nd cycle of alternating current (AC) would reverse the polarity to remove the built-up positive charges, resulting in a repeated oxide bombardment and deposition. A sufficient power and pressure are also required for plasma generation. For example, 50 W, 2 mTorr, 20 sccm of Ar at room temperature conditions are required for metal depositions such as Pt and Ti. For oxides such as MgO (60% Mg and 40%

O) and HfO_2 , 50 W, 1.5 mTorr, 20 sccm of Ar at room temperature conditions are required. Figure 2.4(a) show two sputter deposition systems capable of achieving ultra-high vacuum base pressures of 10^{-8} Torr and are connected by a common load-lock chamber to facilitate material depositions from different chambers. Each of these sputter systems consist of 8 targets shown in Figure 2.4(b) while RRAM samples are being placed on a cassette, which is placed on the transfer arm of the deposition system as shown in Figure 2.4(c). The deposition rate of each sputter target is also calibrated regularly to ensure the correct material thickness in the RRAM devices during deposition. The calibration would require deposition on patterned wafers followed by a lift-off process to investigate the deposited step-height using AFM, which will be discussed further in Section 2.3.1. In addition, prior to the deposition of layers, a process known as pre-sputtering will be performed on an empty cassette to remove any contaminants on the surface targets. These contaminants could be caused by previous rounds of depositions which are not intended to be deposited on the RRAM devices.

(a)

(b)

(c)

Figure 2.4(a) Magnetron sputtering system exhibiting the working processes, (b) 8-gun targets of each sputtering chamber, (c) 9 samples after the deposition process (placed on the cassette on the transfer arm).

2.2 Electrical Characterizations

Predominantly, there are two modes of electrical characterizations, *i.e.* DC and AC which are used for different kinds of characterizations in RRAM. DC is mainly used for I - V sweep measurements to investigate basic RRAM characteristics such as ON/OFF ratio, switching voltage, current output and to investigate the conduction physics of ions and electrons in the RRAM. AC on the other hand is a faster characterization method used for pulsed measurements such as pulsed switching and pulsed endurance. ON/OFF ratio can also be obtained from the pulsed endurance as well, which will be discussed in greater detail in Section 2.2.3. The electrical testing setup was exhibited in Figure 2.5(a) and will be discussed in detail in Sections 2.2.1 and 2.2.2. Figure 2.5 (b) shows the exterior of the probe station set-up, while Figures 2.5(c) exhibited the zoomed-in image of the probed sample or device under test. The probe stations used in the electrical measurements of the RRAM devices are Cascade Microtech with Keithley 4200 semiconductor analyzer with a one pulse measurement unit (PMU) and two source measurement units (SMUs) configuration. While the source measurement unit (SMU) supplies the voltage/current and pulse measurement unit (PMU) controls the pulse, the remote amplifier (RPM) is the circuit element that controls the amount of voltage and the channel in which the voltage is directed to.

Figure 2.5(a) Electrical testing setup with 1 PMU & 2 SMUs connected to the RRAM device, (b) probe station with in-situ heater, (c) zoomed-in probe sample on the stage without in-situ heater, (d) zoomed-in probe sample on the stage with in-situ heater.

2.2.1 Direct Current (DC) Measurements

A DC measurement of RRAM devices is an I - V sweep characterization where an external voltage is applied across the top and bottom electrodes and the current is measured. The application of external voltage was performed by using two SMUs as shown in Figure 2.5(a), one acting as a ground unit to the bottom electrode while the other acting as either a positive or negative voltage source unit. Figure 2.6 shows a full DC I - V characterization cycle of a typical RRAM device where it started from a low current state and the current was increased with increasing voltage ① until a breakdown voltage is reached ② where there is a sudden surge in current, indicating a change in the state of the RRAM. A voltage sweep back was performed at ③ and a negative bias was applied thereafter, resulting in an increase in current

with increasing negative voltage ④. This continues until there is sufficient energy for the RRAM to change its state back to the low current state ⑤. Unlike ② where there is always a sudden surge in current, ⑤ could be a more gradual decrease in current and ⑥ is the sweep back process, thus completing the DC I - V cycle. Regions ①, ③, ④, ⑥ are the non-switching or the conduction parts of the curve, which can reveal the ionic and electronic behavior prior to switching. On the other hand, regions ② and ⑤ are the switching parts of the curve, which reveal the filament behavior during switching or changing of state. DC measurements are usually a pre-determinant of the electrical characteristics of the RRAM during the alternating (AC) measurements as shown in Section 2.2.2.

Figure 2.6 A complete DC I - V cycle of a typical RRAM device

2.2.2 Alternating Current (AC) / Pulsed Measurements

Similar to DC measurements, AC or pulsed measurements are used to measure the switching current or voltage characteristics of the RRAM except that the response is with respect to time. Typically, pulses consist of the rising, constant and falling voltage segments as indicated by ①, ② and ③, respectively as shown in Figure 2.7(a). The rising voltage segment in ① increased from 0 V to a desired switching voltage for a time period known as the rise time, the constant voltage segment in ② remained at the same voltage for a time period known as pulse width, while the falling voltage segment in ③ decreased from a desired switching voltage to 0 V for a time period known as the fall time. The pulse width could also be defined

in a different manner where it is taken from the half-way point of the rise time to the half-way point of the fall time as shown in Figure 2.7(b). However, for the AC measurements of the RRAM devices in this work, the pulse width was defined as per Figure 2.7(a). While there are numerous write schemes, Figure 2.7(c) shows a typical pulse measurement starting with a positive SET switching pulse, followed by a positive read pulse, and a negative RESET switching pulse, followed by another positive read pulse. These pulsed waveforms require both pulse generation and reading using two timed synchronized RPM channels of the PMU as shown in Figure 2.5(a), where the system can perform current measurements up to 80 ns response time.

Figure 2.7(a) Definition 1 of a pulse where pulse width ranges from end of rising voltage segment and start of falling voltage segment, (b) Definition 2 of a pulse where pulse width ranges from the middle of rising voltage segment and middle of falling voltage segment, (c) A typical pulse measurement consisting of SET, RESET and read pulse.

2.2.3 Endurance using DC & Pulsed Measurements

Endurance is a measure of stress on a device on the number of times the data can be programmed and erased without excessive degradation of device performance. Endurance can be performed either using DC or AC as shown in Figure 2.8(a) and (b), respectively where the resistance was extracted and plotted against the number of program/erase cycles. As DC switching requires a full I - V sweep, it is much slower and about 2000 endurance cycles were obtained as shown in Figure 2.8(a). On the other hand, AC are much faster, which in this case 100 ns pulse width was used and $\sim 5 \times 10^5$ endurance cycles were obtained as shown in Figure 2.8(b). It can be observed that over time, the HRS and LRS converge and if they exceed a certain margin, it would be considered as a failure.

Figure 2.8 Endurance measurement using (a) A DC switching generating $\sim 2 \times 10^3$ cycles of Pt/MgO/Cu RRAM devices and (b) An AC pulsed switching generating $\sim 5 \times 10^5$ cycles of Pt/HfO₂/Ti RRAM devices.

2.2.4 Retention Measurements using Voltage-stress and Temperature-stress

Similar to endurance, retention is another type of stress technique used to predict the time period in which data can be retained after storing it, typically over 10 years at 85°C or 125°C. Figure 2.9(a) and (b) shows two different retention measurement techniques. The first technique utilizes constant voltage stress where a low read voltage such as 0.1V is used to read the resistance state over time for both HRS and LRS as shown in Figure 2.9(a). This period could be extrapolated as indicated by the horizontal lines and the data retention can be estimated. The other technique shown in Figure 2.9(b) uses temperature stress to intentionally

accelerate the failure of the device at high temperatures. The RRAM devices are first switched to a particular state and stressed at a high temperature until failure where the failure time is recorded. The failing criteria is where the state is lost during the stress, *e.g.* HRS switched to LRS. This process was repeated for various temperatures where the time to fail was plotted against the inverse of temperature and extrapolated to 85°C or 125°C to find out the retention time at these temperatures. In general, the device is expected to fail faster at higher temperatures and the activation energy (E_a) can be extracted using Arrhenius equation.

Figure 2.9 Different failure acceleration techniques for retention measurement of Ru/MgO/Cu and Ru/MgO/Ta RRAM devices using (a) Voltage-stress exceeding 3 hours, and (b) Temperature stress using Arrhenius equation, exceeding 10 years at 85°C.

2.3 Material Characterizations

Material characterizations such as atomic force microscopy (AFM), transmission electron microscopy (TEM), scanning electron microscopy (SEM) and X-ray Photoelectron Spectroscopy (XPS) revealed more about the atomic and material composition characteristics which can be supplemented with the electrical characterization data. The SIMS-EPD technique mentioned in Section 2.1.2 is also part of the material characterization where the mass of the elemental ions was measured, and the particle count was detected.

2.3.1 Atomic Force Microscopy (AFM)

As part of the fabrication of the RRAM devices in this work, AFM is mainly used to measure the ion milling depth in step ⑤ of the fabrication process flow shown in Figure 2.1

to estimate the thickness of bottom electrode to be deposited in step ⑥. This will require a sacrificial sample to be lifted-off for the measurement of the ion milling depth. The AFM is also used to regularly calibrate the rate of the deposited films before the material depositions as shown in steps ⑥, ⑪ and ⑫. In this work, the imaging was performed in the non-contact mode where the AFM tip interact with the sample surface using atomic forces to investigate the material characteristics. The movement and atomic force response of the cantilever across the sample surface are tracked by a laser beam and is detected by a photodiode detector. The detected signal is feedback into the system to keep the cantilever deflection constant in the Z-direction during the imaging process. Figure 2.10(a) shows an AFM system on the left and the controllers on the right, while Figure 2.10(b) shows an AFM image of one of the typical RRAM devices used in this work. While the TE is clearly visible under AFM, the BE might not be as visible due to the similar lateral height as the Si/SiO₂ wafer explained by step ⑦ of the process flow shown in Figure 2.1. Hence, the BE was outlined in dotted white lines to exhibit its structure. However, the same BE structure can be observed under SEM in Figure 2.12(c) in Section 2.3.2.

Figure 2.10(a) AFM system (left) with controllers on the right, (b) AFM image showing the top view of a typical RRAM device used in this work.

2.3.2 Transmission Electron Microscopy (TEM) & Scanning Electron Microscopy (SEM)

TEM uses a broad beam of electrons to scan the internal material structure, *i.e.* the morphology, composition, and crystallinity of the sample as shown in Figure 2.11(a). SEM uses a fine beam of electrons to scan the surface material structure, *i.e.* topography and

elemental composition of the sample as shown in Figure 2.11(b). The similar working principles of TEM and SEM derives from an electron source that passes through multiple set of lenses, but SEM is usually coupled with detectors for secondary electron and X-ray detections. In addition, TEM is often performed after a focused ion beam (FIB) process to thin down the thickness of the sample to sub-100 nm scale.

Figure 2.11 (a) Transmission electron microscopy setup and (b) Scanning electron microscopy setup, exhibiting their respective working processes of electron source passing through a series of lenses.

Figure 2.12 and 2.13 shows the TEM and SEM images of the RRAM devices used in this work, respectively. Figure 2.12 shows the different TEM magnifications of 40,000 $\times$, 80,000 $\times$, 400,000 $\times$ and 1,200,000 $\times$ as per (a), (b), (c) and (d), respectively. Higher magnifications shown in Figures 2.12(c) and (d) clearly identified oxide and metals as amorphous and crystalline structures, respectively. Figure 2.13 shows the different SEM magnifications of 100 $\times$, 1,000 $\times$, 10,000 $\times$ as per (a), (b), (c), respectively. It can be seen from Figure 2.13 that the RRAM devices used in this work are all fabricated as a cross-point structure, with TE and BE perpendicular to each other.

(a)

(b)

(c)

(d)

Figure 2.12 TEM image of the different layers of Pt/HfO₂/Ti RRAM devices at magnifications of (a) 40,000 $\times$, (b) 80,000 $\times$ (c) 400,000 $\times$ and (d) 1,200,000 $\times$.

(a)

(b)

(c)

Figure 2.13 SEM image of fabricated Pt/HfO₂/Ti RRAM devices at magnifications of (a)100×, (b) 1,000× and (c) 10,000×.

2.3.3 X-ray Photoelectron Spectroscopy (XPS)

XPS are performed using Electron Spectroscopy for Chemical Analysis (ESCA), a widely used technique for measuring the chemical composition of material surfaces. The spectral peak energy, intensity, and structural analysis were used to determine the composition and chemical state of the material species.[150] The XPS working process is shown in Figure 2.14(a), where X-rays were emitted and reflected from a sample surface to an energy analyzer, which reveal the various characteristic elemental spectrums. In an example of HfO₂ thin film, the atomic concentrations were calculated to be ~67% oxygen and ~33% hafnium or HfO₂ with an error of 0.25%. Figure 2.14(b) and (c) exhibited the typical Hf, 4f and O, 1s peaks, indicating the characteristic binding energies at various intensities.

(a)

(b)

(c)

Figure 2.14 (a) Working processes of XPS showing the emission and reflection of x-rays with characteristic elemental spectrums detected, (b) XPS profile of Hf 4f, and (c) XPS profile of O 1s of HfO₂ films.

Chapter 3

Conduction Mechanisms of MgO and HfO₂-based RRAMs

This chapter focuses on investigating the conduction mechanisms of MgO and HfO₂-based RRAM devices, exploring the behavior of ions and electrons before switching. While Schottky Emission was found to be the dominant conduction mechanisms of Ru/MgO/Cu and Ru/MgO/Ta RRAM devices, hopping conduction was found to be the dominant conduction mechanism of Pt/MgO/Cu and Pt/HfO₂/Ti RRAM devices. This suggests that all layers of the RRAM have a role to play in determining the dominant conduction mechanisms. Material studies such as TEM and EDX have also shown Cu to be the filament in Ru/MgO/Cu and Pt/MgO/Cu devices while material studies have shown that MgO-based devices exhibit a high retention of more than 10 years at 85°C.

3.1 Ru/MgO/Ta and Ru/MgO/Cu RRAM Devices

The investigation of Ru(10nm)/MgO(10nm)/Cu(30nm) and Ru(10nm)/MgO(10nm)/Ta(30nm) RRAM devices is focused on the conduction mechanism physics and performances between the two main switching mechanisms in RRAM, *i.e.* ECM and VCM, respectively. Cu is widely known to form a metallic bridge as the RRAM filament while Ta is known to form V_o^+ as the RRAM filament, which provided a good material choice as active electrodes for performance comparison. Ru on the other hand is an inert electrode, for filaments to start forming but it does not need to be too thick (*i.e.* 10nm is sufficient) because only the interfacial layer of atoms is important. 10 nm of MgO was deposited to create sufficient filaments to bridge between the active and inert electrodes, as too thick of an oxide will result in a higher switching voltage and hence a higher power consumption. The active electrodes on the other hand, needs to be thicker (*i.e.* 30 nm) because redox reactions will occur for a few layers as atoms are oxidized into ions. The RRAM devices were fabricated using standard fabrication processes of UV lithography, etching and deposition as described in Section 2.1.

Part of this chapter has been reproduced from Scientific Reports Springer Nature under the Creative Commons License: <http://creativecommons.org/licenses/by/4.0/>.¹

3.1.1 Electrical Characteristics of Ru/MgO/Ta and Ru/MgO/Cu RRAM Devices

In the investigation of conduction mechanisms in MgO-based RRAM devices, single 1R cells with dimensions 30 μm x 30 μm were characterized, as shown in Figure 3.1 and 3.2. 50 cycles of semi-log I – V curves of annealed Ru/MgO/Ta and Ru/MgO/Cu RRAM devices were exhibited in Figure 3.1(a) and (b), respectively. It was observed that the switching voltage distribution of Ru/MgO/Ta RRAM devices was found to be more consistent than Ru/MgO/Cu RRAM devices. The average ON/OFF ratios of Ru/MgO/Ta and Ru/MgO/Cu RRAM devices were found to be 10^2 . Box plots for 5 devices of 50 cycles each for Ru/MgO/Ta and Ru/MgO/Cu RRAM devices were shown in Figure 3.2(a) and (b), respectively. As seen from Figure 3.1 and 3.2, Ru/MgO/Ta resistive switching memory (RRAM) devices have a much

¹ This Chapter is partly published as a peer-reviewed journal as Desmond Jia Jun Loy, Putu Andhita Dananjaya, Xiao Liang Hong, Danny Pak-Chum Shum and Wen Siang Lew, "Conduction Mechanisms on High Retention Annealed MgO-based Resistive Switching Memory Devices" – Scientific Reports, 8, 14774 (2018). <https://doi.org/10.1038/s41598-018-33198-0>

tighter high resistance state (HRS) distribution as compared to Ru/MgO/Cu RRAM devices. This could be explained by the higher diffusivity effect of Cu as compared to Ta atoms into the MgO dielectric layer, which results in a larger variation of filament formation/rupture for Ru/MgO/Cu RRAM devices as compared to Ru/MgO/Ta RRAM devices. The variation of filament formation/rupture in turn results in a greater HRS variation for Ru/MgO/Cu RRAM devices as compared to Ru/MgO/Ta RRAM devices. The same reasoning can be used to explain the larger switching voltage variation in Ru/MgO/Cu RRAM devices as compared to Ru/MgO/Ta RRAM devices.

Figure 3.1 50 semi-log I - V cycles of annealed (a) Ru/MgO/Ta and (b) Ru/MgO/Cu RRAM devices. It can be observed that the switching voltage distribution of Ru/MgO/Ta RRAM devices was found to be more consistent than Ru/MgO/Cu RRAM devices. The average ON/OFF ratio of the RRAM devices was found to be 10^2 .

Figure 3.2 Box plots of 5 (50 cycles each) annealed (a) Ru/MgO/Ta and (b) Ru/MgO/Cu RRAM devices. Ru/MgO/Ta RRAM devices exhibited a much better distribution and less variation in terms of HRS as compared to Ru/MgO/Cu RRAM devices.

The statistical cycle-to-cycle resistance variations of non-annealed and annealed RRAM devices were compared in Figure 3.3(a) and (b), respectively. The cumulative probability was obtained by categorizing the RRAM resistance of different cycles, and arranging them in ascending order, starting with the lowest cumulative probability. It was shown that despite having a lower ON/OFF ratio of annealed RRAM devices, they can exhibit better cycle-to-cycle resistance variations as compared to non-annealed RRAM devices. The low variation in cycle-to-cycle resistance is imperative to conduction mechanism studies because the conduction of ions and electrons needs to be consistent.

Figure 3.3 Statistical cycle-to-cycle resistance variations between (a) non-annealed and (b) annealed Ru/MgO/Ta RRAM devices. It is evident that despite a lower ON/OFF ratio, annealed RRAM devices exhibit less cycle-to-cycle resistance variation as compared to non-annealed ones.

3.1.2 Schottky Emission of Ru/MgO/Ta and Ru/MgO/Cu RRAM Devices

Prior to performing the conduction mechanism fittings, the conduction mechanism for the MgO-based RRAM was suggested to be an electrode-limited type rather than bulk-limited type. This can be attributed to Ru being the inert electrode for the MgO-based RRAM devices. It was reported that the conduction band offset ΔE_C between MgO and Si is 1.5 eV,[24] while the electron affinity of Si and work function of Ru are 4.05 eV and 4.71 eV, respectively.[81, 151] This means that the ΔE_C between MgO and Ru has to be 2.16 eV, which is about 1 eV lower than the energy barrier between Pt and MgO as reported.[70] While the Pt/MgO barrier is a bulk-limited conduction mechanism due to the high energy barrier, the Ru/MgO interface should be dominated by electrode-limited conduction mechanism due to its lower energy barrier. In this work, it would suggest that electrode-limited conduction mechanism is dominant in Ru/MgO/Cu and Ru/MgO/Ta RRAM devices.

The first conduction mechanism investigated was Schottky emission (SE), which takes place when thermally activated electrons gained enough energy to jump into the conduction band of the dielectric layer. SE is the most observed conduction mechanism and is an electrode-limited conduction mechanism as shown in Equation 1, exhibiting the current density expression for SE:

$$J_{SE} = \frac{4\pi q m^* (kT)^2}{h^3} \exp \left[\frac{-q(\Phi_B - \sqrt{qE/4\pi\epsilon})}{kT} \right], \quad (1)$$

where q is the electron charge, m^* is the electron effective mass in the oxide, k is Boltzmann's constant, T is the absolute temperature, h is Planck's constant, Φ_B is the junction barrier height, E is the electric field across the oxide, and ϵ is the permittivity of the oxide.[76, 83] FN-tunneling was investigated as another form of electrode-limited conduction mechanism. It occurs in high electric fields where the thickness of the dielectric is more than 3 nm, which fits the criteria of the investigated MgO layer thickness. Equation 2 exhibits the current density expression for FN-tunneling and the parameters used in Equation 2 are similar to those used in Equation 1.[76, 83]

$$J_{FN} = \frac{q^2}{8\pi h \Phi_B} E^2 \exp \left[\frac{-8\pi \sqrt{2q m^*} \Phi_B^{3/2}}{3hE} \right] \quad (2)$$

In the investigation of SE, the temperature was varied from 300 K to 375 K in intervals of 25 K while I–V curves were characterized. Equation 3 shows the SE fitting curve of the form $\ln(I_{SE})$ vs. $\sqrt{V}$ which in turn generated the slope, M for each of the stated temperatures 300 K, 325 K, 350 K and 375 K as shown in Figure 3.4(a) to (d), respectively. The linear fit shows that Ru/MgO/Ta RRAM devices exhibit SE conduction mechanism. TEM was used to further verify the SE conduction mechanism by comparing the actual and calculated values of d , the distance between the tip of the filament and the MgO/Ru interface. d can be calculated from M as shown in Equations 4 and 5. The values of M and d are shown in Table IV.

$$\ln(I_{SE}) = \ln \left(\frac{4\pi q m^* (kT)^2 A}{h^3} \right) + \frac{-q\Phi_B}{kT} + \frac{q\sqrt{q/4\pi\epsilon d}}{kT} \sqrt{V} \quad (3)$$

$$M = \frac{\sqrt{q^3 / \pi \epsilon_r \epsilon_0 d}}{2kT} \quad (4)$$

$$d_{SE} = \frac{q^3}{(2kTM)^2 \pi \epsilon} \quad (5)$$

In Table IV, it can be generally observed that with an increase in temperature, the distance d decreases. This coincides with the fact when d increases (decreases), the HRS resistance increases (decreases) proportionally, as more (less) filament is being ruptured. A TEM image of the Ru/MgO/Ta RRAM device as exhibited in Figure 3.5 where a thin layer of ~ 2.5 nm Ta was diffused into MgO. The diffusivity of Ta into MgO was attributed to the annealing process which agitates the Ta/MgO interfacial atoms, causing the Ta atoms to cross over the grain boundaries of MgO atoms. It can be concluded that the diffusivity of Ta into MgO had resulted in a lower thickness of MgO (actual $d = 7.5$ nm vs. calculated $d = 8.84$ nm at 300 K) and further validated the SE conduction mechanism of the Ru/MgO/Ta RRAM device.

Figure 3.4 $\ln(\text{current})$ vs. $\sqrt{\text{voltage}}$ and linear fitting for Ru/MgO/Ta RRAM devices at (a) 300 K, (b) 325 K, (c) 350 K, (d) 375 K. The linear fitting shows that Ru/MgO/Ta RRAM devices exhibit SE.

Figure 3.5 TEM image of Ru/MgO/Ta RRAM device showing uniformly deposited layers. TEM was employed to investigate the thickness of MgO and it was observed that a thin layer of Ta of ~2.5 nm was diffused into MgO.

Table IV Relationship between temperature, T , gradient of linear fit, M and the distance between the tip of the filament and the MgO/Ru interface, d for Ru/MgO/Ta devices. The general trend shows that with an increase in temperature, d decreases.

T/K	M	d/m
300	5.06	8.84×10^{-9}
325	5.35	6.73×10^{-9}
350	4.81	7.18×10^{-9}
375	4.92	5.98×10^{-9}

The same characterization and analysis were performed for Ru/MgO/Cu RRAM devices. The same conclusions can be made about Ru/MgO/Cu RRAM devices as shown in Figure 3.6 (a) to (d) where it was shown that SE is also the main conduction mechanism. Similar analysis and discussions exhibited that FN-tunneling conduction mechanism was rejected as the main conduction mechanism for the RRAM devices due to the poorly fitted curves shown in Appendix A1: FN-Tunneling Investigations. Other electrode limited conduction mechanisms such as direct tunneling were eliminated based on the thickness of the MgO, because it has been reported that only less than 3 nm of oxide will direct tunneling occur, such that electrons can directly tunnel from one electrode to the other. [76, 83]

Figure 3.6 $\ln(\text{current})$ vs. $\sqrt{\text{voltage}}$ and linear fitting for Ru/MgO/Cu RRAM devices at (a) 300 K, (b) 325 K, (c) 350 K, (d) 375 K. The linear fitting shows that Ru/MgO/Cu RRAM devices also exhibit SE.

3.1.3 Retention of Ru/MgO/Cu and Ru/MgO/Ta RRAM Devices

Aside from investigating the physics, it is also important to investigate the data retention of the RRAM devices. Ru/MgO/Cu and Ru/MgO/Ta RRAM devices were heated using various high temperatures to accelerate the rate of failure. At the same time, the devices were characterized to obtain their resistance values at fixed intervals of time. The retention data were plotted in Figure 3.7 and was fitted using Arrhenius equation[152, 153] where the time to fail (archival time) for each RRAM device was plotted against the reciprocal of the heated temperature. The archival time was obtained from Arrhenius equation shown in Equation 6, where B is a pre-exponential factor the accounts for the frequency of atomic collisions and

orientations, E_a the activation energy of the reactions in the RRAM devices, k the Boltzmann constant while T is the absolute temperature supplied to the system.

$$\text{Archival Time} = B \cdot \exp\left(\frac{E_a}{kT}\right) \quad (7)$$

An extrapolation of the data points shows that both Ru/MgO/Cu and Ru/MgO/Ta RRAM devices were able to retain its memory for more than 10 years at 85°C. Ru/MgO/Cu RRAM devices performed better as compared to Ru/MgO/Ta RRAM devices as Cu filaments are known to be more stable as compared to V_o^+ filaments. This is due to the metallic bridge which is more robust as opposed to one made up of V_o^+ . It was also found from Equation 6 that the E_a for the redox reactions during the retention process of Ru/MgO/Ta RRAM devices was 0.7 eV. This value is very close to the activation energy for the retention process of flash memories of 0.6 eV,[154] which shows that the retention of Ru/MgO/Ta RRAM devices fabricated in this work is comparable to the retention capabilities of flash memories. Similarly, the E_a of Ru/MgO/Cu RRAM devices was calculated to be 1.17 eV. However, it is believed that the pre-exponential factor, B varies with different types of insulators and electrode materials, thus producing different E_a in the process. Hence, an RRAM with a higher E_a does not directly represent a better retention, even though it generally suggests so.

Figure 3.7. Retention data of Ru/MgO/Cu and Ru/MgO/Ta RRAM devices were obtained using *in-situ* temperature stress. An extrapolation shows that the Ru/MgO/Cu and Ru/MgO/Ta RRAM devices were able to retain its memory for more than 10 years at 85°C.

3.1.4 TEM Ru/MgO/Cu RRAM Devices showing Cu atoms inside MgO

TEM studies were also performed to investigate the filament formation in Ru/MgO/Cu RRAM devices. These studies were performed in Ru/MgO/Cu rather than Ru/MgO/Ta RRAM devices as copper filaments in ECM Ru/MgO/Cu RRAM devices are more easily observed as compared to V_o^+ in VCM Ru/MgO/Ta RRAM devices. In the filament analysis of Ru/MgO/Cu RRAM devices, $0.5\ \mu\text{m} \times 0.5\ \mu\text{m}$ devices were specially designed via electron beam lithography (EBL). A smaller RRAM device size of $0.5\ \mu\text{m} \times 0.5\ \mu\text{m}$ was used for the purpose of concentrating and confining filaments to a small region.

The TEM images of pristine and SET state Ru/MgO/Cu RRAM devices were shown in Figures 3.8(a) and (b), respectively, where the TEM image exhibited in Figure 3.8(b) was obtained after a voltage of 2 V was applied. Observing the insulator layer in Figure 3.8(b), the region concentrated at the center consists of crystalline atoms belonging to Cu atoms, while the regions away from the center consists MgO atoms which are less crystalline (or amorphous). With this observation, it can be concluded that the crystalline atoms located at the center belongs to Cu atoms, thus making up the Cu filament. It was also observed that the width of the filament is about 15 nm from the MgO/Cu interface, with a decreasing width to 5 nm at the Ru/MgO interface, which averaged to be about 10 nm.

Figure 3.8(a) TEM image of pristine Ru/MgO/Cu, (b) TEM image of SET state Ru/MgO/Cu. The TEM image shown in (b) was obtained after applying a voltage of 2 V. The average width of the filament was observed to be about 8 nm.

3.2 Pt/MgO/Cu RRAM Devices

Similar studies were performed on Pt(10nm)/MgO(10nm)/Cu(30nm) RRAM devices due to higher retention stability discussed in Section 3.1.3 earlier, along with a further investigation of a Cu filament, which has been easily observed in Section 3.1.4. This Section is to investigate whether a change in the inert electrode, *i.e.* Pt could affect the conduction physics and performance of the RRAM devices. This Section is partly published as a conference proceeding as “Hopping Conduction Temperature Investigations on High Retention Electrochemical Metallization MgO-based Resistive Switching Devices in the Low Resistance State” – EDTM, IEEE (2019). DOI: [10.1109/EDTM.2019.8731244](https://doi.org/10.1109/EDTM.2019.8731244)

3.2.1 Electrical Characteristics of Pt/MgO/Cu RRAM Devices

In the electrical characterization, 100 DC I - V cycles of Pt/MgO/Cu RRAM devices were performed as shown in Figure 3.9(a). It indicated a good ON/OFF ratio between 10^3 to 10^4 , while exhibiting SET and RESET voltages of 4 V and -3 V, respectively. A good cycle-to-cycle variability was also observed in Pt/MgO/Cu RRAM devices, which was further confirmed by the tight vertical box plot ranges of the Pt/MgO/Cu RRAM devices as indicated in Figure 3.9(b). Furthermore, the abrupt switching observed from both SET and RESET processes suggests the possibility of Cu filament formation and rupture in Pt/MgO/Cu RRAM devices, which is a distinctive feature of ECM.[102]

Figure 3.9(a) 100 DC I - V cycles indicating a SET and RESET voltage of 4V and -3 V, respectively with ON/OFF ratio of 10^3 to 10^4 , (b) HRS & LRS box plots of Pt/MgO/Cu devices indicating good cycle-to-cycle variability, maintaining at least an ON/OFF ratio of 10^3 to 10^4 .

3.2.2 Hopping Conduction of Pt/MgO/Cu RRAM Devices

The conduction mechanisms investigated in the Pt/MgO/Cu RRAM devices were suggested to be bulk-limited as the ΔE_C between MgO and Pt was reported to be 3.1 eV as shown in the inset of Figure 3.10.[70] Therefore, the temperature dependent bulk-limited conduction mechanisms investigated in the low resistance state were Poole Frenkel emission, variable range hopping and hopping conduction, as indicated by Equations 7 to 9, respectively.

$$J_{PF} = q\mu N_C E \exp \left[\frac{-q(\Phi_T - \sqrt{qE / \pi\epsilon})}{kT} \right], \quad (7)$$

$$J_{VRH} = \sigma_0 E \exp \left[-\frac{T_0}{T} \right]^{1/4}, \quad (8)$$

$$J_{HC} = qanv \exp \left[\frac{qaE}{kT} - \frac{E_a}{kT} \right], \quad (9)$$

where J is the current density, E is the electric field, T is the varied temperature, a is the mean hopping distance, n is the electron concentration in the conduction band, f is the frequency of thermal vibrations of electrons at trap sites and E_a the hopping barrier between traps.

In the conduction mechanism investigations, temperatures were varied from 300 K to 350 K at intervals of 25 K. Poole Frenkel emission was investigated by plotting $\ln(I/V)$ vs. $\sqrt{V}$, while variable range hopping and hopping conduction were investigated by plotting J vs. E . It was found that P-F is not a good fit, but variable range hopping and hopping conduction exhibited a very good fit in Pt/MgO/Cu RRAM devices. However, it was observed that the resistance state increases as temperature increases, which led to the conclusion that hopping conduction was the dominant mechanism for Pt/MgO/Cu RRAM devices. In the fitting, the most critical parameter is the energy difference between field-driven barrier lowering (qaE) and hopping barrier between traps (E_a) as shown in the inset of Figure 3.10. It is the most critical parameter because it determines whether electrons have sufficient energy to hop from site to site to overcome the trap energy in the MgO dielectric material. Plotting $\ln J$ vs. $1/T$ generates the slope in which the energy difference qaE and E_a was found to have an average value of 0.18 eV.[155]

Figure 3.10 Hopping conduction of Pt/MgO/Cu RRAM devices at different temperatures, indicating that as temperature increases, resistance increases as well.

3.2.3 Endurance and Retention of Pt/MgO/Cu RRAM Devices

In verifying the performance of Pt/MgO/Cu RRAM devices, endurance and retention measurements were performed. DC endurance of Pt/MgO/Cu RRAM devices began with a 10^5 ON/OFF ratio and decreased to an ON/OFF ratio of 10^3 after 750 cycles up to the 2000th cycle as shown in Figure 3.11(a). The retention of Pt/MgO/Cu RRAM devices was also measured and was found to exhibit more than 10 years at 125°C using the Arrhenius equation as shown in Figure 3.11, where the lifetimes of devices were plotted against the reciprocal of the varied temperatures, *i.e.* 270°C, 280°C and 290°C.[21] The devices were first set to a particular resistance state, *e.g.* LRS and was heated *ex-situ* for a certain amount of time using an oven before bringing it back to room temperature to measure the resistance state again. If the LRS has switched to HRS, it means that the devices have failed and the time to fail was recorded. This process was repeated for another two temperature points and was plotted and extrapolated to 10 years. As compared to Ru/MgO/Cu, Pt/MgO/Cu RRAM devices was observed to have a better retention due to the higher work function of the Pt (5.65 eV) as compared to Ru (4.71 eV). As the work function represents the minimum thermodynamic energy required to remove an electron to its vacuum, it will require a higher temperature to cause an instability or change in chemical reaction of the Cu filaments in Pt-based RRAMs as compared to Ru-based RRAMs.

Figure 3.11(a) DC endurance showing at least 2000 cycles starting at 10⁵ ON/OFF ratio and decreased to an ON/OFF ratio of 10³ after 750 cycles, (b) Above 10 years of retention at 125°C using an Arrhenius equation extrapolation.

3.2.4 TEM & EDX of Pt/MgO/Cu RRAM Devices

TEM was performed on the MIM layers as shown in Figure 3.12(a). However, while the TEM shows uniformly deposited layers of Pt/MgO/Ta, it alone was unable to conclude any presence of Cu filaments within MgO. Therefore, an energy-dispersive X-ray spectroscopy (EDS) line profile was performed to investigate the presence of a Cu filament as exhibited in Figure 3.12(b). It was shown in Figure 3.12(b) as indicated by the black Cu line and the red arrow that there exists a certain amount of Cu atoms within the MgO layer. While it might be challenging to confirm the location of the Cu filament using TEM, it can be suggested that Cu filaments are present in the MgO layer using EDX.[20] Furthermore, the accumulation of oxygen ions at the MgO/Cu₂O interface could result in a lowering of the electric field in MgO and a strong increase of the electric field across Cu₂O. Therefore, metal ions at the Cu anode are subjected to a strong field, causing the Cu injection into MgO.[156]

Figure 3.12(a) TEM image exhibiting uniform layers of Pt/MgO/Cu, (b) EDX line profile with black Cu line overlapping in the MgO region (circled in red) suggests the presence of Cu in MgO.

3.3 Hopping Conduction of Pt/HfO₂/Ti RRAM Devices

While the previous Sections in this chapter investigated the conduction mechanisms of MgO-based RRAM devices, similar analysis were also performed on the I - V plots of Pt/HfO₂/Ti RRAM devices to compare and explore the conduction mechanisms between MgO-based and HfO₂-based RRAM devices. It was found that the hopping conduction was the dominant conduction mechanism for $V_{stop} = -0.9$ V to -1.3 V at intervals of -0.1 V as shown in Figure 3.13. The hopping conduction used for the analysis was shown in Equation 10:

$$J = qanv \exp\left(\frac{qaE - \phi_T}{kT}\right), \quad (10)$$

where $n = 5 \times 10^{24} \text{ m}^{-3}$ is the electron concentration in conduction band,[157] $v = 2 \times 10^{13} \text{ Hz}$ is the frequency of thermal vibration of electrons in trap site,[158] a is the mean distance between traps and ϕ_T is the energy level of traps site below the conduction band.[20] The linear fitting of hopping conduction was performed by taking the natural log on Equation 10 followed by a $\ln(I)$ vs V plot as shown in Figure 3.13. The selected fitting voltage range of -0.9 V to -1.3 V with a corresponding current range of ~ 2 orders exhibited a good fit with linear

correlation. The gradient (M) and vertical intercept (C) from Equations 11 and 12 can also be extracted from the fitting $\ln(I) = MV + C$:

$$M = \frac{qa}{kTd}, \quad (11)$$

$$C = \ln(qanvA) - \frac{\phi_T}{kT}, \quad (12)$$

where d is the distance between the top and bottom electrode, while a and ϕ_T can be obtained from Equations 11 and 12, respectively. The parameters a and ϕ_T extracted from Equations 11 and 12 were shown to increase as V_{stop} increases from -0.9V to -1.3V at intervals of -0.1 V in Table V. As V_{stop} increases, V_o^+ became further apart as indicated by the larger a to be overcome, thus resulting in a decrease in n_D , while ϕ_T remained fairly constant at 0.86 eV . A more detailed study of Pt/HfO₂/Ti RRAM devices can be found in Section 4.2 later. Similarly, due to poor fittings, conduction mechanisms such as FN-Tunneling and Trap-Assisted Tunneling (TAT) were eliminated as discussed in Appendix A2.

Figure 3.13. Hopping conduction analysis of V_{stop} from -0.9 V to -1.3 V at intervals of -0.1 V .

Table V Hopping distance (a) extracted from Figure 3.13 at different V_{stop} indicated an increasing trend with increasing V_{stop} .

V_{stop} [V]	-0.9	-1.0	-1.1	-1.2	-1.3
Trap-to-trap Distance, a [nm]	0.83	0.84	0.88	0.91	0.93

3.4 Chapter Summary

The annealing effect of MgO-based RRAM devices was shown to improve the cycle-to-cycle resistance variability, resulting in consistent $I-V$ paths for conduction mechanism studies. Schottky emission was found to be the dominant conduction mechanism at temperatures of 300 K, 325 K, 350 K and 375 K. This was further validated by TEM where the diffusion of Ta atoms into MgO was found to match with extracted values. TEM analysis of Ru/MgO/Cu devices also revealed a Cu filament by the difference in crystallinity, where the filament width was measured to be ~ 10 nm. Another TEM analysis also revealed Cu filaments within MgO of Pt/MgO/Cu RRAM devices, as shown by an EDS line profile. Hopping conduction was found to be the dominant conduction mechanism where the energy barrier was found to be 0.18 eV. Similarly, Pt/HfO₂/Ti devices also exhibited an increase of trap-to-trap distance from 0.83 nm to 0.93 nm from the HRS hopping conduction fittings as V_{stop} increased from -0.9 V to -1.3 V. The MgO-based RRAM devices also revealed a high retention of 10 years at 85°C using an Arrhenius extrapolation. These studies provided a better understanding of the pre-switching ion and electron behavior integral for stack optimization, while the next chapter will build up on this chapter by discussing more about their behavior during the switching process.

Chapter 4

Switching Dynamics in MgO and HfO₂-based RRAMs

This chapter discusses the switching dynamics of MgO and HfO₂-based RRAMs, focusing on the multi-level state properties for both DC and AC modes of switching. Various MgO and HfO₂-based RRAMs were investigated to identify any relationship between the slope angle of the RESET switching process and the consistency of the multi-level states, i.e. the number of distinguishable multi-level states. Multi-level states are important because it provides an alternative solution to improve the density of the memory devices as compared to the traditional binary state memory. This process requires stack engineering by changing both electrodes and dielectric layers to identify the optimized stack for multi-level state switching. Thereafter, further studies such as material characterizations, temperature studies and modelling were used to investigate the selected stack characteristics and its multi-level switching properties.

4.1 Multi-level states in MgO-based RRAM Devices

In this Section, the MgO-based RRAM devices were investigated for multi-level states, focusing on the RESET switching process. While the SET state is usually abrupt in RRAM, the RESET state can be either abrupt or gradual. This makes the RESET process a clear factor to look for in determining whether multi-level states are possible in any RRAM stack.[106, 159] A gradual switching would allow different resistance states to be obtained by varying V_{stop} , however the slope of the gradual switching also plays a role in determining whether multi-level states can be obtained.[127]

Part of this chapter has been adapted with permission from Desmond Jia Jun Loy, Putu Andhita Dananjaya, Somsubhra Chakrabarti, Kuan Hong Tan, Samuel Chen Wai Chow, Eng Huat Toh and Wen Siang Lew, “Oxygen Vacancy Density Dependence with Hopping Conduction Mechanism in Multi-Level Switching Behavior of HfO₂-Based RRAM Devices” ACS Applied Electronic Materials 2(10), 3160-3170 (2020). Copyright 2021 American Chemical Society.²

4.1.1 Absence of Multi-level states in Pt/MgO/Cu RRAM Devices

Figure 4.1 shows 100 DC I - V cycles of Pt/MgO/Cu RRAM devices but both SET and RESET processes are abrupt switching, making it difficult to observe any multi-level switching during RESET. The abrupt switching from both SET and RESET processes also suggest that Pt/MgO/Cu RRAM devices are ECM by nature with a Cu filament formed and ruptured during the SET and RESET processes, respectively.[102] This phenomenon was also supported by the EDX line profile in Section 3.2, indicating the presence of Cu filaments in MgO.[20]

² This Chapter is partly published as a journal paper “Oxygen Vacancy Density Dependence with Hopping Conduction Mechanism in Multi-Level Switching Behavior of HfO₂-Based RRAM Devices” – ACS Applied Electronic Materials 2(10), 3160-3170 (2020). <https://doi.org/10.1021/acsaelm.0c00515>.

Figure 4.1 100 DC I - V Cycles of Pt/MgO/Cu RRAM devices indicating abrupt SET and RESET processes.

4.1.2 Multi-level states in Pt/MgO/Ta RRAM Devices

Pt/MgO/Ta RRAM devices on the other hand, exhibited a slightly gradual RESET, providing possibility for multi-level states in the RESET process. Figure 4.2(a) to (e) shows 100 cycles of I - V curves indicating larger ON/OFF ratio and higher HRS from -1.1 V to -1.5 V of V_{stop} . This shows that Pt/MgO/Ta RRAM devices can exhibit multi-level states in DC I - V switching. Figure 4.2(f) exhibited the average curves of 100 cycles of the I - V curves in Figure 4.2(a) to (e), verifying that the ON/OFF ratio and HRS increases from -1.1 V to -1.5 V of V_{stop} . However, a closer observation revealed that at higher voltages such as -1.3 V to -1.5 V, the spacing between HRS are very close to one another, which might suggest a difficulty in differentiating between the different HRS for the multi-level states. Furthermore, the $\sim 70^\circ$ RESET switching process slope angle as indicated in Figure 4.2(e) might suggest a challenge in successfully distinguishing multi-level states. This issue was exhibited more distinctly in the cumulative probability resistance plot in Figure 4.3 where 200 ns RESET pulses of pulse height from -1.1 V to -2.0 V were used to switch the Pt/MgO/Ta RRAM devices. As indicated by the red circles, clearly there are only two main states, which imply that Pt/MgO/Ta RRAM devices could have binary states, and that any optimization of multi-level states could be challenging.

Figure 4.2 100 DC I - V Cycles of Pt/MgO/Ta RRAM devices indicating abrupt SET but gradual RESET processes for V_{stop} at (a) -1.1 V, (b) -1.2 V, (c) -1.3 V, (d) -1.4 V, (e) -1.5 V, (f) Average of 100 curves of (a), (b), (c), (d) & (e).

Figure 4.3 100 cycles of RESET pulse heights from -1.1 V to -2.0 V with 200 ns pulse widths of Pt/MgO/Ta RRAM devices showing two states.

4.1.3 Multi-level states in Pt/MgO/Ti RRAM Devices

In the stack engineering of MgO-based devices from Cu to Ta to Ti, the 100 DC I - V curves of Pt/MgO/Ti devices in Figure 4.4 shows that the slope angle of the gradual RESET switching process was $\sim 45^\circ$, which is more gradual as compared to the $\sim 70^\circ$ slope angle as shown by Pt/MgO/Ta devices in Figure 4.2(d) at -1.5 V of V_{stop} . Clearly, these two slope angles *i.e.* $\sim 45^\circ$ and $\sim 70^\circ$ of the gradual RESET switching process are smaller as compared to the 90° slope angle of the abrupt RESET switching process Pt/MgO/Cu devices in Figure 4.1. It was shown in the cumulative probability resistance plot in Figure 4.5 that by tuning the RESET pulse height of Pt/MgO/Ti devices from -1.7 V to -2.0 V at 1 μ s pulse width while the SET pulse was -1.7 V at 200 ns pulse width, multi-level states were observed. However, the SET and RESET pulse heights of Pt/MgO/Ti devices are much higher as compared to their DC SET & RESET voltages, which requires more stack engineering to optimize the RRAM stack. Typically, pulses have very small widths, *i.e.* 200 ns in this case, which is a trade-off with the pulse height. Either a small pulse height and large pulse width or a large pulse height and small pulse width is required to achieve the same switching effect. Therefore, given a small pulse width, compensation with a larger pulse height is required to achieve the same switching effect

as DC switching, which on the other hand can be taken to be cumulative pulses with increasing pulse height and constant pulse widths.

These findings suggest that the slope angle of the RESET process could have a role to play in determining whether multi-level states can exist or if they can be controlled well. In the proving of this hypothesis and noting that the Ti electrode provided multi-level states capabilities in both DC and AC, stack engineering was performed to replace MgO with HfO₂ as the latter has been reported to exhibit multi-level switching capabilities. It was found that Ti was able to create multi-filament pathways in the oxide, with individual filament contribution to different resistance states.[41, 42] Hence, in the next and subsequent Sections, the multi-level properties of Pt/HfO₂/Ti RRAM devices and its characteristics will be discussed in detail.

Figure 4.4 100 DC I - V Cycles of Pt/MgO/Ti RRAM devices indicating abrupt SET but gradual RESET processes for -1.5 V of V_{stop} , exhibiting a gradual RESET switching angle of $\sim 45^\circ$.

Figure 4.5 100 cycles of RESET pulse heights from -1.7 V to -2.0 V with 200 ns pulse widths of Pt/MgO/Ti RRAM devices exhibiting multi-level states

4.2 Multi-level states of Pt/HfO₂/Ti RRAM Devices

As per the previous Section, the same analysis was performed on 100 DC I – V cycles of Pt/HfO₂/Ti RRAM Devices at -1.4 V of V_{stop} and it was observed that the RESET process was even more gradual with $\sim 20^\circ$ slope angle. The switching process was also observed to be more consistent as compared to the MgO-based RRAM devices. Thereafter, AC pulsed studies were also performed by varying the pulse height and widths as shown in the cumulative probability resistance plots in Figure 4.7 and 4.8, respectively. The Pt/HfO₂/Ti RRAM devices were set at 1.2 V of SET pulse height and the RESET pulse height was varied from -0.9 V to -2.0 V at intervals of -0.1 V as shown in Figure 4.7 and at least 3 bits of multi-level states were exhibited. The SET and RESET pulse widths were kept constant at 200 ns. In comparison to varying the pulse heights, varying the RESET pulse width from 200 ns to 2000 ns at intervals of 200 ns with a constant SET pulse height of 1.2 V and constant RESET pulse height at -1.5 V as shown in Figure 4.8 shows little difference between the multi-level states. This requires more optimization with a longer pulse width (*i.e.* in orders of 10), but it might be impractical as the high pulse width will result in a high energy per bit.

Regardless, the investigation of MgO-based and Pt/HfO₂/Ti RRAM devices have validated the hypothesis where a more gradual RESET process (*i.e.* a smaller angle) will result

in higher number of multi-level states and more controllable multi-level states. Therefore, more focus will be placed on Pt/HfO₂/Ti RRAM devices in the next Sections to investigate its material characteristics, temperature, and gap dynamics in the HRS state. However, for completeness, the multi-level state property was also investigated by varying the compliance current of 1 mA and 1 μ A as shown in the DC I - V graphs and cumulative probability graphs of Figure 4.9(a) and (b) respectively.

Figure 4.6 100 DC I - V Cycles of Pt/HfO₂/Ti RRAM devices indicating abrupt SET but gradual RESET processes for -1.4 V of V_{stop} , exhibiting a gradual RESET switching angle of $\sim 20^\circ$.

Figure 4.7 100 cycles of RESET pulse heights from -0.9 V to -2.0 V with constant 200 ns pulse widths of Pt/HfO₂/Ti RRAM devices showing more than 3-bits of multi-level states.

Figure 4.8 100 cycles of RESET pulse widths from 200 ns to 2000 ns with a constant SET pulse height of 1.2 V and constant RESET pulse height at -1.5 V of Pt/HfO₂/Ti RRAM devices showing at least 2-bits of multi-level states.

Figure 4.9 (a) Semilog I – V plots of Pt/HfO₂/Ti resistive switching devices at different compliance current 1 mA & 200 μ A, (b) Cumulative probability plot for three multi-level states at different compliance currents.

4.2.1 Current-Voltage, XPS & TEM Characterizations of Pt/HfO₂/Ti RRAM Devices

The I - V characteristics of Pt/HfO₂/Ti resistive switching devices were investigated to better understand the switching behavior and high resistance state (HRS) multi-level switching properties. A consistent switching process could be observed in Figure 4.10(a) where 50 I - V cycles of one device were plotted. In the 50 I - V cycles, it was found that the average SET voltage is 0.5 V while the RESET stop voltage is fixed at -1.2 V, giving an ON/OFF ratio of about 50 $\times$. The forming voltage was observed to be at 1.8 V at a compliance current of 1 mA while the read voltage (V_{read}) was performed at -0.1 V and the compliance current was set at 700 μ A. While there was consistent switching and low cycle-to-cycle variability, it was more important to observe the presence of gradual switching characteristics in the RESET state, thus confirming the existence of multi-level states in the HRS.[106, 159] In the investigation of multiple device characteristics, the device-to-device variability of the resistive switching devices with average SET voltage 0.5 V and RESET stop voltage -1.2 V were also shown in a resistance box plot in Figure 4.10(b). It was found that the median ON/OFF ratio was about 50 $\times$, a ratio large enough for multiple level resistance switching states to occur.

Figure 4.10(a) Semilog I - V plots of Pt/HfO₂/Ti resistive switching devices exhibiting the forming and first 50 I - V cycles with an ON/OFF ratio of about 50 $\times$, (b) resistance box-plot of Pt/HfO₂/Ti resistive switching devices exhibiting device-to-device variability.

Endurance studies were also performed at SET/RESET pulse heights of 0.6 V/ -1.3 V at 100 ns pulse widths as shown in the flow chart of Figure 4.11(a). Two read/write schemes A & B were implemented at different cycles as shown in the flow charts of Figure 4.11(a) and (b). While scheme A was implemented to every (1st, 2nd, 5th) $\times 10^n$ cycle where $n = 0, 1, 2, 3$,

4, scheme B was implemented to every cycle in between. Scheme A reads the resistance state after every SET & RESET write while scheme B adopts a current-blind pulsed voltage stress (PVS) method where there is only SET & RESET writing but no reading.[142] At least 5×10^5 endurance cycles at an average ON/OFF ratio of $50\times$ were observed as the LRS of the 10^{6th} cycle converged to that of HRS as shown in Figure 4.11(c), indicating a failure. However, these results show that Pt/HfO₂/Ti resistive switching devices exhibited a good endurance, an attribute necessary to maintain multi-level HRS switching after multiple endurance cycles.

Retention studies were also performed using an Arrhenius equation where the lifetime of each device is plotted against an inverse of temperature as shown in Figure 4.11(d). The devices were first switched to LRS and heated up to 310°C, 330°C and 350°C while checking its resistance state using a read voltage of +0.1 V. The device is considered failed when the device switched to HRS unintentionally and its corresponding time to fail was recorded. These three temperature points were plotted and extrapolated to 10 years ($\sim 3.154 \times 10^8$ s). The extrapolation shows that the retention exceeds 10 years at 125°C, exhibiting strong retention capabilities in Pt/HfO₂/Ti RRAM devices. E_a was also extracted to be 1.72 eV, which is higher than 0.6 eV of FLASH.[153] However, the pre-exponential factor, B varies with different types of insulators and electrode materials, thus producing different E_a in the process.[21] For a stable RRAM such as Pt/HfO₂/Ti, the endurance and retention of multi-states would be as robust as their binary state counterparts as shown in Figure 4.11(c) and (d) because they are made up of the same type of filament processes. However, a HRS endurance margin/buffer needs to be made to account for the HRS variability.

(a)

(b)

(c)

(d)

Figure 4.11(a) Read/write schemes of endurance performed at SET/RESET pulse heights of 0.6 V/−1.3 V at 100ns pulse widths, (b) An endurance flow chart where scheme A was implemented to every $(1^{\text{st}}, 2^{\text{nd}}, 5^{\text{th}}) \times 10^n$ cycle where $n = 0, 1, 2, 3, 4$, while scheme B was implemented to every cycle in between, (c) At least 5×10^5 endurance cycles with $\sim 50\times$ ON/OFF ratio where LRS converged to HRS at the 10^6 th cycle, (d) An Arrhenius plot showing that the retention exceeds 10 years at 125°C.

Material studies such as transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS) were also performed on Pt/HfO₂/Ti resistive switching devices and HfO_x films, respectively. TEM was performed on the Pt/HfO₂/Ti resistive switching devices to investigate the uniformity of deposited films and its crystallinity, while XPS studies were performed on HfO₂ films to verify the Hf and O peaks. The TEM analysis in Figure 4.12(a) exhibited uniformly deposited layers of the RRAM and the inset of Figure 4.12(a) shows an amorphous HfO_x structure.

In the XPS profiles, the O 1s peaks indicated broad and multiple overlapping components while the Hf 4f peaks indicated well-separated spin-orbit components as shown in Figure 4.12(b) and its inset, respectively.[150] The de-convolution of the Gaussian O 1s spectrum revealed two different oxygen components of binding energies 530.0 eV and 531.8 eV, respectively, as shown in Figure 4.12(b). With an energy resolution of 0.1 eV, the 530.0 eV peak is characteristic to O²⁻, the higher binding energy of 531.8 eV can be attributed to V_o⁺. [160-162] The amount of oxygen vacancies was found to be 4.79% of the entire oxygen content of the HfO_x material by taking the proportion of areas under the two oxygen peaks in Figure 4.12(b). Similarly, the binding energies of the Hf 4f peaks were found to be 16.8 eV and

18.3 eV as shown in the inset of Figure 4.12(b), which were characteristic to Hf.[163] While Burrell *et al.* discussed about using spectral peak energy, intensity, and structural analysis to determine the composition and chemical state of the material species, Luo *et al.* performed XPS on their HfO₂ films by capturing the energy of X-ray ejected photo-emitted electrons specific to the chemical state and compounds. These analysis culminated in the area calculations under the material profiles such that by comparing the areas under the curve of the O 1s and Hf 4f profiles,[150, 164, 165] the atomic concentrations revealed ~67% oxygen and ~33% hafnium of HfO₂ with an error of 0.25%.[164, 165]

Figure 4.12(a) Characteristic XPS profile of O 1s showing two oxygen states indicating 4.79% of oxygen vacancies with XPS profile of Hf 4f (inset) of HfO₂ films, (b) TEM of Pt/HfO₂/Ti resistive switching devices showing uniformly deposited layers.

4.2.2 Temperature Characterization & Arrhenius Equation Relation between High Resistance State and Temperature

Temperature studies were also performed at -40°C , 25°C , 75°C , 125°C and 50 cycles of I – V curves were measured at each temperature as shown in Figure 4.13(a) to (d), respectively.[166] The SET voltage ranged from 0.5 V to 0.75 V, the RESET voltage was -1.2 V while the ON/OFF ratio is about $50\times$ at the same $V_{\text{read}} = -0.1$ V. While the SET processes might not exhibit thermal stability, the RESET processes have shown stable HRS switching and maintained $\sim 50\times$ ON/OFF ratio at -40°C , 25°C , 75°C and 125°C . These observations indicated a good thermal stability in Pt/HfO₂/Ti resistive switching devices in the HRS even at

low temperatures, indicating that the multi-level HRS is resilient at different temperature ranges.

Figure 4.13. 50 cycles of semilog I - V plots of Pt/HfO₂/Ti resistive switching devices measured at (a) -40°C (b) 25°C (c) 75°C (d) 125°C .

Temperatures at -40°C , 25°C , 75°C , 125°C and 175°C were performed on devices 1, 2 & 3 to exhibit the full operating range of Pt/HfO₂/Ti RRAM devices. An I - V sweep of -0.6 V to 0.6 V was performed on devices 1, 2 and 3 where the HRS decreases with an increasing temperature trend as shown in Figure 4.14(a), (b) and (c), respectively. An Arrhenius equation indicated by Equation 13 was linearly fitted as shown in Figure 4.14(d) where an exponential relation between HRS and temperature was observed. The HRS was read at 0.4 V in Figure 4.14(d) and Equation 13 is stated as follows:

$$R_{HRS} = R_0 \exp\left(\frac{E_{AC}}{kT}\right), \quad (13)$$

where R_{HRS} is the HRS, R_0 is the constant factor of the exponential function, E_{AC} is the activation energy of HfO_2 , k is the Boltzmann constant, and T is the corresponding temperature of the performed measurement. The value of R_0 is inversely related to n_D , which is indicative of the n_D present in Pt/ HfO_2 /Ti devices and is characteristic to different RRAM stack configurations. Equation 1 shows that R_0 is proportional to R_{HRS} , thus making R_{HRS} inversely related to n_D . At the same time, Equation 1 also shows that R_{HRS} is inversely proportional to temperature, [130]. which would result in the increase of n_D with increasing temperature. More intuitively, n_D increases with increasing temperature because a higher temperature lowers the resistance of the RRAM device, which increases n_D . [127, 129, 130, 167] The decreased resistance of the device could be attributed to a less significant filament rupture, which in turn is caused by a higher n_D . A less significant rupture is represented by a lower extent of recombination between O^{2-} and V_o^+ , thus causing the density of V_o^+ to be higher, *i.e.* n_D is higher. E_{AC} and R_0 were found to exhibit average values of 0.022 eV and 152.18 Ω , respectively from the fittings shown in Figure 4.14(d). The value of E_{AC} was also found to be at a consistent range to the values reported by Larcher *et al.* and Bersuker *et al.* for HfO_x -based devices. [168, 169] The R_{HRS} vs. $1/T$ trend has remained similar for all three devices, indicating that R_{HRS} increases with decreasing temperature.

(a)

(b)

Figure 4.14. Temperature dependence of I – V curves of (a) Device 1, (b) Device 2, (c) Device 3, (d) An Arrhenius relationship, R vs. $1/T$ with a linear fit of the average I – V results of the devices at each temperature read at 0.4 V.

4.2.3 Switching Model Between Activation Energy, Reset Stopping Voltage and Reset Multi-Level Resistance States

The E_{AC} of HfO_2 was further investigated in its relationship with n_D , which is related to the V_{stop} . Multi-level state investigations were performed by varying the V_{stop} from -0.9 V to -1.3 V at intervals of -0.1 V as shown in Figure 4.15(a) to (e), respectively. It could be observed that as the V_{stop} increases from -0.9 V to -1.3 V, HRS increases and n_D decreases. Further investigations of the multi-level states were performed where 200 I – V cycles in each voltage of -0.9 V to -1.3 V at intervals of -0.1 V shown in Figure 4.15(a) to (e) were averaged and combined into Figure 4.15(f). Thereafter, the cumulative probability for all 200 I – V cycles shown in Figure 4.15(a) to (e) were plotted at $V_{read} = -0.1$ V in Figure 7(g). It can also be observed from the cumulative probability plot in Figure 4.15(g) that the HRS increased at an increasing rate as voltage increases. Therefore, an exponential relationship model was proposed to explain the filament evolution and its relationship with multi-level states in Equation 14:

$$R_{HRS} = \alpha \exp(\beta V_{stop}), \quad (14)$$

where R_{HRS} is again the HRS, α is the constant factor of the exponential function and β is a factor of the exponent. R_{HRS} is plotted against V_{stop} in Figure 4.15(h) and α was found to be

86.34 and β was found to be 5.42 at the 50th percentile. The 25th and 75th percentiles were also plotted as the range of the error bars, mostly exhibiting non-overlap between different multi-level states. As Equation 13 relates R_{HRS} to E_{AC} and Equation 14 relates R_{HRS} to V_{stop} which is a function of E_{AC} , the relationship between E_{AC} and V_{stop} can be established in Equation 15 by combining Equation 13 and 14.

$$E_{AC} = [\ln(\alpha) - \ln(R_0)]kT + \beta V_{stop}kT \quad (15)$$

As the R_{HRS} vs. V_{stop} measurement was performed at room temperature, Equation 15 was simplified into Equation 16 where γ and ϕ are constants:

$$E_{AC} = \gamma + \phi V_{stop} \quad (16)$$

Hence, a reduction in n_D due to increasing V_{stop} resulted in a higher R_{HRS} , which in turn resulted in a larger E_{AC} as shown in Equation 16 was in line with reported literatures.[126, 127] Intuitively, a larger filament rupture is caused by a larger V_{stop} due to more recombination between O^{2-} and V_o^+ , thus resulting in a lower n_D .

Figure 4.15. Semilog I - V plots of Pt/HfO₂/Ti resistive switching devices with V_{stop} (a) -0.9 V, (b) -1.0 V, (c) -1.1 V, (d) -1.2 V, (e) -1.3 V, indicating an increasing HRS trend, (f) the mean of each semilog I - V plot from (a) to (e) and, (g) its corresponding cumulative probability plot at $V_{read} = -0.1$ V of 200 I - V cycles in each voltage of -0.9 V to -1.3 V at intervals of -0.1 V, (h) R_{HRS} vs. V_{stop} with an exponential fit with 25th to 75th percentile as the range of error bars.

4.3 Chapter Summary

The switching dynamics investigations of MgO and HfO₂-based RRAM devices revealed a higher number and better controllability of multi-level states in Pt/HfO₂/Ti RRAM devices. This was confirmed by the gentler 20° slope of the gradual RESET process of DC I – V curves as compared to the steeper slopes of the MgO-based RRAMs. The Pt/HfO₂/Ti switching model shows multi-level resistance states obtained from increasing V_{stop} to be directly related to E_{AC} but inversely related to n_D . The average E_{AC} value was extracted from an Arrhenius equation to be 0.022 eV at a wide temperature range of –40°C to 175°C and was shown to be inversely proportional to n_D as part of our proposed switching model. The multi-level high resistance states were achieved at V_{stop} from –0.9V to –1.3 V at intervals of –0.1 V. In the validation of the relationship between n_D and V_{stop} , kMC simulations exhibited a decrease in n_D at increasing V_{stop} at different regions of the filament. The uniformly fabricated Pt/HfO₂/Ti devices exhibited at least 5×10^5 endurance cycles at 100 ns with a retention for more than 10 years at 125°C. With good thermal stability and multi-level state capabilities, Pt/HfO₂/Ti RRAM devices and their proposed models have great potential for neuromorphic engineering in automobiles.

Chapter 5

Area Independent Filamentary RRAM and HfO₂-based RRAM Modelling

This chapter first discusses filamentary RRAM found in MgO and HfO₂-based RRAM devices using an I–V analysis on different device areas. To further investigate the filamentary RRAM characteristics, kinetic Monte Carlo (kMC) and Simulation Program with Integrated Circuit Emphasis (SPICE) compact modelling were performed on Pt/HfO₂/Ti devices. The switching behavior of Pt/HfO₂/Ti resistive random-access memory (RRAM) devices has been investigated in this filament evolution study where the defects were analyzed quantitatively via kMC methods. The rate of change of defects and the number of defects at different voltages were analyzed at different filament regions. Thereafter, the kMC model parameters were used in the SPICE model. The aims of this chapter are to understand filamentary RRAM as well as its evolution from the kMC perspective and to devise kMC and SPICE models which are well-represented with Pt/HfO₂/Ti experimental results. These models can be readily integrated to predict 1T1R behavior for future industrial applications.

5.1 Filamentary RRAM in MgO & HfO₂-based RRAM Devices

The filamentary nature of RRAM is the most common where one dominant or multiple chains of filaments define the switching in RRAM devices. The filamentary nature can also be suggested by the abrupt SET process of MgO and HfO₂-based RRAM devices as shown in Section 4.1.[170] In this Section, these RRAM devices were further investigated for their filamentary characteristics by considering the current trends at different area sizes ranging from $5 \times 5 \mu\text{m}^2$ to $50 \times 50 \mu\text{m}^2$.³

5.1.1 Area Dependence of Pt/MgO/Cu RRAM Devices

In Section 3.2.4, Cu filaments were suggested in the switching of Pt/MgO/Cu devices from the TEM and EDX analysis. In this Section, I - V electrical measurements were used to investigate whether the Cu filament is filamentary by varying different device areas. Figure 5.1(a) shows the I - V curves of the pre-forming process of different device areas from $10 \times 10 \mu\text{m}^2$ to $50 \times 50 \mu\text{m}^2$. It was observed that as the device area decreases, the current flowing through the RRAM devices decreases as well, which is exhibited by the arrow indicating a trend. Given that the height of all the RRAM devices is the same, this is commonly known as the resistance of an electrical wire which is inversely proportional to its cross-sectional area.[171] This means that the as-fabricated RRAM devices behave as a resistor due to the absence of filament, where its resistance is inversely proportional to its area. Figure 5.1(b) and (c) exhibited the I - V curves of the HRS and LRS of different device areas from $10 \times 10 \mu\text{m}^2$ to $50 \times 50 \mu\text{m}^2$, respectively. However, unlike the pre-forming process, no current vs. area trend could be observed this time for both HRS and LRS. This suggests that the Cu filament characteristics are filamentary by nature as the filament size (~ 10 nm as shown in Section 3.1.4) is independent of the area of the device.[104, 171-173] The absence of current vs. area trend also suggests that the difference in current could be attributed to the device-to-device variability of Pt/MgO/Cu devices as shown in Figure 3.9(b) from Section 3.2.1.

³ This Chapter is partly under revision as a peer-reviewed journal as "Filament Evolution and Compact Modelling of Multi-level Resistance HfO₂-based RRAM Devices" – IEEE Transactions on Electron Devices

Figure 5.1(a) Pre-forming, (b) HRS, (c) LRS *I-V* sweep of different Pt/MgO/Cu RRAM device areas from $10 \times 10 \mu\text{m}^2$ to $50 \times 50 \mu\text{m}^2$.

5.1.2 Area Dependence of Pt/MgO/Ta RRAM Devices

The same analysis was applied to Pt/MgO/Ta RRAM devices where Figure 5.2(a) shows the *I-V* curves of the pre-forming process of different device areas from $5 \times 5 \mu\text{m}^2$ to $50 \times 50 \mu\text{m}^2$. Similarly, it was observed that as the device area decreases, the current flowing through the RRAM devices decreases as well, which is exhibited by the arrow indicating a trend.[171] This shows that the as-fabricated RRAM devices behave as a resistor due to the absence of filament, where its resistance is inversely proportional to its area, just like the Pt/MgO/Cu RRAM devices. Figure 5.2(b) and (c) exhibited the *I-V* curves of the HRS and LRS of different

device areas from $5 \times 5 \mu\text{m}^2$ to $50 \times 50 \mu\text{m}^2$, respectively. Similarly, no current vs. area trend could be observed for both HRS and LRS. This suggests that the filament characteristics of Pt/MgO/Ta devices are filamentary by nature as the filament size is independent of the area of the device.[104, 171-173]

Figure 5.2(a) Pre-forming, (b) HRS, (c) LRS I - V sweep of different Pt/MgO/Ta RRAM device areas from $5 \times 5 \mu\text{m}^2$ to $50 \times 50 \mu\text{m}^2$.

5.1.3 Area Dependence of Pt/HfO₂/Ti RRAM Devices

Similar observations also suggest that Pt/HfO₂/Ti RRAM devices are filamentary as per reported.[104] Figure 5.3(a) shows the I - V curves of the pre-forming process of different device areas from $5 \times 5 \mu\text{m}^2$ to $50 \times 50 \mu\text{m}^2$. Similarly, it was observed that as the device area

decreases, the current flowing through the RRAM devices decreases as well, which is exhibited by the arrow indicating a trend.[171] It could be observed that the $5 \times 5 \mu\text{m}^2$ and $10 \times 10 \mu\text{m}^2$ devices have a much lower pre-forming current as compared to the larger area devices from $20 \times 20 \mu\text{m}^2$ to $50 \times 50 \mu\text{m}^2$, suggesting an inverse relationship between the resistance and area of the Pt/HfO₂/Ti RRAM devices. Figure 5.3(b) and (c) exhibited the I – V curves of the HRS and LRS of different device areas from $5 \times 5 \mu\text{m}^2$ to $50 \times 50 \mu\text{m}^2$, respectively. Similarly, no current vs. area trend could be observed for both HRS and LRS. This suggests that the filament characteristics of Pt/HfO₂/Ti devices are filamentary by nature as the filament size is again independent of the area of the device.[104, 171-173]

Comparing the pre-forming characteristics of Pt/MgO/Cu, Pt/MgO/Ta and Pt/HfO₂/Ti RRAMs in Figures 5.1(a), 5.2(a) and 5.3(a) respectively, the pre-forming voltage of Pt/MgO/Cu is higher because a higher energy is typically required for the redox reactions forming a metallic Cu filament than a V_o^+ filament. However, after the filaments are established, the SET and RESET voltages are comparable between Pt/MgO/Cu, Pt/MgO/Ta and Pt/HfO₂/Ti RRAMs.

Figure 5.3(a) Pre-forming, (b) HRS, (c) LRS I - V sweep of different Pt/HfO₂/Ti RRAM device areas from $5 \times 5 \mu\text{m}^2$ to $50 \times 50 \mu\text{m}^2$.

The filamentary characteristics of Pt/HfO₂/Ti RRAM devices were further investigated through a filament evolution study using GinestraTM, a kMC physics modelling software, by considering the defect density at different regions of the filament. The good fitting of experimental LRS and HRS curves enabled the extraction of physical parameters such as thermal ionization energy and the electron tunneling effective mass. Thereafter, filament evolution in HfO₂-based devices was also investigated in different regions of the filament. As the filament behavior at the oxide/electrode during reset process is largely debated in terms of the definition of a gap between the tip of the filament and the electrode, the gap region was represented in the form of oxygen vacancy concentration (n_c). The non-gap region of the filament was also investigated, and though less significant, it was found that the non-gap region contributed to the rupture during the reset process as well. The gap and non-gap regions were varied at different proportions and the relationship between V_{stop} and n_c revealed a negative linear correlation while the different gap and non-gap regions affected the slope of V_{stop} and n_c . While the kMC model considers oxygen vacancy-based filaments,[174] this is not to imply that the possibility of cationic filaments is ignored, however we are considering the most general case for this stack where density functional theory, oxide/electrode interface engineering and literatures of a high tendency of an oxygen vacancy-based filaments reported in this stack.[100, 103-105] Figure 5.4 shows a flowchart of the models and the parameters extracted from the kMC model, literature and experimental results which were utilized to model multi-level resistance states by controlling V_{stop} . The definition of the parameters will be further elaborated in Tables V & VI in Sections 5.2 and 5.3, respectively. The kMC and compact model results have also shown to agree well with experimental results.

Figure 5.4 Flowchart describing the model parameters between the kMC and compact model with parameters defined in Tables V & VI in Sections 5.2 and 5.3, respectively.

5.2 Pt/HfO_x/Ti as a 3D Kinetic Monte Carlo (KMC) RRAM Model

In this Section, a kMC model and a compact model were investigated on Pt/HfO₂/Ti RRAM devices, where the simulated curve was fitted with experimental I – V curves. While MgO-based devices were not explored using kMC or compact modelling, the filament evolution is expected to be less predictable with little to no multi-level states, as observed from the experimental findings in Chapter 4. Therefore, the modelling focus is on HfO₂-based RRAM devices. The parameters of these two HfO₂-based models were obtained from literatures, experimental calculations, and fittings. GinestraTM is a 3D kMC modelling software which applies comprehensive physics to simulate defect evolution, where the electric field and potential profiles are calculated by solving Poisson's and charge continuity equations.[174] While the charge continuity equations are solved for electrons, holes and traps, the power dissipated and its temperature profile can be obtained in a 3D map by solving Fourier's heat flow equation as shown in Equation 17.[141]

$$P(x, y, z) = k_{TH} \cdot \nabla^2 T(x, y, z), \quad (17)$$

where k_{TH} is the thermal conductivity of the dielectric and T is the temperature profile. In the generation of defects associated to the breakage of Hf-O bonds during the set operation, the rate of generation of O^{2-} and V_O^+ , G_F is calculated by thermochemical theory as shown in Equation 18.[141, 175]

$$G_F(x, y, z) = v \cdot \exp\left(-\frac{E_A - p_0 \cdot [(2+k)/3] \cdot F(x, y, z)}{k_B \cdot T(x, y, z)}\right), \quad (18)$$

where v is the effective vibration frequency, E_A is the zero field effective activation energy to break the metal-oxygen bond, F is the electric field, k_B is the Boltzmann's constant, p_0 is the dielectric molecular dipole moment, and k is the relative dielectric constant. Similarly, during the reset process, the diffusion and recombination of carriers play an important role and their rate can be calculated by Equations 19 and 20.[141]

$$R_D(x, y, z) = v \cdot \exp\left(-\frac{E_{A,D} - k_D \cdot F_{EFF}(x, y, z)}{k_B \cdot T(x, y, z)}\right), \quad (19)$$

$$R_R(x, y, z) = v \cdot \exp\left(-\frac{E_{A,R}}{k_B \cdot T(x, y, z)}\right), \quad (20)$$

where R_D is the diffusion rate, $E_{A,D}$ is the diffusion activation energy, k_D is a factor based on atomic material properties, F_{EFF} is the electric field component along the diffusion direction, R_R is the recombination rate, and $E_{A,R}$ is the recombination activation energy.[141, 148, 176] Due to the stochastic nature of the kMC physical processes during the reset processes, the randomness of the recombination and diffusion processes resulted in cycle-to-cycle variability.

5.2.1 kMC Model Fitting and Verification with Experimental Results

With a good understanding of the kMC model physics, the Pt/HfO₂/Ti experimental I - V curve was simulated in the HRS and LRS as shown in Figure 5.5. The best fit also allowed an extraction of material parameters such as thermal ionization energy found to be in the range of 2.2 eV to 2.3 eV, which is very close to the measured value of 2.32 eV for HfO₂ V_O^+ species.[177] The density of the filament was also extracted to be $4 \times 10^{22} \text{ cm}^{-3}$, in line with the reported defect density in HfO₂. [178] The model parameters used in this work are shown

in Table VI where they were obtained from a combination of literature findings and fitting / extracted parameters.

Table VI Model parameters used and obtained from literatures and fittings / extraction, respectively for the kMC model.

Parameters obtained from Literatures			
Parameters	Description	Value	Reference
E_{REL}	relaxation energy of an isolated HfO_x defect	1.19 eV	[179]
r_t	HfO_x defect radius	5.64 Å	[141]
k	HfO_x relative dielectric constant	21	
k_{TH}	HfO_x thermal conductivity	0.005 W/cmK	[180]
ν	effective O-Hf bond vibration frequency	7×10^{13} Hz	[181]
p_0	O-Hf bond polarization factor	5.2 eA	[181]
E_A	O-Hf bond breakage zero-field effective activation energy	2.9 eV	[181]
$E_{A,D}$	Generation activation energy	vacancies: 1.5 eV ions: 0.7 eV	[182]
$E_{A,R}$	Recombination activation energy	0.2 eV	[183]
Extracted Parameters based on Fig 5.2 Experimental fitting			
E_T	Thermal ionization energy of HfO_2 defects	2.2 eV	[177]
N_{crit}	Critical defect density for the transition between TAT and drift conduction regimes	$4 \times 10^{22} \text{ cm}^{-3}$	[178]

Figure 5.5 Pt/HfO₂/Ti Experimental I – V data with good LRS and HRS fittings

5.2.2 Filament Evolution Analysis at Different Regions of the Filament

The filament evolution was investigated for the Pt/HfO₂/Ti stack and Figure 5.6(a) to (h) show the rupture of the filament as V_{stop} increases and more recombination occurs between V_o^+ and O^{2-} species. It could be observed that the rupture started from ~ -0.7 V as the voltage required is sufficient for recombination to occur between the tip of the filament and the top electrode known as the gap. However, as there is no clear gap until after -1.1 V where the rupture becomes more visible, it would be worth investigating the filament evolution at different regions of the filament. The filament in the Pt/HfO₂/Ti kMC model was separated into top and bottom regions to represent gap and non-gap regions, respectively as indicated in Figure 5.6(h) for quantitative analysis. Figure 5.7 shows the decrease in n_o as V_{stop} increases throughout the entire filament, which can be described by the fittings at different voltages on the plot. Absolute values of V_{stop} were used in Figure 5.7 to improve visibility. It was observed that the number of oxygen vacancies (V_o^+) started decreasing at a gradual rate until -0.7 V but experienced a sudden and sharp decrease from -0.7 V to -0.75 V as soon as the energy is sufficient for recombination, which was followed by a more gradual decrease in the n_o from -0.75 V to -1.5 V. Furthermore, this sudden decrease in n_o from -0.7 V to -0.75 V was revealed by the first derivative graph in Figure 5.7, exhibiting a turning point as indicated by a sharp downward pointed peak.

Figure 5.6 Filament evolution of Pt/HfO₂/Ti KMC model for V_{stop} at (a) -0.1 V, (b) -0.3 V, (c) -0.5 V, (d) -0.7 V, (e) -0.9 V, (f) -1.1 V, (g) -1.3 V, (h) -1.5 V, where filament rupture was first observed around -0.7 V. The numbers at the bottom right corner of each sub-Figure represents the number of oxygen vacancies corresponding to the respective V_{stop} . The filament regions in Pt/HfO₂/Ti kMC model was separated into top and bottom regions in (h) to represent gap and non-gap regions, respectively.

Figure 5.7 Number of oxygen vacancies (n_o) vs. V_{stop} of Pt/HfO₂/Ti kMC model for V_{stop} from 0 V to 1.5 V over the entire filament with its 1st derivative emphasizing a turning point at ~ 0.7 V to 0.75 V.

It has been defined in Figure 5.6(h) at $V_{stop} = -1.5$ V that the Pt/HfO₂/Ti kMC model was separated into top and bottom regions to represent gap and non-gap regions, respectively for quantitative analysis. Here, 5 types of gap and non-gap regions, *i.e.* (1) 10% gap, 90% non-gap, (2) 20% gap, 80% non-gap, (3) 30% gap, 70% non-gap, (4) 40% gap, 60% non-gap, (5) 50% gap, 50% non-gap were analyzed. The filament evolution behavior of cases (1) to (5) were exhibited in Figure 5.8 & 5.9 where it shows a decreasing n_o with increasing V_{stop} at the gap regions similar to that described in the analysis of Figure 5.7. In addition, n_o was observed to decrease faster when a larger gap region was considered, as shown in Figure 5.8(a) comparing the gradient of the slopes beyond -0.7 V. Similar analysis was also performed on the n_o in the non-gap region which exhibited a similar trend as its gap region counterparts as shown in Figure 5.8(b). As n_o was observed to decrease at different non-gap regions, this shows that the non-gap region also has a role to play during the rupture or recombination process.

Figure 5.8(c) to (g) exhibited the behavior of n_o at gap, non-gap and entire filament regions based on cases (1) to (5), respectively. Going from cases (1) through (5), it can be observed that the plots represented by the gap and non-gap regions converge and eventually overlap in case (5) in Figure 5.8(g). However, case (5) where the both gap and non-gap regions are 50% of the filament height is highly unlikely because the n_o at the gap should be less than the non-gap region.⁴³⁻⁴⁷ Similarly, case (4) where the gap region is 40% and non-gap region is 60% of the filament height is also unlikely because n_o at the gap regions is only 10% less than the n_o at the non-gap regions. Hence, both cases (4) and (5) were omitted, and the more probable cases are 10% to 30% gap where 1 nm to 3 nm was suggested to be the rupture gap length.

Further analysis was also performed on the cumulative decrease of n_o with respect to time in Figure 5.9(a) to (g) representative of cases (1) to (5), respectively. In these cases, the rate of decrease of n_o with respect to time can be inferred from the gradient of the plots. The rate of simulation of the switching process was defined to be 1 V/s, where a faster rate of decrease of n_o with respect to time can be suggested by a steeper slope. The vertical axis of Figure 5.9(a) to (g) was plotted in percentage decrease to better illustrate the decrease of n_o over time as V_{stop} increases with reference to the LRS at the start of the simulation. Figure 5.9(a) shows a gradual decrease of n_o at the gap regions until ~ 0.7 s where the rupture started and a very fast decrease in n_o was suggested due to the steep slope observed from 0.7 s to 0.75 s. The sudden and quick decrease of n_o can also be attributed to the V_{stop} sufficient for the recombination to occur, thus resulting in a sudden lowering of barrier energy for the rupture to occur. As the time exceeded

0.75 s, n_o was found to decrease at a slower rate. Similarly, the decrease in n_o in the non-gap regions as shown in Figure 5.9(b) suggests that the n_o at the non-gap also participated in the filament rupture, where the highest cumulative decrease in n_o was observed in the largest non-gap region, 90%. However, it is worthy to note that the decrease in n_o at the gap regions are still dominant as compared to the non-gap regions as observed from the larger cumulative decrease in n_o at the gap regions than at non-gap regions.

Similarly, Figure 5.9(c) to (g) exhibited the cumulative decrease n_o at the gap, non-gap and entire filament regions based on cases (1) to (5), respectively. Due to its larger percentage fluctuations over time, the decrease of n_o at the gap regions are more dominant as compared to the non-gap regions. It can also be observed that the rate of decrease of n_o at the gap regions were up to $\sim 10\times$ larger as compared to that of non-gap regions. In the investigation of Figure 5.9(c) to (g), the cumulative decrease of n_o in the gap region was found to be of a lesser extent for 40% and 50% gap regions as compared to 10%, 20% and 30% gap regions. The cumulative decrease in gap regions at 40% and 50% gap regions again show that they are least probable cases as the n_o was still observed to be about 20% to 30% in those regions. Similar explanations suggested that the most probable rupture gap length is still between 10% to 30% of the filament, *i.e.* 1 nm to 3 nm in this case of 10 nm HfO₂ thickness. Building up to the next Section, the rupture gap length will be estimated in greater detail when different V_{stop} are considered.

Figure 5.8 Number of oxygen vacancies (n_o) vs. V_{stop} of Pt/HfO₂/Ti kMC model at (a) different gap regions at 10% gap to 50% gap based on cases (1) to (5), (b) different non-gap regions at 90% non-gap to 50% non-gap based on cases (1) to (5), (c) all regions at 10% gap based on case (1), (d) all regions at 20% gap based on case (2), (e) all regions at 30% gap based on case (3), (f) all regions at 40% gap based on case (4), (g) all regions at 50% gap based on case (5).

Figure 5.9 Cumulative decrease of oxygen vacancies (n_o) vs. time of Pt/HfO₂/Ti kMC model at (a) different gap regions at 10% gap to 50% gap based on cases (1) to (5), (b) different non-gap regions at 90% non-gap to 50% non-gap based on cases (1) to (5), (c) all regions at 10% gap based on case (1), (d) all regions at 20% gap based on case (2), (e) all regions at 30% gap based on case (3), (f) all regions at 40% gap based on case (4), (g) all regions at 50% gap based on case (5).

5.2.3. Investigation of Ruptured Gap at different RESET Stopping Voltages

The ruptured gap between the tip of the filament and the top electrode was investigated. The number of oxygen vacancies referenced from the top electrode (n_T) was analyzed at different oxide heights with different V_{stop} as shown in Figure 5.10(a). It was observed that n_T decreases with oxide height as the rupture occurs at the interface between the top electrode and the dielectric as shown in Figure 5.6(h). For instance, at 10 nm of oxide height, n_T is close to zero while at 1 nm of oxide height, n_T is at least 2000, depending on the V_{stop} . The V_{stop} values investigated coincide with those shown in Figure 5.6(h), which played a role in determining n_T as different V_{stop} values will result in different extent of recombination between O^{2-} and V_o^+ . Specifically, when V_{stop} increases, n_T decreases as indicated by the arrow in Figure 5.10(a). The inset of Figure 5.10(a) shows the structure of the entire filament at -1.5 V where the V_o^+ spread out towards the top electrode but is empty at the top 2 nm due to the rupture process.

The findings in Figure 5.10(a) were extended to investigate the rupture gap length at different V_{stop} in Figure 5.10(b) enlarged from the bottom right highlighted box of Figure 5.10(a). As the rupture occurs between the top electrode and oxide interface, only the region of oxide height from 7 nm to 10 nm were studied. As mentioned previously that the rupture only occurs at ~ -0.7 V of V_{stop} , linear fittings were performed from the top of the oxide, *i.e.* 10 nm to an oxide height level where the gradient of n_T vs. filament height is changed significantly. The change in the gradient refers to an increase in the number of oxygen vacancies, which suggests the non-ruptured part of the filament. As shown in Figure 5.10(b), the filaments heights where the gradient of n_T vs. filament height is changed significantly are 9.25 nm, 9 nm, 8.75 nm, 8.25 nm and 8 nm for $V_{stop} = -0.7$ V, -0.9 V, -1.1 V, -1.3 V, -1.5 V, respectively. The 8 nm of filament height at $V_{stop} = -1.5$ V corresponds to 2 nm of ruptured gap, which corresponds to the ~ 1 nm to 3 nm suggested filament height discussed in the previous Section.

(a)

(b)

Figure 5.10 Number of oxygen vacancies decreasing with filament height ranging from (a) 0 nm to 10 nm with inset showing the filament (b) 7 nm to 10 nm (shaded box of (a)) at -0.1 V to -1.5 V corresponding to the cases in Figure 5.6. Part (b) also included the estimated filament length where the gradient of the slope started to change, representing a difference in oxygen vacancies between the ruptured and main part of the filament.

5.3 Pt/HfO_x/Ti as a SPICE Compact RRAM Model

After investigating the kMC model, the parameters shown in the flowchart of Figure 5.4 were used as inputs of the compact modelling of Pt/HfO₂/Ti devices where they were integrated with a 40 nm NFET in the Cadence library as a current limiter. The transport equations used in the compact model are very similar to Equations 18 to 20 while the filament extends and ruptures in both lateral and vertical directions during the set and reset processes as well, which shows a relation between the physics and compact model. The main difference between the compact model and the kMC physics-based model used in this work is that the former does not consider the filament in an atomic scale but as a group of atoms migrating during the formation and rupture. In the modelling of conduction, the I - V equation commonly used in compact models is shown in Equation 21 where the hopping current (I) is correlated with the voltage (V) and gap distance (x) by:

$$I = I_0 \exp(-x/x_T) \sinh(V/V_T), \quad (21)$$

where x is the gap height, x_T is the characteristic distance and V_T is the characteristic voltage. [143-148]

5.3.1 Compact Model Fitting and Verification with Experimental Results

x_T is the characteristic distance and V_T is the characteristic voltage, which are fitting parameters extracted from HRS I - V curve, and are found to be 0.39 and 0.31, respectively.[144] The parameters used in this compact model were obtained from literatures, kMC model simulation results, and measurements as shown in Table VII. Parameters γ , f , and E_i are the voltage enhancement factor, V_o vibration frequency, and average activation energy, respectively which contribute to the generation and recombination of oxygen vacancies in both set and reset processes.[138] E_i is the energy barrier between the electrode and oxide interface, which will limit the oxygen ions from moving back to the electrode and oxide interface during the reset process. R_{th} is the effective thermal resistance used in the calculation of the temperature dynamics which play a significant role in both generation and recombination processes.[138] The parasitic effects were also considered in this model to make it more representative of the parasitic effects experienced by the experimental device during

characterization. C_p and R_h are the parasitic capacitance and resistance, respectively from the oxide material, while R_i is the contact resistance between the filament and the electrodes.[146]

Table VII. Compact model parameters obtained from literatures, kMC model simulation results, and measurements.

Parameters from Literatures			
Parameters	Description	Value	Reference
a	distance between adjacent V_o	0.25 nm	[146]
f	vibration frequency of V_o	1×10^{13} Hz	[138]
E_i	Energy barrier at electrode/oxide interface	1.2 eV	[146]
α_i	energy enhancement factor in E_i	0.75 nm	[138]
α_h	energy enhancement factor in E_h	0.75 nm	[138]
γ	voltage enhancement factor	1.5	[146]
Z	charge number & unit charge	1 & e	
R_{th}	effective thermal resistance	5×10^5 K/W	[184]
R_h	parasitic resistance between electrodes	200 M Ω	[147]
R_i	parasitic contact resistance of electrodes	20 Ω	[147]
C_p	parasitic capacitance between electrodes	20 fF	[147]
w_0	initial filament width	20 nm	[145]
w_{eff}	effective filament extending width	0.5 nm	[146]
Parameters obtained from fabrication & experiments			
T_0	ambient temperature	300 K	
L_0	switching layer thickness	10 nm	
W_{CF}	switching layer width	10 μ m	
E_h	hopping barrier of oxygen ions	0.82 eV	
Parameters utilized from kMC model simulations in the I–V fitting from Fig. 1			
E_a	average activation energy of V_o	0.55 eV	
ρ	resistivity of CF	2.5×10^{-5} Ω m	

In the compact model simulation, the initial filament gap length x_0 was set to 0 nm, while a negative pulse and a positive pulse were applied by a voltage source V1 at 50 μ s rise and fall time with 0 s pulse width, representing a DC sweep.[146, 185] V1 pulses were applied to the top electrode of the RRAM model successively to simulate the reset and set processes with a

delay of 100 μ s between them. V2 is a 1.6 V DC gate voltage source, which provided a current of ~ 700 μ A in the saturation region of the NFET. Figure 5.11(a) shows the output voltage waveform of V1 as well as the voltage applied and current read across the RRAM as calculated by $V1 - V_{out}$. Figure 5.11(b) exhibited a good fitting in both HRS and LRS parts of the averaged experimental curve of 200 DC cycles at -1.3 V of V_{stop} , where the fitting was obtained from the parameters in Table II and the voltage inputs defined by V1 & V2. In a better representation of the RRAM device stochasticity observed experimentally, variations parameters were applied to the model, and 10 consecutive cycle-to-cycle variability were observed by the colored lines in Figure 5.11(c). Furthermore, good $I-V$ fittings on multi-level states experimental results at different V_{stop} were observed in Figure 5.11(d), where x_T and V_{stop} were varied while all other parameters remained constant. The good fitting between simulation and experimental results can also be observed in the inset of Figure 5.11(d) at 0.2 V read voltage.[186] Overall, the circuit configuration of the compact model exhibited an accurate waveform of the voltage across the Pt/HfO₂/Ti devices, while the simulated graphs exhibited a similar fitting and trend representative of the experimental results of the multi-level states. Further details of the model fitting can be found in Appendix A3 SPICE Model Parameter Investigations.

Hence, the kMC and compact modelling of HfO₂-based RRAM devices can be applied to other RRAM material systems if material and transport properties were altered accordingly. Fittings and analysis will still be required to match the simulated data with experimental data. As this process will take up a lot of time, it would be efficient if the simulation is performed on optimized RRAM devices with good performance.

Figure 5.11(a) The simulated waveform of output voltages V1, voltage across RRAM, $V1 - V_{out}$ and the current I_{RRAM} through the RRAM, (b) A good fitting of LRS and HRS of simulated result at $V_{stop} = -1.3$ V according to Table VII parameters on $I-V$ experimental results, (c) 10 consecutive simulation cycles exhibiting cycle-to-cycle variability at -1.3 V of V_{stop} which shows a good fitting on the experimental $I-V$ curve, (d) A good fitting of simulated results on experimental multi-level states at different V_{stop} by varying V_{stop} and fitting parameter x_T .

5.3.2 Prediction Analysis Studies of RRAM integrated with GlobalFoundries 40 nm transistor model

Prediction analysis is an important aspect in modelling as it can predict the necessary RRAM device performance suitable for the transistor. In a typical 1T1R configuration, the voltage drop across the RRAM (V_{RRAM}) is the bit line (BL) voltage (V_d) less the voltage drop across the transistor. This means that the voltage drop across the RRAM is lower than V_d and hence to meet the corresponding SET and RESET voltage across the RRAM, the amount of resistance of the LRS and HRS needs to be predicted or vice versa. Figure 5.12 shows the 1T1R simulations of a regular resistor integrated with GlobalFoundries 40 nm transistor model using HSPICE simulation software, a similar SPICE simulation software as Cadence Virtuoso. The gate voltages (V_g) were varied from 1.2 V to 2.2 V at intervals of 0.2 V and the V_d was set to 1.2 V and the transistor width was fixed at 180 nm. Considering the case where $V_g = 1.6$ V and considering 0.7 V to be the voltage drop across the RRAM or SET voltage, the amount of LRS required is at least 5 k Ω as shown by the dotted lines. This model is hence able to predict the required minimum LRS to SET the RRAM. This also works vice versa, using LRS to predict the minimum SET voltage. For example, if only the transistor width is increased to 500 nm while keeping the other conditions same as the case of Figure 5.12(a), the SET voltage can afford to be higher *i.e.* ~1.04 V at LRS of 5 k Ω as shown in the dotted line of Figure 5.12(b). If only the V_d was increased to 1.4 V while keeping the other conditions same as the case of Figure 5.12(a), the SET voltage can afford to be higher *i.e.* ~0.8 V at LRS of 5 k Ω as shown in the dotted line of Figure 5.12(c). Finally, if both transistor width and V_d is increased to 500 nm and 1.4 V, respectively, the SET voltage can afford to be even higher *i.e.* ~1.2 V at LRS of 5 k Ω as shown in the dotted line of Figure 5.12(d).

Figure 5.12 Modelling of SET voltage across the RRAM to predict its corresponding resistance and vice versa in (a) transistor width 180 nm, $V_d = 1.2$ V, (b) transistor width 500 nm, $V_d = 1.2$ V, (c) transistor width 180 nm, $V_d = 1.4$ V, (d) transistor width 500 nm, $V_d = 1.4$ V cases.

Similarly, this prediction analysis can be extended to HRS to predict the RESET voltage and its corresponding resistance and vice versa. Considering the case where $V_g = 1.6$ V and considering 0.7 V to be the voltage drop across the RRAM or RESET voltage, the amount of HRS required is at least 100 kΩ as shown by the dotted lines. This model is hence able to predict the required minimum HRS to RESET the RRAM. This also works vice versa, *i.e.* using HRS to predict the minimum RESET voltage. For example, if only the transistor width is increased to 500 nm while keeping the other conditions same as the case of Figure 5.13(a), the RESET voltage can afford to be higher *i.e.* ~0.78 V at HRS of 100 kΩ as shown in the dotted line of Figure 5.13(b). If only the V_d was increased to 1.4 V while keeping the other conditions same as the case of Figure 5.13(a), the RESET voltage can afford to be slightly higher *i.e.* ~0.7 V at HRS of 100 kΩ as shown in the dotted line of Figure 5.13(c). Finally, if both transistor

width and V_d is increased to 500 nm and 1.4 V, respectively, the RESET voltage can afford to be even higher *i.e.* ~ 0.8 V at HRS of 100 k Ω as shown in the dotted line of Figure 5.13(d). More analysis can be found in Appendix A4 SPICE Model Prediction Analysis where the V_g was explored at a wider range from 1.2 V to 3.0 V, while V_d was up to 2.5 V.

Figure 5.13 Modelling of RESET voltage across the RRAM to predict its corresponding resistance and vice versa in (a) transistor width 180 nm, $V_d = 1.2$ V, (b) transistor width 500 nm, $V_d = 1.2$ V, (c) transistor width 180 nm, $V_d = 1.4$ V, (d) transistor width 500 nm, $V_d = 1.4$ V cases.

5.4 Chapter Summary

The filamentary nature of Pt/HfO₂/Ti RRAM devices was proven by the area independence in both LRS and HRS and modelled using kMC and SPICE, providing a comprehensive physics study and analysis. In the kMC study, the decrease in V_o^+ was found to occur throughout the entire filament, including the part of the filament where the rupture did not occur. The cumulative decrease of V_o^+ in the ruptured gap region was revealed to be up to $\sim 10\times$ faster as compared to the remaining part of the filament. Further analysis shows that the gap height between the tip of the filament to the top electrode was about 20% of the oxide thickness at a V_{stop} of -1.5 V. The experimental I - V results of the devices was well-fitted using the kMC physics-based model where extracted parameters such as thermal ionization energy and defect density values were verified. Compact modelling of the devices integrated with 40 nm NFET as a current limiter also revealed a good agreement with experimental results of multi-level states. The SPICE modelling was also shown to be able to predict the SET voltage, RESET voltage, HRS and LRS of the devices when integrated to the 40 nm transistor. Overall, the kMC models and multi-level states SPICE models have a great potential for stack prediction analysis for future 1T1R industrial and neuromorphic applications.

Chapter 6

Conclusions and Future Works

This chapter concludes this PhD work on MgO-based and HfO₂-based RRAM physics investigations and discusses about future works on integrating the HfO₂-based RRAM to the GlobalFoundries 40 nm transistor. It will summarize the main findings, which includes the conduction mechanisms, switching dynamics, multi-level states and modelling of the RRAMs. This will provide a comprehensive physics platform to integrate with the GlobalFoundries 40 nm transistor and explore finite element modelling (FEM) on RRAM devices and transistors.

6.1 Conclusions

The annealing effect on MgO-based RRAM devices has been shown to improve cycle-to-cycle resistance variability while producing consistent I - V curves for conduction mechanism studies. These studies revealed Schottky Emission as the dominant conduction mechanism at temperatures ranging from 300 K to 375 K. Schottky Emission was further validated by TEM on Ru/MgO/Ta RRAM devices where Ta diffusion resulted in a smaller MgO thickness, matching the extracted values. TEM analysis on Ru/MgO/Cu RRAM devices identified a Cu filament by a difference in crystallinity, with the filament width measured to be ~ 10 nm. Another TEM analysis on Pt/MgO/Cu RRAM devices revealed Cu filaments within the MgO layer, observed from the EDS line profile. Hopping conduction was found to be the dominant conduction mechanism in Pt/MgO/Cu RRAM devices where the energy barrier was calculated to be 0.18 eV. Similarly, hopping conduction in Pt/HfO₂/Ti devices revealed an increase of trap-to-trap distance from 0.83 nm to 0.93 nm as V_{stop} increased from -0.9 V to -1.3 V. The retention of these MgO and HfO₂-based devices were found to be more than 10 years at 85°C using an Arrhenius plot. Therefore, these conduction mechanism and performance studies provided a better understanding of the pre-switching ion and electron behavior, integral for stack optimization.

Angular studies on the gradual RESET process of MgO and HfO₂-based RRAM devices was found to correlate with number and controllability of multi-level states. A gentler RESET slope angle of 20° in Pt/HfO₂/Ti devices exhibited more distinct multi-level states than its MgO-based counterparts that exhibited steeper slope angles. The multi-level state switching of Pt/HfO₂/Ti resistive switching devices was validated with the proposed E_{AC} and V_{stop} switching model. The average E_{AC} value was also extracted from an Arrhenius equation to be 0.022 eV at a wide temperature range of -40°C to 175°C and was suggested to be inversely proportional to n_D . Furthermore, the multi-level high resistance states were achieved at V_{stop} -0.9 V to -1.3 V at intervals of -0.1 V. In the validation of the relationship between n_D and V_{stop} , kMC simulations exhibited a decrease in n_D at increasing V_{stop} at different regions of the filament. The uniformly fabricated Pt/HfO₂/Ti devices exhibited at least 5×10^5 endurance cycles at 100ns with a retention for more than 10 years at 125°C . With these good electrical, thermal and multi-level state capabilities, Pt/HfO₂/Ti RRAM devices and their proposed models have great potential for applications such as neuromorphic engineering in automobiles.

The filamentary nature of Pt/HfO₂/Ti RRAM devices was proven by the area independence in both LRS and HRS and modelled extensively using kMC and SPICE. In the kMC study, the decrease in V_o^+ was found to occur throughout the entire filament, where the decrease of V_o^+ in the ruptured gap region was revealed to be up to $\sim 10\times$ faster as compared to other parts of the filament. Further analysis on filament evolution estimated a ruptured gap to be ~ 2 nm at a V_{stop} of -1.5 V. The experimental $I-V$ results of Pt/HfO₂/Ti RRAM devices was well-fitted using the kMC physics-based model where extracted parameters such as thermal ionization energy and defect density values were verified. Compact modelling also revealed a good agreement with multi-level states experimental results. The SPICE modelling was able to predict the SET and RESET voltages, HRS and LRS of the RRAM when integrated to the 40 nm transistor. These kMC model along with the multi-level states SPICE capabilities have great potential for stack prediction analysis for future 1T1R industrial and neuromorphic applications.

The performance of the RRAM devices investigated in this work were summarized and compared with the industry specifications in Table VIII. While MgO-based RRAMs need a lot of improvements in terms of performance, HfO₂-based RRAMs only need to improve on its size and switching current to meet the industry specifications, which is the most suitable RRAM structure in future. Overall, this work extends the existing conduction physics, switching dynamics and modelling of MgO and HfO₂-based RRAM devices, deepening the understanding of area, temperature, material, and electrical performance studies. These new findings will provide a stable platform for numerous applications such as neuromorphic computing, automobiles, and temperature sensors, when integrated with transistors.

Table VIII. Summary of RRAM devices investigated in this work and comparison to industry specifications.

Parameters	RRAMs in this Work				Industry Goto Specs (FLASH)
<div>Efficient</div> <div>Acceptable</div> <div>Needs Improvement</div> <div>Not efficient</div>	Ru/MgO/Ta	Ru/MgO/Cu	Pt/MgO/Cu	Pt/HfO ₂ /Ti	Selected Material
Cell area	30 × 30 um ²	30 × 30 um ²	10 × 10 um ²	10 × 10 um ²	100 x 100 nm ²
Multi-bit	No	No	No	Yes	Not required
Switching Speed	NIL	NIL	NIL	200 ns	200 ns
Switching Voltage	3 V	3 V	3 V	~1.2 V	1.2 V
Switching Current	1 mA	1 mA	1 mA	1 mA	100 uA
ON/OFF Ratio	100x	100x	1000x	50x	100x
Endurance	NIL	NIL	2 x 10 ³ cycles	5 x 10 ⁵ cycles	10 ⁵ cycles
Data Retention	>10 years at 85°C	>10 years at 125°C	>10 years at 125°C	>10 years at 125°C	>10 years at 125°C

6.2 Future Works

The findings in this work will mainly be brought over to the industry where the RRAM device and their models will be integrated with transistors in different configurations such as 1T1R, 1T2R and arrays.

6.2.1 Integration of Pt/HfO₂/Ti with GlobalFoundries 40 nm transistors

The future works will be to integrate the investigated Pt/HfO₂/Ti RRAM to the GlobalFoundries 40 nm transistor as shown in Figure 6.1 in a standard 1T1R integration process where the RRAM is fabricated above a metal line, often connected with a via.[187, 188] This process usually takes months of process fabrication from the front end of line (FEOL) to the back end of line (BEOL), where the RRAM integration process is part of the BEOL. Other than a 1T1R integration process, 1T2R and array configurations will also be investigated to demonstrate their performance capabilities.[189, 190] However, some considerations during the integration process would be to ensure that the deposited RRAM layers are uniformly calibrated, the etching of the RRAM stack is optimized as a vertical-shaped pillar, and that the metal lines are well-connected to the vias linked to the RRAM devices.

Figure 6.1 Standard 1T1R integration schematic.

So far, only the GlobalFoundries 40 nm transistor was characterized where the drain current (I_d) was plotted against the V_d when the V_g was varied from 0 V to 2.0 V at intervals of 0.25 V as shown in Figure 6.12(a). It shows a very consistent and increasing trend of higher I_d as V_d increases which is non-ideal as the I_d does not saturate at a current value. The source current (I_s) was also plotted against the source voltage (V_s) when V_g was varied from 0 V to 2.0 V at intervals of 0.25 V as shown in Figure 6.12(b). Similarly, it shows a very consistent and increasing trend of higher I_s as V_s increases which is non-ideal as the I_s does not saturate at a current value. Figures 6.12(c) and (d) shows the I_d plotted against V_g and I_s plotted against V_g , respectively at 2 V of V_d where I_d and I_s increases when V_g increases. All these trends exhibited a transistor performance and the RRAM will be integrated to the transistor for 1T1R and other configurations.

Figure 6.2(a) I_d vs. V_d with increasing V_g , (b) I_s vs. V_s with increasing V_g , (c) I_d vs. V_g at V_d of 2 V, (d) I_s vs. V_g at V_d of 2 V of GlobalFoundries 40 nm transistors.

Another area of exploration when integrated with the transistor would be to investigate the multi-level states of the Pt/HfO₂/Ti RRAM. There have been many methods proposed to improve the scalability of 1T1R devices, either by shrinking the transistor technology node or stacking up in 3D which usually involves complex fabrication processes and additional masks, thus increasing the cost per bit. Exploring multi-level states would be a cost-saving approach which would improve the number of bits per cell. However, multi-level states would require numerous optimizations and strict resistance margin rules to prevent states from overlapping one another. This means that the multi-level states need to be distinctive from one another to avoid writing or reading the incorrect memory information.

6.2.2 Finite Element Model for RRAM & Transistor devices

While kMC modelling are based on defects generation and recombination in RRAM, FEM are used to investigate the switching characteristics and its local dynamics of defect concentration. Ielmini reported a numerical model of filament growth based on thermally activated ion migrations on both SET and RESET switching, which was improved by Ambrogio *et al.* to incorporate Monte Carlo switching statistics in HfO_x-based RRAM models.[125, 191] Other FEM models also include temperature and the geometry of the depleted gap during the switching process where partial differential equations (PDEs) relating to heat, electrons and defects are solved.[192] One such model was reported by Kim *et al.* where filament evolution was demonstrated using a drift/diffusion continuity equation for V_o^+ transport, a current continuity equation for electrical conduction, and a Fourier equation for Joule heating. With these PDEs, the V_o^+ density in the conductive filament region of the Pt/TaO_x/Ta₂O₅/Pt and Pd/TaO_x/Ta₂O₅/Pd models were investigated when a different voltage is applied.[128, 193] Fantini *et al.* also explored the impact of load resistances and ramp rates on the output current of the TiN/HfO₂/Hf/TiN device models,[194] which was further improved by Niraula *et al.* more recently to incorporate filament evolution, gap dynamics, temperature and energy as a comprehensive FEM model.[195]

Finite element model (FEM) simulations such as COMSOL and TCAD would also be useful in analyzing and predicting the transistor behavior.[196] Figure 6.3(a) and (b) shows the electric potential in 2D and 3D metal oxide semiconductor field effect transistor (MOSFET) simulation which is useful to design and study the transistor in detail, prior to any fabrication processes. These COMSOL and TCAD simulations can save fabrication time as optimizations of the transistors can be performed from simulations, prior to any fabrication.

Figure 6.3(a) A 2D MOSFET model, (b) A 3D MOSFET model in COMSOL

A Pt(10nm)/HfO₂(10nm)/Ti(100nm)/Pt(10nm) model was built using COMSOL Multiphysics using a 2D axisymmetric plane which will be rotated 360° throughout the vertical axis to create a 3D model. In the model simulation, the electric currents module, heat transfer in solids module and the Multiphysics module of COMSOL were utilized. The filament region is 6 nm in radius (r), and the entire device is 10nm in radius as shown in Figure 6.4(a) and (b). Figure 6.4(a) shows the model with the SET configuration where the BE is grounded while the TE is applied with a positive voltage. On the other hand, Figure 6.4(b) represents the RESET configuration where the BE is still grounded but the TE is applied with a negative voltage. The 3D model is designed such that it is both electrically and thermally insulated.

Figure 6.4 Pt/HfO₂/Ti RRAM COMSOL model in (a) SET and (b) RESET configurations respectively.

As the Pt/HfO₂/Ti devices were shown experimentally to exhibit hopping conduction in Chapter 3, a variation of hopping, i.e. phonon assisted hopping is suitable to describe the electrical conduction of the Pt/HfO₂/Ti devices through optimum hopping chains or paths.[197, 198] The conductivity of the optimum hopping paths are given by Equations 22 & 23.

$$\sigma_{cf} = \sigma_{0f} \exp\left(-\frac{E_{Gf}}{kT}\right) \exp\left(\sqrt{\frac{eV}{kT}}\right), \quad (22)$$

$$\sigma_{cg} = \sigma_{0g} \exp\left(-\frac{E_{Gg}}{kT}\right) \exp\left(\sqrt{\frac{eV}{kT}}\right), \quad (23)$$

where E_G is the energy difference between the Fermi-level (E_F) and mobility edge (E_C) as shown in Figure 6.5, while subscripts f and g refer to filament and gap respectively.

Figure 6.5 Electrons hopping through the optimum hopping sites from dielectric trap-to-trap, with E_G is the energy difference between the Fermi-level (E_F) and mobility edge (E_C).

Equation 24 shows the threshold voltage required for the switching to occur while Equations 25 and 26 show the free energy of the filament and dielectric. The free energy consists of thermal energy due to Joule heating, electrostatic energy, and chemical energy (surface & volume).

$$V_T = V \left[\ln\left(\frac{V}{\lambda\tau_0}\right) \right]^{-1} \text{ where, } V = \frac{hW_0}{kT} \sqrt{\frac{3\pi^2\alpha^3\Lambda W_0}{32\epsilon r_c^3}} \quad (24)$$

where h is the filament height, W_0 is the nucleation barrier, T is the temperature, α is the ratio of minimum filament radius and critical nucleus radius (r_c), Λ is a multiplier logarithmically dependent on the embryo (initial filament) aspect ratio, λ is the voltage ramp-rate, τ_0 is the characteristic atomic-vibration time, and ϵ is the permittivity of HfO_2 .

$$F = \int \rho C_p \delta T dx^3 + \frac{1}{2} \int \epsilon |E|^2 dx^3 + 2\pi r h \sigma + \pi r^2 h \delta \mu_1, \quad (25)$$

$$F = \int \rho C_p \delta T dx^3 + \frac{1}{2} \int \epsilon |E|^2 dx^3 + 2\pi r l \sigma + \pi r^2 l \delta \mu_2, \quad (26)$$

where ρ is the mass density, C_p is the specific heat, δT is the change in temperature, E is the electric field, r is the filament radius, h is the filament length, l is the gap width, σ is the surface tension or interfacial energy, and $\delta \mu_1$ is the chemical potential difference between the *uc*-phase and the *i*-phase while $\delta \mu_2$ is the chemical potential difference between the *uc*-phase and the *mc*-phase considering that SET and RESET processes are endothermic. Figure 6.6 exhibited the triple well chemical potential of the HfO_2 dielectric represented by the 3 different phases, i.e. insulating (*i*), unstable conducting (*uc*) and metastable conducting (*mc*).[199]

Figure 6.6 Triple potential well indicating the various chemical potentials in the insulating (*i*), unstable conducting (*uc*) and metastable conducting (*mc*) phases.

The parameters used in Equation 24 to 26 can also be found in Table IX & X which exhibits the material properties and the model parameters of the 4 fittings shown in Figure 6.7 with respect to the experimental data.

Table IX Properties of materials used in the Pt/HfO₂/Ti model [195]

Material	Electrical Conductivity σ [S/m]	Thermal Conductivity κ [W/K.m] [200]	Specific heat capacity C_p [J/kg.K]	Relative Permittivity ϵ_r	Density ρ [kg/m ³]
SiO ₂	10 ⁻⁹	1.38	703	3.9	2.2 x 10 ³
Pt	$\exp(\sigma_c(T))$	$\sigma_c(T)TL$	133	-10 ⁶	2.15 x 10 ⁴
Ti	$\exp(\sigma_c(T))$	$\sigma_c(T)TL$	520	-10 ⁶	4.5 x 10 ³
HfO ₂	10	0.5	120	25	10 ⁴
HfO _{2-x}	$\sigma_{0f} \exp\left(-\alpha_f \ln\left(\frac{\tau}{\tau_0}\right)\right) \exp\left(\sqrt{\frac{eV}{kT}}\right)$	$\sigma_c(T, V)TL$	140	-10 ⁶	1.2 x 10 ⁴
Gap	$\sigma_{0g} \exp\left(-\alpha_g \ln\left(\frac{\tau}{\tau_0}\right)\right) \exp\left(\sqrt{\frac{eV}{kT}}\right)$	κ_{eff} $\sigma_c(T, V)TL$	140	25	10 ⁴

Table X Pt/HfO₂/Ti Model parameters of the 4 fittings shown in Figure 5.17 [195]

Parameters	Symbols	Fitting 1	Fitting 2	Fitting 3	Fitting 4	Units
Circuitry [194]						
Load Resistance	R _L	2	2	2	2	kΩ
Set Voltage Amplitude	V _{amp(+ve)}	1.6	1.6	1.6	1.6	V
Reset Voltage Amplitude	V _{amp(-ve)}	-1.5	-1.5	-1.5	-1.5	V
Ramp rate	λ	100	100	100	100	V/s
Electrical Conductivity (gap/filament)						
Electrical conductivity of filament	σ _{0f}	7000	7000	7000	7000	kS/m
Electrical conductivity of gap	σ _{0g}	1000	2000	1000	1000	kS/m
Pre-logarithmic constant of filament	α _f	-0.09	-0.09	-0.07	-0.09	—
Pre-logarithmic constant of gap	α _g	0.09	0.09	0.07	0.09	—
V _{amp} /λ	τ	0.016	0.016	0.016	0.016	s
Atomic Vibration	τ ₀ (τ _{min})	0.1	0.1	0.1	0.1	ps
Thermal Conductivity (gap)						
Thermal conductivity	κ _{eff}	10	10	10	10	—
Chemical Energy [199]						
Surface Tension	σ	0.01	0.01	0.01	0.01	J/m ²
Difference between unstable conductive and insulating chemical potentials	δμ ₁	20	15	15	15	GJ/m ³

Difference between unstable conductive and metastable conductive chemical potentials	$\delta\mu_2$	9.5	9.5	9.5	9.5	GJ/m ³
Fitting parameter of $\delta\mu_1$	β_1	0.35	0.35	0.45	0.35	GJ/m ³
Fitting parameter of $\delta\mu_2$	β_2	0.5	0.5	0.5	0.5	GJ/m ³
Change in maximum and minimum random thermodynamic barriers in the unstable conductive phase	ΔW_{Buc}	1	1	1	1	eV
Change in maximum and minimum random thermodynamic barriers in the insulator phase	ΔW_{Bi}	0.1	0.1	0.1	0.1	eV
Change in maximum and minimum random thermodynamic barriers in the metastable conductive phase	ΔW_{Bmc}	0.3	0.3	0.3	0.3	eV
Filament Nucleation [201]						
Filament height	h	5	5	5	5	nm
Nucleation Barrier	W_0	2.5	2.5	2.5	2.5	eV
Multiplier logarithmically dependent on embryo aspect ratio	Λ	6.6	6.6	6.6	6.6	–
Critical nucleus radius	r_c	2.9	2.9	2.9	2.9	nm
Minimum filament radius	r_{min}	0.6	0.6	0.6	0.6	nm
r_{min}/r_c	α	0.21	0.21	0.21	0.21	–

In the variation of model parameters as per Table IX and X, fittings 1 to 4 were obtained as shown in Figure 6.7 with respect to the experimental data. Similar to the kMC model in Section 5.2, the focus will be on the rupture part of the filament in the investigation of the gap, which is on the negative voltage part of the I – V curve. Figure 6.7 shows a relatively good fitting of the I – V curve, which shows that hopping conduction is suitable to model Pt/HfO₂/Ti RRAM devices. These fittings were performed by varying different modelling parameters as shown in Appendix Section A5. Figure 6.8(a) to (d) shows the relationship between device resistance, length of gap, average filament temperature and average gap temperature respectively with increasing RESET voltage. For basic checking, Figure 6.8(a) shows the correct relationship

where reset voltage increases as resistance increases, indicating a higher resistance state. The increase in resistance is also supported by the larger gap length as shown in Figure 6.8(b). As the rupture of the filament becomes larger due to the larger reset voltage, the gap widens where there is a larger amount of dielectric material, this increasing the resistance of the device as lesser current can pass through the shorter filament. This range of gap length is also consistent to the analysis of filament gap evolution in Section 5.2.2 where the gap length was found to be between 1 nm to 3 nm from the kMC model. The filament and gap temperatures were also found to increase with reset voltage as shown in Figure 6.8(c) and (d) respectively. This is likely attributed to Joule heating as the filament and the surrounding regions heats up due to the high voltage applied. The temperatures are consistent with those reported at corresponding reset voltages.[195] Further analysis of the FEM model can be found in Appendix A5 Numerical Model Parameter Investigations.

Figure 6.7 I – V fittings 1 to 4 on experimental data, which shows a relatively good fitting.

Figure 6.8 Relation between (a) Device resistance, (b) Length of gap, (c) Average filament temperature and (d) Average gap temperature at increasing RESET voltage for Pt/HfO₂/Ti COMSOL simulation.

Appendix

This Appendix serves as supporting information for the investigations and modelling in various parts of this thesis. Specifically, the focus will be on conduction mechanism, kMC model, SPICE model and FEM investigations as well as parameter fittings to fill in the gap of this work and to complete the entire investigations.

A1 FN-Tunneling Investigations Pt/MgO/Ta and Pt/MgO/Cu RRAM Devices

This Appendix Section exhibited the FN-Tunneling fittings in relation to Section 3.1.2, showing that FN-Tunneling is not the dominant conduction mechanism due to its non-linear fittings. As compared to Schottky Emission fittings in section 3.1.2, FN-Tunneling would not be suitable as a conduction mechanism.

Figure A1 I/V^2 vs. $1/V$ FN-tunneling fit of (a) HRS Ru/MgO/Ta RSM device, (b) LRS Ru/MgO/Ta RSM device, (c) HRS Ru/MgO/Cu RSM device, (d) LRS Ru/MgO/Cu RSM device. As fitting is not linear, FN-tunneling is regarded as not dominant conduction mechanism.

A2 FN-Tunneling & Trap-Assisted Tunneling Investigations of Pt/HfO₂/Ti RRAM Devices

This Appendix Section exhibited the FN-Tunneling and Trap-Assisted Tunneling (TAT) fittings in relation to Section 3.3, showing that FN-Tunneling and TAT are not the dominant conduction mechanisms due to its non-linear fittings. As compared to hopping conduction fittings in Section 3.3, FN-Tunneling and TAT would not be suitable as a conduction mechanism.

Due to the reciprocal of voltage ($1/V$) in the X -axis, a large part of the model was well-fitted in the lower voltage region as shown in Figure A2.1 & A2.2, while only a small part of the curve fitting is in the high voltage region, *i.e.* towards zero in the X -axis. As the rupture occurs at high negative voltage ranges, it would be more suitable to investigate the high negative voltage (or low negative $1/V$) region more extensively. The focus is mainly on bulk-limited conduction mechanisms as different V_{stop} would determine different gap lengths, where the gap rupture occurs mainly at the bulk at higher voltage regions. FN-tunneling, being an electrode-limited conduction mechanism, would be less suitable in this case. However, we adopted a type of TAT in the hopping regime to investigate trap characteristics in the bulk, specifically to determine the trap-to-trap distance.[202] The increase in trap-to-trap distance was found to coincide with the decrease in n_D at increasing V_{stop} , indicating that the hopping conduction as part of TAT is suitable to interpret the results reported in this paper. Hence, a combination of voltage region, bulk-limited conduction, and trap characteristics determined that hopping conduction is most suitable to interpret our results.

Figure A2.1. FN-Tunnelling with fittings in the low voltage region of V_{stop} at -0.9 V, -1.0 V, -1.1 V, -1.2 V & -1.3 V.

Figure A2.2. TAT with fittings in the low voltage region of V_{stop} at -0.9 V, -1.0 V, -1.1 V, -1.2 V & -1.3 V.

A3 kMC Model Parameter Investigations

This Appendix Section explores the impact of the activation energy (E_a) variation on filament evolution in Table A2, and the filament evolution in Pt/HfO₂/Ti RRAM devices from $V_{stop} = 0$ V to -1.5 V showing an increased rupture as V_{stop} increases. These investigations are in relation to Section 5.2.1.

Table A3 Impact of activation energy (E_a) variation in x,y & z on filament evolution

PtHfO ₂ (10)TiO _x (0.5)Ti	$E_{a,x} = E_{a,y} = 0.80\text{eV}$		$E_{a,x} = E_{a,y} = 0.85\text{eV}$		$E_{a,x} = E_{a,y} = 0.90\text{eV}$	
$E_{a,z} = 0.55\text{eV}$						
$E_{a,z} = 0.60\text{eV}$						
$E_{a,z} = 0.65\text{eV}$

Figure A3 Filament evolution of Pt/HfO₂/Ti RRAM devices from (a) 0 V, (b) -0.1 V, (c) -0.2 V, (d) -0.3 V, (e) -0.4 V, (f) -0.5 V, (g) -0.6 V, (h) -0.7 V, (i) -0.8 V, (j) -0.9 V, (k) -1.0 V, (l) -1.1 V, (m) -1.2 V, (n) -1.3 V, (o) -1.4 V, (p) -1.5 V.

A4 SPICE Model Parameter Investigations

This Appendix Section exhibited the parameter variations of the compact model in relation to Section 5.3.1, in building the compact model for Pt/HfO₂/Ti RRAM devices.

(a)

(b)

(c)

(d)

(e)

(f)

(g)

(h)

(i)

(j)

(k)

(l)

Figure A4 (a) Hopping Current Density, (b) Hopping Distance between Traps, (c) Activation Energy, (d) Hopping Barrier of O^{2-} , (e) Interface Barrier, (f) Energy Enhancement Factor (RESET), (g) Energy Enhancement Factor (SET), (h) Voltage Enhancement Factor, (i) Characteristic Gap (j) Effective Thermal Resistance, (k) Initial Gap Length (l) Switching Layer Width (m) Effective Width of CF, (n) Initial CF Width, (o) Characteristic Voltage.

A5 SPICE Model Prediction Analysis

This Appendix Section exhibited an extension of the SPICE model prediction analysis in relation to Section 5.2.2.

Figure A5.1 Modelling of SET voltage across the RRAM to predict its corresponding resistance and vice versa in (a) transistor width 180 nm, $V_d = 1.2$ V at different V_g from 1.2 V to 3.0 V, (b) transistor width 180 nm, $V_d = 1.5$ V at different V_g from 1.2 V to 3.0 V (c) transistor width 180 nm, $V_d = 2.0$ V at different V_g from 1.2 V to 3.0 V (d) transistor width 180 nm, $V_d = 2.5$ V.

(a)

(b)

(c)

(d)

Figure A5.2 Modelling of RESET voltage across the RRAM to predict its corresponding resistance and vice versa in (a) transistor width 180 nm, $V_d = 1.2$ V at different V_g from 1.2 V to 3.0 V, (b) transistor width 180 nm, $V_d = 1.5$ V at different V_g from 1.2 V to 3.0 V (c) transistor width 180 nm, $V_d = 2.0$ V at different V_g from 1.2 V to 3.0 V (d) transistor width 180 nm, $V_d = 2.5$ V.

A6 Numerical Model Parameter Investigations

This Appendix Section includes the parameter variation of the COMSOL model to investigate the effect of parameter change on the I – V curve for fitting purposes in Section 6.2.2. The parameters in Table A5 correspond to Figures A5(a) to (p).

Table A6 Parameters & values used for the COMSOL model in Section 6.2.2.

Figure	Parameters	Symbols
Circuitry [194]		
	Load Resistance	R_L
(a)	Set Voltage Amplitude	$V_{\text{amp}(+ve)}$
(b)	Reset Voltage Amplitude	$V_{\text{amp}(-ve)}$
	Ramp rate	λ
Electrical Conductivity (gap/filament)		
(d)	Electrical conductivity of filament	σ_{0f}
(j)	Electrical conductivity of gap	σ_{0g}
(c)	Pre-logarithmic constant of filament	α_f
(i)	Pre-logarithmic constant of gap	α_g
	V_{amp}/λ	τ
(k)	Atomic Vibration	τ_0 (τ_{min})
Thermal Conductivity (gap)		
(l)	Thermal conductivity	κ_{eff}
Chemical Energy [199]		
(e)	Surface Tension	σ
(f)	Difference between unstable conductive and insulating chemical potentials for SET process	$\delta\mu_1$
(g)	Difference between unstable conductive and metastable conductive chemical potentials for RESET process	$\delta\mu_2$
(h)	Fitting parameter of $\delta\mu_1$	β_1
(m)	Fitting parameter of $\delta\mu_2$	β_2
(n)	Change in maximum and minimum random thermodynamic barriers in the unstable conductive phase	ΔW_{Buc}
(p)	Change in maximum and minimum random thermodynamic barriers in the insulator phase	ΔW_{Bi}
(o)	Change in maximum and minimum random thermodynamic barriers in the metastable conductive phase	ΔW_{Bmc}

(a)

(b)

(c)

(d)

(e)

(f)

(g)

(h)

(i)

(j)

(k)

(l)

(m)

(n)

(o)

(p)

Figure A6 with descriptions shown in Table A5

Publications List

Peer-Reviewed Journals Published & Submitted

- 1) Desmond Jia Jun Loy, Putu Andhita Dananjaya, Xiao Liang Hong, Danny Pak-Chum Shum and Wen Siang Lew, "Conduction Mechanisms on High Retention Annealed MgO-based Resistive Switching Memory Devices" – Published in Scientific Reports, 8, 14774 (2018).
- 2) Desmond Jia Jun Loy, Putu Andhita Dananjaya, Somsubhra Chakrabarti, Kuan Hong Tan, Samuel Chen Wai Chow, Eng Huat Toh and Wen Siang Lew, "Oxygen Vacancy Density Dependence with Hopping Conduction Mechanism in Multi-Level Switching Behavior of HfO₂-Based RRAM Devices" – Published in ACS Applied Electronic Materials 2(10), 3160-3170 (2020).
- 3) Desmond Jia Jun Loy, Kunqi Hou, Mun Yin Chee, Samuel Chen Wai Chow, Putu Andhita Dananjaya, Somsubhra Chakrabarti, Eng Huat Toh, Wen Siang Lew, "Filament Evolution and Compact Modelling of Multi-level Resistance HfO₂-based RRAM Devices" – Under revision in IEEE Transactions on Electron Devices.
- 4) Xiao Liang Hong, Desmond Jia Jun Loy, Putu Andhita Dananjaya, Funan Tan, Chee Mang Ng & Wen Siang Lew, "Oxide-based RRAM materials for neuromorphic computing" – Published in Journal of Materials Science, 53, 8720 (2018).
- 5) Putu Andhita Dananjaya, Desmond Jia Jun Loy, Samuel Chen Wai Chow, Wen Siang Lew, "Unidirectional threshold switching induced by Cu migration with high selectivity and ultralow OFF current under gradual electroforming treatment" – Published in ACS Applied Electronic Materials, 1, 2076 (2019).
- 6) Nagaraj Lakshmana Prabhu, Desmond Jia Jun Loy, Putu Andhita Dananjaya, Eng Huat Toh, Wen Siang Lew, Nagarajan Raghavan, "Exploring the Impact of Variability in

Resistance Distributions of RRAM on the Prediction Accuracy of Deep Learning Neural Networks” – Published in Electronics, 9, 414 (2020).

Conferences Presented & Published

- 1) Desmond Jia Jun Loy, Putu Andhita Dananjaya, Wai Cheung Law, Gerard Joseph Lim, Funan Tan, Xiao Liang Hong, Samuel Chen Wai Chow, Eng Huat Toh and Wen Siang Lew, “Hopping Conduction Temperature Investigations on High Retention Electrochemical Metallization MgO-based Resistive Switching Devices in the Low Resistance State” – Published in Electron Devices Technology and Manufacturing Conference, IEEE (2019).
- 2) Desmond Jia Jun Loy, Putu Andhita Dananjaya, Wai Cheung Law, Gerard Joseph Lim, Funan Tan, Xiao Liang Hong, Samuel Chen Wai Chow, Eng Huat Toh and Wen Siang Lew. “Nearest Neighbor Hopping in High Retention MgO-based Resistive Switching Devices in the High Resistance State” – Presented in Materials Research Society Conference (2019).
- 3) Desmond Jia Jun Loy, Putu Andhita Dananjaya, Somsubhra Chakrabarti, Kuan Hong Tan, Samuel Chen Wai Chow, Mun Yin Chee, Jia Rui Thong, Kun Qi Hou, Jia Min Ang, Gerard Joseph Lim, Yong Chiang Ee, Wen Siang Lew, “Impact of Stopping Voltage and Hopping Conduction on the Oxygen Vacancy Concentration of Multi-Level HfO₂-Based Resistive Switching Devices” – Published in Silicon Nanoelectronics Workshop (2020).
- 4) Putu Andhita Dananjaya, Desmond Jia Jun Loy, Wen Siang Lew, “Correlation Between Traps Jumping Distance and Gradual Conductance Change Under Different Conductance Update Schemes in Ti/HfO₂/TiN Memristive Devices” – Presented in Materials Research Society Conference (2019).
- 5) Nagaraj Lakshmana Prabhu, Desmond Jia Jun Loy, Putu Andhita Dananjaya, Eng Huat Toh, Wen Siang Lew, Nagarajan Raghavan, “Exploring the Power – Prediction Accuracy Trade-Off in a Deep Learning Neural Network using Wide Compliance

RRAM Device” – Published in International Symposium on Next-Generation Electronics, IEEE (2019).

- 6) Putu Andhita Dananjaya, Desmond Jia Jun Loy, Mun Yin Chee, Samuel Chen Wai Chow, Jia Min Ang, Kun Qi Hou, Jia Rui Thong, Somsubhra Chakrabarti, Yong Chiang Ee, Wen Siang Lew, “Bulk-limited Effect in Gradual Conductance Switching Behaviour of HfO_x-based Memristive Devices for Analog Synaptic Device Applications” – Published in Silicon Nanoelectronics Workshop (2020).
- 7) Somsubhra Chakrabarti, Jia Min Ang, Jia Rui Thong, Kun Qi Hou, Mun Yin Chee, Putu Andhita Dananjaya, Desmond Jia Jun Loy, Yong Chiang Ee, Wen Siang Lew, “Effects of Thermal Annealing on Ta₂O₅ based CMOS compatible RRAM” – Published in Silicon Nanoelectronics Workshop (2020).

Patents Awarded & Filed

- 1) Desmond Jia Jun Loy, Danny Pak-Chum Shum, Wen Siang Lew, “Non-volatile memory devices, RRAM devices and methods for fabricating RRAM devices with magnesium oxide insulator layers” – Awarded June 2019, US 15/711,370, Patent No: 10,312,442.
- 2) Desmond Jia Jun Loy, Eng-Huat Toh, Bin Liu, Shyue Sheng Tan, “Non-Volatile Memory Elements with Filament Confinement” – Awarded Nov 2020, US 16/447,460, Patent No.: 10,847,720
- 3) Desmond Jia Jun Loy, Eng-Huat Toh, Shyue Sheng Tan, “A Memory Device and A Method for Forming the Memory Device” – Awarded Jan 2021, US 16/513,745, Patent No.: 20210020834
- 4) Desmond Jia Jun Loy, Bin Liu, Eng-Huat Toh, Shyue Sheng Tan, “A Memory Device and A Method for Forming the Memory Device” – Awarded Feb 2021, US 16/532,522, Patent No.: 20210043637

- 5) Desmond Jia Jun Loy, Eng-Huat Toh, Shyue Sheng Tan, Steven Soss, “A Memory Device and a Method for Forming the Memory Device” – Filed Nov 2019, US 16/672,632.
- 6) Desmond Jia Jun Loy, Bin Liu, Eng-Huat Toh, Sriram Balasubramanian, Shyue Sheng Tan, “Non-Volatile Memory Elements with One-Time or Multiple-Time Programmability” – Filed Dec 2019, 101013.00134.
- 7) Desmond Jia Jun Loy, Eng-Huat Toh, Shyue Sheng Tan, “Memory Devices and Methods of Forming Memory Devices” – Filed Feb 2020, US 16/802,562.
- 8) Desmond Jia Jun Loy, Eng-Huat Toh, Shyue Sheng Tan, “Logic Gate Devices and Methods of Forming a Logic Gate Device” – Filed Mar 2020, US 16/816,361.
- 9) Desmond Jia Jun Loy, Eng-Huat Toh, Shyue Sheng Tan, “Memory Devices and Methods of Forming Memory Devices” – Filed May 2020, US 16/882,795.
- 10) Desmond Jia Jun Loy, Eng-Huat Toh, Shyue Sheng Tan, “Memory Devices and Methods of Forming Memory Devices” – Filed Jun 2020, US 16/903,503.
- 11) Desmond Jia Jun Loy, Eng-Huat Toh, Shyue Sheng Tan, “Non-Volatile Memory Elements with a Multi-level Cell Configuration” – Filed Jun 2020, US 16/896,788.
- 12) Desmond Jia Jun Loy, Eng-Huat Toh, Shyue Sheng Tan, “Resistive Random Access Memory Devices” – Filed Aug 2020, US 16/994,647.
- 13) Desmond Jia Jun Loy, Eng-Huat Toh, Shyue Sheng Tan, “Resistive Memory Elements having Conductive Islands Embedded within the Switching Layer” – Filed Sep 2020, US 17/009,288.
- 14) Desmond Jia Jun Loy, Eng-Huat Toh, Shyue Sheng Tan, “Resistive Random Access Memory Devices” – Filed Sep 2020, US 17/026,303.
- 15) Desmond Jia Jun Loy, Eng-Huat Toh, Shyue Sheng Tan, “Multi-Level Cell Configurations for Non-Volatile Memory Elements in a Bitcell” – Filed Dec 2020, US 17/111,996.

- 16) Desmond Jia Jun Loy, Eng-Huat Toh, Shyue Sheng Tan, “Memory Devices and Methods of Forming Memory Devices” – Filed Dec 2020, US 17/136,133.
- 17) Desmond Jia Jun Loy, Chang Wei, Eng-Huat Toh, Shyue Sheng Tan, “Semiconductor Devices with Memory Cells” – Filed Jan 2021, US 17/146,439.
- 18) Desmond Jia Jun Loy, Eng-Huat Toh, Shyue Sheng Tan, “Semiconductor Memory Devices” – Filed Feb 2021, US 17/172,085.

References

- [1] Y. Chen, "ReRAM: History, Status, and Future," *IEEE Transactions on Electron Devices*, vol. 67, no. 4, pp. 1420-1433, 2020.
- [2] R. Micheloni, *3D Flash Memories*. New York: Springer, 2016.
- [3] J. Boukhobza, S. Rubini, R. Chen, and Z. Shao, "Emerging NVM: A Survey on Architectural Integration and Research Challenges," *ACM Trans. Des. Autom. Electron. Syst.*, vol. 23, no. 2, p. Article 14, 2017.
- [4] A. Chen, "Electronic Effect Resistive Switching Memories," in *Emerging Nanoelectronic Devices*, A. Chen, J. Hutchby, V. Zhirnov, and G. Bourianoff, Eds., 2014, pp. 162-180.
- [5] C. S. Hwang, "Prospective of Semiconductor Memory Devices: from Memory System to Materials," *Advanced Electronic Materials*, vol. 1, no. 6, p. 1400056, 2015/06/01 2015.
- [6] S. Yu, *Resistive Random Access Memory (RRAM): From Devices to Architectures*. Arizona: Morgan & Claypool Publishers, 2016.
- [7] S. Yu, *Resistive Random Access Memory (RRAM) (Synthesis Lectures on Emerging Engineering Technologies, no. 5)*. San Rafael, CA, USA: Morgan & Claypool Publishers, 2016, pp. 1-79.
- [8] A. Grossi, C. Zambelli, and P. Olivo, "Reliability of 3D NAND Flash Memories," in *3D Flash Memories*, R. Micheloni, Ed. Dordrecht: Springer Netherlands, 2016, pp. 29-62.
- [9] H. S. P. Wong and S. Salahuddin, "Memory leads the way to better computing," *Nature Nanotechnology*, vol. 10, no. 3, pp. 191-194, 2015/03/01 2015.
- [10] H. Wang and X. Yan, "Overview of Resistive Random Access Memory (RRAM): Materials, Filament Mechanisms, Performance Optimization, and Prospects," *physica status solidi (RRL) – Rapid Research Letters*, vol. 13, no. 9, p. 1900073, 2019.
- [11] V. Gupta, S. Kapur, S. Saurabh, and A. Grover, "Resistive Random Access Memory: A Review of Device Challenges," *IETE Technical Review*, pp. 1-14, 2019.
- [12] L. Goux, "OxRAM technology development and performances," in *Advances in Non-volatile Memory and Storage Technology 2nd Edition*, B. M.-K. Yoshio Nishi, Ed. Duxford, UK: Woodhead Publishing, 2019, pp. 3-33.

- [13] X. Ding, Y. Feng, P. Huang, L. Liu, and J. Kang, "Low-Power Resistive Switching Characteristic in HfO₂/TiO_x Bi-Layer Resistive Random-Access Memory," *Nanoscale Research Letters*, vol. 14, no. 1, p. 157, 2019/05/09 2019.
- [14] E. Ambrosi, A. Bricalli, M. Laudato, and D. Ielmini, "Impact of oxide and electrode materials on the switching characteristics of oxide ReRAM devices," *Faraday Discussions*, 10.1039/C8FD00106E vol. 213, no. 0, pp. 87-98, 2019.
- [15] M. Biglari, T. Lieske, and D. Fey, "High-Endurance Bipolar ReRAM-Based Non-Volatile Flip-Flops with Run-Time Tunable Resistive States," presented at the Proceedings of the 14th IEEE/ACM International Symposium on Nanoscale Architectures, Athens, Greece, 2018. Available: <https://doi.org/10.1145/3232195.3232217>
- [16] Z.-Y. He *et al.*, "Atomic Layer-Deposited HfAlO_x-Based RRAM with Low Operating Voltage for Computing In-Memory Applications," *Nanoscale Research Letters*, vol. 14, no. 1, p. 51, 2019/02/07 2019.
- [17] D. I. Rainer Waser, Hiro Akinaga, Hisashi Shima, H.-S. Philip Wong, Joshua J. Yang, Simon Yu, "Introduction to Nanoionic Elements for Information Technology," in *Resistive Switching: From Fundamentals of Nanoionic Redox Processes to Memristive Device Applications*, R. W. Daniele Ielmini, Ed. Hoboken, NJ, USA: Wiley, 2016, pp. 1-30.
- [18] C. Nail *et al.*, "Understanding RRAM endurance, retention and window margin trade-off using experimental results and simulations," in *2016 IEEE International Electron Devices Meeting (IEDM)*, 2016, pp. 4.5.1-4.5.4.
- [19] W. Banerjee, Q. Liu, and H. Hwang, "Engineering of defects in resistive random access memory devices," *Journal of Applied Physics*, vol. 127, no. 5, p. 051101, 2020.
- [20] D. J. J. Loy *et al.*, "Hopping Conduction Temperature Investigations on High Retention Electrochemical Metallization MgO-based Resistive Switching Devices in the Low Resistance State," in *2019 Electron Devices Technology and Manufacturing Conference (EDTM)*, 2019, pp. 163-165.
- [21] D. J. J. Loy, P. A. Dananjaya, X. L. Hong, D. P. Shum, and W. S. Lew, "Conduction Mechanisms on High Retention Annealed MgO-based Resistive Switching Memory Devices," *Scientific Reports*, vol. 8, no. 1, p. 14774, 2018/10/03 2018.
- [22] I. H. Inoue and A. Sawa, "Resistive Switchings in Transition-Metal Oxides," in *Functional Metal Oxides*, S. B. Ogale, T. V. Venkatesan, and M. G. Blamire, Eds., 2013, pp. 443-463.

- [23] Y. S. Chen *et al.*, "Highly scalable hafnium oxide memory with improvements of resistive distribution and read disturb immunity," in *2009 IEEE International Electron Devices Meeting (IEDM)*, 2009, pp. 1-4.
- [24] D. Ielmini, F. Nardi, and C. Cagli, "Universal Reset Characteristics of Unipolar and Bipolar Metal-Oxide RRAM," *IEEE Transactions on Electron Devices*, vol. 58, no. 10, pp. 3246-3253, 2011.
- [25] D. Jana *et al.*, "Conductive-bridging random access memory: challenges and opportunity for 3D architecture," *Nanoscale Research Letters*, vol. 10, no. 1, p. 188, 2015/04/18 2015.
- [26] L. Zhu, J. Zhou, Z. Guo, and Z. Sun, "An overview of materials issues in resistive random access memory," *Journal of Materiomics*, vol. 1, no. 4, pp. 285-295, 2015/12/01/ 2015.
- [27] A. Hanada, K. Kinoshita, K. Matsubara, and S. Kishida, "Developmental Mechanism for the Memory Effect in Perovskite Oxide-Based ReRAM Consisting of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ Bulk Single Crystal," *Procedia Engineering*, vol. 36, pp. 411-418, 2012/01/01/ 2012.
- [28] D. Panda and T.-Y. Tseng, "Perovskite Oxides as Resistive Switching Memories: A Review," *Ferroelectrics*, vol. 471, no. 1, pp. 23-64, 2014/10/26 2014.
- [29] R. Waser, R. Dittmann, G. Staikov, and K. Szot, "Redox-Based Resistive Switching Memories – Nanoionic Mechanisms, Prospects, and Challenges," *Advanced Materials*, vol. 21, no. 25-26, pp. 2632-2663, 2009/07/13 2009.
- [30] H. P. Wong *et al.*, "Metal–Oxide RRAM," *Proceedings of the IEEE*, vol. 100, no. 6, pp. 1951-1970, 2012.
- [31] D. Ielmini, "Resistive switching memories based on metal oxides: mechanisms, reliability and scaling," *Semiconductor Science and Technology*, vol. 31, no. 6, p. 063002, 2016/05/16 2016.
- [32] X. Hong, D. J. Loy, P. A. Dananjaya, F. Tan, C. Ng, and W. Lew, "Oxide-based RRAM materials for neuromorphic computing," *Journal of Materials Science*, vol. 53, no. 12, pp. 8720-8746, 2018/06/01 2018.
- [33] E. Ambrosi *et al.*, "Electrochemical metallization ReRAMs (ECM) - Experiments and modelling: general discussion," *Faraday Discussions*, 10.1039/C8FD90059K vol. 213, no. 0, pp. 115-150, 2019.

- [34] M. M. M. N. Kozicki, I. Valov, "Electrochemical Metallization Memories," in *Resistive Switching: From Fundamentals of Nanoionic Redox Processes to Memristive Device Applications*, R. W. Daniele Ielmini, Ed. Hoboken, NJ, USA: Wiley, 2016, pp. 1-30.
- [35] I. Valov, R. Waser, J. R. Jameson, and M. N. Kozicki, "Electrochemical metallization memories—fundamentals, applications, prospects," *Nanotechnology*, vol. 22, no. 25, p. 254003, 2011/05/16 2011.
- [36] R. Zhang *et al.*, "Role of Oxygen Vacancies at the TiO₂/HfO₂ Interface in Flexible Oxide-Based Resistive Switching Memory," *Advanced Electronic Materials*, vol. 5, no. 5, p. 1800833, 2019.
- [37] S.-S. Li and Y.-K. Su, "Oxygen-Vacancy Induced Resistive Switching Effect in Mn-Doped ZnO Memory Devices," *physica status solidi (RRL) – Rapid Research Letters*, vol. 13, no. 2, p. 1800453, 2019.
- [38] R. D. Christian Lenser, John Paul Strachan, "Valence Change Observed by Nanospectroscopy and Spectromicroscopy," in *Resistive Switching: From Fundamentals of Nanoionic Redox Processes to Memristive Device Applications*, R. W. Daniele Ielmini, Ed. Hoboken, NJ, USA: Wiley, 2016, pp. 1-30.
- [39] Z. Zhang *et al.*, "Memory materials and devices: From concept to application," *InfoMat*, vol. 2, no. 2, pp. 261-290, 2020/03/01 2020.
- [40] M. Azzaz *et al.*, "Endurance/Retention Trade Off in HfO_x and TaO_x Based RRAM," in *2016 IEEE 8th International Memory Workshop (IMW)*, 2016, pp. 1-4.
- [41] V. Milo *et al.*, "Multilevel HfO₂-based RRAM devices for low-power neuromorphic networks," *APL Materials*, vol. 7, no. 8, p. 081120, 2019.
- [42] Z. Alamgir, K. Beckmann, J. Holt, and N. C. Cady, "Pulse width and height modulation for multi-level resistance in bi-layer TaO_x based RRAM," *Applied Physics Letters*, vol. 111, no. 6, p. 063111, 2017/08/07 2017.
- [43] L. L. Bin Gao, Jinfeng Kang, "Investigation of the synaptic device based on the resistive switching behavior in hafnium oxide," *Progress in Natural Science: Materials International*, vol. 25, no. 1, pp. 47-50, 2015.
- [44] B. Jain *et al.*, "Multilevel Resistive Switching in Hf-Based RRAM," *ECS Transactions*, vol. 89, no. 3, pp. 39-44, 2019/04/23 2019.
- [45] T.-C. Chang, K.-C. Chang, T.-M. Tsai, T.-J. Chu, and S. M. Sze, "Resistance random access memory," *Materials Today*, vol. 19, no. 5, pp. 254-264, 2016/06/01/ 2016.

- [46] M. Gupta and J. Kedia, "A Review on Resistive Random Access Memory," *International Journal of Advanced Research in Electronics and Communication Engineering*, vol. 7, no. 3, pp. 184-191, 2018.
- [47] S. Shirinzadeh and R. Drechsler, "In-Memory Computing: The Integration of Storage and Processing," in *Information Storage – A Multidisciplinary Perspective*, R. D. Cornelia S. Große, Ed. Basel, Switzerland: Springer Nature, 2020, pp. 79-110.
- [48] D. Ielmini and S. Ambrogio, "Neuromorphic computing with resistive switching memory devices," in *Advances in Non-volatile Memory and Storage Technology 2nd Edition*, B. M.-K. Yoshio Nishi, Ed. Duxford, UK: Woodhead Publishing, 2019, pp. 3-33.
- [49] D. Ielmini, "Brain-inspired computing with resistive switching memory Devices, synapses and neural networks(RRAM)," *Microelectronic Engineering*, vol. 190, pp. 44-53, 2018.
- [50] K. Moon *et al.*, "RRAM-based synapse devices for neuromorphic systems," *Faraday Discussions*, 10.1039/C8FD00127H vol. 213, no. 0, pp. 421-451, 2019.
- [51] W. Kim *et al.*, "Forming-free nitrogen-doped AlOX RRAM with sub- μ A programming current," in *2011 Symposium on VLSI Technology - Digest of Technical Papers*, 2011, pp. 22-23.
- [52] M. Trapatseli, A. Khia, S. Cortese, A. Serb, D. Carta, and T. Prodromakis, "Engineering the switching dynamics of TiOx-based RRAM with Al doping," *Journal of Applied Physics*, vol. 120, no. 2, p. 025108, 2016/07/14 2016.
- [53] Y. Lin *et al.*, "Performance Improvement of CuOx RRAM for Non-volatile Applications," *ECS Transactions*, vol. 18, no. 1, pp. 281-286, 2019/12/18 2019.
- [54] X. L. Hong, D. J. J. Loy, P. A. Dananjaya, F. Tan, C. M. Ng, and W. S. Lew, "Oxide-based RRAM materials for neuromorphic Computing," *Journal of Material Science*, vol. 53, no. 9, 2018.
- [55] M. Lanza, "A Review on Resistive Switching in High-k Dielectrics: A Nanoscale Point of View Using Conductive Atomic Force Microscope," (in eng), *Materials (Basel, Switzerland)*, vol. 7, no. 3, pp. 2155-2182, 2014.
- [56] C.-F. Liu *et al.*, "Resistive Switching Characteristics of HfO₂ Thin Films on Mica Substrates Prepared by Sol-Gel Process," *Nanomaterials*, vol. 9, no. 1124, pp. 1-11, 2019.

- [57] C.-A. Lin, C.-J. Huang, and T.-Y. Tseng, "Impact of barrier layer on HfO₂-based conductive bridge random access memory," *Applied Physics Letters*, vol. 114, no. 9, p. 093105, 2019.
- [58] B. Gao, L. Liu, and J. Kang, "Investigation of the synaptic device based on the resistive switching behavior in hafnium oxide," *Progress in Natural Science: Materials International*, vol. 25, no. 1, pp. 47-50, 2015/02/01/ 2015.
- [59] W. Chung *et al.*, "A study of the relationship between endurance and retention reliability for a HfO_x-based resistive switching memory," *IEEE Transactions on Device and Materials Reliability*, pp. 1-1, 2020.
- [60] F.-Y. Yuan *et al.*, "Conduction Mechanism and Improved Endurance in HfO₂-Based RRAM with Nitridation Treatment," *Nanoscale Research Letters*, vol. 12, no. 1, p. 574, 2017/10/26 2017.
- [61] H. Y. Lee *et al.*, "HfO_x Bipolar Resistive Memory With Robust Endurance Using AlCu as Buffer Electrode," *IEEE Electron Device Letters*, vol. 30, no. 7, pp. 703-705, 2009.
- [62] H. Y. Lee *et al.*, "Low-Power and Nanosecond Switching in Robust Hafnium Oxide Resistive Memory With a Thin Ti Cap," *IEEE Electron Device Letters*, vol. 31, no. 1, pp. 44-46, 2010.
- [63] Z. Zhang, Y. Wu, H. P. Wong, and S. S. Wong, "Nanometer-Scale HfO_x RRAM," *IEEE Electron Device Letters*, vol. 34, no. 8, pp. 1005-1007, 2013.
- [64] B. Govoreanu *et al.*, "10×10nm² Hf/HfO_x crossbar resistive RAM with excellent performance, reliability and low-energy operation," in *2011 International Electron Devices Meeting*, 2011, pp. 31.6.1-31.6.4.
- [65] S. Pi *et al.*, "Memristor crossbar arrays with 6-nm half-pitch and 2-nm critical dimension," *Nature Nanotechnology*, vol. 14, no. 1, pp. 35-39, 2019/01/01 2019.
- [66] C. B. L. Myoung-Jae Lee, Dongsoo Lee, Seung Ryul Lee, Man Chang, Ji Hyun Hur, Young-Bae Kim, Chang-Jung Kim, David H. Seo, Sunae Seo, U-In Chung, In-Kyeong Yoo, Kinam Kim "A fast, high-endurance and scalable non-volatile memory device made from asymmetric Ta₂O_{5-x}/TaO_{2-x} bilayer structures," *Nature Materials*, vol. 10, pp. 625–630, 2011// 2011.
- [67] Y. Zhang, N. Deng, H. Wu, Z. Yu, J. Zhang, and H. Qian, "Metallic to hopping conduction transition in Ta₂O_{5-x}/TaO_y resistive switching device," *Applied Physics Letters*, vol. 105, no. 6, p. 063508, 2014/08/11 2014.

- [68] A. Prakash, J. Park, J. Song, J. Woo, E. Cha, and H. Hwang, "Demonstration of Low Power 3-bit Multilevel Cell Characteristics in a TaOx-Based RRAM by Stack Engineering," *IEEE Electron Device Letters*, vol. 36, no. 1, pp. 32-34, 2015.
- [69] M. Yu *et al.*, "Novel Vertical 3D Structure of TaOx-based RRAM with Self-localized Switching Region by Sidewall Electrode Oxidation," *Scientific Reports*, vol. 6, no. 1, p. 21020, 2016/02/17 2016.
- [70] F.-C. Chiu, W.-C. Shih, and J.-J. Feng, "Conduction mechanism of resistive switching films in MgO memory devices," *Journal of Applied Physics*, vol. 111, no. 9, p. 094104, 2012/05/01 2012.
- [71] E. Miranda *et al.*, "Effects of the electrical stress on the conduction characteristics of metal gate/MgO/InP stacks," *Microelectronics Reliability*, vol. 49, no. 9, pp. 1052-1055, 2009/09/01/ 2009.
- [72] W. Lu, W. Chen, Y. Li, and R. Jha, "Self Current Limiting MgO ReRAM Devices for Low-Power Non-Volatile Memory Applications," *IEEE Journal on Emerging and Selected Topics in Circuits and Systems*, vol. 6, no. 2, pp. 163-170, 2016.
- [73] L. M. Guerra *et al.*, "Unipolar Nonvolatile Resistive Switching in Pt/MgO/Ta/Ru Structures Deposited by Magnetron Sputtering," *Journal of Nanoscience and Nanotechnology*, vol. 17, no. 2017, pp. 564–567, 2017.
- [74] M. Menghini *et al.*, "Resistive switching on MgO-based metal-insulator-metal structures grown by molecular beam epitaxy," *physica status solidi c*, vol. 12, no. 1-2, pp. 246-249, 2015/01/01 2015.
- [75] O. Jambois, P. Carreras, A. Antony, J. Bertomeu, and C. Martínez-Boubeta, "Resistance switching in transparent magnetic MgO films," *Solid State Communications*, vol. 151, no. 24, pp. 1856-1859, 2011/12/01/ 2011.
- [76] E. W. Lim and R. Ismail, "Conduction Mechanism of Valence Change Resistive Switching Memory: A Survey," *Electronics*, vol. 4, pp. 586-613, 2015.
- [77] J.-J. Huang, C.-W. Kuo, W.-C. Chang, and T.-H. Hou, "Transition of stable rectification to resistive-switching in Ti/TiO2/Pt oxide diode," *Applied Physics Letters*, vol. 96, no. 26, p. 262901, 2010/06/28 2010.
- [78] W. Zhu, T. P. Chen, Y. Liu, and S. Fung, "Conduction mechanisms at low- and high-resistance states in aluminum/anodic aluminum oxide/aluminum thin film structure," *Journal of Applied Physics*, vol. 112, no. 6, p. 063706, 2012/09/15 2012.

- [79] J.-K. Lee *et al.*, "Accurate analysis of conduction and resistive-switching mechanisms in double-layered resistive-switching memory devices," *Applied Physics Letters*, vol. 101, no. 10, p. 103506, 2012/09/03 2012.
- [80] F.-C. Chiu, S. Mondal, and T. M. Pan, "Structural and Electrical Characteristics of Alternative High-k Dielectrics for CMOS Applications," in *High-k Gate Dielectrics for CMOS Technology*, G. He and Z. Sun, Eds.: Wiley-VCH Verlag GmbH & Co. KGaA, 2012, pp. 111-184.
- [81] S. M. Sze and K. K. Ng, "Physics and Properties of Semiconductors—A Review," in *Physics of Semiconductor Devices*: John Wiley & Sons, Inc., 2006, pp. 5-75.
- [82] Y. Yee Chia *et al.*, "Direct tunneling gate leakage current in transistors with ultrathin silicon nitride gate dielectric," *IEEE Electron Device Letters*, vol. 21, no. 11, pp. 540-542, 2000.
- [83] F.-C. Chiu, "A Review on Conduction Mechanisms in Dielectric Films," *Advances in Materials Science and Engineering*, vol. 2014, p. 18, 2014, Art. no. 578168.
- [84] H.-D. Kim, M. J. Yun, J. H. Lee, K. H. Kim, and T. G. Kim, "Transparent Multi-level Resistive Switching Phenomena Observed in ITO/RGO/ITO Memory Cells by the Sol-Gel Dip-Coating Method," *Scientific Reports*, vol. 4, no. 1, p. 4614, 2014/04/09 2014.
- [85] Y. H. Tseng, W. C. Shen, and C. J. Lin, "Modeling of electron conduction in contact resistive random access memory devices as random telegraph noise," *Journal of Applied Physics*, vol. 111, no. 7, p. 073701, 2012/04/01 2012.
- [86] C. Chen, F. Pan, Z. S. Wang, J. Yang, and F. Zeng, "Bipolar resistive switching with self-rectifying effects in Al/ZnO/Si structure," *Journal of Applied Physics*, vol. 111, no. 1, p. 013702, 2012/01/01 2012.
- [87] S. M. Hong, H.-D. Kim, M. J. Yun, J. H. Park, D. S. Jeon, and T. G. Kim, "Improved resistive switching properties by nitrogen doping in tungsten oxide thin films," *Thin Solid Films*, vol. 583, pp. 81-85, 2015/05/29/ 2015.
- [88] B. T. Phan, T. Choi, A. Romanenko, and J. Lee, "Hopping and trap controlled conduction in Cr-doped SrTiO₃ thin films," *Solid-State Electronics*, vol. 75, pp. 43-47, 2012/09/01/ 2012.
- [89] N. D. Ye Zhang, Huaqiang Wu, Zhiping Yu, Jinyu Zhang, and He Qian, "Metallic to hopping conduction transition in Ta₂O_{5-x}/TaO_y resistive switching device," *Applied Physics Letters*, vol. 105, p. 063508, 2014// 2014.
- [90] Z. Xu *et al.*, "Low-energy Resistive Random Access Memory Devices with No Need for a Compliance Current," *Scientific Reports*, vol. 5, no. 1, p. 10409, 2015/05/18 2015.

- [91] S. Kim, H. Y. Jeong, S.-Y. Choi, and Y.-K. Choi, "Comprehensive modeling of resistive switching in the Al/TiO_x/TiO₂/Al heterostructure based on space-charge-limited conduction," *Applied Physics Letters*, vol. 97, no. 3, p. 033508, 2010/07/19 2010.
- [92] Q. Liu, W. Guan, S. Long, R. Jia, M. Liu, and J. Chen, "Resistive switching memory effect of ZrO₂ films with Zr⁺ implanted," *Applied Physics Letters*, vol. 92, no. 1, p. 012117, 2008/01/07 2008.
- [93] I. Valov and M. N. Kozicki, "Cation-based resistance change memory," *Journal of Physics D: Applied Physics*, vol. 46, no. 7, p. 074005, 2013/02/01 2013.
- [94] G. Bersuker *et al.*, "Grain boundary-driven leakage path formation in HfO₂ dielectrics," *Solid-State Electronics*, vol. 65-66, pp. 146-150, 2011/11/01/ 2011.
- [95] B. Long, Y. Li, S. Mandal, R. Jha, and K. Leedy, "Switching dynamics and charge transport studies of resistive random access memory devices," *Applied Physics Letters*, vol. 101, no. 11, p. 113503, 2012/09/10 2012.
- [96] S. Menzel, E. Linn, and R. Waser, "Redox-based Resistive Memory," in *Emerging Nanoelectronic Devices*, A. Chen, J. Hutchby, V. Zhirnov, and G. Bourianoff, Eds., 2014, pp. 137-161.
- [97] U. Celano, "Filamentary-Based Resistive Switching," in *Metrology and Physical Mechanisms in New Generation Ionic Devices*, U. Celano, Ed. Cham: Springer International Publishing, 2016, pp. 11-45.
- [98] e. a. A. Mehonic, "Quantum Conductance in Silicon Oxide Resistive Memory Devices," *Scientific Reports*, vol. 3, no. 2708, pp. 1 - 8, 2013.
- [99] A. Wedig *et al.*, "Nanoscale cation motion in TaO_x, HfO_x and TiO_x memristive systems," *Nature Nanotechnology*, vol. 11, no. 1, pp. 67-74, 2016/01/01 2016.
- [100] Y. Dai, Z. Pan, F. Wang, and X. Li, "Oxygen vacancy effects in HfO₂-based resistive switching memory: First principle study," *AIP Advances*, vol. 6, no. 8, p. 085209, 2016/08/01 2016.
- [101] S. Privitera *et al.*, "Microscopy study of the conductive filament in HfO₂ resistive switching memory devices," *Microelectronic Engineering*, vol. 109, pp. 75-78, 2013/09/01/ 2013.
- [102] S. Chandrasekaran, F. M. Simanjuntak, R. Aluguri, and T.-Y. Tseng, "The impact of TiW barrier layer thickness dependent transition from electro-chemical metallization memory to valence change memory in ZrO₂-based resistive switching random access memory devices," *Thin Solid Films*, vol. 660, pp. 777-781, 2018/08/30/ 2018.

- [103] P. Calka *et al.*, "Engineering of the Chemical Reactivity of the Ti/HfO₂ Interface for RRAM: Experiment and Theory," *ACS Applied Materials & Interfaces*, vol. 6, no. 7, pp. 5056-5060, 2014/04/09 2014.
- [104] Y. Lu, J. H. Lee, and I. W. Chen, "Scalability of voltage-controlled filamentary and nanometallic resistance memory devices," *Nanoscale*, 10.1039/C7NR02915B vol. 9, no. 34, pp. 12690-12697, 2017.
- [105] M. Thammasack, G. Micheli, and P.-E. Gaillardon, "Effect of O₂- migration in Pt/HfO₂/Ti/Pt structure," *Journal of Electroceramics*, vol. 39, pp. 137-142, 04/01 2017.
- [106] F. Zahoor, T. Z. Azni Zulkifli, and F. A. Khanday, "Resistive Random Access Memory (RRAM): an Overview of Materials, Switching Mechanism, Performance, Multilevel Cell (mlc) Storage, Modeling, and Applications," *Nanoscale Research Letters*, vol. 15, no. 1, p. 90, 2020/04/22 2020.
- [107] S. Park *et al.*, "A non-linear ReRAM cell with sub-1 μ A ultralow operating current for high density vertical resistive memory (VRRAM)," in *2012 International Electron Devices Meeting*, 2012, pp. 20.8.1-20.8.4.
- [108] S. Kim, J. Zhou, and W. D. Lu, "Crossbar RRAM Arrays: Selector Device Requirements During Write Operation," *IEEE Transactions on Electron Devices*, vol. 61, no. 8, pp. 2820-2826, 2014.
- [109] N. L. Prabhu, D. J. J. Loy, P. A. Dananjaya, W. S. Lew, E. H. Toh, and N. Raghavan, "Exploring the Impact of Variability in Resistance Distributions of RRAM on the Prediction Accuracy of Deep Learning Neural Networks," *Electronics*, vol. 9, no. 3, p. 414, 2020.
- [110] W. Kim, S. Menzel, D. J. Wouters, R. Waser, and V. Rana, "3-Bit Multilevel Switching by Deep Reset Phenomenon in Pt/W/TaOX/Pt-ReRAM Devices," *IEEE Electron Device Letters*, vol. 37, no. 5, pp. 564-567, 2016.
- [111] S. Yu, Y. Wu, and H. S. P. Wong, "Investigating the switching dynamics and multilevel capability of bipolar metal oxide resistive switching memory," *Applied Physics Letters*, vol. 98, no. 10, p. 103514, 2011/03/07 2011.
- [112] G. Sassine *et al.*, "Hybrid-RRAM toward Next Generation of Nonvolatile Memory: Coupling of Oxygen Vacancies and Metal Ions," *Advanced Electronic Materials*, vol. 5, no. 2, p. 1800658, 2019/02/01 2019.
- [113] Y.-L. Chung, W.-H. Cheng, J.-S. Jeng, W.-C. Chen, S.-A. Jhan, and J.-S. Chen, "Joint contributions of Ag ions and oxygen vacancies to conducting filament evolution of

- Ag/TaOx/Pt memory device," *Journal of Applied Physics*, vol. 116, no. 16, p. 164502, 2014/10/28 2014.
- [114] D. Zhu, Y. Li, W. Shen, Z. Zhou, L. Liu, and X. Zhang, "Resistive random access memory and its applications in storage and nonvolatile logic," *Journal of Semiconductors*, vol. 38, no. 7, p. 071002, 2017/07 2017.
 - [115] C. Wang, H. Wu, B. Gao, T. Zhang, Y. Yang, and H. Qian, "Conduction mechanisms, dynamics and stability in ReRAMs," *Microelectronic Engineering*, vol. 187-188, pp. 121-133, 2018/02/05/ 2018.
 - [116] E. Yalon, I. Karpov, V. Karpov, I. Riess, D. Kalaev, and D. Ritter, "Detection of the insulating gap and conductive filament growth direction in resistive memories," *Nanoscale*, 10.1039/C5NR03314D vol. 7, no. 37, pp. 15434-15441, 2015.
 - [117] T. Tang, R. Luo, B. Li, H. Li, Y. Wang, and H. Yang, "Energy efficient spiking neural network design with RRAM devices," in *2014 International Symposium on Integrated Circuits (ISIC)*, 2014, pp. 268-271.
 - [118] H. Liu *et al.*, "Uniformity Improvement in 1T1R RRAM With Gate Voltage Ramp Programming," *Ieee Electron Device Letters*, vol. 35, pp. 1224-1226, 12/01 2014.
 - [119] K. Chang *et al.*, "Dual Ion Effect of the Lithium Silicate Resistance Random Access Memory," *IEEE Electron Device Letters*, vol. 35, no. 5, pp. 530-532, 2014.
 - [120] X. Wu *et al.*, "Evolution of Filament Formation in Ni/HfO₂/SiO_x/Si-Based RRAM Devices," *Advanced Electronic Materials*, vol. 1, no. 11, p. 1500130, 2015/11/01 2015.
 - [121] J. Shin *et al.*, "Effect of Program/Erase Speed on Switching Uniformity in Filament-Type RRAM," *IEEE Electron Device Letters*, vol. 32, no. 7, pp. 958-960, 2011.
 - [122] C. Li *et al.*, "Direct Observations of Nanofilament Evolution in Switching Processes in HfO(2) -Based Resistive Random Access Memory by In Situ TEM Studies," (in eng), *Adv Mater*, vol. 29, no. 10, p. 1602976, Mar 2017.
 - [123] T.-H. S. Yi-Jen Huang, Lan-Hsuan Lee, Cheng-Yen Wen, and Si-Chen Lee, "Low-power resistive random access memory by confining the formation of conducting filaments," *AIP Advances*, vol. 6, pp. 065022-1 - 065022-7, 2016.
 - [124] K. H. Masashi Arita, Yasuo Takahashi, Kazuhisa Sueoka, Tamaki Shibayama, "In Situ Transmission Electron Microscopy for Electronics," in *The Transmission Electron Microscope - Theory and Applications*, K. Maaz, Ed.: IntechOpen, 2015.
 - [125] D. Ielmini, "Modeling the Universal Set/Reset Characteristics of Bipolar RRAM by Field- and Temperature-Driven Filament Growth," *IEEE Transactions on Electron Devices*, vol. 58, no. 12, pp. 4309-4317, 2011.

- [126] P. Bousoulas, P. Asenov, I. Karageorgiou, D. Sakellariopoulos, S. Stathopoulos, and D. Tsoukalas, "Engineering amorphous-crystalline interfaces in $\text{TiO}_2\text{-x/TiO}_2\text{-y}$ -based bilayer structures for enhanced resistive switching and synaptic properties," *Journal of Applied Physics*, vol. 120, no. 15, p. 154501, 2016.
- [127] S. Larentis, F. Nardi, S. Balatti, D. C. Gilmer, and D. Ielmini, "Resistive Switching by Voltage-Driven Ion Migration in Bipolar RRAM—Part II: Modeling," *IEEE Transactions on Electron Devices*, vol. 59, no. 9, pp. 2468-2475, 2012.
- [128] S. Kim *et al.*, "Physical electro-thermal model of resistive switching in bi-layered resistance-change memory," *Scientific Reports*, vol. 3, no. 1, p. 1680, 2013/04/22 2013.
- [129] F.-C. Chiu, P.-W. Li, and W.-Y. Chang, "Reliability characteristics and conduction mechanisms in resistive switching memory devices using ZnO thin films," *Nanoscale Research Letters*, vol. 7, no. 1, p. 178, 2012/03/08 2012.
- [130] G. Khurana, P. Misra, and R. S. Katiyar, "Forming free resistive switching in graphene oxide thin film for thermally stable nonvolatile memory applications," *Journal of Applied Physics*, vol. 114, no. 12, p. 124508, 2013.
- [131] S. Chakrabarti *et al.*, "Negative voltage modulated multi-level resistive switching by using a Cr/BaTiOx/TiN structure and quantum conductance through evidence of H₂O₂ sensing mechanism," *Scientific Reports*, vol. 7, no. 1, p. 4735, 2017/07/05 2017.
- [132] S. Samanta *et al.*, "Understanding of multi-level resistive switching mechanism in GeOx through redox reaction in H₂O₂/sarcosine prostate cancer biomarker detection," *Scientific Reports*, vol. 7, no. 1, p. 11240, 2017/09/11 2017.
- [133] Y. Bai *et al.*, "Study of Multi-level Characteristics for 3D Vertical Resistive Switching Memory," *Scientific Reports*, vol. 4, no. 1, p. 5780, 2014/07/22 2014.
- [134] M. Qi, C. Guo, and M. Zeng, "Oxygen Vacancy Kinetics Mechanism of the Negative Forming-Free Process and Multilevel Resistance Based on Hafnium Oxide RRAM," *Journal of Nanomaterials*, vol. 2019, no. 6724018, pp. 1-9, 2019.
- [135] A. L. Jagath, C. H. Leong, T. N. Kumar, and H. F. Almurib, "Insight into physics-based RRAM models – review," *The Journal of Engineering*, vol. 2019, no. 7, pp. 4644-4652, 2019.
- [136] F. O. Hatem, P. W. C. Ho, T. N. Kumar, and H. A. F. Almurib, "Modeling of bipolar resistive switching of a nonlinear MISM memristor," *Semiconductor Science and Technology*, vol. 30, no. 11, p. 115009, 2015/10/09 2015.
- [137] A. L. Jagath, T. N. Kumar, and H. A. F. Almurib, "Modeling of Current Conduction during RESET Phase of Pt/Ta₂O₅/TaOx/Pt Bipolar Resistive RAM Devices," in *2018*

- IEEE 7th Non-Volatile Memory Systems and Applications Symposium (NVMSA)*, 2018, pp. 55-60.
- [138] X. Guan, S. Yu, and H. P. Wong, "On the Switching Parameter Variation of Metal-Oxide RRAM—Part I: Physical Modeling and Simulation Methodology," *IEEE Transactions on Electron Devices*, vol. 59, no. 4, pp. 1172-1182, 2012.
 - [139] S. Yu, X. Guan, and H. P. Wong, "On the Switching Parameter Variation of Metal Oxide RRAM—Part II: Model Corroboration and Device Design Strategy," *IEEE Transactions on Electron Devices*, vol. 59, no. 4, pp. 1183-1188, 2012.
 - [140] E. Abbaspour, S. Menzel, A. Hardtdegen, S. Hoffmann-Eifert, and C. Jungemann, "KMC Simulation of the Electroforming, Set and Reset Processes in Redox-Based Resistive Switching Devices," *IEEE Transactions on Nanotechnology*, vol. 17, no. 6, pp. 1181-1188, 2018.
 - [141] A. Padovani, L. Larcher, O. Pirrotta, L. Vandelli, and G. Bersuker, "Microscopic Modeling of HfOx RRAM Operations: From Forming to Switching," *IEEE Transactions on Electron Devices*, vol. 62, no. 6, pp. 1998-2006, 2015.
 - [142] M. Lanza *et al.*, "Recommended Methods to Study Resistive Switching Devices," *Advanced Electronic Materials*, vol. 5, no. 1, p. 1800143, 2019.
 - [143] F. M. Puglisi, P. Pavan, A. Padovani, and L. Larcher, "A compact model of hafnium-oxide-based resistive random access memory," in *Proceedings of 2013 International Conference on IC Design & Technology (ICICDT)*, 2013, pp. 85-88.
 - [144] X. Guan, S. Yu, and H. P. Wong, "A SPICE Compact Model of Metal Oxide Resistive Switching Memory With Variations," *IEEE Electron Device Letters*, vol. 33, no. 10, pp. 1405-1407, 2012.
 - [145] H. A. Marc Bocquet, Weisheng Zhao, Yue Zhang, Santhosh Onkaraiah, Christophe Muller, Marina Reyboz, Damien Deleruyelle, Fabien Clermidy, Jean-Michel Portal "Compact Modeling Solutions for Oxide-Based Resistive Switching Memories (OxRAM)," *Journal of Low Power Electronics and Applications*, vol. 4, no. 1, pp. 1-14, 2014.
 - [146] P. Huang *et al.*, "A Physics-Based Compact Model of Metal-Oxide-Based RRAM DC and AC Operations," *IEEE Transactions on Electron Devices*, vol. 60, no. 12, pp. 4090-4097, 2013.
 - [147] H. Li, P. Huang, B. Gao, B. Chen, X. Liu, and J. Kang, "A SPICE Model of Resistive Random Access Memory for Large-Scale Memory Array Simulation," *IEEE Electron Device Letters*, vol. 35, no. 2, pp. 211-213, 2014.

- [148] F. M. Puglisi, L. Larcher, A. Padovani, and P. Pavan, "Bipolar Resistive RAM Based on HfO₂: Physics, Compact Modeling, and Variability Control," *IEEE Journal on Emerging and Selected Topics in Circuits and Systems*, vol. 6, no. 2, pp. 171-184, 2016.
- [149] I. V. Tudose *et al.*, "Chapter 2 - Chemical and physical methods for multifunctional nanostructured interface fabrication," in *Functional Nanostructured Interfaces for Environmental and Biomedical Applications*, V. Dinca and M. P. Suchea, Eds.: Elsevier, 2019, pp. 15-26.
- [150] M. C. Burrell, "Chemical Analysis, Electron Spectroscopy," in *Encyclopedia of Materials: Science and Technology*, K. H. J. Buschow *et al.*, Eds. Oxford: Elsevier, 2001, pp. 1142-1149.
- [151] H. B. Michaelson, "The work function of the elements and its periodicity," *Journal of Applied Physics*, vol. 48, no. 11, pp. 4729-4733, 1977/11/01 1977.
- [152] V. K. and H. U., *Understanding MSP430 Flash Data Retention*. Dallas, Texas: Texas Instruments, 2018.
- [153] M.-J. Lee *et al.*, "A fast, high-endurance and scalable non-volatile memory device made from asymmetric Ta₂O₅-x/TaO₂-x bilayer structures," *Nature Materials*, vol. 10, no. 8, pp. 625-630, 2011/08/01 2011.
- [154] I. A. E. Agency, *Thermophysical Properties of Materials for Nuclear Engineering: A Tutorial and Collection of Data*. Vienna: International Atomic Energy Agency, 2008.
- [155] R. I. Ee Wah Lim, "Conduction Mechanism of Valence Change Resistive Switching," *Electronics*, vol. 4, no. 3, pp. 586-613, 2015// 2015.
- [156] M. Saadi *et al.*, "On the mechanisms of cation injection in conducting bridge memories: The case of HfO₂ in contact with noble metal anodes (Au, Cu, Ag)," *Journal of Applied Physics*, vol. 119, no. 11, p. 114501, 2016.
- [157] V. A. Gritsenko *et al.*, "Oxygen Vacancy in Hafnia as a Blue Luminescence Center and a Trap of Charge Carriers," *The Journal of Physical Chemistry C*, vol. 120, no. 36, pp. 19980-19986, 2016/09/15 2016.
- [158] O. Dominguez, T. L. McGinnity, R. K. Roeder, and A. J. Hoffman, "Optical characterization of polar HfO₂ nanoparticles in the mid- and far-infrared," *Applied Physics Letters*, vol. 111, no. 1, p. 011101, 2017.
- [159] J.-H. Oh, K.-C. Ryoo, S. Jung, Y. Park, and B.-G. Park, "Effect of Oxidation Amount on Gradual Switching Behavior in Reset Transition of Al/TiO₂-Based Resistive Switching Memory and Its Mechanism for Multilevel Cell Operation," *Japanese Journal of Applied Physics*, vol. 51, p. 04DD16, 2012/04/20 2012.

- [160] S. Jain, J. Shah, N. S. Negi, C. Sharma, and R. K. Kotnala, "Significance of interface barrier at electrode of hematite hydroelectric cell for generating ecopower by water splitting," *International Journal of Energy Research*, vol. 43, no. 9, pp. 4743-4755, 2019/07/01 2019.
- [161] J. Gan *et al.*, "Oxygen vacancies promoting photoelectrochemical performance of In(2)O(3) nanocubes," (in eng), *Scientific reports*, vol. 3, pp. 1021-1021, 2013.
- [162] X. Lu *et al.*, "Oxygen-Deficient Hematite Nanorods as High-Performance and Novel Negative Electrodes for Flexible Asymmetric Supercapacitors," *Advanced Materials*, vol. 26, no. 19, pp. 3148-3155, 2014/05/01 2014.
- [163] L. Zhang *et al.*, "ALD preparation of high-k HfO₂ thin films with enhanced energy density and efficient electrostatic energy storage," *RSC Advances*, 10.1039/C6RA27847G vol. 7, no. 14, pp. 8388-8393, 2017.
- [164] D. David and C. Godet, "Derivation of dielectric function and inelastic mean free path from photoelectron energy-loss spectra of amorphous carbon surfaces," *Applied Surface Science*, vol. 387, pp. 1125-1139, 2016/11/30/ 2016.
- [165] X. Luo *et al.*, "Investigation of HfO₂ Thin Films on Si by X-ray Photoelectron Spectroscopy, Rutherford Backscattering, Grazing Incidence X-ray Diffraction and Variable Angle Spectroscopic Ellipsometry," *Crystals*, vol. 8, no. 6, p. 248, 2018.
- [166] C. Walczyk *et al.*, "Impact of Temperature on the Resistive Switching Behavior of Embedded HfO₂-Based RRAM Devices," *IEEE Transactions on Electron Devices*, vol. 58, no. 9, pp. 3124-3131, 2011.
- [167] F. M. Puglisi, A. Qafa, and P. Pavan, "Temperature Impact on the Reset Operation in HfO₂ RRAM," *IEEE Electron Device Letters*, vol. 36, no. 3, pp. 244-246, 2015.
- [168] L. Larcher, F. M. Puglisi, P. Pavan, A. Padovani, L. Vandelli, and G. Bersuker, "A Compact Model of Program Window in HfO_x RRAM Devices for Conductive Filament Characteristics Analysis," *IEEE Transactions on Electron Devices*, vol. 61, no. 8, pp. 2668-2673, 2014.
- [169] G. Bersuker *et al.*, "Metal oxide resistive memory switching mechanism based on conductive filament properties," *Journal of Applied Physics*, vol. 110, no. 12, p. 124518, 2011/12/15 2011.
- [170] W. Zhang *et al.*, "Analog-Type Resistive Switching Devices for Neuromorphic Computing," *physica status solidi (RRL) – Rapid Research Letters*, vol. 13, no. 10, p. 1900204, 2019/10/01 2019.

- [171] D. Ielmini *et al.*, "Scaling analysis of submicrometer nickel-oxide-based resistive switching memory devices," *Journal of Applied Physics*, vol. 109, no. 3, p. 034506, 2011/02/01 2011.
- [172] H. Kim, H. An, E. B. Lee, and T. G. Kim, "Stable Bipolar Resistive Switching Characteristics and Resistive Switching Mechanisms Observed in Aluminum Nitride-based ReRAM Devices," *IEEE Transactions on Electron Devices*, vol. 58, no. 10, pp. 3566-3573, 2011.
- [173] H. Y. Peng *et al.*, "Electrode dependence of resistive switching in Mn-doped ZnO: Filamentary versus interfacial mechanisms," *Applied Physics Letters*, vol. 96, no. 19, p. 192113, 2010/05/10 2010.
- [174] A. M. Ginestra™. (2020). *APPLIED MDLX™ GINESTRA™ SIMULATION SOFTWARE*. Available: <http://www.appliedmaterials.com/products/applied-mdlx-ginestra-simulation-software>
- [175] A. Padovani and L. Larcher, "Time-dependent dielectric breakdown statistics in SiO₂ and HfO₂ dielectrics: Insights from a multi-scale modeling approach," in *2018 IEEE International Reliability Physics Symposium (IRPS)*, 2018, pp. 3A.2-1-3A.2-7.
- [176] L. Larcher and A. Padovani, "Multiscale modeling of oxide RRAM devices for memory applications: from material properties to device performance," *Journal of Computational Electronics*, vol. 16, no. 4, pp. 1077-1084, 2017/12/01 2017.
- [177] J. L. Gavartin, D. Muñoz Ramo, A. L. Shluger, G. Bersuker, and B. H. Lee, "Negative oxygen vacancies in HfO₂ as charge traps in high-k stacks," *Applied Physics Letters*, vol. 89, no. 8, p. 082908, 2006/08/21 2006.
- [178] J. Robertson and R. Gillen, "Defect densities inside the conductive filament of RRAMs," *Microelectronic Engineering*, vol. 109, pp. 208-210, 2013/09/01/ 2013.
- [179] L. Vandelli, A. Padovani, L. Larcher, R. G. Southwick, W. B. Knowlton, and G. Bersuker, "A Physical Model of the Temperature Dependence of the Current Through SiO₂/HfO₂ Stacks," *IEEE Transactions on Electron Devices*, vol. 58, no. 9, pp. 2878-2887, 2011.
- [180] M. A. Panzer *et al.*, "Thermal Properties of Ultrathin Hafnium Oxide Gate Dielectric Films," *IEEE Electron Device Letters*, vol. 30, no. 12, pp. 1269-1271, 2009.
- [181] A. Padovani, L. Larcher, G. Bersuker, and P. Pavan, "Charge Transport and Degradation in HfO₂ and HfO_x Dielectrics," *IEEE Electron Device Letters*, vol. 34, no. 5, pp. 680-682, 2013.

- [182] A. S. Foster, A. L. Shluger, and R. M. Nieminen, "Mechanism of Interstitial Oxygen Diffusion in Hafnia," *Physical Review Letters*, vol. 89, no. 22, p. 225901, 11/12/ 2002.
- [183] R. Govindaraj, C. S. Sundar, and R. Kesavamoorthy, "Atomic scale study of oxidation of hafnium: Formation of hafnium core and oxide shell," *Journal of Applied Physics*, vol. 100, no. 8, p. 084318, 2006/10/15 2006.
- [184] U. Russo, D. Ielmini, C. Cagli, and A. L. Lacaita, "Self-Accelerated Thermal Dissolution Model for Reset Programming in Unipolar Resistive-Switching Memory (RRAM) Devices," *IEEE Transactions on Electron Devices*, vol. 56, no. 2, pp. 193-200, 2009.
- [185] J. Noh *et al.*, "Development of a Semiempirical Compact Model for DC/AC Cell Operation of HfOx-Based ReRAMs," *IEEE Electron Device Letters*, vol. 34, no. 9, pp. 1133-1135, 2013.
- [186] M. Bocquet *et al.*, "Robust Compact Model for Bipolar Oxide-Based Resistive Switching Memories," *IEEE Transactions on Electron Devices*, vol. 61, no. 3, pp. 674-681, 2014.
- [187] N. Sedghi *et al.*, "The role of nitrogen doping in ALD Ta₂O₅ and its influence on multilevel cell switching in RRAM," *Applied Physics Letters*, vol. 110, no. 10, p. 102902, 2017.
- [188] M. Arita *et al.*, "Oxygen Distribution around Filament in Ta-O Resistive RAM Fabricated Using 40 nm CMOS Technology," in *2018 IEEE International Memory Workshop (IMW)*, 2018, pp. 1-4.
- [189] S. Lim, M. Kwak, and H. Hwang, "One transistor-two resistive RAM device for realizing bidirectional and analog neuromorphic synapse devices," *Nanotechnology*, vol. 30, no. 45, p. 455201, 2019/08/21 2019.
- [190] A. M. S. Tosson, S. Yu, M. H. Anis, and L. Wei, "1T2R: A novel memory cell design to resolve single-event upset in RRAM arrays," in *2017 IEEE 12th International Conference on ASIC (ASICON)*, 2017, pp. 12-15.
- [191] S. Ambrogio, S. Balatti, A. Cubeta, A. Calderoni, N. Ramaswamy, and D. Ielmini, "Statistical Fluctuations in HfOx Resistive-Switching Memory: Part I - Set/Reset Variability," *IEEE Transactions on Electron Devices*, vol. 61, no. 8, pp. 2912-2919, 2014.
- [192] D. Ielmini and V. Milo, "Physics-based modeling approaches of resistive switching devices for memory and in-memory computing applications," *Journal of Computational Electronics*, vol. 16, no. 4, pp. 1121-1143, 2017/12/01 2017.

- [193] S. Kim, S. Choi, and W. Lu, "Comprehensive Physical Model of Dynamic Resistive Switching in an Oxide Memristor," *ACS Nano*, vol. 8, no. 3, pp. 2369-2376, 2014/03/25 2014.
- [194] A. Fantini *et al.*, "Intrinsic Switching Behavior in HfO₂ RRAM by Fast Electrical Measurements on Novel 2R Test Structures," in *2012 4th IEEE International Memory Workshop*, 2012, pp. 1-4.
- [195] D. Niraula and V. Karpov, "Comprehensive numerical modeling of filamentary RRAM devices including voltage ramp-rate and cycle-to-cycle variations," *Journal of Applied Physics*, vol. 124, no. 17, p. 174502, 2018/11/07 2018.
- [196] F. M. Puglisi, A. Padovani, P. Pavan, and L. Larcher, "3 - Advanced modeling and characterization techniques for innovative memory devices: The RRAM case," in *Advances in Non-Volatile Memory and Storage Technology (Second Edition)*, B. Magyari-Köpe and Y. Nishi, Eds.: Woodhead Publishing, 2019, pp. 103-135.
- [197] B. I. Shklovskii, "Nonohmic Hopping Conduction," *SOV PHYS SEMICON*, vol. 10, no. 8, pp. 855-860, 1976.
- [198] E. I. Levin, R. I. M., and B. I. Shklovskii, "Transverse hopping conductivity of amorphous films in strong electric fields," *Sov. Phys. Semicond.*, vol. 22, pp. 401–408, 1988.
- [199] V. G. Karpov, D. Niraula, I. V. Karpov, and R. Kotlyar, "Thermodynamics of Phase Transitions and Bipolar Filamentary Switching in Resistive Random-Access Memory," *Physical Review Applied*, vol. 8, no. 2, p. 024028, 08/30/ 2017.
- [200] D. Niraula and V. G. Karpov, "Heat Transfer in Filamentary RRAM Devices," *IEEE Transactions on Electron Devices*, vol. 64, no. 10, pp. 4106-4113, 2017.
- [201] I. V. Karpov, M. Mitra, D. Kau, G. Spadini, Y. A. Kryukov, and V. G. Karpov, "Evidence of field induced nucleation in phase change memory," *Applied Physics Letters*, vol. 92, no. 17, p. 173501, 2008/04/28 2008.
- [202] A. Gehring and S. Selberherr, "Modeling of tunneling current and gate dielectric reliability for nonvolatile memory devices," *IEEE Transactions on Device and Materials Reliability*, vol. 4, no. 3, pp. 306-319, 2004.