Advanced oxide based resistive random access memories (RRAMs) : switching mechanisms and material solutions

Wang, Zhongrui

2014

Wang, Z. (2014). Advanced oxide based resistive random access memories (RRAMs) : switching mechanisms and material solutions. Doctoral thesis, Nanyang Technological University, Singapore.

<https://hdl.handle.net/10356/61763>

<https://doi.org/10.32657/10356/61763>

**ADVANCED OXIDE BASED RESISTIVE RANDOM
ACCESS MEMORIES (RRAMs): SWITCHING
MECHANISMS AND MATERIAL SOLUTIONS**

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**School of Electrical and Electronic Engineering
A Thesis Submitted to the Nanyang Technological
University in Partial Fulfillment of the Requirement of the
Degree of Doctor of Philosophy**

2014

Abstract

This thesis reports a study of the resistive switching phenomena in oxide based material systems, practically hafnium and graphene oxide based Resistive Random Access Memories (RRAMs), in aspects of device fabrication, electrical and physical characterization, and theoretical calculation.

Both hafnium and graphene oxide based RRAMs have been fabricated. Through variation of the configuration of material systems and deposition techniques, boosts of performance in terms of uniformity, forming-free property and self-compliance are realized in the hafnium oxide based RRAM. On the other hand, impact of electrodes, critical role for graphene oxide RRAM, has been studied for its influence to the switching directions.

Electrical and physical characterization are employed to unravel the underlying transport and switching mechanisms. Frequency and temperature dependent dielectric loss characterization, implementing on the hafnium oxide RRAM, provides the evidence of the existence of small polaron adiabatic hopping in the high resistance state, consistent with the analysis of activation energy and field dependence. On the other hand, a weak metallic nature in transport is identified in the low resistance state. In graphene oxide RRAM, same technique reveals the fact that the combination of both oxygen related functional groups absorption/release and electrode metal ions diffusion are responsible for the multi-directional switching.

Theoretical calculation, using hybrid functional in first principle simulation, is performed to interpret the observed metal-insulator transitions in the hafnium oxide based RRAM. Computational evidence is found for oxygen vacancy-bound small polarons migration and Mott type localization-delocalization transition. Adiabatic polaron hopping between equivalent threefold oxygen vacancies are of anisotropic barriers, in both the bulk and ($\bar{1}11$) surface slab models, consistent with the

characterization findings. Phonon correlation to the hopping of the small polaron is explored where the important roles of the vacancy neighboring threefold oxygen atoms are unveiled.

Acknowledgement

First and foremost, I would like to express my sincere gratitude to Professor Hong-yu Yu, Professor Weiguang Zhu and Doctor Jun Wei, supervisors of the RRAM project, who have provided me with this excellent opportunity to work on the resistive switching devices. Their passion and enthusiasm in research has greatly impressed me. It is my great pleasure to be a student of them. Their valuable guidance and constant support are crucial to the advancements of this project.

Dr. Haibin Su, professor of the school of material science and engineering with expertise in condensed matter physics, has offered me invaluable help. Without his imparting of the insightful ideas through many times of discussions, I think the attempts in theoretical calculations will be in vain.

During my candidature, I owe many thanks to all current and former members of our research team. In particular, I would like to thank Dr. Wenjun Liu, Mr. Zheng Fang, Mr. Ling Wu, Mr. Xuan Anh Tran, Ms. Tianli Duan, Mr. Jinghao Wang and many others for their generous help, valuable discussions and kind encouragement. They are irreplaceable sources of thoughts and support, and I have really learnt a lot from them in these years. I would also like to take this opportunity to thank all the technical staffs of Nanyang Nano Fabrication Centre and Computational Nano Electronics Lab for their kindly help and assistance during my candidature.

Finally, my deepest gratitude is with my grandparents, parents and wife Ms. Shanshan Yin, for their unconditional love and support through the years. Your encouragements have kept me up in the hardest time.

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List of Abbreviations

ALD	Atomic Layer Deposition
	Becke 3-Parameter (Exchange), Lee, Yang and Parr
B3LYP	(Correlation) Functional
BEOL	Back End of Line
CAFM	Conductive Atomic Force Microscopy
CMOS	Complementary Metal–Oxide–Semiconductor
CPE	Constant Phase Element
C _v	Coefficient of Variation
dc	Direct Current
DOS	Density of States
DRAM	Dynamic Random Access Memory
ECM	Electrochemical Metallization Memory
EDX	Energy-dispersive X-ray Spectroscopy
EELS	Electron Energy Loss Spectroscopy
GGA	Generalized Gradient Approximation
HAXPES	Hard X-ray Photoelectron Spectroscopy
HRS	High Resistance State
HRTEM	High Resolution Transmission Electron Microscopy
I-V	Current-Voltage
LDA	Local Density Approximation
LRS	Low Resistance State
MIM	Metal-Insulator-Metal
MRAM	Magnetoresistive Random-Access Memory
PBE	Perdew–Burke–Ernzerhof Functional

PBE0	Hybrid Perdew–Burke–Ernzerhof Functional
PCM	Phase Change Memory
RRAM	Resistive-switching Random Access Memory
RHRS	Resistance of High Resistance State
RLRS	Resistance of Low Resistance State
SRAM	Static Random Access Memory
sX	Screened Exchange Functional
TCM	Thermochemical Memory
VCM	Valence Change Memory
VRESET	Voltage of RESET Transition
VSET	Voltage of SET Transition
XPS	X-ray Photoelectron Spectroscopy
XRD	X-ray Diffraction

List of Symbols

ps	Picosecond
A	Ampere
Å	angstrom
cm	Centimetre
e	Electron charge
mA	Miniampere
V	Volt
yr	Year
μA	Microampere

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Chapter 1 Introduction

1.1 Background

Resistance switching, which refers to the alternating of conductance triggered by an external electrical field, is a very fundamental physical phenomena of dielectrics. This unique feature meets the requirements of the non-volatile memory, which yields the emergence of the RRAM, a MIM capacitor which tunable resistance. Upon its birth, RRAM has attracted the attention of both the industry and academia. This is because the current market of non-volatile memory, established within the last decade, is experiencing an unprecedented expansion due to technical advancements. The non-volatile memory has being increasingly used in portable electronics (i.e. mobile phones, tablets, and digital cameras), person/enterprise storage, and industrial & transportation. Unlike the volatile DRAM, it is widely recognised that the non-volatile memory market is not fledged. The current non-volatile memory market is dominated by the flash NAND devices. However, in the coming future, the performance of the emergent non-volatile memories, especially MRAM, PCM, and RRAM, will be greatly improved and will spark many new applications which will trigger a further increment of the market demand.

Driving by the market, RRAM is extensively studied in the recent years. Top memory manufacturers including Samsung, Micron, and Sandisk have all invested on the development of non-volatile memory including RRAM, which drastically boosts the research of this field. For RRAM, the number of tracked papers published in the interval of 2000 to 2011 reaches 10000 according to the database Compendex, which marks the RRAM as one of the most competitive and popular research areas of microelectronics.

Historically, resistive switching is frequently witnessed to take place in thin film dielectrics, with first experimental report from Hickmott et al. in 1962. [1] The observation of Hickmott was soon examined and confirmed by Geppert et al. [2]. And similar switching behaviors were identified in other material systems shortly. For instance, the first experimental observation of resistive switching in polymer was made by Mann et al. on thin silicone polymer film [3]. Table 1.1 lists some of the most pioneering works on research of resistive switching.

Reference	Material System	Time of Submission
[1]	Al/SiO ₂ /Au, Al/Al ₂ O ₃ /Au, Ta/Ta ₂ O ₅ /Au, Zr/ZrO ₂ /Au, and Ti/TiO ₂ /Au	Feb-05-1962
[2]	Nb/Nb ₂ O ₅ /Hg	Oct-05-1962
[4]	Al/Al ₂ O ₃ /Hg	Oct-11-1962
[5]	Nb/Nb ₂ O ₅ /Metal (Metal=Ag, Al and Au)	Mar-26-1963
[6]	Nb/Nb ₂ O ₅ /Metal (Metal=Au, Cu and W)	Sep-17-1963
[3]	Thin silicone polymer film	Nov-20-1963
[7]	Al/Al ₂ O ₃ /Metal (Metal=Au, Cu, Co, Pb, Sn, Bi, In, Al, Mg)	Dec-13-1963
[8]	Al/Al ₂ O ₃ /Se/Au	Jan-23-1964
[9]	Ni/NiO/Ag	Mar-30-1964
[10]	Nb/Nb ₂ O ₅ /Metal (Metal=Ag and Au), Ti/TiO ₂ /Metal, Ta/Ta ₂ O ₅ /Metal	Jun-10-1964
[11]	Nb/Nb ₂ O ₅ /Bi	Dec-29-1964

Table 1.1. Pioneering works on resistive switching.

Interests of researchers was not confined to the materials listed above. Instead, observation of resistive switching in a more wide range of materials were reported shortly. Most of them were non-crystalline metal oxide compounds. In 1970, Dearnaley et al. had written a famous article on resistive switching which for the first time

reviewed the switching and transport mechanisms in details, and the concept of RRAM was thus established [12]. In 1973, A special issue of IEEE Transactions on Electron Devices (Volume 20, Issue 2) was devoted to amorphous switching devices for their potential of being novel memory devices. Despite oxide based material systems, excellent switching performance had also been demonstrated in other systems. For instance, an ultrafast (500 ps switching time) switching RRAM with AlN switching layer, as reported by Rutz et al. from IBM, still ranks high in terms of speed among those recently developed memories [13].

However, practical memory application was not realized in last century, particularly due to technical challenging in material processing and device integration. With the advancement of CMOS technology, RRAM has regained the attention of researchers in the beginning of this century as a prominent candidate of next generation non-volatile memory due to its scaling ability, low cost, and compatibility of being integrated in BEOL process in CMOS fabrication. Beck et al. reported SrZrO₃:Cr based RRAM devices as potential candidate of next generation non-volatile memory [14]. In 2002, Zhuang et al. successfully developed perovskite material based RRAM [15]. In 2004, NiO based RRAM was demonstrated by Seo et al., which prospered subsequent studies on various transition metal oxide based RRAM systems. Resistive switching and RRAM have been reviewed by several groups recently thanks to the fast pace in technology development and overwhelming interest in RRAM. The subsequent research, with a concentration on device fabrication and optimization, blooms due to the driving force of the non-volatile memory market. Vast literature is dedicated to RRAM research in the past ten years where part of the recent reviews on resistive switching and RRAM are presented in Table 1.2.

Ref	Material Scope	Mechanisms	Remarks
-----	----------------	------------	---------

[16]	Inorganic Materials	VCM and ECM	
[17]	Transition Metal Oxide	TCM and VCM (homogeneous)	Ti/LSMO/SRO is reported as charge injection type RRAM also.
[18]	Oxide	VCM(homogeneous)	
[19]	Inorganic Materials	TCM, VCM and ECM	
[20]	Metal Oxide (binary)	TCM and VCM	
[21]	Inorganic Material	TCM, VCM , ECM, Phase Change and Spin Polarization	
[22]	TiO ₂ , WO ₃ , GeSe, SiO ₂ , and MSQ	VCM and ECM	
[23]	TiO ₂	TCM, VCM	
[24]	Inorganic Materials	ECM	
[25]	binary oxide	TCM	
[26]	Metal Oxide	TCM	

Table 1.2. Recent reviews on resistive switching and RRAM.

1.2 RRAM Classification

RRAM is a board definition refers to all types of MIM structures which exhibit electric field triggered resistance changes. RRAM can be classified according to different criteria, including mechanisms, operation polarities, and materials.

1.2.1 Classification by Mechanisms

One of the well-accepted schemes, proposed by Waser et al. and adopted by ITRS 2010, is to classify RRAMs based on the switching mechanisms [19]. Waser et al. claimed that there are five different switching mechanisms, corresponding to the five sub-categories in Figure 1.1. They are Phase Change Memory (PCM), Thermal Chemical Memory (TCM), Valence Change or Mixed Valence Memory (VCM), Electrochemical Metallization (i.e. Program Metal Cell or Atomic Switch) (ECM), and Electrostatic/Electronic Effects Memory (i.e. Ferroelectric Barrier Cell, Mott Insulator Cell, or Charge Trapping Cell) (EEM).

Figure 1.1. RRAM classification. Reproduced from ITRS 2010.

According to Waser et al., the resistive switching in phase change memory mainly relies on reversible heat induced phase transformation. On the contrast, electrostatic/electronic mechanism memory purely operates on electronic effect. The other three types are based on redox-related chemical effects, and they share strong resemblance in terms of operation mechanism. Therefore, TCM, VCM and ECM are typically grouped as Redox RAM which occasionally serves as a narrow definition of RRAM. The scope of this review is limited to Redox RAM.

1.2.2 Classification by Polarity

There are three types of switching behaviors according to operation voltage polarity which are unipolar, bipolar, and nonpolar operation. The origin of polarity dependence in resistive switching comes from the underlying mechanism as depicted in Figure 1.1.

As revealed by its names, unipolar switching features for that SET and RESET transitions can take place under the same polarity of the applied electric field (See Figure 1.2). In other word, the unipolar RRAM can be programmed with voltage pulses of single polarity. And typically switching can be made with either polarity of applied field especially in symmetrically configured material systems. That is why it is also named nonpolar RRAM. Both SET and RESET transitions are dependent on the strength of electric field. Compared to RESET transition, a smaller threshold of the field strength is desired to trigger a SET transition. Unipolar operations are more favorable for ultimate RRAM application because of memory array integration.

For bipolar resistive switching, SET and RESET transitions take place under opposite polarity of electric field, as shown in Figure 1.2.

Figure 1.2. RRAM classification by polarity. Reproduced with permission from [17].
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There is possibility of coexistence of both unipolar and bipolar operations, or nonpolar operation. The terminology “nonpolar switching” was first used by Akinaga in his work on Pt / CoO / Pt RRAM where the device was found of both unipolar and bipolar characteristics in operation.[27]

1.2.3 Classification by Materials

A family of materials which comprises of compounds of similar chemical properties typically show similarities in resistive switching if all of them are switchable. Therefore, a natural way to group resistive switching systems is based on material families. Table 1.3 lists some frequently reported material families used for resistive switching.

Family	TCM	VCM	ECM
Carbon and Polymer	Diamond-like Carbon, Reduced GO*, CNT*, PVK: Au NP/PEDOT- PSS*, MSQ/Ag*	GO/PrCaMnO ₃	PI/GO-PI/PI*, GO, PEO+AgClO ₄ *

Chalcogenide Glass			GeSe, GeTe
Metal Carbide			CuC
Metal Nitride	AlN, CuN		
Metal Oxide	CuO, SiO ₂ , HfO ₂ , Nb ₂ O ₅ , NiO, SnO ₂ , Ta ₂ O ₅ , TiO ₂ , ZnO, ZrO ₂	Al ₂ O ₃ , SiO ₂ , GeO ₂ , HfO ₂ , Nb ₂ O ₅ , Ta ₂ O ₅ , TiO ₂ , WO ₃ , ZnO, ZrO ₂	Al ₂ O ₃ , CoO ₂ , CuO, SiO ₂ , Ta ₂ O ₅ , ZrO ₂
Metal Sulfide			AgS, CuS, GeS
Perovskite Structure	BaTiO ₃ , PrCaMnO ₃ , SrTiO ₃ , SrZrO ₃	LaCaMnO ₃ , PrCaMnO ₃	
*GO=graphene oxide, CNT=carbon nanotube, PVK=poly(N-vinylcarbazole), NP=nanoparticles, PEDOT-PSS=poly(3, 4-ethylenedioxythiophene)- poly(styrenesulfonate), MSQ=methylsilsesquioxane, PI=polyimide, PEO=polyethylene oxide			

Table 1.3. RRAM classification by material family.

1.3 Expectations

The update of IRTS 2010 considered RRAM to be one of the emerging memory devices along with Nano-mechanical memory, polymer memory and molecular memory due to their long duration of technology development and polishing. Redox based RRAM, together with STT-MRAM, were recommended by the committee to receive additional focus in research and development to accelerate progress towards commercialization.

In order to compete with floating gate memory devices and fulfill the circuit requirements of ultrahigh density device integration, performance expectations which were acknowledged by ITRS 2010 were proposed by Waser et al. [19].

Figure 1.3. Requirements of RRAM. Reproduced from ITRS 2010.

The endurance expectation of RRAM is 10^7 , which stands for a longer lifespan compared to current floating gate memory devices. Resistance ratio > 10 is preferred to simplify the circuit of sense amplifier and accelerate reading process. Expectation value of read current is at the level of 1 μA for fast detection. And most importantly, as a candidate of sub-22 nm node nonvolatile memory, RRAM is supposed to possess a good scalability for < 22 nm integration or a feasibility of 3D stacking.

A less than 5 V write voltage will benefit RRAM by eliminating the V_{pp} generate circuit used in flash memory programming with 5 V USB power supply. Optimal read voltage should be around 10% of the write voltage, due to concerns of circuit design. Speed of writing is expected to be less than 100 ns, which is similar to that of DRAM. And a ten years life time is also essential.

There are many inborn advantages of RRAM over other candidates of the next generation non-volatile memory thanks to its unique operation mechanism. For instance, filaments based RRAM is possible to be scaled down to 10 nm resulting in ultrahigh

density integration. Another advantage comes from the switching speed where less than 10 ns switching cycle has been demonstrated in AlN based RRAM, which is of similar performance with SRAM. Possible unipolar operation further benefits the density of integration because there is no demand of active devices (i.e. transistor) in memory matrix. On the other hand, being a two-edged sword, the mechanism of RRAM is also associated with drawbacks which hinders its application in consumer electronic devices. One of the major tough issues comes from its unpredictable reliability. The pros and cons of RRAM are listed in Table 1.4.

Pros	Cons
Good potential for scaling below 10nm generation (small cell size ~ DRAM size)	Need better understanding of physical SET/RESET processes; need quantitative physical models
Fast read and write times switching < 10ns	Fractal structure; robustness of filament structure (reliability issue)
Low write current in mA range (needs further reduction for DRAM application)	Temperature dependence of Read disturb (reliability issue)
Compatible with CMOS (materials, processing)	Need better Endurance and Retention (reliability issue)
Possible unipolar operation	Unstable Unipolar operation (reliability issue)
Possible crossbar structure with potential for multiple layers	Need a reliability model
Multibit/cell storage	Currently requires an initial forming process
Reasonable endurance ~ 10^9 (needs improvement for SRAM application)	Per bit cost savings of 3-D stacked RRAM is questionable
Reasonable retention time @ 150°C	
Large ON/OFF ratio	

Table 1.4. Pros and Cons of Redox RAM. Reproduced from ITRS 2010.

1.4 Challenges and Motivations

As partially summarized in Table 1.4, the cons of the RRAM may halt the commercial application of RRAM. Those issues can be classified into two categories, the challenges to engineer RRAM as a device with decent performance and the challenges to understand its underlying operations. The work of this thesis originates from the efforts in these two directions.

1.4.1 Electrical Performance

As mentioned in the previous section, many materials have been demonstrated with repeatable resistive switching characteristics including metal oxide, perovskite, metal sulfide, metal nitride and carbon based materials. Among all these materials, the transition metal oxide based RRAM is one of the most promising candidates which have potential of commercial application. However, the following technique challenges have to be addressed, otherwise they will hinder the wide application of the transition metal oxide RRAM.

The first issue comes from the forming voltage. According to the theory of filament switching which will be discussed in the next chapter, RRAM desires high electric field strength in forming process to establish a conductive filament.

Secondly, in RESET transition, a current compliance is of a critical role to prevent RRAM from suffering hard dielectric breakdown. And this compliance relies on the external circuit, which thus greatly complicates the design of supplementary macro.

Last but not the least, the electro-chemical reactions, including filament formation and rupture processes, are stochastic that the observed R_{HRS}/R_{LRS} and V_{SET}/V_{RESET} are different from cycle to cycle. These problems also challenges the supplementary circuit which is used to sense the data stored.

1.4.2 Mechanism Investigation

The nature of the transport and switching in the resistive switching devices is of great importance to the improvement of the RRAM performance. Since transition metal oxide, especially HfO_2 , is one of the most extensively studied RRAM types due to the compatibility with the high- κ transistors, investigation of its operation mechanism is crucial along with its performance optimization. Proposed interpretations on current transport mechanisms include modification of Schottky barrier at interface between electrode and dielectric layer, migration of ions from electrode (or diffusion of impurity metal ions), space charge limited current, Mott type variable range hopping, and filamentation of oxygen deficiency [33-38]. However, no unified transport mechanism and switching theory have been developed yet. Recent reports on physical characterization of HfO_x [28], NiO_x [29, 30], SiO_x [31], SrTiO_x [32], and TiO_x [33] have speculated oxygen vacancies to be responsible for the valence change type bipolar resistive switching in oxides. Further analysis of electronic properties of these materials shows strong correlation to the local configuration of oxygen vacancies [45, 46]. Spectroscopic ellipsometer measurements revealed that oxygen vacancies are the dominant native defects in HfO_x . [34] Although various models have been developed to qualitatively account the observed switching, the exact role of oxygen vacancies in carrier transport is still unknown. [35-38]

On the other hand, it is generally accepted that charge carriers tend to create small polarons in high- κ transition metal oxides due to significant electron-phonon interaction [47, 48]. For instance, TiO_2 and HfO_2 , are highly polarizable medium where charge carriers in intrinsic TiO_2 and HfO_2 will be self-trapped by forming small polarons [39, 40]. Free polarons, with possible charge trapping hard to be distinguished from disorder influence, have been predicted in crystalline $m\text{-HfO}_2$ [41, 42]. But the

population of free polarons is limited by large band gap. Bound polarons, as suggested by Gavartin, are likely to occur in the vicinity of pre-existed defects; and trapping of extra electrons in negatively charged oxygen vacancies is polaronic [40]. And the ability that oxygen vacancies can trap up to two extra electrons is believed to have originated from polarization [40, 43]. This further complicate the nature of the transport and switching of the transition metal oxide RRAM.

Despite the transition metal oxide RRAM, the investigation of working mechanism of GO RRAM is another challenge. Motivated by small fabrication cost, GO based RRAM is widely studied for its competitive and potential use as a low cost flexible memory device. (GO oxide RRAM is fabricated by spin-casting GO solution onto substrates and thus of much smaller cost compared to either reactive sputtering or ALD used for transition metal oxide RRAM.[44-46]) However, they may suffer from inherent temperature instability, which results in poor reliability. All of these correlate to the switching and transport mechanism of the randomly stacked GO flakes which constitute the switching layer.

1.5 Scope of the Project

In this dissertation, oxides based resistive switching systems, including hafnium oxide and graphene oxide based RRAMs, have been developed. Performance optimization has been implemented by evaluating various configurations of material systems fabrication techniques. Electrical as well as physical characterization is employed to investigate the underlying mechanisms, especially charge transport and switching mechanisms of the corresponding systems.

On the other hand, attempts on theoretically modeling of the observed transport behaviors are implemented by using density functional theory. Hybrid functional based transition state search approach is used to unveil the observed small polaron migration

process in HfO_x based RRAM. Impact of the presence of surfaces is explored. Phonon calculation is performed to understand its coupling to the carrier transport.

1.6 Organization of Thesis

This thesis comprises of seven chapters. Chapter 1 is about the background of the resistive switching, with an overview of the history of research on the phenomena of resistive switching. In addition, popular ways of classification of resistive switching are discussed.

Chapter 2 consists of a detailed review of literature on the redox based resistive switching systems, including TCM, VCM, and ECM type switching systems. Information is provided on the configurations of material system, electrical properties as well as underlying switching and transport mechanisms. This chapter also covers the theoretical formulation of the dielectric loss technique which is intensively used for charactering the electronic properties of the dielectrics in the subsequent chapters. Literature review of the resistive switching, including a discussion of the operation directions, in graphene oxide is also presented.

Chapter 3 tackles the performance issues, listed in Sec. **Error! Reference source not found.**, by introducing Ge doping in conventional HfO_x based RRAM. Electrical and physical characterizations have been performed to identify the difference in performance induced by the doping. The self-compliance is realized by employing proper deposition techniques and annealing conditions which may lead to unbreakable resistance in series. The large amount of leakage current caused by oxygen deficiency brings RRAM the property of being forming free. Improvement of uniformity is achieved by the decrement of formation energy of oxygen vacancies in the vicinity of the Ge dopants, as implied by the ab-initio density functional calculation.

Chapter 4 intends to meet the challenges in mechanism study discussed in Sec. 1.4.2 via dielectric loss based techniques. Here low frequency ac conductivity

measurements at various temperatures are performed to investigate the electronic properties of the oxygen deficient filaments. Both HRS and LRS cells are observed of an additional frequency independent conductance component in addition to the power law term inherited from pristine cells. For cells in HRS, such a term is found of significant temperature dependence while the counterpart in LRS is almost temperature independent. The conduction in HRS suits the model of small polaron adiabatic hopping in the temperature range above half of the Debye temperature. A weak metallic behavior is identified in transport of LRS. *Ab-initio* calculation has been employed to probe oxygen vacancies on the surface of HfO_x . $(\bar{1}11)$ and (111) surfaces are found of lowest surface energy among various facets. The formation energy of oxygen vacancy at the vicinity to surface has been predicted to be significantly lower than that in the bulk. One of the stable oxygen vacancy configurations is found to be chain-like along $[101]$ direction. And the weak metallic nature of LRS may stems from the delocalization of the impurity orbitals with t_{2g} character within the band gap.

Chapter 5 presents the efforts on theoretical modeling of the transport based on the experimental observations of Chapter 4. Computational evidence is presented for the motion of bound polarons in HfO_x and localization-delocalization transitions due to correlation, with direct implication to transport and switching behaviors of HfO_x based resistive memory. Using hybrid functional based linear/quadratic synchronous transit scheme, we find highly anisotropic hopping barriers for bound small polarons jumping between equivalent threefold oxygen vacancies. Phonon structures have been calculated which indicates large vibration is with vacancy-neighboring threefold oxygen atoms. Symmetrical hopping paths in the presence of $(\bar{1}11)$ surface are calculated, and the vibration mainly concerns surface modes localized on vacancy-neighboring threefold oxygen atoms.

Chapter 6 is about the mechanism study of graphene oxide RRAMs which are novel devices attempting to address the cost issue of the RRAM. Various commonly used metal electrodes are testified. Coexistence of different reproducible switching directions has been observed. These switching directions are correlated to the underlying switching mechanisms as revealed by field dependence, temperature dependence and area dependence, suggesting that both oxygen related functional groups absorption/release and electrode metal ions diffusion are involved in the resistive switching of GO.

Last but not the least, chapter 7 is a summary of the significances of research works carried out in this thesis along with the recommendations for future studies.

Chapter 2 Literature Review

2.1 Thermal Chemical Mechanism RRAM Material System

2.1.1 General Properties

As mentioned in the previous chapter, one of the most important features of Thermal Chemical Mechanism (or Fuse/Anti-fuse) RRAM is its unipolar or non-polar type of operation which makes it different from bipolar operation VCM or ECM RRAM. This property stems from the significant Joule heating effect caused by the filament which serves as the driving force of RESET transition. TCM RRAM also features for the advantage of unipolar operation as no active elements in the memory matrix are desired.

2.1.1.1 Area Dependence of Resistance

In literature, the low resistance state (LRS) resistance of a TCM RRAM is frequently reported of area independence, which is a natural consequence of its filament nature switching (See Figure 2.1 and Figure 2.2).

On the other hand, for high resistance state (HRS), both area dependent conduction and area independent conduction have been reported (See Figure 2.1 and Figure 2.2). A possible explanation is that there is competition between carriers flowing through the partially ruptured/shrunk filament and carriers passing through the homogeneous bulk dielectric film. If carriers flowing through ruptured/shrunk filament dominate the transport, the I-V characteristics will lose area independence. In this case, HRS behaves like as a weak LRS.

Figure 2.1. Area independent LRS resistance and dependent HRS resistance. Reproduced with permission from [47]. © 2007 IEEE.

Figure 2.2. Area independent LRS and HRS resistance. Reproduced with permission from [48]. © The Electrochemical Society.

2.1.1.2 Temperature Dependence of Resistance

For TCM RRAM, LRS has been reported of very weak temperature dependence where the activation energy is typically less than 10 meV in most of the cases, as shown in Figure 2.3 (a). The current at 300K/450K is $\sim 30/33 \mu\text{A}$, implying a temperature-independent transport, in accordance to the claim that the filament of LRS is of a weak metallic nature.

On the contrast, HRS is typically of much larger activation energy which is material system dependent. This signifies that the transport process is thermally facilitated (See Figure 2.3).

Figure 2.3 Temperature dependence of the current for (a) LRS and (b) HRS of n^+ -Si/HfO_x/Ni device. The applied voltage is 0.2 V. Reproduced with permission from [49]. © 2011 IEEE.

2.1.1.3 Frequency Dependence of Admittance

A very critical piece of information on the transport analysis of RRAM is the conductance (real part of admittance) as a function of frequency. The imaginary part of the admittance is correlated to the conductance by Kramer-Kronig transformation.

Typically the admittance of pristine devices follows the power law for polycrystalline/amorphous materials as illustrated in Figure 2.4.

Figure 2.4. Frequency dependence of the real (closed symbols) and imaginary (open symbols) parts of the intrinsic admittance of TiO₂ at the various resistance states: fresh state (FS), high resistance state (HRS), low resistance state (LRS) on (a) linear and (b) log scales. In FS, $Re(Y_{FS})$ shows a power law behaviour. In HRS, $Re(Y_{HRS})$ is almost constant until the ac conductance becomes dominant. In LRS, the dc conductance is high enough to hide the ac conductance. Reproduced with permission from [50]. ©

On the contrary, LRS is of pretty weak frequency dependence in the low frequency range because its admittance consists of large a frequency independent component caused by the weak metallic filament. The behavior of RRAM in HRS is somehow between pristine and LRS.

2.1.2 TCM Material Combinations

As mentioned in the previous section, there is a large diversity in materials explored for unipolar switching. Majority of materials reported of TCM switching are metal oxides. In addition, perovskite structure materials, carbon based materials and polymers have also been reported with repeatable unipolar switching behaviors. Table 2.1 lists some typical unipolar switching systems reported recently.

Type	Switching Region	Thickness	BE	TE	Device Size	Current	Voltage	Speed Endurance	Retention	Remarks	Ref
Carbon and Polymer	Diamond-like Carbon	22nm	W	Pt	0.24 μ m diameter	38 μ A	<1.5V	>10 ³ (SET/RE SET: 50ns/10ns)	>10hrs @ 300C in Ar		[51]
	Reduced Graphene Oxide or Multiwall Carbon Nanotube	20nm or 150nm	ITO	Al or Ar	3mm diameter	<1 or 4 μ A	<7.5 or 15V	(SET/RE SET: 10 μ s/10 μ s)	>2 $\times$ 10 ³ s		[52]
	PV: Au NP/PEDOT-PSS	(120nm or 360nm)/70nm	Al	Al	0.04mm ²	<10mA	<5V/<10V	NS	>10 ⁴ s @ RT		[53]
	MSQ/Ag	150/12nm	Pt	Pt	0.1 $\times$ 0.1 μ m ² (vertical)	<0.7 mA (vertical)	<1V (vertical)	>2 $\times$ 10 ³ (SET/RE SET: 0.1ms/0.1ms)	>6 $\times$ 10 ⁴ s @ 85C		[54]
Simple Metal Oxide	Cu ₂ O	190nm	Pt	Cr	NS	<10mA	<2V	>10 ⁴	NS		[55]
	SiO _x /HfSiON	2.5nm	Si	NiSi	0.12 μ m ²	<0.2 mA	<4V	>50 (DC)	>10 ⁴ s @ 150C	Both bipolar and unipolar	[56]
	HfO ₂	30nm	Si	Ni	NS	<2.5 mA	<4V	(SET/RE SET: 500ns/100ns)	>10 ⁴ s @ 85C		[57]

HfO ₂	5-20nm	Ni	Ti N	0.1 × 0.1mm ²	<0.2 mA (lowest Ic)	<1.5V (lowest Ic)	>10 ⁴ (bipolar) 10 ³ (unipolar)	>20hrs @ 150C	Both bipolar and unipolar	[58]
HfO ₂	3nm	Si	Ni	5625-99225μm ²	<1mA	<2.5V	>10 ⁵ (SET/RE SET: 50ns/50ns)			[49]
HfO ₂ /Al ₂ O ₃	4.2nm	Si	Ni	NS	<1mA	<1.5V	>10 ⁶ (SET/RE SET: 10ns/30ns)	>7 × 10 ³ s @ 120C		[59]
InGaZnO	60nm	Cu	Cu	0.5mm diameter	<1mA	<2V	>150 (DC)	NS	Flexible	[60]
NbO	40nm	Pt	Pt	50 × 50 μm ²	<10mA	<4V	>150 (DC)	NS		[61]
NiO	35nm	W	Au	180nm diameter	<4mA	<1.5V	>200 (DC)	>3 × 10 ⁶ s @ 125C		[62]
NiO:W	50nm	Pt or Ti N	Pt	40 × 40 μm ²	<10mA	<2V or <2.5V	NS	NS		[63]
Al ₂ O ₃ /NiO /Al ₂ O ₃	4/40/4nm	Pt	Ti N	0.4mm diameter	<10mA	<2.5V	>250 (DC)	>10 ⁴ s @ RT		[64]
NiO Nanodot	30nm	Au	Au	30nm diameter	<0.1nA	<0.8V	>200 (DC)	NS	Lateral Wire Structure	[65]
SiO	50nm	W	Cu	40 × 40 μm ²	<2mA	<6V	NS	>10 ⁴ s @ 100C		[66]
SiO	20nm	Pt	Cu	4.9 × 10 ⁻⁴ cm ²	<1mA	<3V	NS	NS	Both bipolar and unipolar	[67]
SnO ₂	50nm	Ti	Ag	0.635/1.778/2.413mm diameter	<10mA	<1.25V	>30 (DC)	>10 ⁴ s @ RT		[68]
TaO _x	~40nm	Pt	Pt	30 × 30 μm ²	<0.1A	<2.5V	NS	NS	Bipolar with Ta ₂ O ₅ layer	[69]
TiO:Gd	40nm	Pt	W	NS	<15mA	<1.5V	NS	NS		[70]
TiO ₂	60nm	Pt	Pt	2 × 2 μm ²	<10mA	NS	>4 × 10 ³	NS		[71]
ZnO	40/90/140nm	Al	Al	0.2mm diameter	<10mA	<2/2.5/3V	NS	NS		[72]
ZnO:La	200nm	Pt or Si	Pt	0.2mm diameter	<20mA	<3V	>150 (DC)	>10 ⁶ s		[73]

	ZnO, NiO/ZnO or WO ₃ /ZnO	50, 50/50 or 50/50nm	Pt/ Au	Pt/ Au	2×2 - 10×10µm ²	<10,1 00 or 10m A	<2V	NS	NS		[7 4]
	Zn _{0.98} Cu _{0.02} O	80nm	IT O	Ag	1mm diameter	<20m A	<15V	NS	>10 ³ s	Both bipola r and unipol ar	[7 5]
	ZrO ₂ /Cu/Z rO ₂	20/3/20n m	Pt	Cu	0.1×0.1 mm2	<70m A	<2.5V	NS	NS		[7 6]
Perovs kite Struct ure	SrTiOx	60nm	Pt	Pt	25×25µm ²	NS	NS	NS	>60s		[7 7]
	Pr _{0.7} Ca _{0.3} M nO ₃	400nm	Pt	Au, Ag, Cu or Al	0.3mm diameter	<150 mA	<7V	>100 (DC)	>24hr s	Both bipola r and unipol ar	[7 8]
	SrTiO ₃	300nm	Pt	Au	0.1mm diameter	<30m A	<1.5V	NS	>14da ys	Both bipola r and unipol ar	[7 9]
	SrTiO ₃	200nm	Pt	Pt	0.2mm diameter	<50m A	<6V	NS	>10 ⁵ s	Both bipola r and unipol ar	[8 0]
	SrZrO ₃	100nm	Pt	Pt	0.2mm diameter	<200 mA	<15V	>600 (DC)	NS		[8 1]
	BaTiO ₃ :Co	400nm	Pt	Au	0.1mm diameter	<30m A	<7.5V	>10 ⁵ (SET/RE SET: 8ns/69ns)	>7×10 ⁴ s		[8 2]

Table 2.1. Recent reports on TCM based RRAM systems.

2.1.3 TCM Mechanism Study

It is believed that TCM switching is filament based. With electric field applied, pristine device experiences dielectric breakdown due to migration of either cations or anions. Once a filament is bridged between two electrodes, the RRAM cell is in its LRS state with good conductance. However, for TCM RRAM, Joule heating caused temperature gradient is a more dominant force than electric field in driving cations or anions to migrate under the condition of large current flow. Thus, the filament will be ruptured by Joule heating if the current is beyond a threshold and this is the mechanism

of RESET transition. As mentioned in Table 1.2, specific TCM mechanism reviews have been given by Ielmini et al. [26, 83] and Kim et al. [25].

2.1.3.1 Physical Characterization Study

Recently, for NiO system, Yoo et al. have reported of the direct observation of creation and rupture of a portion of percolation network, which takes the form of grain boundary under the inspection of HRTEM [29] (See Figure 2.5).

Figure 2.5. Observation of soft breakdown boundaries in NiO thin films during resistance switching. (a) A grain boundary is indicated by red lines in the virgin NiO thin film. (b) New boundaries with yellow lines appeared after resistance switching. It is believed that conducting clusters (percolating network) are formed in both grain boundaries and breakdown boundaries during resistance switching. Reproduced with permission from [29]. © 2010 IEEE.

The chemical composition analysis of percolation path has been taken by Li et al. via EELS analysis [84]. The weight of Ni cations and oxygen vacancies in filament

are significantly higher than the neighboring volume as shown in Figure 2.6.

Figure 2.6. Ni and O EELS line profiles acquired at three locations indicated in the inserted TEM micrograph. At the filament location, O diffuses to the NiSi gate, while Ni moves into the gate dielectrics and Si substrate. The Si epitaxy region shows low Ni intensity as a result of Si protrusion from the substrate. Reproduced with permission from [84]. © 2010 American Institute of Physics.

HAXPES has been used to identify the change of valence state of Ni atoms before and after dielectric breakdown by Calka et al. [85] (See Figure 2.7). During forming, occupied bandgap states are created near NiO Fermi level (E_F), which coincides with oxygen deficient NiO bandgap structure. Besides, metallic Ni atoms weight is observed to increase after forming process. And it is noted that the increment is relatively small, which may suggest that filament is confined in a small volume.

Figure 2.7. Ni core level spectrum. The decomposed area for metallic peak (851eV) increases after forming process. The inset shows the bandgap spectrum. The bandgap states are attributed to oxygen vacancies. Reproduced with permission from [85]. © 2011 American Institute of Physics.

Kondo et al. have reported their TEM observation of breakdown NiO also [30]. As shown by Figure 2.8, a ~400nm diameter conductive spot was observed of significant change of surface morphology. The EDX analysis of NiO underlying reveals of oxygen deficiency.

Figure 2.8. (a) SEM image of conductive spot, (b) and (c) corresponding TEM images. In (c), the edge of conductive spot is enlarged, where the conductive path (filament) is thought to be formed. Around this area, compositional analyses of NiO were performed by EDX. The triangles, squares, and circles correspond to positions with composition ratios of Ni:O = 1:1, 2:1, and 9:1, respectively. Reproduced with permission from [30]. © 2011 The Japan Society of Applied Physics.

Despite Ni based material system, another system has been frequently reported is TiO_2 . Kwon et al. have reported the observation of Ti_4O_7 (Magnéti phase) filament in TiO_2 unipolar RRAM by using HRTEM [86] (See Figure 2.9). Ti_4O_7 is oxygen deficient compared TiO_2 and of metallic nature above $\sim 150\text{K}$. Both properties have been confirmed to exist in TiO_2 RRAM.

Figure 2.9. (a) High-resolution image, diffraction pattern and fast Fourier transformed micrograph of the Magnéti structure before RESET. (b) The corresponding images after RESET. The diffraction spot (marked as a circle in c) from the Magnéti structure disappeared after RESET. Reproduced with permission from [86] © 2010 Macmillan Publishers Limited.

Despite Ti_4O_7 , another Magnéti phase Ti_5O_9 has also been identified of its presence in TiO_2 RRAM, as reported by Kim et al. [71] (See Figure 2.10).

Figure 2.10. HRTEM image of the hourglass shape conductive filament. Insets show

the fast Fourier transformed diffraction patterns. Reproduced with permission from [71].

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2.1.3.2 Switching and Conduction Mechanisms

Switching mechanisms as well as conduction mechanisms have been proposed by several groups to account for observations in electrical and physical characterization.

Precise *ab-initio* modeling of the SET/RESET transition process is a big challenge. This is because the concerned atomic system is of a large atomic population and severe disorder which lead to unaffordable computational cost. And the exact atomic configurations before and after switching are very difficult or impossible to be probed experimentally. In this case, empirical or classical treatments have been reported with success for unipolar RRAM. Regarding switching mechanisms, despite the mentioned review articles, a quantitative computational model based on switching parameters has been developed by Russo et al. [87]. By considering temperature gradient drove ion motions and the redox reactions, Bocquet et al. have simulated the I-V characteristics and sweep rate as functions of SET voltage by solving the partial differential equation [88]. Their simulated SET and RESET transitions behaviors are shown in Figure 2.11.

Figure 2.11. Simulated SET and RESET operations. Reproduced with permission from

[88]. © 2011 American Institute of Physics.

More sophisticated approach, by using molecular dynamical simulation with Matsui–Akaogi potential, has been performed by Zhao et al. on Ti and O ions distribution subjecting to external electric field [89]. The temperature profile has been calculated, and the filament melting has been demonstrated in their calculation (See Figure 2.12).

Figure 2.12. (a) SET simulation (b) RESET simulation. Blue dots: Ti atoms. Red dots: Oxygen atoms. Reproduced with permission from [89]. © 2011 IEEE.

For NiO system, a novel model has been proposed to interpret its unique switching behavior based on Ni_2O_3 by Chien et al. [90]. Their proposed model suggests that, in HRS state, switching region is of the stoichiometry NiO. NiO will transform itself into Ni and Ni_2O_3 if local temperature is higher than the critical decomposing point. Joule heating is responsible for the temperature rising. Metallic Ni atoms are capable to bridge a metallic path which enables large current flow in LRS state. However, Ni_2O_3 is not thermally stable also. It may easily decompose to NiO by release oxygen ions at even higher temperature. The released oxygen ions will oxidize metallic Ni atoms, which will eventually rupture the conductive filament. Their claim is supported by photo emission spectrum shown in Figure 2.13.

Figure 2.13. Photon emission spectra of Ni $2p_{3/2}$ and O $1s$ taken in the original NiO film. (a) and (b) the ON spot (c) and (d), and the OFF spot (e) and (f). Reproduced with permission from [90]. © 2011 American Institute of Physics.

For carrier transportation, assumption of metallic impurity band due to oxygen vacancies is proposed by several groups to explain the observed weak metallic nature of LRS. For instance, Park et al., using density functional theory calculation, has claimed that aligned neutral oxygen vacancies chains in TiO_2 may form delocalized impurity bands due to overlapping of t_{2g} orbitals [91] (See Figure 2.13).

Figure 2.14. Isosurface ($0.1 \text{ e}/\text{\AA}^3$) of band decomposed charge density of all defect states. (a) $[110]$ vacancy chain. (b) $[001]$ vacancy chain. Reproduced with permission from [91]. © 2011 IEEE.

Similar calculation has also been implemented on NiO by Magyari et al. [92]

(See Figure 2.15). And the calculated formation energy of oxygen vacancies indicates neutral oxygen vacancy is preferred if Fermi level of external electron reservoirs aligns at the middle of the bandgap.

Figure 2.15. Partial charge density within (E_F , $E_F + 0.3$ eV) in the (100) plane including oxygen vacancies and a Ni metal chain (E_F is the Fermi level). Reproduced with permission from [92]. © 2011 IOP Publishing Ltd.

For HRS state, Ielmini et al. have proposed the oxygen vacancy/defects concentration impact on activation energy [83]. A gradual change can be seen in Figure 2.16. The role of the oxygen vacancies is believed to be dopants like. Therefore, in LRS, high local density of oxygen vacancies will trigger metal-insulator transition in a similar manner with the degenerately doped semiconductors.

Figure 2.16. Arrhenius plot of resistances for different nanofilament states (left) and corresponding schematic band structures (right). LRS display a metallic conductivity behavior, where resistance increases with T , as revealed by the negative apparent activation energy. This suggests that the Fermi level is pinned in the conduction (or valence) band as for a degenerately doped semiconductor. For increasing resistance, the nanofilament behavior becomes increasingly semiconductor-like, showing an increasing activation energy. The corresponding physical picture is a semiconductor with a different Fermi level with respect to the band edge. Reproduced with permission from [83]. © 2011 IOP Publishing Ltd.

2.2 Valence Chemical Mechanism RRAM Material System

2.2.1 General Properties

Unlike TCM switching, there are two different types of VCM switching RRAM, which are filament type and homogeneous switching type, based on experimental observations. Filament VCM memory shows very similar properties with TCM memory. Indeed, as mentioned in the previous chapter, some material systems feature for coexistence of both unipolar and bipolar switching properties because of the reason that Joule heating and electric field are two competing forces in RESET processes. The

only difference is that, for TCM cells, the RESET actions are mainly thermal driven and thus nonpolar, while the anions, which are typically oxygen ions, were drifted by electric fields and therefore showing bipolar switching in filament VCM RRAM.

2.2.1.1 Area Dependence of Resistance

Most VCM RRAM are filament based, showing strong resemblance in properties with TCM based RRAM that LRS typically has area independent resistance. But the resistance of HRS of VCM RRAM may either be area independent (See Figure 2.18) or dependent (See Figure 2.17), depending on whether the current contribution of the ruptured/shrunk filament can dominate or not.

Figure 2.17. Area independent LRS resistance and dependent HRS resistance. Reproduced with permission from [93]. © 2008 IEEE.

Figure 2.18. Area independent LRS and HRS resistance. Reproduced with permission from [94]. © 2011 IEEE.

The other type of VCM RRAM, the interface switching memory, is experiencing homogenous change of interface properties during switching process. As depicted in Figure 2.19, resistance of both LRS and HRS are scaling with area.

Figure 2.19. Device area dependence of resistance values in HRS and LRS. Reproduced with permission from [95]. © 2011 American Institute of Physics.

2.2.1.2 Temperature Dependence of Resistance

For VCM RRAM, majority cases (either filament oriented or homogeneous interface oriented) are reported of the feature that LRS resistance is of very weak temperature dependence. Along with its Ohmic field dependence, these transport properties imply that LRS is of a weak metallic nature, which is same with the TCM case. And similarly, HRS is found to be temperature sensitive suggesting a thermally facilitated transport type (See Figure 2.20).

Figure 2.20. Temperature independent LRS resistance and dependent HRS resistance. Reproduced with permission from [96]. © 2007 IEEE.

However, there are also reports of ultralow conductance LRS VCM RRAM in which the LRS behaves like typical HRS which is of significant temperature dependence. And the HRS of such a device is of even poor conductance close to that of a pristine device (See Figure 2.21).

Figure 2.21. Temperature dependent LRS and HRS resistance. Reproduced with permission from [97]. © 2007 IEEE.

2.2.1.3 Frequency Dependence of Admittance

Similar to TCM cells, the real part of admittance of pristine VCM RRAM cells is generally following the universal power law for polycrystalline/amorphous semiconductors. On the contrary, LRS is typically dominated by a large frequency independent component, possibly a consequence of the metallic filament, in low frequency range. And HRS is of a state in between pristine state and LRS (See Figure 2.22).

Figure 2.22. Frequency dependence of the C and G in the ON and OFF states, as a function of the top electrode size. Reproduced with permission from [98]. © 2010 American Institute of Physics.

2.2.2 VCM Material Combinations

Similar to TCM RRAM, VCM resistive switching is observed in a large variety of material families, including carbon based materials, polymer based materials, metal nitride, metal oxide, and perovskite structure materials. Table 2.2 consists of some common seen examples of VCM RRAM from recent publications.

Type	Switching Region	Thickness	BE	TE	Device Size	Current	Voltage	Speed Endurance	Retention	Remarks	Ref
Carbon and Polymer	GO/PCMO	30/25nm	Pt	Pt	NS	<3mA	<1V	>125	>10 ⁴ s @ 85C		[99]
Metal Nitride	AlN	150nm	Pt	Ti	50-200μm diameter	<10μA	<2V	>10 ⁸ (SET/RESE T: 10ns/10ns)	>10 ⁵ s @ 85C		[100]
	AlN	130nm	ITO	ITO	0.2mm diameter	<10mA	<3V	>10 ⁸ (SET/RESE T: 10ns/10ns)	>10 ⁵ s @ 85C		[101]
	Cu _x N	~80nm	Cu	Ni	0.1mm diameter	<0.2mA	<0.8V	>50 (DC)	NS		[102]

Metal Oxide	Al ₂ O ₃ /RuN Cs/Al ₂ O ₃	10/3/1 0nm	Pt	TaN	0.1mm diamet er	<100m A	<1.5V	>10 ³	>10 ⁵ s @ RT		[1 03]
	AlO _x /WO _x	5/20nm	W	Al	0.22×0.22 - 300×300μm ²	<30μA	<2V	>10 ³ (SET/RESE T: 1μs/1μs)	NS		[9 4]
	CoSiO _x	30nm	Pt	TiN	1- 64μm ²	<10mA	<2V	>100 (DC)	NS		[1 04]
	GeO _x or GeO _x /SrZr O _x	5, 8, 12/5 or 12/8 nm	TaN	Ni	11304 μm ²	<1μA (for SrZrOx /GeOx, 12/8nm)	<1.5V (for SrZrOx /GeOx, 12/8nm)	>10 ⁶ (SET/RESE T: 50ns/50ns)	NS		[1 05]
	GeO _x /HfO N	8.5/7.5 nm	TaN	Ni	11300 μm ²	<0.1μA	<3V	>10 ⁶ (SET/RESE T: 20ns/20ns)	NS		[9 7]
	HfO _x /TiO _x / HfO _x /TiO _x	4/2/4/2 nm	Pt	TiN	100μm ²	<1mA	<1.5V	>500 (DC)	NS		[1 06]
	ZrO _x /HfO _x	NS/3nm	NS	Pt	50×50 μm ² or 250nm diamet er	NS	NS	NS	NS		[1 07]
	SiO _x /HfSiO N	2.5nm	Si	NiSi	0.12μ m ²	<1μA	<2.3V	>30 (DC)	>10 ⁴ s @ 85C	Both bipol ar and unipo lar	[1 08]
	HfO ₂	20nm	Pt or TiN	Au	2mm diamet er	<0.1mA	<6V	NS	NS		[1 09]
	HfO ₂ :Gd	20nm	Pt	TiN	NS	NS	<2.7V	(SET/RESE T: 1μs/1μs @ 1.1/1.2V)	>10 ⁴ s @ 120C		[1 10]
	Nb ₂ O ₅	50nm	Pt	TiN/Ti	0.4mm diamet er	<20mA	<1.5V	>10 ³ (DC)	>5×1 0 ⁴ s @ RT		[1 11]
	Ta ₂ O ₅ /TaO _x	5/20nm	Pt	Pt	30×30 μm ²	<0.1mA	<2.5V	>10 ⁶ (SET/RESE T: 10μs/10μs)	NS		[1 12]
	TiO ₂ - ₈ /La _{2/3} Sr _{1/3} MnO ₃	100/10 0nm	LA O	In	NS	<1mA	<5V	NS	NS		[1 13]
	Ti/TiO ₂	5/20nm	TiN	TiN	NS	<1mA	<1.5V	NS	NS		[1 14]

	Ti/HfO ₂	10/5nm	TiN	TiN	50×50 nm ² - 40×40 μm ²	<1mA	<2V	>4×10 ⁴ (SET/RESET: 0.5ms/0.5ms)	>3×10 ⁴ s @ 200C		[15]
	WO _x	46nm	W	Pt	50nm diameter - 0.1×0.1mm ²	<5mA	<1.2V	>10 ⁷ (SET/RESET: 10μs/10μs)	NS		[16]
	ZnO:Ga (H ₂ : 5%)	240nm	ZnO:Ga	ZnO:Ga	NS	<0.1mA	<2V	>20 (SET/RESET: 0.5ms/0.5ms)	NS		[17]
	Ga ₂ O ₃ -ZnO-Ga ₂ O ₃	50/120/50nm	ZnO:Ga	ZnO:Ga	0.03, 0.8 or 10mm ²	<100mA	<15V	>50 (DC)	>10 ⁵ s		[18]
	ZrO ₂	19nm	Pt	Ti	25μm ²	<25μA (single level)	<3V	>4×10 ³	2640s (150C) 1100s (175C) 470s (200C)		[19]
Perovskite	Pr _{0.7} Ca _{0.3} MnO ₃	60nm	Pt	Multilayer Graphene	~900-20000 μm ²	<0.1mA	<5V	>10 ³ (SET/RESET: 10μs/10μs)	>10 ⁴ s @ 85C		[95]
	Pr _{0.7} Ca _{0.3} MnO ₃	40nm	Pt	Ge ₂ Sb ₂ Te ₅ /Ti	150nm diameter	<0.1μA	<4V	>10 ⁵ (SET/RESET: 100μs/20μs)	>10 ⁴ s @ 125C	Possible of being charge injection type []	[20]
	La _{0.7} Ca _{0.3} MnO ₃	200nm	Pt	Ag, Al or Ag-Al	50μm diameter	<50mA (10nm Al top)	<2.5V (10nm Al top)	>1.1×10 ⁴ (SET/RESET: 5μs/5μs)(10nm Al top)	>10 ⁵ s (10nm Al top)	Possible of being Mott Insulator-Transition type []	[21]

Table 2.2. Recent reports on VCM based RRAM systems.

2.2.3 VCM Mechanism Study

Like TCM RRAM, the forming process and SET transition in VCM RRAM cause migration of cations or anions for both filament oriented device or homogenous switching device. However, in RESET process, electric field is overwhelming that temperature gradient loses its control over ion migrations. The reversed field polarity caused inverted motion of ions leads to the rupture of the formed conducting bridge or filament. Detailed VCM mechanisms have been reviewed by several groups as listed in Table 1.2.

2.2.3.1 Physical Characterization

Because there is strong resemblance between TCM and VCM filament switching systems, the physical characterizations for some TCM RRAM (i.e. TiO_2 RRAM) can also be applied to VCM systems. This is a natural consequence that bipolar switching in unipolar system is frequently spotted. (i.e. TiO_2 RRAM). In 2006, Szot et al. have reported the observation of conduction spots of SrTiO_3 RRAM formed by thermal reduction (as SET, to create oxygen vacancies) and oxidation (as RESET, to annihilate oxygen vacancies) [32]. CAFM has detected the conducting spots which are of nanometer level size as shown in Figure 2.23.

Figure 2.23. (a) Conductivity map of the surface of a SrTiO_3 single crystal as recorded by the LC-AFM. Filamentary paths with enhanced conductance are present on the

surface after thermal reduction and re-oxidation under ambient conditions. Inset: spot with a dimension of 1–2 nm, where the main current is concentrated in a region corresponding to the size of the core of a typical edge-type dislocation. (b) Line scan across the selected spot (D denoting distance along AB) showing the dynamic range of the resistance change as a result of the application of a negative tip voltage bias, that is, selective electroformation. Right: Conductivity maps of the selected spot before (n1) and after electroformation (n15) with an increase in diameter at the surface from 5 to 10 nm. Reproduced with permission from [32]. © 2006 Nature Publishing Group.

Similar direct observation of conductive spots by CAFM on WO_x based RRAM has been reported by Shang et al. recently [122] (See Figure 2.24). They also claim that carriers flux is mainly confined at grain surface rather than grain boundary surface.

Figure 2.24. Local I–V characteristics at grain surface (a) and grain boundary surface (b) measured by the CAFM tip with the external biases ranging from -3 to 3 V. The current compliance is 100 pA. Upper left and lower right insets in (a) show the current mappings after negative and positive voltage sweep, respectively. Inset in (b) shows the current mappings after negative voltage sweep. The current images were obtained under the tip bias of -0.5 V. Reproduced with permission from [122]. © 2011 IOP Publishing Ltd.

2.2.3.2 Switching and Conduction Mechanism

Although oxygen vacancies have been identified of important roles in the resistive switching of VCM RRAM, the detailed mechanism has not been unveiled. Different models have been proposed by different groups.

Regarding the switching mechanism, McKenna et al. have made an important claim that segregation energy of neutral and positively charged oxygen vacancies is lower at the (101) grain boundary by performing first principles calculation, as shown in Figure 2.25. This may imply that grain boundaries are energetically favorable for percolation paths [36].

Figure 2.25. Segregation energies (E_s) for neutral and double positively charged oxygen vacancy defects in the vicinity of the (101) twin boundary. O sites with different coordination number (i.e., number of nearest Hf neighbours) are separated for clarity. Reproduced with permission from [36]. © 2009 American Institute of Physics.

Gao et al. have developed an ion-transport-recombination model as an account of the switching phenomena in VCM RRAM, with prediction of oxygen profile, switching speed and endurance [123] (See Figure 2.26).

Figure 2.26. (a) Calculated O^{2-} concentration distribution as a function of depth from the interface with different interface barrier. (b) Calculated time evolution of O^{2-}

concentration at different point. Reproduced with permission from [123]. © 2011 American Institute of Physics.

A similar model is proposed by Chang et al. with qualitative description [124]. Joule heating effect is taken into consideration by Yu et al., which further advance the ion migration model [125].

Theoretical investigation of transport mechanism is mainly focus on the electronic properties of the states induced by oxygen vacancies. In 2006, Broqvist et al. have calculated the electronic structure of HfO_2 with oxygen vacancy at different charge state as well as its formation energy [126]. Hybrid functional was used to reduce the self-interaction caused underestimation of bandgap (See Figure 2.27).

Figure 2.27. (a) Kohn-Sham energy levels for neutral and charged oxygen vacancies in $m\text{-HfO}_2$. The valence (VB) and conduction band (CB) edges are indicated. (b) Formation energy vs. electron chemical potential for the O vacancy in $m\text{-HfO}_2$. The midgap and conduction band (CB) levels are indicated by dashed and solid vertical lines, respectively. The most stable charge states are highlighted. Reproduced with permission from [126]. © 2006 American Institute of Physics.

In 2007, Ho et al. suggested that the transport in HRS of VCM RRAM is dominated by variable-range hopping of electrons, while LRS is of metallic nature [96]. Gao et al. have proposed a universal model for carriers transport in bipolar RRAM in 2009 based on thermal assisted hopping of electrons through the chain of oxygen vacancies [127]. Momida et al. have calculated electronic properties of isolated oxygen vacancy in amorphous Al_2O_3 under the different charge conditions. The calculated DOS

is shown in Figure 2.28 [128].

Figure 2.28. Density of states (DOS) for the Vo^q in the amorphous model of the most energetically favorable configuration. Reproduced with permission from [128]. © 2011 American Institute of Physics.

Recently, a trap-assisted-tunneling model has been reported by Yu et al. [129].

2.3 Electrochemical Metallization RRAM Material System

2.3.1 General Properties

ECM type RRAMs are sometimes called atomic switches. They have received more attention in the early stage of RRAM development due to its evident switching mechanism. Different from TCM and VCM type RRAM, the active components in TCM RRAM are electrodes which can release and absorb ions. And the bulk dielectric insulating layer serves as a solid electrolyte. The mechanism has projected special requirements on selection of electrode materials that they should be easily oxidized and reduced during switching process. And the ions must have reasonable mobility in corresponding electrolyte.

2.3.1.1 Area Dependence of Resistance

In ECM RRAM, because the metal ions form filaments bridging the two electrodes, LRS resistance typically does not possess area dependence.

For HRS, both size dependent and size independent resistance has been observed. The underlying reason may be the same with that of TCM and VCM cases, which is caused by competition between current flow through ruptured filament and current flow through the rest of homogeneous dielectric layer (See Figure 2.29 and Figure 2.30).

Figure 2.29. Area independent LRS resistance and dependent HRS resistance. Reproduced with permission from [130]. © The Electrochemical Society.

Figure 2.30. Area independent LRS and HRS resistance. Reproduced with permission from [131]. © 2008 IEEE.

2.3.1.2 Temperature Dependence of Resistance

HRS may be of semiconductor behaviors where most of the reported cases show that its transport is thermally activated (See Figure 2.31).

Figure 2.31. (a) HRS current at -2V measured at elevated temperatures. (b) Corresponding HRS resistance at -2V of at temperatures up to 120 °C. Reproduced with permission from [132]. © Oldenbourg Wissenschaftsverlag, München.

In low temperature region, quite a number of papers consider the temperature dependence of LRS in the same manner with metallic nanowires (Figure 2.32). However, in high temperature region, the behaviors of LRS of ECM RRAM may severely deviate from predictions based on metallic nanowire due to temperature driven ions diffusion.

Figure 2.32. Metallic like LRS in low temperature range. Reproduced with permission from [133]. © 2011 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

2.3.1.3 Frequency Dependence of Admittance

Very few reports concern admittance (or impedance, which is the reciprocal of the admittance) as a function of frequency in ECM RRAM. According to the reported cases, similar behaviors with TCM or VCM RRAM cells have been witnessed. The circuit model of the ECM RRAM could be thought as a resistor-like filament in parallel with a non-ideal capacitor presenting the rest of the dielectric layer. For pristine device, the resistance of the filament is very large and thus non-ideal capacitor dominates the low frequency dielectric response. On the contrary, since filament in LRS is of low resistance, the low frequency response will be a direct consequence of the nanowire-like filament. (See Figure 2.33)

Figure 2.33. Impedance analysis of CuTCNQ-based memory cells in LRS (a) and HRS (b) together with the circuit model including a thin Al_2O_3 interface layer at the interface between CuTCNQ and Al top electrode. Reproduced with permission from [134]. © 2009 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

2.3.2 Material Combinations

Materials exhibiting ECM switching behaviors are of some common features that their electrodes are generally made of Ag or Cu. Table 2.3 lists some recent publications on ECM type RRAMs.

Type	Switching Region	Thickness	B E	TE	Device Size	Current	Voltage	Speed Endurance	Retention	Remarks	Ref
Carbon and	PI/GO-PI/PI	10/30/10nm	ITO	Ag	0.5mm diameter	<1mA	<5V	>130 (DC)	>1400s		[135]

Polymer	GO	30nm	Pt	Ag, Au, Cu or Ti	0.2mm diameter	<10mA (Cu/GO/Pt)	<1V (Cu/GO/Pt)	>100 (DC)	>8×10 ⁴ s		[136]
	PEO+AgClO ₄	125-500nm	Pt	Ag	50×50 μm ²	<0.1mA	<2.5V	>400 (SET/RESET: 8.3ms/8.3ms)	>10 ⁵ s		[133]
Chalcogenide Glass	Amorphous or Crystalline Ag ₁₀ Ge ₁₅ Te ₇₅	200nm	Pt	Ag	0.2mm diameter	<0.3 or 1mA	<0.3 or 0.15V	>1.5×10 ⁵ or 3.5×10 ⁵ (SET/RESET: 100ns/100ns)	NS		[137]
	Ge _{0.3} Se _{0.7}	30-120nm	Pt	Cu	50×50 - 400×400 μm ²	<0.5mA	<1V	NS	NS		[138]
	GeTe: Cu	100nm	W	Cu	2×2 μm ²	<50mA	<1V	>10 ⁶ (SET/RESET: 200ns/500ns)	>5×10 ³ s		[139]
Metal Carbide	CuC or CuC/BO	NS	Pt	Pt	50×50 μm ²	<10mA	<1.5 or 2.5V	>10 ³ (SET/RESET: 1μs/500ns)	NS	BO=Buffer Oxide	[140]
Metal Oxide	Al ₂ O ₃	50nm	Si	Cu-Te	3mm diameter	<5μA	<1V	>10 ³ (DC)	>10 ⁴ s @ 85C		[141]
	Li _x CoO ₂	100nm	Si	Au	0.1×0.4mm ²	<0.1mA	<4V	>12 (DC)	NS		[142]
	CuO	200nm	ATO	Cu	NS	<10mA	<5V	NS	NS		[143]
	SiO ₂	20nm	Pt	Cu	NS	NS	NS	NS	NS	Complementary Cell	[144]
	Ta ₂ O ₅	15nm	Pt	Cu	20×20 μm ²	<1mA	<2V	>100 (DC)	NS		[145]
	ZrO ₂ :Cu	40nm	Pt	Cu	200×100 nm ²	<0.1mA	<0.8V	NS	NS		[146]
Metal Sulfide	Ag ₂ S	<120nm	Ag	CAFM tip	44nm	<100nA	<0.5V	NS	>10hr		[147]
	Cu ₂ S	100nm	Cu	Ti	2mm diameter	<1mA	<0.4V	NS	NS		[148]

	GeS	8-60nm	Cu	Pt-Ir	<20nm diameter	<0.5 μ A	<4V	NS	NS	TE=STEM tip	[149]
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Table 2.3. Recent reports of ECM based RRAM systems.

2.3.3 ECM Mechanism Study

Microscopic inspection and identification of metal atom bridge in ECM type resistive switching system can date back to 1976 when Ag filament in Ag/As₂S₃/Ag RRAM was observed by Hirose et al. [150]. What they have discovered is that SET and RESET transitions correspond to the creation and annihilation of this metallic ion bridge, respectively. Recently, with the advancement of electron microscopy, more clear pictures of nanoscale filaments have been taken.

2.3.3.1 Physical Characterization

As shown in Figure 2.34, in a GeS resistive switching system, Fujii et al. have reported the direct observation of Cu filament by TEM with *in situ* Pt-Ir tip electrode[149]. The progressive formation and annihilation transitions have also been seen. EDX profile implies that Cu peak significantly intensifies when the electric field is applied across the filament region.

Figure 2.34. (a) TEM image and (b) SAD pattern before voltage application. Clear spots caused by Pt–Ir and weak Debye-ring patterns were observed. The latter diffraction, which did not change during the resistance switching operation, may come from the Ge nanocrystals. The indices are those of Pt–Ir. (c) TEM image and (d) SAD pattern during voltage application of 1 V. The filamentlike deposit and the appearance of fine and sharp diffraction spots forming Debye-rings were recognized. They are thought to be

from Cu nanocrystals, four of which corresponded with reflection indices. Reproduced with permission from [149]. © 2011 American Institute of Physics.

In situ observation of filament formation in GeTe electrolyte has been reported by Choi et al. [151]. HRTEM images, as shown in Figure 2.35, are about the central region of the dielectric layer where filaments locate. Such a region experiences significant changes in terms of chemical composition with voltage biasing applied.

Figure 2.35. (a) HRTEM of the middle region in electrolyte of the Pt-Ir/GeTe:Cu/Cu RRAM with $V=0$ applied at top electrode, (b) HRTEM image of the same location with $V=-0.8$ V, (c) EDS analysis of Cu/Te ratio under different biasing. Reproduced with permission from [151]. © 2011 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

For GeSe system, Chen et al. have reported time dependent evolution of precipitation and percolation of Ag cations [152] (See Figure 2.36).

Figure 2.36. (a) As deposited film (b) (c) (d) (e) 3, 60, 180, 480 minutes of electric field

(f) Zoom of (e) which shows network type precipitation. Reproduced with permission from [152]. © 2009 American Institute of Physics.

Similar observations have been made by Rahaman et al. They have identified Cu filaments in GeSe electrolyte by using HRTEM [130]. After having a few switching cycles, the GeSe electrolyte of the RRAM is inspected where the formation of Cu filament is confirmed by EDX analysis.

Figure 2.37. (a) HRTEM image of W/Ge_{0.4}Se_{0.6}/Cu memory device without external bias (i.e., fresh device), (b) HRTEM image with a small scale bar of 20 nm, (c) HAADF-STEM image of W/Ge_{0.4}Se_{0.6}/Cu memory device, (d) EDX spectrum in Ge_{0.4}Se_{0.6} layer, (e) HRTEM image with external bias and 4×10^3 cycles (i.e., LRS), and (f) HRTEM image after cycles with small scale bar of 10 nm. A Cu filament is observed clearly. (g) HAADF-STEM image after cycles (i.e., LS) and (h) EDX spectrum in Ge_{0.4}Se_{0.6} layer after P/E cycles. Reproduced with permission from [130]. © The Electrochemical Society.

An interesting visualization of Ag filaments in Ag/H₂O/Pt switching system has been reported by Guo et al. [153] (See Figure 2.38). Tree shape Ag dendrites grow from the Pt electrode towards the Ag electrode. Once the front-most dendrite has a touch of the Ag electrode, the cell will be switched on.

Figure 2.38. The switching-on process while applying -1 V to a Pt/H₂O/Ag cell with a Pt/Ag gap of $3\text{ }\mu\text{m}$: (a) I-t curve, (b), (c), and (d) SEM images showing the Ag dendrite growth after applying -1 V for about 1, 2, and 4 s, respectively. Reproduced with permission from [153]. © 2007 American Institute of Physics.

A novel way to indirectly probe the underlying electrochemical reaction is achieved by employing strain image to sense the tiny changes of volume associated with filaments by Takata et al. [148]. They employ periodic voltage signal to drive the switching in RRAM, and use AFM to record the periodic change of surface morphology (See Figure 2.39).

Figure 2.39. 20-mm-square (a) topographic, and (b) amplitude images taken with 0.5 V_{pp} at 60 kHz . 1-mm-square (c) topographic, and (d) amplitude images of the square region in (a) and (b). Reproduced with permission from [148]. © 2011 Elsevier B. V.

2.3.3.2 Switching and Conduction Mechanism

Quantitative formulation of metal cations migration in ECM type switching memory can be found from reviews by Valov et al. and Waser et al. [19, 24]. In 2009, Chen et al. have employed Monte Carlo simulation to imitate the evolution of filament

growth and rupture [154]. The electric field driven conduction bridge formation is given in Figure 2.40.

Figure 2.40. Four snapshots are taken from an evolution, and the phase-separated lattice consisted by high-conductance phase (red or dark gray) and insulating (cyan or light gray) sites. The inset is the AGS conductance as a function of MCS. The red line (solid cycle) shows the result under the positive bias and the blue line (ring) exhibits the result under the reversed bias. Reproduced with permission from [154]. © 2009 American Institute of Physics.

Similar results have been obtained by Feng et al. [155, 156] (See Figure 2.41).

Figure 2.41. Filament topographies obtained at different voltage levels. (a) Initial state. (b) $V = 0.05$ V. (c) $V = 0.25$ V. (d) $V = 0.35$ V. (e) $V = 0.8$ V. (f) $V = 2$ V. The arrows in (d) with labels “h” and “w” indicate the thickness of isotropic deposition and the average width of the filament, respectively. Reproduced with permission from [156]. © 2011 IEEE

2.4 RRAM System without an Identified Mechanism

The mechanism for some RRAM systems are still obscure, including the GO based RRAM which has been recently explored for its ease of preparation, potential application to flexible memory, and compatibility with all carbon electronics. The resistive switching in GO was first observed by He *et al.* in Cu/GO/Pt structure in 2009 [46], which was soon confirmed by Hong *et al.* on Al/GO/ITO [45, 157, 158]. Studies with different electrodes (i.e. Ag, Au and Ti) and GO recipes (i.e. reduced GO) were reported subsequently [44, 52, 135, 136, 159-161]. The underlying switching mechanisms in GO was under debate as shown in Table 2.4.

	Bipolar Switching				Unipolar Switching	
	Oxygen related functional group absorption/ release at the interface		Metal electrode ions diffusion		Nanoelectromechanical Effect (NEM)	
Physical Characterization	XPS on Al/GO/Al [44]		XPS on Al/GO/ITO [162]		AFM on Al/RGO/ITO [52]	
	REBIC on Al/GO/Al [160]					
	XPS on Al/GO/ITO [162]					
Field Dependence	Non-linear LRS and HRS field dependence	Al/GO/Al [44]	Linear LRS and non-linear HRS field dependence	Cu/GO/Pt [46]	Linear LRS and non-linear HRS field dependence	Al/RGO/ITO [52]
				Al/GO/ITO [45, 157, 158, 162]		
				(Ag,Au,Cu,Ti)/GO/Pt [136]		
				Al/GO/ITO [161]		
Temperature Dependence	N. A.		Temperature Independent R_{LRS} in Cu/GO/Pt [136]		N. A.	
Area Dependence	Area Dependent R_{HRS} , R_{LRS} [162]		N. A.		N. A.	

Table 2.4. Literature summary of mechanisms study on GO based resistive switching.

For bipolar switching, two interpretations had been proposed. The first suggested that the absorption and release of oxygen related functional groups were responsible for the bipolar switching in GO, which shared resemblance with homogeneous Valence Change Mechanism (VCM) type switching in inorganic materials [19]. This explanation received partial support from REBIC profile at the GO/metal interface and XPS depths profile of oxygen where HRS and LRS were identified with distinct oxygen bonding near the interface [44, 160, 162]. Besides, as the switching was homogeneous, it should be accompanied with strong area

dependence, which had been witnessed by Hong *et al.* [162]. The other interpretation of bipolar switching in GO was based on the diffusion of metallic ions from the electrodes, which was similar to the Electrochemical Metallization mechanism (ECM). This was partially supported by the observed Ohmic transport [45, 46, 136, 157, 158, 161, 162] (i.e. linear field dependence in LRS and temperature independent R_{LRS} . See Table 2.4 also). And a recent XPS study on Al/GO/ITO had also suggested the possibility of Al diffusion in GO [162]. Unipolar resistive switching in reduced GO was first reported by Vasu *et al.* in Al/RGO/ITO where the switching had been attributed to Nanoelectromechanical (NEM) effect [52]. Besides, for bipolar switching in GO, different switching directions had been observed (See Table 2.5). The origin of these switching directions and their implication to switching mechanism are of great importance to understand the underlying mechanism.

Switching Direction	Bipolar Switching		Unipolar Switching
	Clockwise (CW)	Anticlockwise (AW)	
	Al/GO/ITO [45, 157, 158, 162]	Cu/GO/Pt [46]	Al/RGO/ITO[52]
		(Ag, Au, Cu, Ti)/GO/Pt [136]	
		Ag/PI/GO:PI/PI/ITO [135]	
		Al/GO/ITO [161]	

Table 2.5. Literature summary of reported bipolar resistive switching direction in GO. Bottom electrode is presumed to be grounded.

2.5 Theory of the Frequency-Dependent Loss in Non-crystalline Semiconductors

The measurement of the low-frequency dielectric response of a resistive switching device is an effective technique to study the underlying electronic properties, especially the band gap states, of the resistive switching semiconductors. The theoretical treatment of the dielectric loss originated from the pioneering works of Pollak.[163] And unified theoretical reviews were accomplished by Long and Elliot which serves as the basis of the mathematical formulation presented in this section.[164, 165]

2.5.1 Definition of A. C. Dielectric Loss

The complex permittivity can be written as $\varepsilon = \varepsilon_0(\varepsilon_1 + j\varepsilon_2)$. The alternative expression of the permittivity is the complex A. C. conductivity which is of the form $\sigma = \sigma_1 + j\sigma_2$. The conversion between permittivity and conductivity is given in Eqn. (2.1) while the correlation between the real part and imaginary part follows the Kramers-Kronig transform.

$$\begin{aligned}\sigma_1 &= \varepsilon_0 \varepsilon_1 \omega \\ \sigma_2 &= \varepsilon_0 \varepsilon_2 \omega\end{aligned}\tag{2.1}$$

2.5.2 Nature of A. C. loss

The objective of doing A. C. current loss measurement is to investigate into the properties of electronic states deep in the principal band gap which dominated the A. C. dielectric loss. The sources of these band gap states are irregularities of the lattice or the discontinuities of atom network.

The presence of these states has impact on electronic properties. In the case of high concentration band gap states, the transport may be dominated by carriers flowing through these states, especially at low temperature. For the system with low

concentration gap states, recombination centres or Fermi level pinning are frequently observed. [163]

Nature of A. C. current loss process comes from the interaction between the gap states and the external varying electric field. Centres develop electron dipole moments under the influence of the applied field. A well acknowledged picture is that centres interact with applied field in pairs. And the interactions of the applied field with such a pair can in general be split into the following two groups. [164]

- Resonant Absorption: This group typically dominates in the high frequency.

Due to the interaction between those paired two centres, or systems of two well coupled harmonic oscillators shown in Figure 2.42, the ground level splitting occurs. The photon causes transition of electron from ground level to the split level.

Figure 2.42 Schematic illustration of the resonant absorption. The ground level splitting is depicted by the two red lines. The electron is represented by the yellow ball. The arrow stands for the photon.

- Dielectric Relaxation (generally for low frequency loss): In relaxation processes, because of applied field, electron transitions between centres occur. The resultant loss is dominated by pairs with relaxation time ω^{-1} .

2.5.3 The Model for Frequency-Dependent Loss by Relaxation

To simplify the modelling of low frequency dielectric loss, the scope is confined to the loss due to the dielectric relaxation rather than the resonant absorption where the latter has limited contribution to the low frequency dielectric loss. In this case, the nature of the loss is due to electron transfer between states deep within the band gap. It should be noted that there is a difference between the D. C. conduction and A. C. conduction. For the D. C. case, continuous percolation paths are desired, while for the A. C. case the transfer of an electron takes place between a pair sites which can be isolated from the rest sites.

2.5.3.1 The Partition Function

Under the pair approximation, each site is capable to accommodate 2 electrons. The Hubbard term is denoted as U , which is same for both sites. The inter-site correlation is defined as E_{12} . The relaxation of the lattice is ignored here for simplicity. The energy and degeneracy of the various occupation states of the joint system is summarized in Table 2.6.

Total Electrons	Site 1	Site 2	Energy of paired sites	Degeneracy
0	0	0	0	1
1	1	0	E_1	$2(\uparrow; \downarrow)$
1	0	1	E_2	$2(\uparrow; \downarrow)$
2	1	1	$E_1 + E_2 + E_{12}$	$4(\uparrow, \uparrow; \uparrow, \downarrow; \downarrow, \uparrow; \downarrow, \downarrow)$
2	2	0	$2E_1 + U$	$1(\uparrow\downarrow)$
2	0	2	$2E_2 + U$	$1(\uparrow\downarrow)$
3	2	1	$2E_1 + E_2 + 2E_{12} + U$	$2(\uparrow\downarrow, \uparrow; \uparrow\downarrow, \downarrow)$
3	1	2	$E_1 + 2E_2 + 2E_{12} + U$	$2(\uparrow, \uparrow\downarrow; \downarrow, \uparrow\downarrow)$
4	2	2	$2E_1 + 2E_2 + 4E_{12} + 2U$	$1(\uparrow\downarrow; \uparrow\downarrow)$

Table 2.6 Configuration, energy and degeneracy of different occupation states of the paired center system.

For the grand canonical ensemble, the temperature is constant, but the population of the particles is not fixed, with the partition function written of the form shown in Eqn. (2.2).

$$\begin{aligned}
Z &= \sum_{N=0}^{\infty} \sum_{\{n_i\}} \prod_i \exp[-\beta n_i (\varepsilon_i - \mu)] \\
&= 1 + 2 \exp[-\beta 2(E_1 - \mu)] \\
&\quad + 2 \exp[-\beta 2(E_2 - \mu)] + 4[-\beta 4(E_1 + E_2 + E_{12} - 2\mu)] \\
&\quad + \exp[-\beta(2E_1 + U - 2\mu)] + \exp[-\beta(2E_2 + U - 2\mu)] \quad (2.2) \\
&\quad + 2 \exp[-\beta 2(2E_1 + E_2 + 2E_{12} + U - 3\mu)] \\
&\quad + 2 \exp[-\beta 2(E_1 + 2E_2 + 2E_{12} + U - 3\mu)] \\
&\quad + \exp[-\beta(2E_1 + 2E_2 + 4E_{12} + 2U - 4\mu)]
\end{aligned}$$

For the treatment of the single electron case, only the first four terms are needed. An additional assumption that U is much larger than the distribution of E_1 and E_2 is made in the subsequent formulation. To make the equation more neat, define the reference zero energy point according to Eqn. (2.3).

$$0 \equiv \mu + kT \ln(2) \quad (2.3)$$

Rewrite the grand partition function yields the form shown in Eqn. (2.4) which is of less terms than that of Eqn.(2.2).

$$Z = 1 + \exp(-\beta E_1) + \exp(-\beta E_2) + [-\beta(E_1 + E_2 + E_{12})] \quad (2.4)$$

The probability of having a single electron in site 1 and nothing in site 2 under thermal equilibrium is thus given by Eqn. (2.5).

$$\begin{aligned}
h_1^0 &= \frac{\exp(-\beta E_1)}{1 + \exp(-\beta E_1) + \exp(-\beta E_2) + [-\beta(E_1 + E_2 + E_{12})]} \\
&= \frac{\exp\left[-\frac{1}{2}\beta(E_1 - E_2)\right]}{2 \cosh\left[\frac{1}{2}\beta(E_1 - E_2)\right] + \exp\left(-\frac{1}{2}\beta E_2\right) 2 \cosh\left[-\frac{1}{2}\beta(E_1 + E_2 + E_{12})\right]} \quad (2.5)
\end{aligned}$$

2.5.3.2 The Rate Equation in the Equilibrium

Under the equilibrium, the net transition rate is zero as revealed by the rate equation Eqn. (2.6) where ω_{ij}^0 stands for the equilibrium transition rate from site i to site j .

$$\frac{\partial h_1^0}{\partial t} = \omega_{21}^0 h_2^0 - \omega_{12}^0 h_1^0 = -\frac{\partial h_2^0}{\partial t} = 0 \quad (2.6)$$

2.5.3.3 The Polarizability

The rate equations may then be linearized and solved for a small perturbation, leading to a polarizability given by Eqn. (2.7). [164] The expression of polarizability is a function of the frequency, energies, and separation.

$$\begin{aligned}
 \alpha(\omega, E_1, E_2, E_{12}, R_{12}) &= \frac{e^2 R_{12}^2}{2kT} \frac{\omega_{21}^0 h_2^0 + \omega_{12}^0 h_1^0}{\omega_{21}^0 + \omega_{12}^0} \frac{1}{1 + i\omega\tau(E_1, E_2, R_{12})} \\
 &= \frac{e^2 R_{12}^2}{2kT} \frac{2h_1^0 h_2^0}{h_1^0 + h_2^0} \frac{1}{1 + i\omega\tau(E_1, E_2, R_{12})} \\
 &= \frac{e^2 R_{12}^2}{4kT} \frac{1}{1 + i\omega\tau(E_1, E_2, R_{12})} \frac{1}{\cosh\left[-\frac{1}{2}\beta(E_1 - E_2)\right]} \\
 &\quad \frac{1}{\left\{ \cosh\left[\frac{1}{2}\beta(E_1 - E_2)\right] + \exp\left(-\frac{1}{2}\beta E_2\right) \cosh\left[-\frac{1}{2}\beta(E_1 + E_2 + E_{12})\right] \right\}}
 \end{aligned} \tag{2.7}$$

2.5.3.4 Conduction in terms of Frequency, Energies, and Relaxation Time

Assume the density of band gap states is g_0 and all pairs are uniformly distributed with all possible energy combinations, inter-site distances, and orientations. For a specific site 1 associated with energy E_1 , it's necessary to integrate all the possible site 2 energy E_2 and inter-site distance R_{12} . Since there is an applied field, it's also necessary to integrate over all possible orientation of paired sites θ to give the average polarizability $\bar{\alpha}$. [164]

$$\bar{\alpha}(\omega, E_1) = \int dE_2 \int dR_{12} \int d\theta \alpha(E_1, E_2, E_{12}, R_{12}) 2\pi g_0 R_{12}^2 \sin \theta \tag{2.8}$$

In integrate the Eqn. (2.8) over all possible E_1 and introduce a prefactor 0.5 for twice counting, the frequency dependent conductance is given by Eqn. (2.9).

$$\begin{aligned}\sigma(\omega) &= \frac{i\omega}{2} \int dE_1 \bar{\alpha}(E_1) g_0 \\ &= \frac{\pi}{6} e^2 \beta g_0^2 \int dR_{12} \int dE_1 \int dE_2\end{aligned}\quad (2.9)$$

$$\frac{R_{12}^4 \frac{i\omega}{1+i\omega\tau(E_1, E_2, R_{12})}}{\cosh\left[-\frac{1}{2}\beta(E_1 - E_2)\right] \left\{ \cosh\left[\frac{1}{2}\beta(E_1 - E_2)\right] + \exp\left(-\frac{1}{2}\beta E_{12}\right) \cosh\left[-\frac{1}{2}\beta(E_1 + E_2 + E_{12})\right] \right\}}.$$

The real part of the conductance is thus given by Eqn. (2.10).

$$\begin{aligned}\sigma_1(\omega) &= \frac{\pi}{6} e^2 \beta g_0^2 \int dR_{12} \int dE_1 \int dE_2 R_{12}^4 \\ &\quad \frac{\omega^2 \tau(E_1, E_2, R_{12})}{1 + \omega^2 \tau^2(E_1, E_2, R_{12})} \cosh^{-1}\left[-\frac{1}{2}\beta(E_1 - E_2)\right] \\ &\quad \left\{ \cosh\left[\frac{1}{2}\beta(E_1 - E_2)\right] + \exp\left(-\frac{1}{2}\beta E_{12}\right) \cosh\left[-\frac{1}{2}\beta(E_1 + E_2 + E_{12})\right] \right\}^{-1}\end{aligned}\quad (2.10)$$

2.5.3.5 Relaxation Time of Different Mechanisms

The conductance in Eqn. (2.9) is a function of the relaxation time τ . Depending on the energy of excitation, the relaxation time may have different forms. For the relatively high energy excitation corresponding to multi-phonon process, the relaxation time can be approximated by τ_{high} in the Eqn. (2.11). For relatively small energy excitation due to single-phonon process, the relaxation time is better represented by τ_{low} . [164]

$$\begin{aligned}\tau_{\text{high}}(E_1, E_2, R_{12}) &= \frac{\tau_0(R_{12})}{2} \left[\cosh\left(\frac{|E_1 - E_2|}{2kT}\right) \right]^{-1} \\ \tau_{\text{low}}(E_1, E_2, R_{12}) &= \frac{1}{B(R_{12})|E_1 - E_2|} \tanh\left(\frac{|E_1 - E_2|}{2kT}\right)\end{aligned}\quad (2.11)$$

Assumption is made that the origin and destination energy levels, E_1 and E_2 , are of small difference compared to kT . This assumption removes the site energy dependence of the relaxation time.

$$\begin{aligned}\tau_{\text{high}}(R_{12}) &\approx \frac{\tau_0(R_{12})}{2} \\ \tau_{\text{low}}(R_{12}) &\approx \frac{1}{B(R_{12})}\end{aligned}\quad (2.12)$$

The term τ_0 of the equations above is dependent on the nature of the transport.

Commonly used forms of τ_0 is summarized in Table 2.7.

Type	Description	Relaxation Time
Electron Tunnelling	Direct coupling due to the overlap of the exponentially decaying wave functions.	Relaxation time is generally a function of separation. The α is a measure of decaying of the localized wavefunction, for multi-phonon high energy excitation. $\tau_0(R_{12}) = 2\tau_{0t} \exp(2\alpha R_{12})$
Electron Hopping (correlated barrier case)	Thermal activation of a charged carrier over the potential.	Relaxation time is generally a function of activation energy. In multi-phonon case, $W(R_{12})$ is the correlated potential barrier for hopping, which is separation dependent. $\tau_0(R_{12}) = 2\tau_{0h} \exp\left[\frac{W(R_{12})}{kT}\right]$
Polaron	Polaron motion is both separation and activation dependent.	r_0 is polaron radius, for small polaron it's 0. W_{H0} is activation energy for polaron tunnelling. In high temperature case, $\tau_0(R_{12}) = 2\tau_{0p} \exp\left[\frac{W_{H0}}{kT} \left(1 - \frac{r_0}{R}\right)\right] \exp(2\alpha R_{12})$ In low temperature region, assume ω_0 is characteristic frequency of lattice vibration $\tau_0(R_{12}) = 2\tau_{0p} \exp\left[\frac{W_{H0}}{\frac{1}{4}\hbar\omega_0} \left(1 - \frac{r_0}{R}\right)\right] \exp(2\alpha R_{12})$

Table 2.7 Relaxation time factor τ_0 of different mechanisms.

2.5.3.6 Typical Analytic A. C. Conductivity

Based on the Table 2.7, the analytic form of relaxation time due to electron tunnelling, correlated barrier hopping, and polaron tunnelling is able to be written down.

Thus, the corresponding A. C. conductivity can be analytically derived.

- **Electron Tunnelling**

For electron tunnelling induced relaxation, the case that intersite correlation E_{12} is negligible will be studied first which presumes a relaxation time based on multi-phonon process. Since $\tau_0(R_{12}) = 2\tau_{0t} \exp(2\alpha R_{12})$, in order to achieve analytic solution, approximation must be used. Note that the relaxation time is varying very fast with R , thus R is varying very slowly with τ . Moreover, $\frac{\omega\tau(R_{12})}{1 + \omega^2\tau^2(R_{12})}$ reaches its maximum value at $\omega\tau(R_\omega) = 1$. Thus, the integral over R_{12} can be replaced by the integral over τ with fixed $R = R_\omega$.

$$\begin{aligned}\tau(R_{12}) &= \tau_{0t} \exp(2\alpha R_{12}) \\ dR_{12} &= \frac{1}{\tau 2\alpha} d\tau\end{aligned}\tag{2.13}$$

The conductivity now takes the form of Eqn. (2.14).

$$\begin{aligned}\sigma_1(\omega) &= \frac{\pi}{6} e^2 \beta g_0^2 \frac{\omega}{2\alpha} \int d(\omega\tau) \frac{R_\omega^4}{1 + \omega^2\tau^2} \\ &\quad \int dE_2 \cosh^{-1} \left[-\frac{1}{2} \beta(E_1 - E_2) \right] \\ &\quad \int dE_1 \int \left\{ \cosh \left[\frac{1}{2} \beta(E_1 - E_2) \right] + \cosh \left[-\frac{1}{2} \beta(E_1 + E_2) \right] \right\}^{-1} \\ &\quad dE_2 \cosh^{-1} \left[-\frac{1}{2} \beta(E_1 - E_2) \right] \\ &= \frac{\pi}{12\alpha} e^2 \beta g_0^2 \omega R_\omega^4 \int dE_1 \int \left\{ \cosh \left[\frac{1}{2} \beta(E_1 - E_2) \right] \right. \\ &\quad \left. + \cosh \left[-\frac{1}{2} \beta(E_1 + E_2) \right] \right\}^{-1} dE_2 \cosh^{-1} \left[-\frac{1}{2} \beta(E_1 - E_2) \right]\end{aligned}\tag{2.14}$$

Assume the bandwidth is much wider than the kT , the integrals in Eqn. (2.14)

can be performed analytically which gives the conductivity in Eqn. (2.15).

$$\sigma_1(\omega) = \frac{\pi^4}{12} \frac{e^2 g_0^2 kT}{2\alpha} \omega R_\omega^4\tag{2.15}$$

To facilitate comparison with experimentally observed frequency and temperature dependence, define the frequency exponent s and temperature exponent n

according to $\sigma_1(\omega) \propto \omega^{s(\omega)} T^{n(\omega)}$. Take derivatives, the frequency exponent s in the case of electron tunnelling is given by Eqn. (2.16).

$$s(\omega) = \frac{\partial [\ln(\sigma_1)]}{\partial [\ln(\omega)]} = 1 + \frac{4}{\ln(\omega \tau_{0t})} \quad (2.16)$$

The value of s in low frequency range is close to 0.8. The temperature exponent n in the case of electron tunnelling is given by Eqn. (2.17).

$$n(\omega) = \frac{\partial [\ln(\sigma_1)]}{\partial [\ln(T)]} = 1 \quad (2.17)$$

Recall that the intersite correlation E_{12} is not considered the derivation above. This applies to the condition that E_{12} is much smaller than the kT . (See Table 2.8) However, in case E_{12} is of similar magnitude with kT , no analytic form can be reached for both E_{12} and the conductivity. If E_{12} is much larger than kT , approximation of E_{12} can be made as given in Table 2.8.

Condition	Approximation of E_{12}
$E_{12} \ll kT$	0
$E_{12} \sim kT$	No analytic form
$E_{12} \gg kT$	$E_{12}(R_{12}) = \frac{e^2}{4\pi\epsilon_0 R_{12}}$

Table 2.8 Approximation of intersite correlation E_{12} in different conditions.

Following the same procedure of derivation, the conductivity in this case is given by Eqn. (2.18). And it can be note that the temperature exponent n is less by 1 if the intersite correlation E_{12} is retained.

$$\sigma_1(\omega) = \frac{\pi^2}{3} \frac{e^4 g_0^2 \omega}{4\pi\epsilon\epsilon_0 2\alpha} R_{\omega}^3 \quad (2.18)$$

- **Correlated barrier hopping**

The reported treatment of correlated barrier hopping case ignores the intersite correlation energy E_{I2} . [164] Recall that the relaxation time is proportional to the exponential of the barrier. (See Eqn. (2.19))

$$\tau_0(R_{12}) = 2\tau_{0h} \exp\left[\frac{W(R_{12})}{kT}\right] \quad (2.19)$$

The barrier function $W(R_{12})$ follows the model of Pike that there are two localized states separated by a potential barrier, as shown in Figure 2.43 (a). The individual states are illustrated in Figure 2.43 (b) and Figure 2.43 (c) [166]

Figure 2.43 (a) Schematics of two localized states separated by a potential barriers (b) The orbital of the state E_1 where the electron localizes on one of the centers (c) The orbital of the state E_2 where the electron mainly localizes on the other center.

Assume E_1 and E_2 are energy levels close to each other, W_m is the energy required to totally ionize/free the electron from these two states. The barrier function is of the form Eqn. (2.20).

$$W(R_{12}) = W_m - \frac{e^2}{\pi\epsilon\epsilon_0 R_{12}} \quad (2.20)$$

The second term of Eqn. (2.20) is due to electric potential. The equation has its minimum value when the electron is just located at the middle of the line contacting the two centres.

Consider the multi-phonon type of relaxation time, same numerical technique (replace integral variable as relaxation time and assume a constant R_ω) applies to the relaxation time.

$$\begin{aligned}
\tau_0(R_{12}) &= 2\tau_{0h} \exp\left[\frac{W(R_{12})}{kT}\right] \\
\tau(R_{12}) &= \tau_{0h} \exp\left[\frac{W(R_{12})}{kT}\right] \\
dR_{12} &= \frac{kT}{\tau} \frac{\partial R_{12}(W)}{\partial W} \Big|_{R=R_\omega}
\end{aligned} \tag{2.21}$$

The integration of the conductivity is given by Eqn. (2.22).

$$\begin{aligned}
\sigma_1(\omega) &= \frac{\pi}{6} e^2 g_0^2 \omega \int d(\omega\tau) \frac{R_\omega^4}{1+\omega^2\tau^2} \frac{\partial R_{12}(W)}{\partial W} \Big|_{R=R_\omega} \\
&\quad \int dE_1 \int \frac{dE_2 \cosh^{-1}\left[-\frac{1}{2}\beta(E_1 - E_2)\right]}{\left\{ \cosh\left[\frac{1}{2}\beta(E_1 - E_2)\right] + \cosh\left[-\frac{1}{2}\beta(E_1 + E_2)\right] \right\}^{-1}} \\
&= \frac{\pi^2}{12} e^2 g_0^2 \omega R_\omega^4 \frac{\partial R_{12}(W)}{\partial W} \Big|_{R=R_\omega} \\
&\quad \int dE_1 \int \frac{dE_2 \cosh^{-1}\left[-\frac{1}{2}\beta(E_1 - E_2)\right]}{\left\{ \cosh\left[\frac{1}{2}\beta(E_1 - E_2)\right] + \cosh\left[-\frac{1}{2}\beta(E_1 + E_2)\right] \right\}^{-1}}
\end{aligned} \tag{2.22}$$

For narrow band limit where the distribution width is much smaller than kT or broad band limit where the distribution is much larger than kT , the integral over E_1 and E_2 can be carried out in the way given by Eqn. (2.23).

$$\begin{aligned}
\sigma_1(\omega) &= \frac{\pi^2}{24} N^2 e^2 \omega R_\omega^4 \frac{\partial R_{12}(W)}{\partial W} \Big|_{R=R_\omega} \\
\sigma_1(\omega) &= \frac{\pi^2}{12} g_0^2 (kT)^2 \omega R_\omega^4 \frac{\partial R_{12}(W)}{\partial W} \Big|_{R=R_\omega}
\end{aligned} \tag{2.23}$$

The frequency dependence exponent s , as given by Eqn. (2.24), decreases with the temperature.

$$s(\omega) = \frac{\partial[\ln(\sigma_1)]}{\partial[\ln(\omega)]} = 1 - 6 \frac{kT}{W_m + kT \ln(\tau_{oh}\omega)} \tag{2.24}$$

The temperature dependence exponent n for narrow band is shown in Eqn. (2.25). On the other hand, broad band temperature dependence exponent n increases by 2.

$$n(\omega) = \frac{\partial [\ln(\sigma_1)]}{\partial [\ln(T)]} = -6 \frac{kT \ln(\tau_{oh} \omega)}{W_m + kT \ln(\tau_{oh} \omega)} \quad (2.25)$$

- Polaron Tunnelling

There are two classes of polarons which are small polarons and large polarons depending on the lattice deformation volume. Small polarons are influential to local bonds. Their distortion of sites are not overlapping. For large polarons, their polarization of lattice feature for long range Coulomb interaction. Small polaron at high temperature has relaxation time factor τ_0 given by Eqn. (2.26).

$$\tau_0(R_{12}) = 2\tau_{0p} \exp\left(\frac{W_{H0}}{kT}\right) \exp(2\alpha R_{12}) \quad (2.26)$$

Eqn. (2.26) shares strong resemblance with that of the single electron tunnelling case because the first exponential factor is separation independent, which can be treated as a constant. The frequency dependence exponent s is given by Eqn. (2.27).

$$s(\omega) = \frac{\partial [\ln(\sigma_1)]}{\partial [\ln(\omega)]} = 1 + \frac{4}{\ln(\omega \tau_{0r}) + \frac{W_H}{kT}} \quad (2.27)$$

Large polaron has a relaxation time τ_0 given by Eqn. (2.28).

$$\tau_0(R_{12}) = 2\tau_{0p} \exp\left[\frac{W_{H0}}{\frac{1}{4}\hbar\omega_0} \left(1 - \frac{r_0}{R}\right)\right] \exp(2\alpha R_{12}) \quad (2.28)$$

Using the barrier function $W(R_{12})$ of Pike, the relaxation factor and relaxation time are of a more neat form given by Eqn. (2.29).

$$\begin{aligned}
\tau_0(R_{12}) &= 2\tau_{0h} \exp\left[\frac{W(R_{12})}{kT}\right] \\
\tau(R_{12}) &= \tau_{0h} \exp\left[\frac{W(R_{12})}{kT}\right] \\
dR_{12} &= \frac{kT}{\tau} \frac{\partial R_{12}(W)}{\partial W} \Big|_{R=R_\omega} \\
dR_{12} &= \frac{d\tau}{\tau \left(2\alpha + \frac{W_{H0}r_0}{kTR_{12}^2}\right)}
\end{aligned} \tag{2.29}$$

The conductivity is thus given by Eqn. (2.30)

$$\begin{aligned}
\sigma_1(\omega) &= \frac{\pi}{6} e^2 \beta g_0^2 \omega \int d(\omega\tau) \frac{R_\omega^4}{1 + \omega^2 \tau^2} \frac{1}{2\alpha + \frac{W_{H0}r_0}{kTR_\omega^2}} \\
&\int dE_1 \int dE_2 \cosh^{-1} \left[-\frac{1}{2} \beta (E_1 - E_2) \right] \\
&\left\{ \cosh \left[\frac{1}{2} \beta (E_1 - E_2) \right] + \cosh \left[-\frac{1}{2} \beta (E_1 + E_2) \right] \right\}^{-1} \\
&= \frac{\pi^2}{12} e^2 \beta^2 g_0^2 \omega \frac{R_\omega^4}{2\alpha + \frac{W_{H0}r_0}{kTR_\omega^2}} \\
&\int dE_1 \int dE_2 \cosh^{-1} \left[-\frac{1}{2} \beta (E_1 - E_2) \right] \\
&\left\{ \cosh \left[\frac{1}{2} \beta (E_1 - E_2) \right] + \cosh \left[-\frac{1}{2} \beta (E_1 + E_2) \right] \right\}^{-1}
\end{aligned} \tag{2.30}$$

Chapter 3 Germanium Doped Hafnium Oxide RRAM with Improved Switching Performance

3.1 Experiment

Six different RRAM samples have been used in this study (See Figure 3.1 (a-f) and Table 3.1). The bottom electrodes of all devices are made of Pt deposited by the electron beam evaporation on the Si substrate with a Ti layer for adhesion purpose. For structures (c), (d) and (f), a thin layer of Ge of thickness 3/3/7.5 nm has been evaporated on top of the Pt electrodes. A HfO₂ layer of thickness 7.5 nm has been formed on the Pt electrodes in both structure (a) and (b), via oxidation of sputtered Hf metal layer and ALD, respectively. A subsequent 4.5 nm ALD HfO₂ layer has been grown on structure (c) and (e). Two additional layers, one 2.5 nm ALD HfO₂ layer followed by a 2 nm ALD Al₂O₃ layer, have been deposited on top of the Ge layer in structure (d). The overall physical thickness of the dielectric stacks in structure (a)-(d) and (f) is around 7.5 nm after the fabrication while the thickness of structure (e) is about 4.5 nm. Nitrogen ambience 425 °C annealing has been applied for all devices. The top TiN electrodes have been deposited by reactive sputtering and patterned by standard lithography processes. All devices concerned in this chapter are of a circular cross-sectional area with diameter of 200 µm. Electrical characterization has been performed by a Keithley 4200 semiconductor analyzer along with a SUSS probe station.

Figure 3.1. Sketch of (a) TiN/HfO₂(PVD,7.5nm)/Pt memory cell, (b) TiN/HfO₂(ALD,7.5nm)/Pt memory cell, (c) TiN/HfO₂(ALD,4.5nm)/Ge(3nm)/Pt memory cell, (d) TiN/Al₂O₃(ALD,2nm)/HfO₂(ALD,2.5nm)/Ge(3nm)/Pt memory cell, (e) TiN/HfO₂(ALD,4.5nm)/Pt memory cell, and (f) TiN/Ge (7.5nm)/Pt memory cell.

Structure	(a)	(b)	(c)	(d)	(e)	(f)
TE	TiN	TiN	TiN	TiN	TiN	TiN
Dielectric Layer	PVD HfO ₂ (7.5nm)	ALD HfO ₂ (7.5nm)	ALD HfO ₂ (4.5nm)	ALD HfO ₂ (2.5nm)/Al ₂ O ₃ (2nm)	ALD HfO ₂ (4.5nm)	N. A.
Ge Layer	N. A.	N. A.	3nm	3nm	N. A.	7.5nm
BE	Pt	Pt	Pt	Pt	Pt	Pt
Average V _{Forming}	3.80V	6.44V	N. A.	N. A.	2.68V	N. A.
Average V _{SET}	1.0V	0.9V	1.1V	1.2V	1.0V	N. A.
Average V _{RESET}	-0.9V	-1.2V	-1.3V	-1.3V	-0.9V	N. A.
Self Compliance	No	Yes	Yes	Yes	Yes	No Switching
R _{PRISTINE}	5.2×10 ⁹	8.6×10 ¹⁰	6.9×10 ²	5.8×10 ²	2.2×10 ⁸	1.1×10 ²

R_{LRS}	5.2×10^2	1.5×10^4	9.7×10^2	7.2×10^2	1.6×10^3	No Switching
R_{HRS}	2.7×10^4	2.4×10^5	1.7×10^4	5.5×10^4	8.7×10^3	
Average ON/OFF	52	16	18	72	5	
$C_V(R_{LRS})$	17.00%	18.00%	5.81%	11.30%	62.40%	
$C_V(R_{HRS})$	32.10%	49.70%	10.28%	16.10%	36.18%	

Table 3.1. Performance summary of the six fabricated devices. The Coefficient of variation (C_V) is defined as the ratio of standard deviation to mean. Value of forming voltage is the average of those of 10 randomly selected devices. Average ON/OFF ratio is calculated as the ratio of HRS mean resistance to LRS mean resistance at $|0.1V|$.

3.2 Results and Discussion

One hundred times dc cycling I-V curves of the 6 different structures are illustrated in Figure 3.2. The structure (f) shows no resistive switching, which may imply that the HfO_2 layer is essential for the reproducible switching. A 10 mA compliance is critical to ensure structure (a) has no risk of facing hard breakdown. The structure (b), (c) and (d) have shown the self-compliance property with maximum LRS current less than 10 mA. As suggested by Bum et al. [167], the random distribution of metallic tantalum atoms is of great importance for self-compliance of Ta_2O_5 RRAM cell because the metal atoms in the dielectric stack are equivalent to unbreakable resistor in series to limit the current in breakdown process. In our case, ALD deposited devices have been post annealed in nitrogen ambience so that metallic hafnium atoms, like the tantalum atoms which could provide the external resistance to prevent breakdown, may exist. As a contrast, the PVD deposited devices have been annealed in oxygen ambience, which results in little remaining of metallic hafnium atoms and therefore not enough unbreakable resistance in series. To verify this assumption, 450 °C

10 minutes oxygen ambience annealing has been applied to the TiN/HfO₂(ALD,7.5nm)/Pt RRAM cell.

Figure 3.2. 100 cycles of dc sweeps at room temperature of the 6 fabricated devices. (a) TiN/HfO₂(PVD,7.5nm)/Pt memory cell, (b) TiN/HfO₂(ALD,7.5nm)/Pt memory cell, (c) TiN/HfO₂(ALD,4.5nm)/Ge(3nm)/Pt memory cell, (d) TiN/Al₂O₃(ALD,2nm)/HfO₂(ALD,2.5nm)/Ge(3nm)/Pt memory cell, (e) TiN/HfO₂(ALD,4.5nm)/Pt memory cell, and (f) TiN/Ge (7.5nm)/Pt memory cell.

As mentioned, the self-compliance in this study is achieved by employing ALD technique due to its precise control of the stoichiometry. Unlike PVD technique of

which oxidation of hafnium metal is done by reactive sputtering or post deposition annealing, ALD avoids excessive oxygen in the film, which is a key step to achieve self-compliance. As depicted in Figure 3.3(a), the leakage current has been suppressed in the forming stage with oxygen ambience annealed samples. Figure 3.3(b) is about the 1st RESET transition stage. The annealed samples feature for large LRS current, which is probably a result of harder breakdown in forming process. And 3 out of 10 oxygen ambience annealed devices have exhibited a two stage SET transitions hitting 10 mA compliance limit, which has been observed in the TiN/HfO₂(PVD, 7.5nm)/Pt sample (no self-compliance) as well (Refer to Figure 3.3(c) and Figure 3.2(a)). Different from all self-compliance of non-annealed devices, this result implies that the post-deposition oxygen ambience annealing has a trend to increase the probability of hard dielectric breakdown, which may stem from oxidation of metallic hafnium or germanium. Thus, the proper deposition and annealing condition are pre-requisites of the self-compliance property of HfO₂ based RRAM. On the other hand, the ALD capping is of the advantage in precise thickness control and high layer conformity, which greatly suppresses the device-to-device performance variation. This originates from the merits of ALD, featuring self-limiting and surface reactions. On the contrary, the PVD sputtering deposition is of a relatively low film conformity, degrading the device-to-device uniformity.

Figure 3.3. (a) Forming process of TiN/HfO₂(ALD,7.5nm)/Pt memory cell before and after oxygen ambience annealing. (b) 1st RESET transition of TiN/HfO₂(ALD,7.5nm)/Pt memory cell before and after oxygen ambience annealing. (c) 1st SET transition of TiN/HfO₂(ALD,7.5nm)/Pt memory cell before and after oxygen ambience annealing.

The origin of the forming free property has been investigated in our study. Figure 3.4 consists of the forming or forming-free I-V characteristics of the 6 devices. It has been observed that the forming voltage increases with the physical thickness of the dielectric oxide. As an example, the forming voltage of TiN/HfO₂(ALD,4.5nm)/Pt is around 2.68V but that of TiN/HfO₂(ALD,7.5nm)/Pt structure is about 6.44V (See Figure 3.4(a), (b) and Table 3.1). However, the introduction of the thin Ge metallic layer makes the structure (c) and (d) forming-free with the same thickness of oxide. A very possible scenario to account this difference is the diffusion of the Ge atoms which, serving as dopants, penetrate into the HfO₂ layer and significantly increase leakage current. The structure (f) is forming-free and of large conductance as depicted by Figure 3.2(f) and Figure 3.4(d), which suggests that Ge is not completely oxidized in this fabrication approach.

Figure 3.4. Forming processes of the 6 fabricated devices. (a) TiN/HfO₂(ALD,4.5nm)/Pt memory cell, (b) TiN/HfO₂(ALD,7.5nm)/Pt memory cell, (c) TiN/HfO₂(PVD,7.5nm)/Pt memory cell, and (d) Forming free memory cells, TiN/HfO₂(ALD,4.5nm)/Ge(3nm)/Pt cell, TiN/Al₂O₃(ALD,2nm)/HfO₂(ALD, 2.5nm)/Ge(3nm)/Pt cell, and TiN/Ge (7.5nm)/Pt cell.

In the early study, ratio of R_{HRS} to R_{LRS} of the HfO₂ based RRAM can be augmented by capping an Al₂O₃ dielectric layer [59]. In this study, capping a thin Al₂O₃ layer without any change to total physical thickness has been testified on structure (d). In contrast to structure (c), ratio of R_{HRS} to R_{LRS} has increased by lowering the current in HRS, which may correlated to the inter-diffusion of Al and Hf atoms and corresponding change of activation energy of transport [168].

Enhancement of the uniformity of the HfO_x based RRAM is most likely contributed by Ge doping. As illustrated in Figure 3.5(a), (c) and (i) and Table 3.1, devices without the Ge doping have Coefficient of Variation C_v (HRS) larger than 30%.

However, it drops to around 9% in structure (c) (See Figure 3.5(e)). $C_v(\text{LRS})$ in undoped samples is larger than 15%. But in structure (c), it is around 5%. Besides, for devices with Al_2O_3 capping layer, although its ratio of R_{HRS} to R_{LRS} and R_{HRS} are of advantage over devices without capping layer, the uniformity is compromised because of ineffective doping in the capping layer.

Another important measure of the uniformity concerns operation voltage. The V_{SET} and V_{RESET} in the structure (a) and (b) had a broad distribution (See Figure 3.5(b)(d)). On the other hand, the structure (c) and (d) have very uniform V_{SET} and V_{RESET} (See Figure 3.5(f) (h)). This most probably stems from the HRS I-V characteristics given in Figure 3.2, where the RESET transitions of the structure (a) and (b) are random and fluctuating, but the RESET transition of the structure (c) is very repeatable. The structure (e) (see Figure 3.5(j)) has improved uniformity of operating voltage over the structure (a) and (b), but it is not as good as the structure (c) and (d) because that small physical thickness reduces the uncertainty associated with internal electric field during SET and RESET transitions. What we propose is that the ruptured or recovered filament in doped RRAM has a small possibility in varying location. As a consequence, there is a good uniformity in operating voltage.

Figure 3.5. Measurements of device performance of 100 continuous dc sweeping cycles. (a)(c)(e)(g)(i) Distribution of resistance (R_{HRS} and R_{LRS}) for structure (a)(b)(c)(d)(e) in Figure 3.1. The measurement of R_{HRS} and R_{LRS} are taken at $|0.1V|$. (b)(d)(f)(h)(j) Distribution of operating voltage (V_{SET} and V_{RESET}). The voltage is defined as the point with maximum slope in the abrupt SET transition and max slope change in the gradual RESET transition.

XPS of the Ge 3d and the Hf 4f electrons of the sputtered structure (c), where top electrode is removed, are depicted in Figure 3.6(a) and (b). The alignment of the spectrum is made to Ar 2p orbital. The existence of GeO_x has been confirmed by inspecting Ge 3d peak at around 34 eV, which implies that Ge atoms have bonding with oxygen atoms of HfO_2 [169]. The Hf 4f_{7/2} and Hf 4f_{5/2} electrons are of energy around 18 eV and 20 eV in consistence with expected values for HfO_x composition. Figure 3.6(c) shows the cross-sectional image of structure (c) under TEM. It has been found that there is no visible interface or boundary between the HfO_2 and the Ge layer after nitrogen ambience annealing, which indicates a non-crystalline nature. This is also verified by the EDX profile illustrated in Figure 3.6(d). The EDX profile again confirms that the as-deposited TiN/ HfO_2 (ALD,4.5nm)/Ge(3nm)/Pt device has a metal atom (Hf and Ge) to oxygen atom ratio slowly changing along the depth (normal to the surface), which reveals that the valence states of Hf and Ge atoms are varying instead of being constant along the depth direction. This is further supported by the observed EELS oxygen k-edge (See Figure 3.6(e)).

For the upper interface between TiN electrode $Hf_xGe_yO_z$ dielectric stack, based on the inset of Figure 3.6(d) and (e), weight of O atoms reaches its peak point while the weight of Ge atoms is relatively small. The composition is close to HfO_x with significant amount of Ti doping where such a case has been investigated by the early work of our group. [170] According to Wu et al., delocalized states may present in

band-gap states due to both Ti atoms and oxygen-deficiency, and the Ti diffusion into the HfO_x layer may be the chemical origin of the observed forming-step free behavior.[170] Therefore, less Hf and Ge atoms show metallic behaviors there because most of them are in oxidized states.

On the contrary, for the lower interface between $\text{Hf}_x\text{Ge}_y\text{O}_z$ dielectric stack and Pt bottom electrode, the inset of Figure 3.6(d) and Figure 3.6(e) suggest that Ge atoms are of their maximal concentration while O atoms are of their minimal weight. This leads to the fact that more Hf and Ge atoms produce metallic behaviors. Density of Hf and Ge atoms are close as revealed by Figure 3.6 (d) if they share similar ionization cross-section. Thus, the composition is of non-stoichiometry due to oxygen deficiency, owning similar electronic properties of oxygen vacancies in crystalline HfGeO_x which has been calculated in first principle by Li *et al.*[171] The presence of dangling bonds leads to the formation of a band-gap state which is mainly composed of the hafnium and germanium atomic orbitals. In the non-crystalline structure, such a state will take the form of a defect band. In case that a mobility edge crosses the band, the delocalized part will contribute to the transport in a metallic manner, equivalent to small resistors within the dielectric film, which may possibly account for the observed self-compliance. The metallic transport, as proposed by Lee *et al.*, provides the random distribution of unbreakable resistors in series to limit the current in breakdown process.[112] Such resistors, serving as leakage paths, may also contribute to the observed forming free property. Despite that, from Figure 3.6(c), no evident grain or crystallinity of metallic Hf or Ge clusters can be identified between the two electrodes. Such an observation coincides with the early report that metallic Ta atoms have a non-uniform vertical distribution that a large percentage of metallic Ta atoms accumulate near the lower interface [167]. Also, there is no observation of visible grains or crystallinity metallic

Ta clusters in the literature. The detection of Ti and N atoms in between the two electrodes comes from atoms diffusion from the top TiN electrode. And the concentration of Ti and N atoms quickly vanish to zero in the bulk of the dielectric stack. Although the penetration of Ti atoms has been reported of advantages to uniformity [93, 106, 172], the reported enhancement in uniformity here comes from the effect of Ge doping rather than the Ti atoms as the TiN capped control sample is used as a contrast.

Figure 3.6 (a)XPS spectra of Ge 3d electrons (b)Hf 4f electrons of argon sputtered TiN/HfO₂(ALD,4.5nm)/Ge(3nm)/Pt structure (alignment with reference to Ar 2p).

Both Ge and Hf atoms are oxidized. (c) Cross-sectional TEM image and (d) EDX profile of the TiN/HfO₂(ALD,4.5nm)/Ge(3nm)/Pt structure. Inset shows a parallel scan with O and Si curves where an O peak is observed in the switching layer. (e) EELS oxygen k-edge taken at the upper and bottom interfaces.

To figure out the change of oxygen vacancy formation energy induced by Ge doping, *ab-initio* calculation has been performed by using CASTEP code [173]. Generalized Gradient Approximation (GGA) is employed to account for the exchange-correlation potential. Plane wave basis is of a cut off at 420 eV. Definition of valence electrons include Hf 5d² 6s², Ge 4s², Ge 4p², O 2s², and O 2p⁴. And the built-in Vanderbilt type ultrasoft pseudopotential represents the effect of core electrons. A supercell of *m*-HfO₂ is constructed which comprises of 96 atoms. Four irreducible K-points are used to sample the Brillouin zone. It has been reported that the threefold oxygen vacancy has a more stable binding with dopant [174]. The calculation here is confined to the threefold oxygen vacancy only. For Ge doping atoms, substitutional doping is assumed based on the XPS observation that Ge is in its oxidized state. One of the three Hf atoms which neighbor the vacancy is replaced by a Ge doping atom. The geometry optimization is performed with a criterion that energy variation is less than 5×10⁻⁶ eV/atom and force is not beyond 0.01eV/Å. The neutral state oxygen vacancy formation energy is defined in Equation (3.1).

$$\Delta H_f^{(O,0)} = E(O,0) - E(0) + (\Delta\mu_O + \mu_O^{solid}) \quad (3.1)$$

where E(O,0) stands for the total energy of a neutral supercell with an oxygen vacancy, E(0) refers to the total energy of an ideal neutral supercell and (Δμ_O+μ_O^{solid}) is defined as the absolute value of the chemical potential of an O atom. The neutral threefold oxygen vacancy formation energy in HfO₂ is calculated with a value of 5.78 eV similar to the reported value in literature [175]. However, with an oxygen atom replaced by a Ge atom, the formation energy is reduced to 3.68 eV. Such a decrement

in formation energy naturally leads to higher density of oxygen vacancies in the vicinity of the Ge dopants. This suppresses the randomness and fluctuation associated with the formation and rupture of the conductive filaments in SET and RESET transitions. As a result, variation of the resistance of HRS is eliminated to some extent and the uniformity of switching parameters is improved.

The dc cycling endurance of the structure (c) is given in Figure 3.7(a) while its retention performance is illustrated in Figure 3.7(b). Although Ge doping induced lowering of the formation energy of oxygen vacancy may cause retention degradation, the negative influence will be negligible if the reduction is within a certain range [168, 176]. Here we report the Arrhenius plots of R_{HRS} and R_{LRS} as functions of reciprocal temperature to probe the impact of the Ge doping and the metallic atoms on the conduction mechanisms for both TiN/HfO₂(PVD, 7.5nm)/Pt and TiN/HfO₂(ALD, 4.5nm)/Ge(3nm)/Pt devices. The activation energy of R_{HRS} is calculated to be around 39 meV for the PVD deposited device implying a thermally facilitated transport process, in consistence with the early report in literature [39, 59, 177]. However, the activation energy of carrier transport has increased to about 75 meV after the introduction of Ge doping atoms and the metallic Hf/Ge atoms. Similar increment of activation energy has been observed in Al doped HfO₂ [59]. This is probably related to the barrier modulation caused by the metallic Hf and Ge atoms which project influences to electron hopping processes in HRS. On the other hand, for both samples, the resistance of LRS almost has no temperature dependence in the same range of temperature [178]. A possible explanation is that the localized oxygen deficient filament is of a weak metallic nature in LRS [179]. Thus, the activation energy of R_{LRS} is immune to the doping Ge atoms. Ac frequency dependent response of the structure (a) and (c) have been carried out in the frequency range from 1 KHz to 1 MHz. The results show that the ac conductance

of LRS sample is dominated by a constant term in the low frequency domain, along with its temperature independent R_{LRS} and the Ohmic I-V curves, which strongly suggests a metallic nature of transport in LRS [50, 98]. However, transport in HRS is very possible to be carrier hopping based [127, 180].

Figure 3.7. (a) Endurance property of 1000 cycles dc sweeps of the TiN/HfO₂(ALD,4.5nm)/Ge(3nm)/Pt memory cell. (b) Retention property of the TiN/HfO₂(ALD,4.5nm)/Ge(3nm)/Pt memory cell tested at 85 °C. (c) Arrhenius plots of R_{HRS} and R_{LRS} as a function of reciprocal temperature ($1/T$) in TiN/HfO₂(ALD,4.5nm)/Ge(3nm)/Pt and TiN/HfO₂(PVD,7.5nm)/Pt memory cell, and (d) ac conductance (real part of admittance) as a function of frequency of both LRS and HRS in TiN/HfO₂(ALD,4.5nm)/Ge(3nm)/Pt and TiN/HfO₂(PVD,7.5nm)/Pt memory cell.

Based on the transport measurement shown in Figure 3.7 (c) and (d), we propose band diagrams of different states of TiN/HfO₂(PVD, 7.5nm)/Pt and TiN/HfO₂(ALD, 7.5nm)/Pt RRAM as plotted in Figure 3.8. (The work function of the TiN is assumed

to be 4.8 eV.[181] The work function of the sputtered platinum electrode is assumed to be 6.1 eV.[182] The gap of the hafnium oxide is assumed to be 5.6 eV while the electron affinity is assumed to be 2.0 eV.[183]) Figure 3.8(a) illustrates the band diagram of a pristine device in thermal equilibrium, owning a typical capacitor structure. Figure 3.8(b) shows a possible transport scenario in HRS where the biasing provokes carriers to hop through the localized defect states within the band-gap. Band diagram of Figure 3.8(c) shows a suggested transport model in LRS where the delocalized states have formed an impurity band within the gap thus exhibiting a metallic I-V characteristic.

Figure 3.8 The band diagram of the Pt/HfO₂/TiN RRAM in (a) pristine state (b) HRS (c) LRS.

For the structures with germanium doping, the resultant dielectric layer is of a chemical formula $Hf_xGe_yTi_zO$ where coefficients x , y , and z are functions smoothly varying with the distance to the interface, as revealed by the EDX profile in Figure 3.6(c). There is insufficient literature on either experiments or calculations of the band information of such an alloy. Thus, investigation of the band diagrams of alloyed $Hf_xGe_yTi_zO$ or $Hf_xAl_yGe_zTi_uO$ RRAM is considered as part of the recommended future work.

3.3 Conclusion

ALD HfO₂ based RRAM of high uniformity, forming free property and self-compliance have been demonstrated. Ge doping is proved to be responsible for the

improvement of the uniformity in both experiments and simulation, which originates from the lowering of the formation energy of oxygen vacancy. The forming free property stems from the oxygen deficiency caused by the Ge doping layer. The self-compliance is realized by the proper choice of deposition techniques and annealing conditions. Combination of these novel features sheds light on the possibility to simplify the RRAM supplementary (i.e. reading/writing macros) circuit design.

Chapter 4 Transport Properties of Hafnium Oxide based RRAM

4.1 Sample Preparation and Physical Characterization

The HfO_x RRAM cells used here have a structure as depicted in Figure 4.1(a). The Pt bottom electrode is grown on SiO_2 substrate by using radio frequency sputtering with a thin Ti adhesion layer. A Hf metal layer is sputtered on top of the Pt electrode which is further annealed in oxygen ambient for 5 minutes at 450°C to form the switching HfO_x layer with a thickness of around 10 nm as revealed by HRTEM image (See Figure 4.1(b)). Top electrodes are deposited by reactive sputtering of a 100 nm thick TiN film, which is then patterned by traditional lithography with a diameter ranging from 100 μm to 500 μm . A Keithley 4200-CVU semiconductor analyzer is deployed for both low-frequency (1KHz to 1MHz) and dc electrical characterization with the aid of a SUSS cryogenic probe station cooled by liquid Helium.

As shown in the HRTEM image (See Figure 4.1(b)), an TiO_xN_y interfacial layer is visible in between the HfO_x dielectric layer and TiN top electrode in as-deposited device, which has also been mentioned by Jorel et al. [184]. The role of this interfacial layer is suspected to be a reservoir of oxygen atoms which can absorb and release oxygen ions during switching process.

XRD spectrum has been taken on exposed HfO_x film without TiN top electrode, where a polycrystalline nature is identified for the underlying film. $(\bar{1}11)$ and (111) phases are dominant in the spectrum with strong peaks in Figure 4.1(c) [185].

Figure 4.1. (a) Schematic illustration of the Pt/HfO_x/TiN RRAM device structure. (b) Cross-sectional HRTEM image. The TiO_xN_y interfacial layer is identified. (c) XRD spectrum of HfO_x RRAM cell. HfO_x is found of the polycrystalline nature with dominant ($\bar{1}11$) and (111) phases.

Repeatable switching of the devices has been demonstrated in the early work [178]. The switching performances is summarized in Table 4.1. The as-deposited devices have a forming voltage about 5 V in general. The cells in LRS can be switched to HRS by exerting a negative voltage on top of the TiN electrode. Typically, RESET voltage is around -1.2 V. To switch the cell back to LRS, the desired SET voltage of an average value around 1.5 V. The ratio between R_{HRS} to R_{LRS} is slightly above 100. In terms of endurance, more than 1000 consecutive switching cycles has been achieved under dc voltage sweeps. Data could be retained without any degradation at 120 °C for more than 10000 s.

Structures	Pt / PVD HfO ₂ (10nm) / TiN
Feature Size (μm)	200 (100-500)
Read Voltage (V)	0.1 V
HRS Read Current (A)	3.9×10 ⁻⁸
LRS Read Current (A)	2.1×10 ⁻⁵
Average ON/OFF Ratio	5.4×10 ²
Average SET Voltage (V)	1.5
Average RESET Voltage (V)	-1.2
Endurance	>10 ³ DC sweeps

Retention	>10 ⁴ s at 120 °C (Projected room temperature life time>10 ⁶ s)
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Table 4.1 Switching performance of the HfO_x based RRAM used in dielectric loss measurement.

4.2 Room Temperature Dielectric Response

The admittance Y is generally defined as the summation of conductance G and susceptance B multiplied by the imaginary unit i .

$$Y = G(\omega, T) + iB(\omega, T) = G(\omega, T) + i\omega C(\omega, T) \quad (4.1)$$

where $G(\omega, T)$ is a function of both the angular velocity ω and the temperature T , while $B(\omega, T)$ has an alternative expression which is the product between equivalent capacitance $C(\omega, T)$ and angular velocity ω .

4.2.1 Pristine State

As illustrated in Figure 4.2(a), pristine devices show a typical non-Debye dielectric response curve which is widely observed in polycrystalline/amorphous semiconductors. This is also regarded as the Curie-von-Schweidler's behavior as given in Eqn. (4.2) [164, 165].

$$G(\omega, T) = G_{const} \omega^{S(\omega, T)} T^{N(\omega, T)} \quad (4.2)$$

Here G_{const} is a real value constant. If the temperature is fixed, the expression of the conductance could be simplified as Eqn. (4.3).

$$G(\omega) = G_0 \omega^{S(\omega)} \quad (4.3)$$

Figure 4.2. (a) Typical room temperature ($T=300\text{ K}$) conductance (G) of pristine, HRS, and LRS devices in the frequency (f) range from 1 KHz to 1 MHz. The solid blank line is the implementation of numerical fitting using Eqn. (4.3). (b) Typical room temperature ($T=300\text{ K}$) equivalent capacitance (C) ($C = \frac{\text{Im}(Y)}{\omega}$) of pristine, high resistance state, and LRS devices in frequency (f) range from 1 KHz to 1 MHz. The solid blank line is the implementation of numerical fitting using Eqn. (4.4). The fitted value of S and G_0 are in consistence with those in (a).

Such a behavior has also been witnessed in HfO_x and TiO_x based thin film devices in the last few years [98, 186, 187]. This non-Debye type response is believed to stem from the localized states deep within the principal band gap. The existence of these defect states is a reflection of disorder effect, such as dislocations and impurities (i.e. oxygen vacancies). Using paired sites approximation, carriers confined in these localized states is capable to move back and forth between the nearest neighboring localized state and the original state driven by external periodic electric field. The exponents S and N in Eqn. (4.2) are affected by both angular velocity and temperature where their frequency and temperature dependence are in strong correlation to the underlying charge transport mechanism, and the non-linear dependence of $\ln(G)$ on $\ln(\omega)$ and $\ln(T)$ at the specified temperature and frequency is frequently used to characterize the transport behaviors. In literature, the

admittance with exponent β was first used by Pollak et al. [163] and adopted in the subsequent studies [164-166, 188-190]. And the temperature exponent N was proposed by Long in his paper [164]. Detailed reviews of the power law given in Eqn. (4.2) have been made by Long and Elliot where semi-classical derivation to the power law is given [164, 165]. As pointed out by Long, the most probable scenario of the dielectric loss is that electrons shuttling between two neighboring defect sites in amorphous or polycrystalline semiconductors under periodic electric field. By constructing the partition function this grand canonical ensemble, rate equation of the equilibrium state can be written down [164]. Modeling the effect of the external field is done by including a small perturbation which affects the occupation probability of the two sites. Based on that, applying Fourier transform leads to the conductivity which is a function of ω , E_1 , E_2 and $\tau(R, E_1, E_2)$, where ω is the angular velocity, E_1 , and E_2 are the energy levels associated with the localized states of the two neighboring sites, and τ is the relaxation time which is transport nature (i.e. correlated barrier hopping, tunneling, small polaron tunnelling or large polaron tunneling) dependent [164]. Suggesting an empirical expression of $\tau(R, E_1, E_2)$, the frequency and temperature dependence of $S(\omega, T)$ and $N(\omega, T)$ can be derived for different types of charge transport mechanisms, as given in the articles by Long and Elliot [164, 165]. A more specific formulation, developed by Emin, for dielectric loss with small polaron adiabatic hopping type of charge transport will be discussed in the following section [191]. In the room temperature, the frequency exponent β is usually approximated as a constant with a value between 0 and 1 in low frequency range where f is smaller than 1 MHz.

As a consequence, the imaginary part of the admittance or equivalently $C = \frac{\text{Im}(Y)}{\omega}$ can be found by using Kramers-Kronig transformation [163-166].

$$C = G_0 \omega^{s-1} \tan\left(\frac{S\pi}{2}\right) \quad (4.4)$$

The fitted s of pristine device is 0.936 in agreement with the fitting of conductance G based on Eqn. (4.3) where the fitted s is 0.939 (See Figure 4.2(a)-(b)). Calculation of the pre-power factor G_0 by both fitting approaches yields the same result also.

The impact of cross-sectional area on dielectric response has been studied. The average value of the exponent s of 5 randomly selected devices is about 0.906, fitted in the frequency range from 1 KHz to 10 KHz, in consistence with previous reports (See Table 4.2) [98, 186, 187, 192, 193]. The corresponding capacitance is thus slightly dropping with increment of frequency. The rationale behind carrying fitting in the low frequency range (See Figure 4.2(a)) is to minimize external circuit influence which is significant in high frequency. Very large value of s which is close to 2 and fast decreasing capacitance have been reported when the frequency approaches 1 MHz [98, 193], which is attributed to parasitic effect of contacts as pointed out by Gonon et al. [98]. The parasitic influence to the capacitance of HRS and LRS is elaborated in the coming section as part of the numerical fitted equivalent circuit model. On the other hand, conductance G of pristine devices is found to be proportional to the cross-sectional area, as revealed in Table 4.2 that the G_0 increases with diameter. The conductance is expected to be linear with area in ideal case, and the observed deviation may be a result of the non-uniformly sputtered HfO_x thin film.

Diameter (μm)	δ	G_0 (S)	$G_{DC,HRS}$ (S)	$G_{DC,LRS}$ (S)
100	0.959	2.30×10^{-11}	1.01×10^{-5}	2.26×10^{-3}
200	0.859	2.93×10^{-10}	1.26×10^{-5}	1.44×10^{-3}
300	0.939	3.51×10^{-10}	1.50×10^{-5}	1.39×10^{-3}
400	0.872	1.21×10^{-9}	9.94×10^{-6}	1.19×10^{-3}
500	0.903	1.45×10^{-9}	1.50×10^{-5}	2.27×10^{-3}

Table 4.2. In the room temperature ($T=300$ K), fitted parameters of conductance (G) in pristine, HRS and LRS devices with diameter ranging from $100 \mu\text{m}$ to $500 \mu\text{m}$. G_0 is of clear area dependence while $G_{DC,HRS}$ and $G_{DC,LRS}$ does not possess evident area dependence (See Eqn.(4.3)(4.5)(4.7)).

The pristine devices have non-Ohmic dc I-V characteristics. For a $D = 100 \mu\text{m}$ device, its resistance generally ranges from $10^7 \Omega$ to $10^9 \Omega$ at 1 V corresponding to a bulk resistivity about $10^8 \Omega \text{ m}$ which falls to the regime of insulating dielectrics.

4.2.2 High Resistance State and Low Resistance State

The conductance of HRS devices is different from that of pristine devices by owning an additional frequency independent component $G_{DC,HRS}(T)$ [187].

$$G(\omega, T) = G_{DC,HRS}(T) + G_0 \omega^{S(\omega, T)} T^{N(\omega, T, S)} \quad (4.5)$$

The frequency independence of that term makes large contribution to the dc conductance that a larger leakage current is with HRS device than that of pristine device.

The capacitance of HRS devices is comparably smaller than that of the pristine device in consistence with literature report [98, 187, 193]. The difference between capacitance in HRS and that in pristine device is suspected to originate from influences of contacts, as it is inevitable to have an external resistor $R_{external}$ in series with the RRAM device in the measurement setup. This leads to the reduction in $\text{Im}(Y)$ as

revealed in Eqn. (4.6), (The other component $L_{external}$ associated with the external circuit is neglected here.) which indicates that a smaller HRS film resistance (R_{HRS}) results in a larger reduction in capacitance. More detailed circuit model with numerical fitting is discussed in the next section.

$$C_{HRS} = \frac{\text{Im}(Y)}{\omega} = \frac{\omega C}{\left(\frac{R_{external}}{R_{HRS}} + 1\right)^2 + (\omega C R_{external})^2} \quad (4.6)$$

Different from G_0 , no evidence shows that $G_{DC,HRS}(T)$ possesses area dependence. (See Table 4.2) Here we postulate that the partially ruptured filament, with no cross-sectional area dependence, is responsible for the frequency independent component $G_{DC,HRS}(T)$. Analysis of $G_{DC,HRS}(T)$ of different devices shows clear stochastic fluctuation, which may correlate to the fact that formation and rupture of filament is not controllable.

Similar to HRS, the conductance of LRS is also a summation two components where one is frequency independent while the other one comes from non-Debye response.

$$G(\omega, T) = G_{DC,LRS}(T) + G_0 \omega^{S(\omega, T)} T^{N(\omega, T, S)} \quad (4.7)$$

In low frequency range from 1 KHz to 1 MHz, the dc component is overwhelming that the second term is almost negligible (See Figure 4.2(a)), where the equation above can be approximated by Eqn. (4.8).

$$G(\omega, T) \cong G_{DC,LRS}(T) \quad (4.8)$$

The capacitance in the LRS device is at the same level with that in HRS and pristine device [98, 187, 193]. As mentioned in the HRS case, the lowering of the overall capacitance compared to the pristine device is contacts oriented (i.e. external

resistance in series with the RRAM device). As $G_{DC,LRS}(T)$ is even larger than $G_{DC,HRS}(T)$, the lowering of capacitance is more significant in the LRS than that in HRS, which results in a small $\text{Im}(Y)$ in LRS. The fast diminution near 1 MHz serves evidence of the existence of external inductance $L_{external}$ in series with the RRAM device, which is further analyzed in the circuit model in the coming section also [98, 193].

$G_{DC,LRS}(T)$ has also no clear area dependence, same with $G_{DC,HRS}(T)$. In literature, area independent resistance is frequently spotted in the LRS of the VCM filamentary switching RRAM. But the transport process in the HRS is not only determined by the ruptured or shrunk filament. Indeed, both the area dependent and the area independent resistance has been reported in HRS of HfO_x based RRAM (See, for instance, the resistance of HRS with clear area dependence has been seen in $\text{TiN/Ti/HfO}_2/\text{TiN}$ RRAM [93], while weakly area dependent resistance in HRS is found in $\text{Pt/ZrO}_2/\text{HfO}_x/\text{TiN}$ RRAM [194]). As mentioned in the previous chapter, this may be caused by the competition between charge transport from the ruptured or shrunk filament and the rest of the dielectric film. In our experiments, both the HRS and LRS of $\text{Pt/HfO}_x/\text{TiN}$ are found of area independent resistance suggesting a dominant role of filament based transport.

4.2.3 Equivalent Circuit Model

Figure 4.3 shows the room temperature Cole-Cole plot, where the pristine device has a behavior of typical non-ideal capacitor, which follows the universal power law given by Eqn. (4.3) for amorphous and poly-crystalline dielectrics.

Figure 4.3. (a) In the room temperature ($T=300 \text{ K}$), Cole-Cole plot of pristine device in frequency (f) range from 1 KHz to 1MHz. The solid line is the implementation of numerical fitting based of the equivalent circuit. The schematics illustrate the possible scenarios of transport in HfO_x . (b) In the room temperature ($T=300 \text{ K}$), Cole-Cole plot of HRS cell in frequency (f) range from 1 KHz to 1MHz. The solid red line is the implementation of numerical fitting based of the equivalent circuit. (c) In the room temperature ($T=300 \text{ K}$), Cole-Cole plot of LRS cell with frequency (f) range from 1 KHz to 1MHz. The solid green line is the implementation of numerical fitting based on the equivalent circuit.

As mentioned in the previous section, the assumption of a constant exponent S is proper in the low frequency range. Concerning the Kramers-Kronig transformation, the impedance of the ideal pristine RRAM device Z_{CPD} is described by Eqn. (4.9).

$$\begin{aligned}
Z_{CPD} &= \frac{1}{G_{pristine}} = \frac{1}{G_0 \omega^S + i\omega C} \\
&= \frac{1}{G_0 \omega^S + iG_0 \omega^S \tan\left(\frac{S\pi}{2}\right)} \\
&= \frac{\cos\left(\frac{S\pi}{2}\right)}{G_0 \omega^S} e^{i\left(-\frac{S\pi}{2}\right)}
\end{aligned} \tag{4.9}$$

Since the phase factor $\left(-\frac{S\pi}{2}\right)$ depends on the exponent S only and S is considered to be a constant here, the phase is thus a constant. Such kind of device is also designated as constant phase element (CPE). However, in the equivalent circuit, only an ideal CPE cannot produce the observed low frequency response of HfO_x RRAM. For instance, an ideal CPE is of zero dc conductance as revealed in Eqn. (4.10).

$$\text{Re}\left[G(\omega)\right]\Big|_{\omega=0} = G_0 \omega^S \Big|_{\omega=0} = 0 \tag{4.10}$$

But practically, dc leakage current could not be avoided in the HfO_x thin film. Therefore, a resistor in parallel is added to account for such leakage current. For the pristine HfO_x device, the largest source of dc leakage current is the native defects. For the HfO_x devices in LRS, percolation of oxygen vacancies is responsible for its dc leakage current. And most probably the dc leakage in HRS is caused by partially ruptured filaments. These postulated scenarios are schematically illustrated in Figure 4.3. As illustrated in Figure 4.3(a), a resistor $R_{external}$ is in parallel with CPE to handle all dc leakage current appearing in the non-ideal dielectric film. Effects of contacts are taken into consideration by a resistor $R_{external}$ and an inductor $L_{external}$, which are in series with the dielectric stack. For pristine device, this contact influence is negligible due to the very large $R_{external}$. The Cole-Cole plot of the pristine device is a straight line in the corresponding frequency range. However, in HRS and LRS devices, the parallel resistance R_{HRS} and R_{LRS} , which are the reciprocals of $G_{DC,HRS}$ and $G_{DC,LRS}$, are

much smaller (Refer to the insets of Figure 4.3(b) and (c) where $G_{DC,HRS} = \frac{1}{R_{HRS}}$ and

$G_{DC,LRS} = \frac{1}{R_{LRS}}$). Hence, their dielectric response is more likely to be influenced by

$R_{external}$ (about 310 Ω) and $L_{external}$ (around 5×10^{-7} H), in agreement with reported $R_{external}$ for devices with similar cross-sectional area which ranges from 4.5 Ω to 1000 Ω [195-197]. For example, ideal HRS device should be of a semicircle curve in the complex impedance plane. However, due to the presence of external inductance $L_{external}$, the center of the circle is slightly below the x-axis [195-197].

The fitted exponent S for CPE is 0.94 (See Figure 4.3), very similar to the previous fitting where $S = 0.936$ (based on Eqn. (4.4)) or 0.939 (based on Eqn. (4.3)). The fitted G_0 is in consistence with the previous fitting result also although the previous fitting does not include the effect of contact resistance and inductance (See Figure 4.2).

The fitted resistance of HRS and LRS are $2.7 \times 10^4 \Omega$ and $1.6 \times 10^2 \Omega$, respectively (See Figure 4.3(b) and (c)). Assume the diameter of the cross-section of a single filament is several tens of nanometer, the resistivity of the filaments in LRS will be around $10^{-5} \Omega \cdot m$, which falls into the category of typical amorphous metal. On the other hand, under the same assumption, the resistivity of filaments in HRS is about $10^{-3} \Omega \cdot m$ which suggests that HRS filaments may be of a semiconductor-like nature [32].

4.3 Temperature Dependent Dielectric Response

Temperature dependent electrical characterization of HfO_x based RRAM has been reported [98, 178]. But systematical investigation of temperature dependent dielectric response of both HRS and LRS in HfO_x is still lacking. Here, for the first

time, by employing temperature dependent dielectric response characterization, we have identified the experimental significance of small polaron hopping in HRS and delocalization of impurity orbitals of oxygen vacancies in LRS.

4.3.1 Pristine State

As thin film of typical polycrystalline/amorphous material, temperature dependence of pristine devices has been summarized in the reviews of Long and Elliot [164, 165]. In the low frequency range, as there is no way to avoid dc leakage current in thin dielectric films, there always exists an $R_{pristine}$ (as depicted in Figure 4.3(a)) which dominates the transport in the low frequency range. Different nature of leakage current leads to different types of temperature dependence of $R_{pristine}$ [164, 165]. On the contrary, presence of R_{HRS} (or $G_{DC,HRS}$) and R_{LRS} (or $G_{DC,LRS}$) is a direct consequence of percolation of oxygen vacancies which form conductive filaments. In the high frequency regime, the power term is of a much larger weight than $R_{pristine}$. Thus, a pristine device shows no difference with a HRS device in terms of dielectric response. Here, in the frequency range from 100 KHz to 1 MHz, which is sufficient high to bypass the potential dc residual component, 300 K to 420 K response is observed of very weak temperature dependence that $G(\omega, T)$ slightly increases with temperature, which is consistent with the findings of HRS presented in the coming section.

4.3.2 High Resistance State

4.3.2.1 Temperature Dependent Cole-Cole Plot

The dc I-V curve of HRS devices has evident temperature dependence as mentioned. However, the underlying mechanism responsible for this dependence has

not been unveiled in the early studies. It has been claimed that resistive switching in redox RRAM can be either due to filament formation or interface modification [20]. According to the theorem of interface resistive switching, the interface between dielectric stack and metal top electrode is a Schottky barrier. The height of the barrier is determined by the chemical property of the beneath dielectric layer, and the change of the barrier height under external electric field results in resistive switching [20]. The origin of the temperature dependence, whether it is caused by the conductive filaments or Schottky barrier at the interface, is analyzed by using temperature dependent Cole-Cole plot. In Figure 4.4(a), the left interceptions of the three curves with x-axis are close to each other, at around $165 \text{ } \Omega$, suggesting a temperature independent $R_{external}$ in the equivalent circuit, which is also reported by Papagianni et al. [195]. This finding excludes the possibility of the Schottky barrier modification at the interface between HfO_x and TiN as Schottky barriers are supposed to possess exponential temperature dependence. The contact between HfO_x and electrode is believed to be Ohmic in HRS due to the following concerns. The first one is that the extracted activation energy of transport is much smaller compared to the expected Schottky barrier based on band diagram, which will be elaborated in the coming section (See Figure 4.4(b) and corresponding text). Similar activation energy has been seen in Si/ HfO_2 /TiN [198], TiN/ HfO_2 /Au [199], and Al/ HfO_2 /Si MIM structures [200]. The other evidence comes from the symmetrical I-V curve of Pt/ HfO_x /TiN which has no rectifying effect as shown in our previous report of electrical characterization [178]. Therefore, $G_{DC,HRS}(T)$, the filament oriented conductance, is inferred to be responsible for the temperature dependent Cole-Cole plot of HRS.

Figure 4.4. (a) Cole-Cole plot for device in HRS at various temperature (from 120 K to 300 K) which indicates that the resistive switching is not caused by interface Schottky barrier effect. (b) Arrhenius plot of dc conductance $G_{DC,HRS}$ in HRS as a function of reciprocal temperature $1000/T$. The observation suggests a transport type of small polaron adiabatic hopping. (c) I-V characteristics of device in HRS at various temperature (from 150 K to 225 K). Solid lines are implementation of numerical fitting based on Eqn. (4.11) which is valid for polaron hopping at temperature larger than half of the Debye Temperature. (d) Arrhenius plot of frequency dependent conductance $G - G_{DC,HRS}$ as a function of reciprocal temperature $1000/T$ in HRS at various frequency f . Solids lines are implementation of numerical fitting based on Eqn.(4.12) of highly polarizable mediums.

4.3.2.2 D. C. Conductance Arrhenius Plot

As discussed, $G_{DC,HRS}(T)$ is clearly temperature dependent which implies that the transport is facilitated by thermal activated processes. Arrhenius plot of dc conductance, measured at the same voltage amplitude (10 mV) with that in dielectric

response characterization, is illustrated in Figure 4.4(b). And similar curves have been spotted in the Arrhenius plots of HfO_x and other polarizable systems where small polarons may exist. For instance, more than one group has found that the curves in Arrhenius plots of HfO_x can be divided into two parts with very different slopes or activation energy [198-200]. The extracted activation energy of is 50 meV in the higher temperature region and 2.5 meV in the lower temperature region as shown in Figure 4.4(b). Compagnoni et al. have reported an activation energy of 87meV (under forward biasing) and 60 meV (under reversed biasing) in the high temperature range and 5 meV in the low temperature range. For other polarizable material systems, like TiO_2 , similar slope transition is exhibited at the half of its Debye temperature [201].

The activation energy of transport in the high temperature range of HfO_x RRAM is of a magnitude of tens meV [198, 200], much smaller compared to the width of the band gap. For the oxygen deficient HfO_x dielectric layer of a RRAM device, the Fermi level depends on the external electron reservoirs which are the Pt and TiN electrodes. The work functions of both metal electrodes are very large that the Fermi level will be several eV below the conduction band edge of HfO_2 [126]. Hence, direct excitation of electrons from defect states of oxygen vacancies to the conduction band edge is extremely great challenging in the room temperature range. A more probable scenario is electron type small polaron adiabatic hopping via metal ions in the vicinity of oxygen vacancies. Such type of polaron hopping transport has been predicted to exhibit the transition of slope, same as what is shown in Figure 4.4(b), by Schnakenber [202]. It is also predicted that the transition temperature is about half of the Debye temperature. Below the transition temperature, polarons will be frozen out due to the phonon distribution. For example, other group IV transition metal oxide material like TiO_x has been reported of a transition of activation energy at half of its Debye temperature, which

is considered as a symbol of adiabatic hopping of small polarons [201]. The observed transition temperature here is about 100 K in our experiment, while the reported Debye temperature of HfO₂ is 220(±10) K, suggesting a polaron hopping based transport mechanism [203]. In addition, the *ab-initio* simulation calculated adiabatic small polaron hopping energy is 50 meV in intrinsic HfO₂ material, which further supports our experimental observation [39].

4.3.2.3 Electric Field impact on temperature dependent I-V Characteristics

Another finding of the experiment which also implies the polaron nature of transport in HRS in high temperature range is the impact of electric field on temperature dependent I-V characteristics (See Figure 4.4(c)). In HfO_x/TiN systems, Poole-Frenkel emission like I-V characteristics have been commonly observed in the high temperature region [199]. Here, as suggested by Emin, we postulate such behaviors should be attributed to polaron related transport in the adiabatic regime rather than direct excitation of electrons to conduction band [204]. Presume a T^{-1} pre-exponential factor due to adiabatic hopping, dc conductance can be expressed as a function of the field strength F in Eqn. (4.11).

$$G_{HRS,DC} \propto \frac{\nu}{T} \exp \left[\frac{-E(\infty) + \sqrt{V_L F a \cos \theta}}{k_B} \left(\frac{1}{T} - \frac{1}{T_0} \right) \right] \quad (4.11)$$

where ν stands for the suitable mean of atomic vibrational frequencies, a is the diffusion length, $E(\infty)$ is the activation energy for polarons with an infinite large distance separation, F is the strength of the electric field which drives the hops, and θ is the angle between the applied field and the direction of hop. The pre-exponential T^{-1} has very negligible influence in high temperature region especially when temperature is larger than 150 K [199]. Thus, the conductance of Eqn. (4.11) shares

strong resemblance with that of the ordinary Poole-Frenkel emission in the high temperature range. Numerical fitting is implemented yielding a fitted $E(\infty)=42$ meV which is consistent with the E_A in Figure 4.4(b).

4.3.2.4 G vs. (1000/T) at Different Frequencies in High Resistance State

As illustrated in Figure 4.4(d), HRS and pristine devices exhibit a similar frequency dependent conductance at low temperature, which is widely seen in polycrystalline/amorphous semiconductors. The contribution of the filament, which is $G_{DC,HRS}(T)$, does not depends on frequency. In the high frequency range, the main factor affecting the dielectric response comes from defect states induced by disorder. Its contribution is given as $G(\omega,T)-G_{DC,HRS}(T)$. When temperature is constant, the $G(\omega,T)-G_{DC,HRS}(T)$ increases with frequency as mentioned in Section 4.2.2. As proved by Long, the quantitative formulation of this dependent conductance is underlying dielectric response nature based [164]. When the angular velocity ω is fixed, $[G(\omega,T)-G_{DC,HRS}(T)]/G_{DC,HRS}(T)$ drops with the temperature. This is equivalent to state that the ac contribution to the total conductance is larger at low temperature. The physical interpretation of these behaviors has been proposed by Emin [191]. At low temperature, spontaneous emission of phonons is essential to trigger the ac polarization. But the dc conduction is associated with thermal assisted hops with high energy barrier. It is appropriate to assume that a very small fraction of carriers ($\sim 0.1\%$) in transition metal oxide is responsible ac conduction at low frequency and low temperature. The polarization-paired centers are of the key roles in the transport process. Carriers can move cooperatively within each polarization-paired center. The conductance is linear versus reciprocal temperature in the ranges from 80 K to 250

K . The ac polaronic conductance has been quantitatively formulated by Emin [191]. The approach used by Emin is different from that of Long in terms of the calculation of relaxation time. In Emin's approach, the reciprocal of relaxation time is linearly proportional to the transition rate from one state of the polarization-paired center to the other. A deformation model is employed to account for the interaction between electrons and long wavelength acoustic phonons where the transition rate is calculated by using Fermi's golden rule. This leads to the expression of dielectric loss in Eqn. (4.12)

$$G(\omega, T) - G_{DC, HRS}(T) = G_0 \frac{\left(\frac{\omega}{\omega_0}\right) \left(\frac{T}{T_0}\right)}{\left[1 - \left(\frac{\omega_0}{\omega}\right)^{\frac{1}{n}} \left(\frac{T}{T_0}\right)\right]^2} \quad (4.12)$$

$$\text{where } G_0 \equiv \frac{A}{l} 2q^2 \langle R^2 \rangle \rho_2(\mu, 0) \omega_0 k_B T_0 \exp\left(-\frac{n^2}{2}\right) \text{ and } \frac{(\omega_0)^{\frac{1}{n}}}{T_0} \equiv \frac{2n^2 k_B \omega^{\frac{1}{n}}}{\delta_0}.$$

A is defined as the cross-sectional area, l stands for the dimension in the direction of current flow, q refers to the electron charge, R is the separation between polarization-paired sites, $\rho_2(\mu, 0)$ is the density of paired sites with local energy μ and no site-to-site energy difference, k_B is Boltzmann's constant, and δ_0 is the peak of a dynamic factor generally rising with ω . In the low temperature range, n is close

to 3 and $\delta_0 \propto \omega^{\frac{1}{3}}$, thus $\frac{(\omega_0)^{\frac{1}{n}}}{T_0}$ is a constant. And $\frac{G_0}{\omega_0 T_0}$ is constant too. As depicted

in Figure 4.4(d), the four curves are fitted with $\left.\frac{(\omega_0)^{\frac{1}{n}}}{T_0}\right|_{n \rightarrow 3} = 0.011 s^{\frac{1}{3}} K^{-1}$, which are

consistent with the theorem of Emin. The exponent S derived from Emin's expression, as given in Eqn. (4.13), is close to unity in low frequency range.

$$S(\omega, T) = \frac{\partial \left\{ \ln \left[G(\omega, T) - G_{DC, HRS}(T) \right] \right\}}{\partial \left[\ln(\omega) \right]} \bigg|_{n \rightarrow 3} = 1 - \frac{2 \left[\frac{(\omega_0)^{\frac{1}{3}}}{T_0} \right] T}{3\omega^{\frac{1}{3}} - 3 \left[\frac{(\omega_0)^{\frac{1}{3}}}{T_0} \right] T} \quad (4.13)$$

Substitute in the value of $\frac{(\omega_0)^{\frac{1}{3}}}{T_0} \bigg|_{n \rightarrow 3}$, the exponent S ranges from 0.86 to 0.98

with an average value of 0.95 consistent with the room temperature dielectric loss fitting in Figure 4.2 and Figure 4.3 in the frequency range of the measurement. The corresponding temperature exponent N is of a fitting value ranging from 1.0 to 1.4 in the frequency and temperature range of the measurement, which shows good agreement with theorems. Therefore, all experimental evidence indicates the existence of polarization-paired centers in the HfO_x which confirms the highly polarizable property of the medium [164, 165].

4.3.3 Low Resistance State Sample Temperature Dependence

Different from HRS devices, LRS devices show weakly temperature dependent resistivity. As shown in Figure 4.5, the dc resistance is about 122 Ω at 10 K and 139 Ω at 225 K.

Figure 4.5. Dc resistance and resistivity (by taking a film thickness of 10 nm and a presumed filament diameter of 10 nm) of a LRS device as a function of temperature (T). The plot exhibits a typical metallic behavior. The inset shows corresponding I-V curves of LRS at different temperature (T) (from 10 K to 225 K) where a clear Ohmic behavior is observed.

The temperature insensitive resistance in LRS has also been observed in WO_x based RRAM, where its reported resistance is $9 \text{ } \Omega$ at 10 K and $11 \text{ } \Omega$ at 300 K [156]. In our study, consider a film thickness of 10 nm and a filament diameter of 10 nm, the corresponding resistivity is around $10^{-6} \text{ } \Omega \cdot \text{m}$. As shown in the inset of Figure 4.5, linear I-V curves at various temperatures are evidence of Ohmic transport. The very low resistance-residue-ratio $R_{225\text{K}} / R_{10\text{K}}$ of 1.14, the resistivity of around $10^{-6} \text{ } \Omega \cdot \text{m}$, as well as the Ohmic characteristics all unveil a weak metallic nature of transport in LRS, which is believed to have strong correlation with impurity states associated with the percolated oxygen vacancies. In literature, Ohmic LRS are have been widely spotted [98, 179, 199]. The contact between HfO_x and electrode is Ohmic in LRS. Recently study by Bersuker unravels that the Ohmic charge transport in LRS is caused by forming a metallic sub-band in the filament because of high local oxygen vacancy concentration in $\text{TiN}/\text{HfO}_x(5\text{nm})/\text{TiN}$ RRAM device [205].

Density functional theory based on Vienna *ab initio* simulation package (VASP) [206-209] with the projected augmented wave pseudopotential [210] is implemented to probe the electronic structure in the LRS of HfO_x RRAM. Hf $5p^65d^26s^2$ and O $2s^22p^4$ are defined as the valence electrons. Functional based on GGA is used [211]. Plane wave basis with a cut-off energy of 500 eV is used to represent the wavefunctions of valence electrons.

Conjugated gradient method is used to optimize all the lattice parameters and internal coordinates of all atoms in the unit cell. The convergence criteria of stress tensor is set to 0.1 GPa, and that of forces on each atom is set to 0.03 eV/Å. Calculation of electronic structures of the filament in SrTiO_x and TiO_x have been reported by using bulk model [32, 212]. But in our experiment, the 8 nm-thick HfO_x dielectric film is found of two dominant facets which are $(\bar{1}11)$ and (111) as shown in the XRD spectrum of Figure 4.1(c). It has been claimed that the oxygen vacancies are preferred to be generated at the grain boundaries [36] as well as surfaces [37]. Therefore, surfaces of HfO_x are of much more critical roles than the bulk phase in the formation of oxygen deficient filaments in the HfO_x device. In the room temperature, the phase of lowest energy of HfO₂ is monoclinic, which transforms to the tetragonal phase at elevated temperature about 1300 K, then to the cubic phase at around 2700 K.[213] In this study, a surface model of monoclinic HfO_x, where oxygen vacancies are incorporated, is used in the calculation of the electronic structure of LRS. Firstly, *ab initio* calculations are performed for bulk monoclinic phase HfO₂ where each Hf atom is coordinated by seven neighboring oxygen atoms. As illustrated in Figure 4.6(a), oxygen atoms form *a*-directional alternating threefold and fourfold planes.

Figure 4.6. (a) Structure of monoclinic HfO_2 used in the calculation, yellow balls are Hf atoms, while red balls stand for O atoms. (b) Structures of $(\bar{1}11)$ and (111) slabs of monoclinic HfO_2 .

The cell parameters of the optimized monoclinic structure ($a=5.135 \text{ \AA}$, $b=5.205 \text{ \AA}$, $c=5.304 \text{ \AA}$, and $\beta=99.6^\circ$), the calculated band gap of 4.0 eV as well as DOS are all in consistence with the results of early studies [212, 214-216].

Secondly, nine different low-index surfaces are selected from the monoclinic HfO_2 . The surface energy density $\gamma(n)$ of a system comprising n layers is defined in Eqn.(4.14) for characterization of the stability of surfaces.

$$\gamma(n) = \frac{E_{\text{tot}}(n) - E_{\text{bulk}}(n)}{2A} \quad (4.14)$$

where $E_{\text{tot}}(n)$ and A represent the total free energy and surface areas per molecular unit, respectively, while $E_{\text{bulk}}(n)$ stands for the free energy in the bulk phase, which comprises of the same molecular units with that of the slab model.

Table 4.3(a) unravels that $(\bar{1}11)$ and (111) surfaces, illustrated in Figure 4.6(b), are more stable than any other low-index surfaces due to lowest surface energy

density, in consistence with the finding of XRD depicted in Figure 4.1(c). The calculated ranking of stability of low-index surfaces in HfO₂ is $(\bar{1}11) > (111) > (\bar{1}01) > (110) > (001) > (011) > (101) > (100) > (010)$, which is of well agreement with the early report [214]. Further calculation is implemented on $(\bar{1}11)$ surface which is the most stable surface. Table 4.3(b) gives the formation energy of oxygen vacancies at different depth to the surface. Evidently, the fourfold oxygen atom is more likely to be removed from HfO₂ than the threefold oxygen atom, which does not depend on the position of vacancy [213, 216]. This trend is also valid in our calculation of formation energy of oxygen vacancies in a bulk model. Table 4.3(b) also unveils that oxygen vacancy on the surface is easier to be formed than that in the interior because of difference in bonding environment. The O atoms deep inside the slab have almost the same crystal environment to those in bulk phase. Thus, the corresponding formation energy is close to that of bulk phase.

(a)		
Surface	Surface energy (J/m ²)	Surface energy [214]
$(\bar{1}11)$	1.015	0.993
(111)	1.193	1.199
$(\bar{1}01)$	1.335	1.322
(110)	1.335	1.388
(001)	1.427	1.416
(011)	1.433	1.484
(101)	1.509	1.550
(100)	1.636	1.667
(010)	1.821	1.878

(b)		
	3-fold V_O (eV)	4-fold V_O (eV)
near surface	$7.05 + \Delta\mu_O$	$6.81 + \Delta\mu_O$
in the middle of slab	$7.15 + \Delta\mu_O$	$7.02 + \Delta\mu_O$
bulk phase	$7.37 + \Delta\mu_O$	$7.22 + \Delta\mu_O$

Table 4.3. (a) Simulated surface energy density of the 9 inequivalent low-index surfaces of monoclinic HfO_2 . The $(\bar{1}11)$ surface is the most stable one consistent with the early report and XRD measurement. (b) Simulated formation energy of oxygen vacancies at $(\bar{1}11)$ surface and bulk phase. Fourfold oxygen vacancies are predicted of lower formation energy in both slab and bulk models. Formation energy is found to be lower in the vicinity to the surface.

The conducting filaments are treated as multiple aligned oxygen vacancies chains along the HfO_x $(\bar{1}11)$ surface. $[101]$ directional vacancy chain, formed by alignment of two threefold and two fourfold oxygen vacancies in $(\bar{1}11)$ slab, is energetically preferred. Figure 4.7(a) shows the DOS of the slab, the valence band states mostly comprises of O $2p$ orbitals hybridized with Hf $5d$ orbitals. Surface states, originating from dangling bonds of surface oxygen atoms, peak at the top of valence band. And thus it mainly consists of O $2p$ states. On the other hand, the conduction band states are constituted of Hf $5d$ orbitals with weak hybridization of O $2p$ orbitals. The introducing of oxygen vacancies create intermediate states deep inside the principal band gap of bulk HfO_2 where the contribution of atomic orbitals mainly comes from $5d$ orbitals of Hf atoms: Unbonded extra electrons stay at the Hf $5d$ orbitals, and Fermi level is lifted up to the valence band. Therefore, the band gap is greatly reduced. Impurity band mainly comprises of the t_{2g} orbitals of Hf, with a relative larger contribution from d_{xz} atomic orbital, as revealed by the decomposition of wavefunction.

And the superposition of t_{2g} wavefunctions of two neighboring Hf atoms may result in weak bonding. Figure 4.7(b) depicts the partial charge density distribution in the real space near Fermi level, unraveling that the wavefunction of defect states in association with [101] vacancy chain is delocalized in compared to that of an isolated oxygen vacancy since the isosurface spans the supercell along the chain of the vacancies which means the carrier is of large possibility of moving to the adjacent supercells along the chain. On the contrary, the isosurface of an isolated oxygen vacancy is confined in a small volume with very weak inter-supercell coupling due to fast decay in the direction perpendicular to the isosurface. Hence, carriers are capable to pass through those oxygen deprived Hf ions in [101] direction under external field. This may serve as a clue for the formation of oxygen deficient conducting filaments, which corresponds to the impurity band in Figure 4.7(a) and provide carriers with travelling paths in the LRS of resistive switching process. Here we postulate that the weak metallic nature of LRS is attributed to the delocalization of the impurity band wavefunctions in association with the aligned vacancies chains. The stability of different directional oxygen vacancy chains is estimated by calculating the corresponding formation energy. It has been found that [101] is of lower energy than other 1-Dimensional low index oxygen vacancy chains. For example, the formation energy of [101] chain is 0.383 eV per formula unit smaller than that of [110] chain, revealing that the chain with dense oxygen vacancies is more energetically favorable.

Figure 4.7. (a) DOS of $(\bar{1}11)$ slabs with $[101]$ oxygen vacancies chain. The Fermi level is located at zero. Extra unbonded electrons stay at the Hf $5d$ orbitals, and the Fermi level is lifted up to the valence band which leads to the intermediate states. (b) Schematics of partial charge density (isosurface value= $0.07 \text{ e}/\text{\AA}^3$) near Fermi level of the $(\bar{1}11)$ slab with $[101]$ directional oxygen vacancies chains. The wavefunctions exhibit the tendency of delocalization which may be the cause of weak metallic nature in LRS.

The delocalization trend is also revealed by the calculated valence electron localization function. (The localization function of CASTEP does not fully span 0 to 1.) As illustrated in Figure 4.8 (a), in an ideal $(\bar{1}11)$ vacuum slab with no oxygen vacancies, the slice of localization function exhibits extreme localization along the chain of oxygen atoms with a value close to 0. On the other hand, in Figure 4.8 (b), the vacancies lead to significant local increment of the electron localization function, a symbol of delocalization of the carriers.

Figure 4.8 (a) Slice of electron localization function of the first layer atoms in (a) a

($\bar{1}11$) slab with no oxygen vacancies (b) a ($\bar{1}11$) slab with $\langle 101 \rangle$ directional oxygen vacancy chain. Dotted circles represent oxygen vacancies. Brown balls are hafnium atoms and red balls are oxygen atoms.

Based on Figure 4.7 (a) and Mott type metal-insulator transition theory, Figure 4.9 schematically delineates the scenarios of carriers' response to the external electric field in the pristine state, LRS and HRS, which is also in accordance to the experimental observations. In Figure 4.9 (a), the carrier shuttles between the localized neighboring sites under AC field, yielding the power law of dielectric loss shown in the Figure 4.2 of the original thesis. In Figure 4.9 (b), a filament, in the form of dense oxygen vacancies, serves as a delocalized channel for carrier transport in a metallic way. In Figure 4.9 (c), the filament is partially ruptured/shrank, where a significant contribution to the transport comes from the hopping of the carriers via localized states, producing the temperature dependences shown in Figure 4.4 of the original thesis.

Figure 4.9 The schematic illustration of the carrier motion in (a) pristine cell under AC field where carriers hop between adjacent localized states (b) LRS cell under DC field where carriers flow through the delocalized filament region (c) HRS cell under DC field where part of the carriers hop via localized states due to oxygen vacancies.

The calculation of PDOS is based on the periodic structure (inherent limitation of supercell approach). With consideration of the fact that the film is of a non-crystalline nature, Figure 4.10 (a) proposes the band diagram of a HRS film. The states in light grey color are localized states while those in dark grey are delocalized states, separated by the mobility edge. Figure 4.10 (b) depicts the carrier transport scenarios based on Figure 4.10 (a) where there is a region that the major contribution to the transport is hopping via localized states. Figure 4.10 (c) corresponds to the proposed metallic LRS where the gap states are partially delocalized due to strong coupling between dense oxygen vacancies as shown in Figure 4.10 (d).

Figure 4.10 (a) Proposed band diagram of the HfO_x in HRS. The band gap states are localized with a narrow dispersion. (b) Proposed transport model of the HRS where carriers hop through the localized states. (c) Proposed band diagram of the film in LRS. The band gap states are partially delocalized. (d) Proposed transport model of LRS where an impurity band is responsible for the observed metallic behavior.

4.4 Conclusion

Employing dc and low frequency ac transport measurements at various temperatures, the pristine state, HRS and LRS of Pt/HfO_x/TiN based RRAM devices have been found of distinct behaviors. Equivalent circuit models are developed for all the three states. The conductance of pristine devices obeys the well-known power law of polycrystalline and amorphous semiconductors. An additional frequency insensitive component is included in HRS and LRS. In HRS, this extra conductance term is found of both the frequency and cross-sectional area independence but strong temperature dependence, which may possess strong correlation with the partially ruptured oxygen vacancy filament. The dc activation energy is about 50 meV at the temperature higher than half of the Debye temperature and 2.1 meV at the temperature below 100 K. Fitting based on small polaron hopping field dependence at high temperature is well implemented for dc I-V curves in HRS. All the evidence points that the HRS conduction is small polaron related, which is further verified by the test of high frequency dielectric loss in HRS. On the other hand, the extra conductance term in LRS is not reliant on frequency and cross-sectional area but slightly dependent on temperature, unveiling a weak metallic nature. The insulator-metal transition is believed to originate from the delocalization of wavefunctions of impurity bands. To investigate the electronic properties of oxygen vacancies in polycrystalline material, *ab-initio* simulation has been taken to study aligned oxygen vacancy chains on the $(\bar{1}11)$ surface of HfO_x. Projected DOS and spatial distribution of the wavefunctions of the impurity states induced by oxygen vacancies implies that the delocalization of impurity band is responsible for the weak metallic nature in LRS.

Chapter 5 Oxygen Vacancy-Bound Small Polarons Migration in Resistive Switching Hafnium Oxide

5.1 Polaron Transfer and Computation Information

Vast literature on electron transfer models exists [217-220]. However, few are with detailed introduction to the polaron transfer. Greater detail is given in the reviews by Holstein [221, 222], Marcus [223], Emin [224], Friedman [225], Alexandrov [226], Austin and Mott [227], where Marcus theory bears resemblance with Emin-Holstein-Austin-Mott theory in spite of their different terminology [228]. Influence of disorder was first included in the review of Austin and Mott for polaron migration [227].

Old computational studies on small polaron transfer focus on parameters of the Marcus model [229-232]. Since the motion of polaron is always associated with the transfer of lattice distortion, Maxisch et al. used density functional theory to implement continuous calculation of the total energy along the entire migration path [233]. The method was adopted in free polaron adiabatic hopping calculations for TiO_2 , $m\text{-HfO}_2$ and MnO_2 with linear extrapolation estimated paths [41, 228, 234]. Migration calculations on impurity bond polarons were applied to Li_2O_x and CeO_x , where the latter used nudged elastic band approach in transition state search [235, 236]. Here we use the total energy plane wave pseudo-potential code CASTEP [237]. And the transition state search is implemented by the built-in combined linear synchronous transit and quadratic synchronous transit schemes with 0.1 eV/Å convergence threshold for the root mean square forces on the atoms.

Strong self-interaction error of GGA and LDA make them not suitable for transition metal oxide study due to inaccurate prediction of phase stability, magnetic and electronic structure. Self-interaction tends to over delocalize d electrons [238]. More sophisticated treatment with the application of a Hubbard U term has been used

[228, 233, 234, 236, 239]. However, the species-specific U parameter makes it less advantageous to the hybrid functionals which incorporate part of the exact Hartree-Fock exchange energy. Recently functionals such as sX, PBE0 and B3LYP have been used in the study of oxygen vacancies in HfO_x [43, 126, 240]. We use B3LYP functional in our calculation, which correctly predicts stoichiometric HfO_2 to be an insulator with a gap of 6.2 eV, consistent with the previous reports, where the overestimation may come from excitonic effect and phonon broadening of band tails [43, 126, 240].

HfO_x is diamagnetic, and the calculation is spin polarized to fulfill spin conservation and Franck-Condon principle [241] (The magnetic moments were initialized in the ground-state diamagnetic configuration). Each supercell contains two unit $m\text{-HfO}_2$ cells and two oxygen vacancies. Although lowest formation energy applies to threefold oxygen vacancy with +2 charges, the system will become insulating which contradicts the experiments. Oxygen vacancy charge has been experimentally identified to be +0.4~+1.3 in CeO_{2-x} [242]. Here the fractional charge per unit cell is set to +1.5. And the net difference in the number of spin-up and spin-down electrons is fixed to 1 per supercell.

K-point convergence test has been done and 5 irreducible k-points are used in sampling. For transition state search related calculations, only Γ point is used to reduce computational cost.

For cell optimization, the cell parameters are optimized in their charge states using PBE version of GGA with norm-conserving pseudopotentials. The geometry is further optimized by B3LYP method with an energy cutoff 450 eV. Phonon dispersion and density of states calculation are implemented by using the built-in finite displacement method of CASTEP [243]. Convergence tests have been carried out to determine the cutoff of the force constant matrix, which is 9 Å in our calculation.

5.2 Results and Discussion

The calculated Mulliken charges are +1.83, -0.89 and -0.94 (in units of the electron charge) on the hafnium, threefold oxygen and fourfold oxygen atoms, respectively, consistent with other report suggesting a partially ionic character of *m*-HfO₂ [43]. The *d* electrons of Hf fill the $d_z^2+p_z$ molecular orbitals. Introducing oxygen vacancy with positive charge will create t_{2g} molecular orbitals with σ symmetry to hafnium-vacancy axis [244].

The oxygen vacancy in *m*-HfO₂ induces changes in the local lattice structure. In the 12.5% concentration case, after B3LYP optimization, translational symmetry breaking occurs in the $1 \times 1 \times 2$ supercell, which clearly differs from perfect lattice case. This symmetry breaking leads to localization of electrons shown in the left of Figure 5.1(a) which displace three neighboring hafnium atoms by ~ 0.2 Å towards each other, on average, about 10% of the O-Hf distance (See the right part of Figure 5.1(a)). In this case, about 50% of the electron spin density is localized predominantly on three Hf ions sharing the missing threefold oxygen atoms, similar to the free electron polaron in *m*-HfO₂ [41]. The distribution is asymmetrical among the ions. The rest spin does not localize on the unoccupied threefold oxygen vacancy site but delocalizes over the remaining atoms. Electron localization function has been calculated from the valence electrons to serve as an approximation to the all-orbital electron localization function (Note that electron localization function values from CASTEP do not span the full range from 0 to 1). Irreducible *f*-localization domain, as shown in Figure 5.1(b), could be defined by comprising the single attractor located at the position of the lower oxygen vacancy. As a contrast, the calculated electron localization function in the vicinity of the higher oxygen vacancy is close to zero, which confirms the asymmetrical spin localization. Figure 5.1(c) shows the atomic projected density of states. The polaron

occupies the spin-up state at the Fermi level, and is mainly composed of hafnium $5d$ orbitals on which the electron is localized. The localization splits the original degenerate bandgap states induced by oxygen vacancies by pushing up the un-occupied spin-down state 2 eV above the Fermi level. Weak coupling between vacancies leads to small polaron band dispersion of around 0.1 eV implying electron localization in the low density limit due to dominant on-site potential [245].

Figure 5.1. (a) Left part is the optimized $1 \times 1 \times 2$ lattice with two threefold oxygen vacancies. Hafnium, oxygen atom, and vacancy are represented by blue, red and grey balls, respectively. An isosurface (Isovalue=0.05) shows the spin distribution. The indicated bond lengths are given in angstroms. Right part shows the inter-atomic distances between the vacancy-neighboring hafnium atoms. Translational symmetry is broken. The spin mainly localizes on the lower oxygen vacancy site. (b) (100) and (001) slicing of the electron localization function calculated from valence electrons of the

configuration in (a). The arrows point to the original positions of the oxygen vacancies. An attractor is located at the site of the lower vacancy while the value of electron localization function of the upper site is close to zero. (c) Atom projected density of states for the upper unit cell (non-polar site) and lower unit cell (polar site) in (a). Fermi level is at zero eV. The polaron state is mainly composed of Hf 5*d* atomic orbital.

As pointed out by Austin and Mott, extent of localization is sensitive to the separation between localization centers [227]. If the separation is sufficiently small, kinetic energy will dominate and electron correlation will be negligible. Mott type metal-insulator transition takes place when bandwidth is larger than correlation [245]. Here we studied the so called oxygen divacancies where two symmetrical vacancies sites are neighboring.

In Figure 5.2(a), no inversion center symmetry is broken after geometry optimization. The local lattice distortion is evenly shared by the two vacancies sites, so as for the symmetrical spin distribution. A single valence attractor rather than a pair of attractors is identified at the center of the two vacancies in Figure 5.2(b). The value of the electron localization function at the attractor is much smaller than that of the attractor in Figure 5.1(b). In addition, the band dispersion increases to 1 eV because of strong coupling between vacancies. All of these signify that the polaron is delocalized over the two vacancies sites. And activation barrier is rapidly tending to zero at separation around 2.5 Å, which gives implication of LRS metallic transport in HfO_x resistive switching memory.

Figure 5.2. (a) Optimized $2 \times 1 \times 1$ lattice with two neighboring threefold oxygen vacancies. Hafnium, oxygen atom, and vacancy are represented by blue, red and grey balls, respectively. An isosurface (Isovalue=0.05) shows the spin distribution. The indicated bond lengths are given in angstroms. Inversion center symmetry is retained. The spin distribution is evenly shared by the two oxygen vacancy sites. (b) (100) and (011) slicing of the calculated valence electron based electron localization function of the configuration in (a). The arrows point to the original positions of the oxygen

vacancies. A single valence attractor rather than a pair of attractors is at the center of the two vacancies. The value of the electron localization function at the attractor is smaller than that of the attractor in Figure 5.1(b).

Energetically, there is a preference for divacancies configuration over separated vacancies configuration. The calculated total energy of a divacancies supercell is 0.8 eV lower than the corresponding separated vacancies supercell. This trend of vacancy clustering is in consistence with the observed filament type switching rather than homogeneous switching in HfO_x based resistive switching memory [246].

Although threefold oxygen vacancies are of the lowest formation energy, we have also explored fourfold oxygen vacancies lattice with same translational symmetry. Different from the threefold case, fourfold oxygen vacancies lattice cannot localize electron polaron under this density. In contrast to Figure 5.1(a), the translational symmetry is almost preserved after geometry optimization, as shown in Figure 5.3(a). The spin distribution in the left half is the same with that in the right half of the 2×1×1 supercell. Such delocalization is also revealed by Figure 5.3(b) where the electron localization function in the vicinity of the two fourfold oxygen vacancies is of smaller value than that of oxygen valence shells. The coupling between fourfold vacancies is much stronger compared to the coupling between threefold vacancies, where the orbitals induced by fourfold oxygen vacancies have a band dispersion of ~3 eV. Such a large band dispersion results in the rupture of bandgap as shown in the partial density of states of Figure 5.3(c). The strong coupling is a possible result of the specific bonding environment of fourfold oxygen atoms which greatly increases the size of the polaron. And the configuration after geometry optimization is stable which is immune to manual displacement of vacancy-neighboring Hf atoms.

Figure 5.3. (a) Optimized $2 \times 1 \times 1$ lattice with two fourfold oxygen vacancies. Hafnium, oxygen atom, and vacancy are represented by blue, red and grey balls, respectively. An isosurface (Isovalue=0.05) shows the spin distribution. The indicated bond lengths are given in angstroms. The translational symmetry is almost retained. The spin distribution in the left half is almost the same with that in the right half. (b) (100) and (011) slicing of the electron localization function calculated from valence electrons of the configuration in (a). The arrows point to the original positions of the oxygen vacancies. Electron localization function in the vicinity of the two fourfold oxygen vacancies is of smaller value than that of oxygen valence shells. (c) Atom projected density of states for the left unit cell (left half) and right unit cell (right half) in Figure 5.3. Fermi level is at zero eV. Orbitals induced by fourfold oxygen vacancies have a band dispersion of ~ 3 eV resulting the rupture of bandgap.

Bound electron polaron migration is expected to be anisotropic in the bulk HfO_x . We study three different polaron transfer directions ($[100]$, $[010]$ and $[001]$), all toward the neighboring vacancy sites. In Table 5.1 we present the barriers calculated for polaron symmetrical hopping between equivalent sites in the bulk along the three low index directions. The transition state of $\langle 100 \rangle$ direction migration is associated with significant lattice distortion. In Figure 5.4 (a), the transition state of $\langle 100 \rangle$ directional migration is accompanied with remarkable lattice distortions. Appreciable changes of bond length are observed, as shown in Figure 5.4 (a). Compared to the charge in the initial localized state, the charge in the same region is reduced when in the transition state. This leads to the increment of the inter-atomic separation between hafnium atoms neighboring the lower oxygen vacancy where the charge is originally trapped. So, the chemical bonding between hafnium and oxygen has covalent component besides the commonly discussed ionic nature. Similar analysis is performed for the hopping along $\langle 010 \rangle$ and $\langle 001 \rangle$ directions. Hopping along $\langle 010 \rangle$ direction experiences the highest barrier as shown in Figure 5.4 (b), where significant changes in bond length are identified between threefold oxygen and hafnium atoms. When hopping is along $\langle 001 \rangle$

direction, the changes in bond lengths are much smaller mainly involving atoms near the vacancies as shown in Figure 5.4 (c). The computed lowest activation energy is 90 meV along the $\langle 001 \rangle$ direction, which is in agreement with the measured thermal activation energy of 87 meV observed by Compagnoni et al. in the temperature range from 135 K to room temperature. [200] Ramo et al. have reported that the electron polaron migration barrier in perfect HfO_2 is 50 meV by linear extrapolation approach.[41]. Compared to hopping of polaron, polaron-like bound state migration is facing a relatively larger barrier.

Hopping barrier in the bulk HfO_x		
Direction	Hopping Barrier (meV)	Distance ($\text{\AA}$)
[100]	661.19	4.62
[010]	2814.79	4.76
[001]	90.47	4.80

Table 5.1. Calculated lowest bound polaron symmetrical migration barriers in the bulk HfO_x along [100], [010] and [001] directions. The hopping barrier is anisotropic. The barrier of [001] direction is in consistence with experimentally observed activation energy of HfO_x in the temperature range above 135 K [200].

Figure 5.4 Calculated transition states of (a) $\langle 100 \rangle$ directional hopping in a $1 \times 1 \times 2$ lattice with two threefold oxygen vacancies (b) $\langle 100 \rangle$ directional hopping in a $1 \times 1 \times 2$ lattice with two threefold oxygen vacancies (c) $\langle 100 \rangle$ directional hopping in a $1 \times 1 \times 2$ lattice with two threefold oxygen vacancies. The black dashed line and labels indicate inter-atomic distances in angstroms between the vacancy-neighbouring hafnium atoms. Green labels are bond length changes in angstroms.

We have calculated the partial phonon density of states, shown in Figure 5.5(a), of the configuration with lowest hopping barrier along $[001]$ direction. Projecting the displacements of the transition state onto the phonon eigenvectors at Γ point, the mode with largest contribution is of 45 meV. The inset of phonon partial density of states reveals the deformation of this mode mainly comes from the threefold oxygen atoms O5 and O6 which neighbor the oxygen vacancies as shown by the changes of bond lengths in Figure 5.5(b). By inspecting the eigenvectors, the vibration of the mode with largest projection is found to be longitudinal. On the other hand, fourfold oxygen atoms are of small displacements in the hopping process, along the fact that it is less favored for polaron localization, suggesting a rigid bonding environment of fourfold oxygen

atoms. Higher order effect of the phonon eigenvectors are also estimated by varying the amplitude of the displacements. The modes could be grouped based on the inter-mode non-harmonic coupling. The transition state displacements is mainly a superposition of two groups of modes, one consists of modes 30, 32, 34 and the other comprises of modes 4, 5, 6, as illustrated in Figure 5.5(b) with green arrows, which mainly concerns the vibration localized on the oxygen atoms O3, O4 and O5.

Figure 5.5. (a) Calculated partial phonon density of states of the $1 \times 1 \times 2$ HfO_x lattice in Figure 5.1. The inset shows the zoomed view from 35 meV to 60 meV of contributions of the labeled threefold oxygen atoms in (b). The mode with largest projection at Γ point is of 45 meV, with major contribution from vibration of O5 and O6 atoms. (b) Illustration of transition state displacements. Only threefold oxygen atoms (in red balls) and hafnium atoms (in blue balls) are shown. Dashed lines and black labels show the change of inter-atomic distances between the hafnium atoms next to the vacancies. Bond length changes are green labels. Major bond length changes are with O5 and O6 atoms. Original positions of the oxygen vacancies are indicated with grey balls and text. Arrows are the superposition of the two dominant phonon groups where vibration is

mainly with O3, O4 and O5 atoms. The polaron localizes on the site of the lower vacancy in the original configuration.

We also investigated the bound polaron migration barriers in the presence of $(\bar{1}11)$ surface which is of the lowest surface energy among low index surfaces [246]. McKenne predicted that grain boundaries act as sinks for oxygen vacancies so percolation paths are preferentially located along grain boundaries [36]. Here we used vacuum slab models to account for the influence of grain boundaries. For simplicity, symmetrical hopping between equivalent sites on $(\bar{1}11)$ surfaces are investigated along either [110] or [101] directions with sixteen different paths. By using two-layer vacuum slab models, the lowest activation barrier is found to be 360 meV along [101] direction over 6.24 Å as given in Table 5.2.

Hopping barrier along the $(\bar{1}11)$ surface		
Direction	Hopping Barrier (meV)	Distance (Å)
[110]	519.70	6.88
[101]	360.93	6.24

Table 5.2. Calculated lowest bound polaron symmetrical migration barriers on the $(\bar{1}11)$ surface of HfO_x along [110] and [101] directions. The barrier of [101] is close to the experimentally observed activation energy of HfO_x in the temperature range from 320 K to 400 K [247].

Experimentally, the trap depth in HfO_2 , which presumes a Poole-Frenkel emission model, was found to fall in the range from 210 meV to 350 meV in the elevated temperature region from 300 K to 400 K [247, 248]. As Poole-Frenkel behaviors is likely to possess an origin of small polaron adiabatic hopping [204, 246], it possibly reveals that long distance hopping along surface can become dominant at high temperature due to its phonon assisted nature. Empirically, if the lowest barrier is considered as the experimental hopping energy, the polaron radius will be ~ 3 Å

according to the equation of Mott, which is just the threshold separation for metal-insulator transition [227].

Figure 5.6(a) and (b) are the corresponding calculated phonon dispersion and partial phonon density of states. We projected the displacements of transition state onto the phonon eigenvectors at Γ point as illustrated in Figure 5.6(c) where the branches with top five absolute contributions are highlighted with red dash lines in Figure 5.6(a). It is also noted that the middle three red dash lines in Figure 5.6(a) passing through the forbidden regions between the bulk continuums at non-zero q -points, which reveals the importance of surface modes to polaron hopping along the surface [249]. These branches are also noticed to be almost dispersionless along the symmetry directions due to the very large mass difference between Hf and O atoms. We have also computed the phonon structure of the $(\bar{1}11)$ surface without oxygen vacancies and strong resemblance is found in dispersion. An exception, however, is that the branches appearing in the forbidden region between the acoustic and optical bulk phonon modes are drastically changed due to oxygen vacancies induced surface relaxation. Inspecting Figure 5.6(b), the dominant contribution to the branches with large projection comes from the vibration of the threefold oxygen atoms. Further analysis of phonon eigenvectors reveal the vibration mainly localizes on the vacancy-neighboring threefold oxygen atoms as reflected by the changes of bond lengths in Figure 5.6(d). The displacements are shear vertically polarized. Like the bulk case, non-harmonic coupling between modes is estimated by varying the amplitude used in the finite displacement method. The displacements of the transition states is mainly composed of the contributions of four groups of modes as illustrated by arrows in Figure 5.6(d), which again shows that the dominant vibration is with the threefold oxygen atoms in the vicinity of the oxygen vacancies.

Figure 5.6. (a) Calculated phonon dispersion of $(\bar{1}11)$ HfO_x 2-layer vacuum slab model with lowest symmetrical migration energy along $[101]$ direction. The projected bulk phonon dispersion of HfO_x is shown by the hatched region. The red dashed branch corresponds to mode with maximum projection in (c). The middle three red dash lines

pass through the forbidden regions between the bulk continuums at non-zero q -points, representing surface modes. (b) Calculated partial phonon density of states. (c) Contribution of different modes to the displacements of transition state. (d) Illustration of transition state displacements. Only threefold oxygen atoms (in red balls) and hafnium atoms (in blue balls) are shown. Dashed lines and black labels show the changes of inter-atomic distances between the hafnium atoms next to the vacancies. Bond length changes are green labels. Large bond length changes are with vacancy-neighboring threefold oxygen atoms. Original positions of the oxygen vacancies are indicated with grey balls and text. Arrows are the superposition of the four dominant phonon groups where vibration is mainly with the vacancy-neighboring threefold oxygen atoms. The polaron localizes on the site of the lower vacancy in the original configuration.

5.3 Conclusion

We calculate oxygen vacancy-bound small polarons migration barrier in HfO_x which shades light on the transport in HRS of HfO_x resistive memory. The barrier vanishes in divacancies case due to delocalization transition with implication to the switching mechanisms of the HfO_x resistive memory. Anisotropic migration barriers of bound small polarons are found for hopping between equivalent threefold oxygen vacancies while the trend of delocalization is observed in fourfold oxygen vacancies. Dominant vibration modes concern the longitudinal motion of the neighboring threefold oxygen atoms. In the presence of $(\bar{1}11)$ surface, lowest migration hopping path is found to be along $[101]$ direction with vibration mostly contributed by the surface branches localized on the vacancy-neighboring threefold oxygen atoms.

Chapter 6 Graphene Oxide based Resistive Switching RRAM: Impact of Electrodes and Switching Mechanisms

6.1 Experiment

In GO RRAM devices (Figure 6.1(a)), Pt electrode of ~40 nm was deposited by electron beam evaporation on Si substrate with a Ti adhesion layer.

Figure 6.1. (a) Sketch of Metal/GO/Pt sandwiched structure. (b) and (c) SEM cross section and top view images of GO film on Pt substrate. Inset of (c) shows the image of a single GO flake. (d) XPS spectrum of C 1s. Main peaks P1, P2 and P3 are at 284.2 eV, 286.1 eV and 288.4 eV, respectively, in consistence with literature report.

The GO solution was prepared by oxidation of graphite powder using modified Hummer's and Offeman's method. Briefly, graphite powder, sodium nitrate and sulfuric acid were mixed and stirred for 10 minutes. Then, potassium permanganate was added while solution was put in ice bath. DI water was added while temperature was raised to 90 °C. After an hour, hydrogen peroxide was added drop wise and the

solution turned yellow. The mixture was filtered while warm and washed with warm DI water. Purification was done by centrifugation to remove un-oxidized particle and graphene oxide flakes. A 60 nm thick GO thin film was deposited by drop-casting method, where the SEM images were shown in Figure 6.1(b) and (c). Four different electrodes, Al, Cu, Ni and Ti were deposited by electron beam evaporation with shadow mask patterning respectively. The top electrode had a thickness of 50 nm and a diameter of 300 μm unless specified otherwise. (See Figure 6.1(a)) Electrical characterization was performed by using a Keithley 4200 semiconductor parameter analyzer and a SUSS probe station.

6.2 Results and Discussion

6.2.1 XPS Examination of GO Film

The GO film was examined by XPS, as shown in Figure 6.1(d). As a heavily oxidized graphene oxide film, there were 3 main peaks from C 1s, denoted as Peak 1 (sp² carbon), Peak 2 [epoxy (C-E) group and hydroxyl group (C-OH)] and Peak 3 [ketones (C=O) or edge groups like carboxyl (COOH)], consistent with the literature report [250].

6.2.2 I-V Characteristics and Cycle-to-cycle Distribution of Switching Parameters

The typical anticlockwise (AW) bipolar resistive switching of GO RRAM with different electrode materials was compared in Figure 6.2(a), (c), (d) and (e) with compliance current $I_C = 1 \text{ mA}$. No switching was found in Ni/GO/Pt RRAM cell, which might be due to the reason that Ni^{2+} could react with hydroxyl group of GO to form conductive $\text{Ni}(\text{OH})_2$ [251, 252]. This might hinder negative voltage sweep from drifting back Ni^{2+} ions. Also, for the absorption of oxygen related functional groups at the Ni/GO interface, the barriers might loss insulating capability due to the formation of

Ni(OH)₂ [253]. For Al/GO/Pt structure and Ti/GO/Pt structure, more than one switching directions were observed (See Figure 6.2(b) and (f)).

Figure 6.2. (a)(c)(e) Typical bipolar AW switching I-V curves of GO with Al, Cu, Ti top electrodes ($I_C=1\text{mA}$). (b) Unipolar switching I-V curves in Al/GO/Pt ($I_C=10\mu\text{A}$). (d) No switching in Ni/GO/Pt. (f) Bipolar CW switching I-V curves in Ti/GO/Pt.

For Al/GO/Pt, with a $10\mu\text{A}$ compliance current, positive voltage sweep brought the as-deposited Al/GO/Pt RRAM cell to the unipolar LRS, which had an I-V curve coinciding with that of bipolar HRS shown in Figure 6.2(a)(b). The V_{RESET} in unipolar switching was $\sim 1.8\text{V}$, relatively higher than the V_{SET} in bipolar switching. As a consequence, unipolar switching might easily trigger a second time breakdown in

RESET process and transform to bipolar AW switching. But no reversed transition was observed. This was probably because the bipolar V_{SET} was lower than the unipolar V_{RESET} , which made bipolar AW switching preferable. The endurance of unipolar switching was typically several tens of cycles. For Ti/GO/Pt structure, clockwise (CW) forming free, self-compliance bipolar switching direction was found (See Figure 6.2(f)). LRS (CW) I-V coincided with HRS (AW) I-V (See Figure 6.2(e) and (f)) too. Since RESET process was of a high voltage ~ 2 V, it might cause a subsequent breakdown. Thus, the device would eventually move to bipolar AW switching after tens of cycles. Also, no reversed transition was found because bipolar AW V_{SET} (~ 1.1 V) was smaller than the maximum sweep voltage (2V). Similar behaviors in Pt/TiO₂/Pt RRAM were reported [159]. The Cu/GO/Pt structure exhibited only single switching direction, which might be caused by huge Cu²⁺ absorption capacity of GO [254]. And diffusion of electrode ions might dominate the switching in the Cu/GO/Pt structure.

Figure 6.3 shows the cumulative probability of R_{HRS} , R_{LRS} , V_{SET} , and V_{RESET} distribution of Al, Cu and Ti electrode RRAM structures. Bipolar (AW) resistance magnitude and On/Off ratio of Cu and Ti top electrode RRAM are consistent with reported value [136]. As mentioned, unipolar LRS resistance of Al/GO/Pt is almost the same as that of bipolar HRS due to similar transport natures (See Figure 6.3(a)). And LRS (CW) state resistance of Ti/GO/Pt coincided with HRS (AW) resistance also (See Figure 6.3(e)).

Figure 6.3. Cumulative probability of bipolar switching (AW/CW) and unipolar switching R_{HRS} (measured at -0.1V) and R_{LRS} (measured at 0.1V) in (a) Al/GO/Pt, (c) Cu/GO/Pt, (e) Ti/GO/Pt. $I_C=1\text{mA}$ in positive voltage range. Cumulative probability of bipolar switching (AW/CW) and unipolar switching V_{SET} (defined as the point with maximum slope change) and V_{RESET} (defined as the point with maximum slope change) in (b) Al/GO/Pt, (d) Cu/GO/Pt, (f) Ti/GO/Pt. $I_C=1\text{mA}$ in positive voltage range.

6.2.3 Electric Field Dependence of Current

Figure 6.4(a) showed that LRS (AW) was of an Ohmic behavior with a slope ~ 1 in log-log I-V plot consistent with literature report [45, 46, 136, 157, 158, 161, 162]

(See Table 2.4 also). HRS (AW) showed non-linear field dependence especially in high field region which was of a slope > 1.8 . This could be explained by space charge limited current where $I \sim aV + bV^2$ [161]. On the contrary, as shown in Figure 6.4(b), bipolar CW switching in Ti/GO/Pt and unipolar switching in Al/GO/Pt had non-Ohmic LRS with slope > 1.5 in high field region. Therefore, conduction mechanisms of different directions might be different. In conclusion, bipolar AW switching was observed with linear field dependence in LRS, which suggested Ohmic transport. But unipolar switching in Al/GO/Pt and bipolar CW switching in Ti/GO/Pt were of non-linear field dependence, which might originate from space charge limited current.

Figure 6.4. (a) Field dependence of bipolar AW switching I-V in Al/GO/Pt, Cu/GO/Pt and Ti/GO/Pt. All LRS (AW) are of slope ~ 1 . (b) Field dependence of unipolar switching in Al/GO/Pt and CW bipolar switching in Ti/GO/Pt. All LRS (Unipolar or CW) are of slope > 1 in the high field region.

6.2.4 Temperature Dependence of Resistance and the Instability

Figure 6.5 showed the Arrhenius plot of resistance in Al/GO/Pt, Cu/GO/Pt and Ti/GO/Pt. Distinct R_{LRS} activation energy was observed. For LRS (AW), the E_A was almost zero, which might suggest Ohmic transport again. For HRS (AW), the E_A was $\sim 46\text{meV}/\sim 78\text{meV}/\sim 0.21\text{eV}$ in Al/Cu/Ti topped GO RRAM cell, respectively,

consistent with literature report, which suggested that the transport was thermally activated [136, 159, 201].

Figure 6.5. (a), (b) and (c) are Arrhenius plot of R_{HRS} and R_{LRS} in Al/GO/Pt, Cu/GO/Pt and Ti/GO/Pt under different switching directions, respectively.

In Figure 6.6(a) and Figure 6.6(b), temperature instability of switching parameters in the Al/GO/Pt and the Ti/GO/Pt RRAM cells were compared. The fluctuation of resistance and operation voltage during cycling was more severe in high temperature range. For Al/GO/Pt sample, bipolar AW R_{HRS} (similar to unipolar R_{LRS}) was subjected to larger temperature instability while R_{LRS} was more regulated by current compliance. On the contrary, for Ti/GO/Pt RRAM cell, bipolar AW R_{HRS} (similar to bipolar CW R_{LRS}) had much less temperature based fluctuation (See Figure

6.6(a)). This clued that unipolar switching in Al/GO/Pt was of different mechanism with bipolar CW switching in Ti/GO/Pt.

Figure 6.6. (a) Distribution of R_{HRS} and R_{LRS} in Al/GO/Pt and Ti/GO/Pt structure at 25 °C and 75 °C. (b) Distribution of V_{SET} and V_{RESET} in Al/GO/Pt and Ti/GO/Pt structure at 25 °C and 75 °C.

As a summary, bipolar AW switching was observed with temperature insensitive R_{LRS} , which again suggested Ohmic transport. On the contrary, the R_{LRS} of the unipolar switching Al/GO/Pt and the bipolar CW switching Ti/GO/Pt were of much larger activation energy, which suggested thermal facilitated transport.

6.2.5 Area Dependence of Resistance

As shown in Figure 6.7, the bipolar AW switching and the unipolar switching are observed of weakly area dependent R_{LRS} , this suggested a filament type transport. However, R_{LRS} of bipolar CW switching in Ti/GO/Pt showed strong area dependence, which was consistent with the oxygen related functional groups release/absorption model [162].

Figure 6.7. Area dependence of R_{HRS} and R_{LRS} in (a) Bipolar AW switching Al/GO/Pt RRAM cell. (b) Unipolar switching Al/GO/Pt RRAM cell. (c) Bipolar AW switching Cu/GO/Pt RRAM cell. (d) Bipolar AW switching Ti/GO/Pt RRAM cell. (e) Bipolar CW switching Ti/GO/Pt RRAM cell.

6.2.6 Retention and Endurance

Figure 6.8(a) was a retention test at room temperature on Ti/GO/Pt structure. Both AW and CW directions were tested, which showed no clear degradation in 10^3 seconds. Similar retention characteristic was found for Al/GO/Pt. Figure 6.8(b) was the D. C. cycling endurance of bipolar AW switching Ti/GO/Pt. The performance could retain up to 500 cycles.

Figure 6.8. (a) Room temperature retention of Ti/GO/Pt. (b) Room temperature D. C. endurance of bipolar AW switching Ti/GO/Pt.

6.2.7 Band Diagram

In order to plot the band diagram of the GO based RRAM, first principle calculation is performed to determine the band structure of the GO film. However, the graphene oxide thin film is a stack of multiple graphene oxide flakes where each individual sheet is amorphous with a constituent determined by the synthesis technique. Thus, structure of graphene oxide is not well established yet. Many attempts have been made, especially using theoretical calculation, to determine the underlying structure of graphene oxide. Most of these approaches employ a periodic structure. Here, we performed the first principle simulation by using the CASTEP code with the PBE type General Gradient Approximation correlation functional. The plane wave basis was of a cutoff at 500 eV and the pseudopotential is ultrasoft. The Brillou zone is sampled by a $5 \times 5 \times 1$ Monkhorst-Pack grid. The model of heavily oxidized GO used in the calculation is of a chemical formula of supercell $C_8(OH)_2O_2$ which has been widely used in the modelling of GO. There are 2 hydroxyl groups and 2 epoxy groups per cell. (See Figure 6.9 (a)) The calculated DOS indicates a band gap about 3.7 eV in Figure 6.9 (b).

Figure 6.9 (a) The optimized supercell of $C_8(OH)_2O_2$ (b) The DOS of the structure with a band gap of 3.7 eV.

Based on the calculation, the band diagram of a pristine Metal/GO/Pt RRAM device in thermal equilibrium may be depicted by Figure 6.10.

Figure 6.10 A possible band diagram of a pristine metal/GO/Pt RRAM device at thermal equilibrium

6.3 Conclusion

Resistive switching in GO based RRAM had been studied with Al, Cu, Ni and Ti top electrodes. Different reproducible switching directions had been found in the Al/GO/Pt and the Ti/GO/Pt RRAM. Through analysis of the field dependence, the temperature dependence and the area dependence, the conduction mechanisms were found to be different in these directions, which were summarized in Table 6.1.

	AW			Unipolar or CW	
	Al/GO/Pt	Cu/GO/Pt	Ti/GO/Pt	Al/GO/Pt	Ti/GO/Pt

Field Dependence	HR S	Non-linear	Non-linear	Non-linear	Non-linear	Non-linear
	LRS	<i>Linear</i>	<i>Linear</i>	<i>Linear</i>	<i>Non-linear</i>	<i>Non-linear</i>
Temperature Dependence	HR S	Strong	Strong	Strong	Strong	Strong
	LRS	<i>Weak</i>	<i>Weak</i>	<i>Weak</i>	<i>Strong</i>	<i>Strong</i>
Area Dependence	HR S	Strong	Strong	Strong	Strong	Strong
	LRS	<i>Weak</i>	<i>Weak</i>	<i>Weak</i>	<i>Weak</i>	<i>Strong</i>
Suggested Mechanism		Electrode metal ions migration			NEM	O-group absorption/release

Table 6.1. Summary of the observed transport characteristics.

The transport measurement indicated switching direction was underlying mechanism oriented (See Table 6.1 also). The bipolar AW switching might associate with the diffusion of metal electrode ions while the bipolar CW switching was due to the absorption/release of oxygen based functional groups, consistent with literature [136, 162]. The unipolar switching in Al/GO/Pt might be caused by NEM effect, as reported in literature [52]. And the coexistence of two bipolar switching directions in Ti/GO/Pt also showed that both the oxygen related functional group absorption/release and the electrode metal ions diffusion play important role in the resistive switching of GO.

Chapter 7 Conclusion and Future Work

7.1 Conclusion

The significance of the work in this thesis is reflected in two directions, the device performance optimization which intends to resolve the performance challenge and the mechanism investigation to meet the challenge in deciphering the underlying RRAM device physics.

For HfO_x based RRAM systems, multiple performance boosts have been demonstrated on the same device for the first time by using the technique of ALD and Ge doping, which equips the HfO_x RRAM with characteristics including high uniformity, forming-free property and self-compliance. Comparative experiments reveal that the uniformity enhancement comes from the Ge doping, which may be due to the reduction of vacancy formation energy. Forming-free property originates from the oxygen deficiency caused by the metallic doping layer. Self-compliance is a consequence of the proper choice of deposition technique and condition.

For device physics, this work is the first one of its kind to apply theories of both dielectric loss and polaron in analysis of the transport in hafnium based RRAM. Transport measurements of both the dc and the low-frequency ac are taken at different temperature for Pt/ HfO_x /TiN RRAM. It is observed that the conductance of the as-deposited devices obeys the power relationship with temperature and frequency. To account for the much larger conductance of both the HRS and LRS, we established the equivalent circuit models to incorporate the effect of oxygen vacancy filaments, which is found to be independent of the cross-sectional area of the device. In HRS, since this component is frequency independent but temperature dependent, we proposed for the first time a small polaron hopping type transport, with an activation energy of 2.1 meV at temperatures above/below half of the Debye temperature, in consistence with the analysis of the electric field dependence and the dielectric loss test. In LRS, via temperature-dependent

characterizations, the additional conductance term is found to be originated from the weak metallic transport. Properties of aligned oxygen vacancy chains on the $(\bar{1}11)$ surface are calculated by *ab initio* simulation. This weak metallic behavior is correlated to the delocalization of the impurity band of the aligned oxygen vacancies, as revealed by the partial DOS and spatial distribution of wavefunctions of the defect states.

Inspired by the experimental significance of small polarons in HfO_x based RRAM, further calculation, using hybrid functional, is performed for the first time to interpret the observed metal-insulator transitions in the hafnium oxide based RRAM. Computational evidence is found for oxygen vacancy-bound small polarons migration and Mott type localization-delocalization transition. Adiabatic polaron hopping between equivalent threefold oxygen vacancies are found of anisotropic barriers, where the [001] directional migration barrier is ~ 90 meV, in agreement with low temperature (> 135 K) experimental finding. Dominant vibration mode mainly concerns the longitudinal motion of the vacancy-neighboring threefold oxygen atoms. In the presence of $(\bar{1}11)$ surface, lowest barrier of symmetrical surface hopping is found to be ~ 360 meV which is close to the experimentally observed barrier in high temperature range (320 K - 400 K) along [101] direction, where significant vibration contribution is from vacancy-neighboring threefold oxygen atoms dominated surface.

On the other hand, resistive switching in Graphene Oxide (GO) based RRAM has been studied in combination with various commonly used electrodes e.g. Al, Cu, Ni and Ti. For the first time, coexistence of different reproducible switching directions has been observed in the Al/GO/Pt and the Ti/GO/Pt RRAM cells. These switching directions are correlated to the underlying switching mechanisms as revealed by field dependence, temperature dependence and area dependence. Our observation also

suggests that both oxygen related functional groups absorption/release and electrode metal ions diffusion play important roles in bipolar resistive switching of GO.

7.2 Recommended Future Work

For the germanium doped HfO_x RRAM, as mentioned in Section 3.2, the composition of the dielectric layer is complicated. The composition, as revealed by the EDX profile in Figure 3.6 (c), varies with the distance to the interface. Electronic properties of such an alloy has not been adequately addressed in literature, resulting in difficulty in plotting corresponding band diagrams of the RRAM devices. First principle calculations are favored for future work due to their ease and precise in modelling the electronic structures of $\text{Hf}_x\text{Ge}_y\text{Ti}_z\text{O}$ and $\text{Hf}_x\text{Al}_y\text{Ge}_z\text{Ti}_u\text{O}$ based on physical characterizations, which is of great importance for achieving a complete understanding of the properties of the complex alloy.

The GO used in this study are more compositional than pristine (2D). They consist of multiple flakes. Since the stacking process of GO flakes is stochastic, the non-crystallinity and irregularity are ineluctable. GO flakes may be stacked or overlapped, which is also observed in other studies.[44] The stacking properties of GO thin films and its influence on switching mechanisms are difficult to be investigated experimentally. An alternative is to theoretically calculate the ion migration barriers in different configurations by using density functional theory simulation. Such a practice will be of great importance in figuring out the impact of graphene oxide structure on switching properties.

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