Nonvolatile resistive switching in metal oxides for the application in resistive random access memory

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NONVOLATILE RESISTIVE SWITCHING IN METAL OXIDES FOR THE APPLICATION IN RESISTIVE RANDOM ACCESS MEMORY

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Nonvolatile Resistive Switching in Metal Oxides for the Application in Resistive Random Access Memory

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Abstract

Title of Dissertation: NONVOLATILE RESISTIVE RANDOM ACCESS
 MEMORY DEVICES: FABRICATION AND
 CHARACTERIZATION

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Division of Physics and Applied Physics

Resistive random access memory (ReRAM or memristor) based on the resistive switching (RS) has been proposed as a potential candidate for next generation nonvolatile memory with high density, fast write and erase access, low power operation, and excellent retention performance. Although most of the transition metal oxides have been reported as the building blocks, the underlying mechanism of the switching is still unclear and controversial, which hinders the further development of ReRAM. The main objective of this dissertation is to report our in-depth scientific research on ReRAM based on transition metal oxides, including the materials preparation and characterization, device fabrication, electrical measurements, and investigation on the mechanisms. The structure of this thesis contains three parts, as follows.

First, we explore a few new ReRAM materials and compare its performance with the existing ones. We report the excellent unipolar RS behaviors in spinel ZnMn_2O_4 and ilmenite ZnMnO_3 , both of which have ON/OFF ratios larger than 10^4 . Good endurance and retention are achieved in both oxides. The conduction mechanism of the OFF state is attributed to the space-charge-limited conduction. The Ohmic behavior of the ON state suggests a filamentary conduction mechanism. This study introduces two new candidates for nonvolatile resistive random access memory devices, and it indicates that formation and rupture of conducting filaments are universal in certain ternary oxides even though they may possess distinct crystalline structures.

Second, based on a well studied material of ZnO, we study the doping and electrode effects on the RS characteristics. We carry out a comparative study on RS in Mn-doped ZnO thin films; samples grown on Pt and Si show unipolar and bipolar switching behaviors, respectively. Fittings of the current-voltage curves reveal the filamentary conduction in Pt/Mn:ZnO/Pt with good data retention. On the other hand, the interfacial effect dominates in Pt/Mn:ZnO/Si, and the low resistance state exponentially relaxes towards the high resistance state. Thus our results suggest that selecting electrodes dictates the RS properties, presumably by affecting the migration dynamics of oxygen vacancies.

Finally, using NiO as an example, we demonstrated a controlled room temperature conversions between nonvolatile memory switching and volatile threshold switching within a single device, by rationally adjusting the stoichiometry and the associated defect characteristics. Moreover, from first-principles calculations and x-ray absorption spectroscopy (XAS) experimental studies, we found that the strong electron correlations

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Chapter 1 Introduction

§ 1.1 Overview and Motivation

In computing, memory refers to a physical device for information storage in the integrated circuit. In the semiconductor industry, memories have taken the largest market portion, which still keeps increasing. Basically, memories can be divided into two main types: volatile memory and nonvolatile memory. Volatile memories consume power when they are used to maintain data, while nonvolatile memories are able to maintain data without a power supply. Random Access Memories (RAMs), such as SRAM and DRAM, which are random accessible with very fast access speed, fall into the group of volatile memories. Read Only Memories (ROMs), such as ROM/PROM/EPROM/EEPROM, which generally possess a low writing speed, fall into the group of nonvolatile memories. While traditional RAMs and ROMs both suffered from their drawbacks, in 1980, Dr. Fujio Masuoka from TOSHIBA invented the FLASH memory, which is both nonvolatile and random accessible with the re-writing speed at the range of milliseconds. Nowadays, FLASH memory has many applications in various portable electronic storage devices.

However, besides its shortcoming in terms of slow access speed and high operation voltage, FLASH memory is also approaching its scaling limit, which is believed to be around 10 nm. The industry is searching desperately for new technologies to further scale down FLASH, such as multilevel cell (MLC) and 3-D stacking. In a seemingly parallel line of investigation, researchers are also exploring other alternative nonvolatile random

access memories to replace the FLASH in order to meet the fast growing electronic market. In the following, several potential candidates will be briefly introduced, followed by a detail review of the research background of ReRAM.

Ferroelectric RAM (FeRAM)

FeRAM has a similar construction to DRAM by using ferroelectric layers instead of dielectric layers. Traditional perovskite ferroelectric materials exhibit a spontaneous polarization due to the displacement of the body-centered atom in the perovskite (ABO_3) structures, as shown in the Figure 1-1. When an external electric field is applied across an insulator thin film, the dielectric dipoles tend to align themselves along with the electrical field, associated with small shifts in the positions of atoms, and shift in the distributions of electronic charge in the crystal structure. When the external electrical field is removed, the remnant polarization state can be still maintained, giving rise to nonvolatile memory. The relationship between the applied electrical field and polarization exhibits a hysteresis feature. Binary "0" or "1" is stored as one of two possible polarizations state in a unit cell. For example, in Figure 1-1, the negative remnant polarization "-Pr" is used to encode "1", and the positive remnant polarization "+Pr" is used to encode "0".

Figure 1-1 Schematic of the relationship between the atomic displacement and the hysteresis loop of the polarization process of a ferroelectric perovskite oxide.

In nonvolatile FeRAM, the polarization states of the ferroelectrics materials must be thermodynamically stable. Moreover, A strong electric electrical field is needed to switch the polarization, but this field should not be larger than the break down field of the ferroelectrics materials.¹

Since the switching of polarization in a ferroelectric material happen in a very low current, one of the main advantages of FeRAM is its low power consumption (30 fJ/bit). Besides, write/erase operation induce subtle change of the crystalline structure in ferroelectric material, which give rise to very good write/erase endurance (10^{14}) of FeRAM.²

Nevertheless, nowadays FeRAM remains a relative small share among the overall semiconductor market due to some technical difficulties. One of the disadvantages of FeRAM is its limited scalability. On the other hand, most of the current commercial available FeRAMs are using either a 1 transistor–1 capacitor (1T-1C) design or a 2 transistor–2 capacitor (2T-2C) design. But the problem of these designs is that the reading

process is the destructive, so it requires the cell to be rewritten after its state was changed by reading. Ferroelectric field-effect transistor concept, which uses ferroelectric material as the gate metal to control the channel current, has been proposed, but no commercial product has been developed yet.

Magnetoresistive RAM (MRAM)

Different from traditional semiconductor memory devices, MRAM utilizes magnetic elements rather than electrical ones to store information. Within a basic MRAM cell, there is a thin insulating layer in the middle sandwiched by two ferromagnetic materials layers. The insulating layer is so thin (typically a few nanometers) that electrons can tunnel from one ferromagnetic layer into the other one, resulting in a tunneling current that is perpendicular to the thin insulating layer. On the other hand, the magnetization direction of the two ferromagnetic layers can be switched individually by an applying magnetic field. Due to the giant magnetoresistance (GMR) effect, if the magnetizations are in parallel, the tunneling current is larger, while if they are in the antiparallel the tunneling current is much smaller, which can be simply interpreted by using Mott's two current model. Therefore, such a magnetic tunneling junction can be switched between low and high resistance states to encode the binary "1" and "0". Reading an MRAM bit can be simply accomplished by passing a small current through the magnetic tunneling junction to measure if it is in the high or low resistance state.

Figure 1-2 Schematic of the relationship between the magnetization direction of each magnetic layers and the hysteresis loop of the magnetoresistance in respects to the applied magnetic field.

Rather than the actual moving of atoms or electrons, writing or erasing a MRAM is basically a switching process of the direction of electron spins, which offers MRAM a very fast operation speed. Furthermore, since the data is stored as a magnetic state, MRAM is having almost unlimited write/erase endurance and is inherently nonvolatile. A main drawback of MRAM is its complicated writing process. Traditionally, a high current is used to generate a magnetic field for the magnetization of the ferromagnetic layer. Apart from its high power consumption, this method also suffers from the false writing to the adjacent cell if the device is further scaled down in size. Most of the MRAM in the market today is using the “toggle” method of writing the bits, which employs a free layer synthetic antiferromagnet and a bit orientation rotated 45° with respect to the writing line. Such a novel method greatly enhanced the selectivity. A newer technique, spin transfer torque (STT), uses spin polarized electrons flowing through the device acquire a spin

polarization from a first layer, referred to as the fixed layer, which then exerts a spin-torque on a second layer. This lowers the magnitude of current required to write the cells, allowing for smaller size scaling. However, high current is still needed to realize high speed operation. The conflicting requirements for MRAM in vertical geometry, such as writing current, high thermal stability, read/write speed and the challenging of integration with CMOS, have been discussed in detail in a recent review paper³.

Phase Change RAM (PCRAM)

Another emerging memory device is called phase change random access memory, in which a phase-change material (usually chalcogenide glass, e.g. $\text{Ge}_2\text{Sb}_2\text{Te}_5$) is used as the storage media. Early in September 1966, Stanford Ovshinsky from Energy Conversion Devices filed first patent on phase change technology. A phase-change material exhibit two or more phases with dramatically different properties and is able to be quickly and repeatedly switched between these phases. Most of the phase-change materials in PCRAM have two phases, the amorphous phase and the crystalline phase. While the former is characterized by a high electrical resistivity, the later shows a low resistivity. By switching the material between these two phases, the change in resistivity can reach about five orders of magnitude.⁴ Simple applying an electrical pulse with very small magnitude, the stored data of a PCRAM cell can be retrieved.

In PCRAM, to obtain the crystalline state (SET), an electrical pulse with moderate magnitude is applied, which is to heat up the phase-change material above its crystallization temperature. This crystallization process corresponds to a threshold switching in the I-V curve. If the duration time of the external electrical stimulus is short,

the phase-change material will return to its initial amorphous state rapidly, resulting in a volatile switching. This is because the stabilization of crystallized state is time consuming. Therefore, the duration of this electrical pulse should be sufficiently long to obtain an stable nonvolatile crystalline state. To obtain the amorphous state (RESET), another electrical pulse with larger magnitude but short duration is required, which is to quench the phase-change material to amorphous form. Therefore, the duration time in RESET process should be short to create a steep drop of temperature.

Figure 1-3 (a) Schematic of a single PCM cell in a cross point array. (b) I-V curves of a phase change material under external field.

Nowadays, major electronic companies, such as Samsung Electronics, Intel, and Micron, have spent tremendous efforts on the development of PCRAM due to its outstanding advantages. Firstly, it has a very fast operation speed, which is commonly at the order of 100 ns. Secondly, it has a very promising scalability. Recently, A 20 nm 1.8 V 8 Gb PCRAM was announced by Samsung Electronics. Besides, PCRAM is also very compatible with the existing semiconductor technology. The main drawback of PCRAM is its requirement of large current and high working temperature.

Resistive RAM (ReRAM)

Early in the 1960s, W. R. Hiatt and T. W. Hickmott from General Electric reported the bistable RS in Nb-Nb₂O₅-Bi, where they found the switching between two resistance states with microsecond pulses was electrode dependent and suggested their device should have had potential advantages in computer memory as a result of their low power, non-destructive read-out and nonvolatile properties.⁵ The current tide of research started from the later 1990s. A. Asamitsu *et al.* reported that the switching of resistive states in a colossal magnetoresistive material Pr_{0.7}Ca_{0.3}MnO₃ could be achieved not only by a magnetic field, but also by an electric field.⁶ The resistance change was more than four orders of magnitude. But their experiments were done at low temperature (20 K) and the operation voltage was as large as 700 V. Afterward, Liu *et al.* reported the RS in the same material. Although the ON/OFF ratios were only about 17, the operation pulse voltage was optimized to ~100 ns with magnitude ± 5 V.⁷ A. Beck *et al.* from IBM also explored the nonvolatile memory devices based on the RS of Cr doped SrZrO₃ films sandwiched between SrRuO₃ bottom electrodes and Au top electrodes.⁸

Subsequently, as more and more efforts had been spared on this topic, a lot of materials were targeted as potential candidates, including binary oxides as NiO⁹, TiO₂¹⁰, ZnO¹¹, MnO₂¹², Fe₃O₄¹³, Al_xO_y¹⁴, SiO₂¹⁵ and multi-element oxides as Pr_{0.7}Ca_{0.3}MnO₃¹⁶, La_{0.7}Ca_{0.3}MnO₃¹⁷, SrTiO₃¹⁸, ZnMnO₃ and ZnMn₂O₄¹⁹. At the same time, various models had been proposed to explain this new phenomenon.

(1) One model is related to the field-induced alternating of the *electronic structure*. In Cr doped SrTiO₃, it is thought that current flowing across the insulator was determined by the bulk instead of the interface. The transition to the conducting state was deemed to

originate from a change of the bulk property which was caused by the carriers trapping in the bulk.²⁰ On the other hand, in Cr doped SrZrO₃ films, intrinsic defects which had different oxidation states and vacancies could form a series of electronic states at various levels within the energy gap. Accordingly, multilevel RS was achieved.⁸

(2) The second proposed mechanism is related to *ordered parameters*. Pb(Zr_{0.52}Ti_{0.48})O₃ is an ferroelectric material with high remanent polarization and its solid solutions exhibit a high piezoelectric response at the morphotropic phase boundary (x=0.5). In Pt/6nm-Pb(Zr_{0.52}Ti_{0.48})O₃/SrRuO₃ junction, the polarization reversal in the ferroelectric barrier was suggested to be the origin of the RS.²¹ This model is also strongly related to the ferroelectric nonvolatile memory. For Pr_{1-x}Ca_xMnO₃, the applied electric field could change the shape of the ferromagnetic clusters and arrange them directionally from an expected random state to an organized state, resulting in a filamentary path. Reversing the electric field could reshape the clusters and rearrange them into a secondary organized state. These two different states may give different conducting characteristics.⁷

(3) *Mixed valence character* may also induce RS in some metal oxides. This model was usually proposed for the metal oxides which contained elements with mixed valence, such as TiO₂²², CuO²³, and SrTiO₃¹⁸. In case of TiO₂ or SrTiO₃, the reduction reaction from Ti⁴⁺ to Ti³⁺ will be filling the Ti 3d band. The reduced valence states of the transition metal cations which are generated by this electrochemical process typically turn the oxide into a metallically conducting phase.

(4) At some oxides interface, the resistance may be changed by tuning the *interface barriers*. The Schottky barrier at the oxide interface is the main origin of the contact

resistance. Due to the migration of oxygen vacancies driven by electrical field, the potential profile of such a Schottky barrier can be modified consequently. According to A. Ruotolo *et al.*'s experimental results, such an atomic arrangement is confined at the space charge area below the interface.²⁴ The RS is thus believed to be due to the change of the contact resistance of the oxide interface.

(5) *Filamentary conduction* tends to be the dominating mechanism at the current stage for many metal-insulator-metal structures. Generally, it is thought that under an electric field, some tiny metallic filamentary paths will be formed in the insulator, corresponding to the ON state. Under a reverse bias, which is often accompanied by Joule heating from huge current flow, the filamentary paths will be broken down, resulting in the initial OFF states.

It should be noted that the above classification is an oversimplified picture, and the real switching event is a complicated electronic or ionic process, which may involve more than one mechanism. In order to address the limits of the ReRAM, further considerable research efforts are indispensable with respect to a systematic understanding of the switching mechanism in a microscopic scale.

§ 1.2 Core Theme and Outline of Dissertation

Fabrication and characterization of the ReRAM with metal-insulator-metal structure, and the research on the role of insulator and electrode that affect the switching characteristics and performance of ReRAM are the theme of this dissertation.

The questions we seek to answer here are:

- (1) For the insulator in the middle: does the switching characteristic or device

performance vary with different crystalline structures? As Mott insulators are frequently used as switching media and shows excellent performance, does the insulator type (Mott-Hubbard insulator or Charge-transfer insulator) affects the switching characteristics of ReRAM?

(2) For the electrodes: Can we modulate the switching characteristics, or even optimize the performance by simply selecting electrode? What problems we may encounter if conducting oxides are used as one of the electrodes.

This dissertation is organized in the following manner:

In Chapter 2, several fabrication methods for the oxide thin films are introduced, including pulse laser deposition, magnetron sputtering deposition, and sol-gel spin coating technique. Electrode patterning methods involving traditional photolithography and novel electron beam lithography are presented. In the rest of this chapter, some commonly used material characterization as well as electrical properties measurement techniques are briefly introduced.

In Chapter 3, a detailed introduction about RS characteristics of ReRAM is presented, including the I - V feature and the related proposed mechanisms.

Intensive research efforts have been spared on advancing ReRAM devices, and there is an urgent need to search for a wider range of complex oxides to find materials with better performances and to further elucidate the underlying physics. In Chapter 4, we give a revelation of zinc manganese oxides to be promising candidates for nonvolatile memory cells. By applying an external electric field, both the Au/ZnMn₂O₄/Pt and Au/ZnMnO₃/Pt devices can hold a stable HRS and LRS. Each state has a good reading endurance and data retention. The LRS follows an Ohmic conduction, where the metallic filament is

formed. The HRS is dominated by space charge limited conduction. This work suggested the two functional materials ZnMn_2O_4 and ZnMnO_3 also have a promising potential application in nonvolatile resistance random access memory devices.

In Chapter 5, we use two of the most important electrode materials in current electronic market, Si and indium tin oxides, as examples, to illustrate the electrode effects on the switching characteristics and devices performance. (1) We obtained unipolar and bipolar RS in Mn-doped ZnO thin films by using bottom electrodes of Pt and Si, respectively. Through nonlinear fitting, we interpret the unipolar RS by filamentary conduction and the bipolar RS by an interfacial effect. A broad distribution of operation voltages was observed in unipolar RS, which is due to the random formation of conducting filaments. In contrast, the bipolar RS is more stable and its switching characteristics can be gradually modulated by reverse biases. In terms of device performance, we observed distinct resistance evolutions – filament-type RS exhibits good retentions for both HRS and LRS; on the other hand, the LRS in interface type RS relaxed quickly towards HRS. (2) In the second half of Chapter 5, we carried out an extensive study of the deterministic conversion between the memory and threshold switching in NiO by using ITO as bottom electrode. First, the oxygen concentration can be enhanced by the use of the transparent oxide substrate ITO. Second, memory switching can be converted to threshold switching by using a large enough compliance current. Third, the threshold switching can be converted back to the memory switching by annealing in vacuum. Regarding to the mechanism, from the Poole-Frenkel conduction model, we derived different dielectric constants for the memory OFF state and the threshold OFF state, as a result of the different oxygen concentrations in NiO. This scenario evolving

oxygen concentration is further confirmed by the secondary ion mass spectrometry (SIMS). Our observations suggest that electrode selection is a general route to achieving different switching characteristics, either volatile or nonvolatile as wished, going beyond the conventional performance of such ReRAM devices.

In Chapter 6, with the prototypical Mott insulator NiO as an example, we shed light on the intricate characteristics of RS from the perspective of strong electron correlation effect. The electron correlation and the associated band structure can be modified by tailoring the device structure, the synthesis conditions, and the measurement protocols. Specifically, stoichiometric NiO is a charge-transfer insulator, where the charge fluctuation is the $p-d$ type, giving rise to the commonly reported memory switching. On the other hand, our first-principles calculations and XAS measurements suggest that the nickel-deficient nickel oxide, namely Ni_{1-x}O , is a negative-charge-transfer insulator, where the charge fluctuation is mainly the $p-p$ type, giving rise to threshold switching. Among the various factors considered so far in literature, the strong correlation effect between electrons has been largely ignored in interpreting RS experiments. Our study suggests that the strong electron correlation effect does profoundly affect the characteristics of RS, and its general role in the operation of memory devices made of transition metal oxides clearly warrants further investigations.

Finally, a summary of the whole dissertation is given in Chapter 7.

Chapter 2 Fabrication and Characterization of ReRAM

§ 2.1 Introduction

The fabrication and testing of a ReRAM device in a lab is not very demanding due to its simple structure. The whole procedure includes thin film growth and characterization, electrode patterning and deposition, and device performance evaluation via electrical measurement.

There are a lot of methods that can be used for the thin films or electrode deposition during the ReRAM fabrication, such as magnetron sputtering, atomic layer deposition, thermal evaporation, pulse laser deposition, molecular epitaxial beam, and sol gel spin coating etc. In the beginning of this chapter, we are going to introduce three methods, pulse laser deposition, magnetron sputtering and sol gel spin coating, which have been frequently used in our experiments.

The device performance is influenced by the quality of the prepared thin films, which was examined by various characterization techniques. For example, the influence of oxygen concentration on the switching characteristics of oxides based ReRAM has been often emphasized. In the second part of this chapter, we are going to introduce several frequently used material characterization methods, including: X-ray diffraction, scanning electron microscope, atomic force microscope, and x-ray absorption spectroscopy.

While photolithography is the most common method used for electrodes patterning,

recently electron beam lithography (EBL) is frequently used for precise electrode patterning with nm resolution. Both of these two methods will be covered in the this chapter, and finally we will introduce the electrical characterization of ReRAM and our measurement set up at the end, depending on the size of a single device and the measurement set up.

§ 2.2 Thin Film Fabrication Techniques

§ 2.2.1 Pulse Laser Deposition

Pulsed laser deposition (PLD) is a material deposition technique that using the high energy focused laser beam to ablate a target, the materials in which is then vaporized and deposited on the substrate facing to the target. It is a versatile method for thin film with not only single layer but multiple layer growth. One superior advantage of PLD is its stoichiometric transfer, which means under optimized condition, the stoichiometric of the deposited thin film can be maintained the same as the target. This merit makes PLD a very unique and powerful technique for the fabrication of ReRAM based on the complex oxides heterostructure, such as $\text{Pr}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ (PCMO)/ $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ (YBCO)⁷, PCMO/Pt²⁵, $\text{SrRuO}_3/\text{SrTi}_{0.99}\text{Nb}_{0.01}\text{O}_3$ ²⁶, $\text{LaAlO}_3/\text{Nb:SrTiO}_3$ ²⁷, and $\text{Sr}_2\text{TiO}_4/\text{Au}$ ²⁸. In addition, currently PLD has also been used to fabricate ReRAM based on diluted magnetic semiconductors (DMS) and multiferroic oxides, in which the interplay between magnetic and transport properties are of interest²⁹⁻³¹.

Figure 2-1 Schematic of a typical PLD system.

A typical set-up for a PLD system is schematically shown in Figure 2-1. In an ultrahigh vacuum (UHV) chamber, targets are struck at a stage with an angle of around 45 degree to the pulse laser beam direction. The area of the focused laser beam is around several millimeters square. The atoms or ions ablated from the target are deposited on substrates, which is facing to the target with a distance around 10 cm. In addition, it is also possible to embed a reflection high-energy electron diffraction device into the same chamber, which makes the in situ monitoring feasible during the thin films deposition. The PLD system which is updated in such a way is sometimes called Laser MBE.

§ 2.2.2 Magnetron Sputtering Deposition

Magnetron sputtering is another physical vapor deposition technique for thin films growth. In the basic sputtering process, a target is bombarded by discharge plasma of energetic ions. Before the sputtering deposition process, a vacuum atmosphere better than 10^{-4} Pa must be achieved in order to minimize the contamination. Once such an appropriate pressure has been reached, an inert gas (such as Argon) is introduced with a well-controlled flowing speed, which raises the pressure to the necessary values that is required for the specific material growth. This bombardment process causes the removal of the atoms, which are deposited as a layer of thin film on a substrate placed facing to the

target. Secondary electrons are also emitted from the surface of the target surface due to the ions bombardment, and these electrons play a vital role in terms of maintaining the plasma. In order to improve the efficiency of momentum transfer, the atomic weight of the gas is usually close to the atomic weight of the elements in target. Besides, reactive gases, such as oxygen or nitrogen, are frequently adopted for the sputtering of oxides or nitrides compounds. The compound can be grown by using the target with the same composition, or using the corresponding metal as the target with the assistance of the reactive gas. There are many parameters that influence the quality of the deposited thin films due to the complex process involved during a sputtering deposition. The availability of various parameters enables sputtering deposition to offer a very wide range of control over the growth of different thin films with various surface morphology and physical properties. Magnetron sputtering and the aforementioned PLD are two of the most generally used methods for the fabrication of metal oxides based ReRAM. The switching characteristics in both cases can be affected by some common parameters, particularly, the oxygen pressure. In the Chapter 5 of this thesis, we will describe two distinct switching behaviors in samples fabricated using PLD with different oxygen pressures. Nevertheless, it should be noted that in this thesis, the magnetron sputtering has only been used for metal electrode deposition.

§ 2.2.3 Sol–gel Spin Coating

The sol-gel method is another traditional method for thin film growth. A sol-gel synthesis procedure involves a transition from a colloidal solution liquid phase ‘sol’ to a ‘gel’ phase. Usually metal or semi-metal alkoxides or their derivatives are used as

precursors. A 'sol', a colloidal suspension, is formed after a series of hydrolysis and polymerization reactions of the precursors. Alcohol is usually used as the co-solvent, and the sol-gel precursor, alkoxide, mixes well with alcohol facilitates the hydrolysis. Then the sol particles condense into a continuous liquid phase (gel), which can be deposited on any substrate by spin coating or dip coating. Further drying and heat treatment converted the 'gel' into dense glass or ceramic materials. Generally, hydrolysis, alcohol condensation, and water condensation are the three main reactions are used to describe sol-gel processes.

§ 2.3 Thin film Characterization Techniques

§ 2.3.1 X-ray Diffraction

As the wavelength of an X-ray (0.01~10 nm) is close to the distance between atoms in the lattice of materials, X-ray diffraction (XRD) can be used to characterize materials in term of crystalline structure, chemical bonds, lattice disorder, and various other physical properties.

Crystals can be regarded as regular arrays of atoms, and X-rays can be considered as electromagnetic waves. The incident X-rays are elastically scattered by parallel atomic planes, resulting in phase difference in the reflected rays. While in most directions, these waves cancel one another out by destructive interference, they interfere constructively in some specific directions, which is determined by Bragg's law:

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

where n is any integer, λ is the wavelength of the incident beam, d is the space between

the planes in the atomic lattice, and θ is the angle between the incident ray and the scattering planes. Therefore the plane spacing can be obtained by $d = n\lambda / 2 \sin \theta$ (generally, $n = 1$).

For specific applications, particular XRD techniques are used depending on the types of specimens and the information that is requested. For polycrystalline samples, powder XRD is capable of characterizing the crystallographic structure, preferred orientation, and grain size, etc. Powder XRD is quick and very convenient for the identification of unknown substances, especially for those with mixed phases. By comparing the obtained pattern to the existing data base, the phases can be determined. Moreover, further structural information on unknown materials can be studied if the powder XRD is coupled with lattice refinement techniques. In addition, there is a relationship between the grains size and the full width at half maximum (FWHM) of the XRD patterns, therefore grains size can be roughly estimated by using the Scherrer equation:

$$\tau = \frac{K\lambda}{\beta \cos \theta}$$

where λ is the beam wavelength, K is a constant, β is the FWHM, and θ is the Bragg angle. τ is the mean size of the crystalline domains, which may be smaller or equal to the grain size. K varies with the shape of the domain, which however, is typically about 0.9.

Figure 2-12 (a) Photograph of a Bruker D8 Advanced X-ray powder diffractometer.
(b) Schematic illustration showing X-rays interact with crystalline lattice.

§ 2.3.2 Scanning Electron Microscope

Scanning Electron Microscopy (SEM) produces images of sample morphologies by scanning it with a electron beam (typically energy: 1~30 keV), which generates signals containing information on surface topography, composition and other properties by interacting with the atoms. In the most common mode, imaging mode, SEM collects the low-energy (<50 eV) secondary electrons which are ejected from the k-orbitals of the specimen atoms (within a few nanometers from the surface) by inelastic scattering interactions with beam electrons. The intensity of the SEM signal is strongly related to the angle between incident beam and the sample surface, resulting in images with a well-defined, three-dimensional appearance.

Back-scattered electrons (BSE) are high-energy electrons originating why the incident beam electrons back-scattered out of the interaction volume by elastic scattering interactions with specimen atoms. BSE imaging can image high contrast between areas that consist of different compositions duo to more strongly backscattering from heavier elements. Additionally, BSE can be affected in backscatter diffraction more, which is capable of determining the crystallographic structure of the specimen.

The size of the electron spot plays an important role in determining the spatial resolution of SEM. And the size depends on both the wavelength of electrons (controlled by the acceleration bias voltage) and the electron-optical system (like magnetic lens). In general, a higher beam energy produces a higher resolution, which will

achieve a resolution between less than 1 nm and 20 nm, depending on the instrument. The resolution of SEM is high enough for observing the morphologies of nanomaterial but not for single atoms.

Due to the possible accumulation of incident electrons, local electric fields may be built up and strongly affect the secondary electron and BSE. Such charging effects dramatically downgrade the resolution of the SEM image by inducing drifting and blurring boundaries. To retrieve clear images, the specimens should be generally conductive. For insulating samples, such charging effects can be compensated by coating a thin conducting thin film, like Au or graphite, on top of the specimen.

§ 2.3.3 Atomic Force Microscopy

Atomic Force Microscopy (AFM) is a versatile and powerful tool to provide a 3D profile of the surface in an atomic resolution, by imaging, measuring and manipulating matter at its surfaces. AFM consists of a cantilever with a sharp probe (typically 20 nm) at the end, which deflects when external force (e.g. mechanical contact force and van der Waals force) exerts on it. The cantilevers and probes are typically made of silicon or silicon nitride. A position sensitive photo detector signals the displacement of a laser beam, which is reflected to magnify a small bending. Hence, during the horizontal scanning, a map of the surface topography is generated by detecting the bending of the cantilever. It is important to realize that the resolution of AFM is generally limited to ~0.1 nm due to the unavoidable thermal vibrations. Another common problem is that the application of AFM is limited when the surface is too rough. It is also not suitable for the samples with nanostructures not rigidly mounted to the substrates such as the out-of-plane

nanowire arrays.

The primary modes of operation for an AFM are contact mode and tapping mode. The tapping mode is usually applied in determining topography and phase morphology of films. In tapping mode operation, the silicon probe tip scans across the sample surface by oscillating at its resonance frequency and only intermittent contacting with the surface. Comparing to amplitude images, height data can give a good image of the height of surface features but not able to show the distinct edges. On the other hand, phase data is a powerful technique for mechanical and composition characterization of the surfaces of the heterogeneous samples, regardless of its complications involved in interpretation.

The conventional AFM measures record the van der Waals force between the cantilever tip and the sample surface. It can also be configured to measure other interactions for specific applications. For example, a magnetized cantilever can be used to measure the magnetic momentum on the sample surface, which is also known as magnetic force microscopy (MFM).

Similarly, a conductive AFM tip (C-AFM mode) is able to sense the electric potentials and conductance, which has extensive applications on ReRAM characterization, especially for the devices with small electrodes ($< 1 \text{ } \mu\text{m}^2$).³² C-AFM uses a small electrical current to extract the surface profile of the sample surface. The current can flow through from the metal (such as Pt-Ir alloy) coated tip of the microscope towards the sample. Ordinary topography profile is also obtained simultaneously with the current sensing process. The combination makes it possible for one to obtain the surface conductivity in term of spatial resolution. On the other hand, as the tip is so small that C-AFM is capable for the characterization of device with very small electrodes.

§ 2.4 Electrode patterning

For a general measurement of a ReRAM device with longitudinal transport geometry, electrode size varies from tens to hundreds of microns. Therefore a shadow mask or common photolithography technique can be used for the electrode patterning. This method is feasible in a common lab and also compatible to existing semiconductor technology, therefore it is extensively adopted for the ReRAM research in both of the university and the industry. For transverse transport geometry, a layer of insulating films or even a treated insulating substrate can directly be used as the switching media where the switching may take place between the adjacent electrodes on top of it.¹⁸ The geometry offers a straightforward way to investigate the mechanism of the switching, since one can use microscope, such as SEM^{33,34} and AFM¹⁸, to in situ monitor the physical or structural change of the material during the occurrence of RS.

§ 2.4.1 Photolithography

Photolithography is an optical method to transfer patterns onto a substrate. It is basically the same process as the one that is used in lithographic printing. A typical photolithography process for electrode patterning includes the following steps: surface preparation, coating, pre-bake, alignment, exposure, development, post-bake, electrode deposition, stripping, and post cleaning. After surface cleaning, photoresist is spin coated onto the substrate. Resist thickness is affected by primarily resist viscosity and secondarily spinner rotational speed. Prebake is used to evaporate the solvent coming along with the photoresist, and to density the photoresist. In the lab, usually a hot plate

can serve for this purpose with a fast speed and controllable temperature. Subsequently, desired patterns are transferred to the photoresist by align-exposure-develop steps, which are summarized in Figure 2-3. Postbake is used to stabilize and dense the developed photoresist prior to the electrode thin film deposition where the resist will serve as a mask. After the electrode deposition, common solvent such as acetone or alcohol is used to remove the photoresist, sometimes assisted by ultra sonic cleaning.

Figure 2-2 overview of align-expose-develop steps

Photolithography is a binary pattern transfer: there is no gray-scale, color, nor depth to the image. Photolithography is nowadays efficient in mass production but the wavelength of exposing light sources limit the further advancing in terms of resolution.

§ 2.4.2 Electron Beam Lithography

Similar to the photolithography mentioned above, but for the purpose to obtain a better resolution, the light source is replaced by electron beams in electron beam lithography (EBL). The shorter wavelength of electron beams enables the EBL to pattern much smaller features down to 10 nm or smaller. For electrode patterning, the procedure of

EBL is similar to ordinary photolithography. Since electrons beam is used instead of light beam, a special resist that is sensitive to electrons has to be used in EBL. In our study, we use PMMA as the resist. For positive exposure, exposing the PMMA to electrons causes the breaking down of the large molecule into small ones, which are then simple washed away. PMMA is changed to negative electron beam resist when over exposed, since large molecules are merged together under high electron doses, resulting in even larger molecules that have smaller solubility in developer. The dose of positive pattern is about an order of magnitude less than that for negative one. EBL is extensively used for specific research and development, but it is limited by its low process speed, and the high cost for large scale patterning over a large area.

§ 2.5 Electrical Properties Characterization Techniques

§ 2.5.1 Probe Station

A probe station is a stage with mechanical manipulators that are used to acquire physical (usually electrical) signals through the small contact of the device under test (DUT). The mechanical manipulators allow the precise three dimensional positioning of several small needles over the surface of the DUT. A probe station is usually equipped with at least one vacuum system and an optical system. The vacuum is to stabilize the DUT to the stage in order to minimize the vibration during measurement, while the optical system comes along with a microscope, a camera, a light source, and a monitor to view the sample under test. The small needles, typically at the range of several microns, are so sharp that they may destroy the surface of the sample or electrode readily. To avoid such damage, the image resolution of the above-mentioned optical system is very important, and additional care has to be taken during the positioning (especially lowering) of the needles towards the sample surface.

Figure 2-4 illustrates how external equipment is connected to the DUT. Generally, both the input and put electrical signals pass through the mechanical arms of a probe station. However, the optional coax and triax sample holders also enable the application of ground or bias to the sample stage.

Figure 2-3 How external equipment is connected to the sample

Particularly, a cryogenic probe station is designed specifically for temperature dependent electrical measurements. Such a system comes with a vacuum chamber, which is evacuated by an additional turbo vacuum system. A transfer line is also needed to carry the cryogen (liquid nitrogen or liquid helium) from a Dewar to the refrigerator in the chamber. And a thermal sensor and heater is installed underneath the sample stage, the temperature of which is controlled through a programmable temperature controller. The controller senses the system temperature and sends DC heater power to the probe station heater as required, balancing the amount of heater power against the cooling power available at the cold head to provide a stable temperature at any set point entered by the user. The controller also balances its time response against that of the probe station in order to achieve a stable temperature without oscillations or unnecessary delays.

§ 2.5.2 Temperature Dependent I-V and C-V Measurement

In our experiment, there are three ways available for temperature dependent I-V and

C-V measurement, namely, closed cycle cryostat, physical property measurement system (PPMS), and cryogenic probe station. To carry out the measurement in the closed cycle cryostat or PPMS, the DUT is connected to the measurement equipment through wire bonding technique. This technique is a common way for general electrical transport measurements, such as resistivity and Hall Effect for thin films or bulk materials. For the characterization of devices with large amounts of small electrodes, however, the wire bonding method is difficult and inefficient. In this case, the cryogenic probe station shows superior convenience in catering many devices.

There are two modes for both DC and pulsed I-V measurements, voltage controlled mode and current controlled mode. For the voltage controlled mode, voltage source is used to sweep voltages to the DUT, while the current passing through the DUT is monitored and recorded. For the current controlled mode, current source is used and voltage is recorded. To protect the DUT from permanent break down, a compliance current (compliance voltage) is used in voltage controlled mode (current controlled mode). For the measurement of ReRAM devices, both measurement modes have been used, although the usage of voltage control mode is frequently reported in literatures.

In a C-V measurement, the voltage applied to the DUT is varied, and the capacitance is recorded and plotted as a function of voltage. To measure the capacitance, a small AC signal is used. C-V testing is a very powerful technique to acquire semiconductor parameters in traditional MOSFET and MOSCAP devices. Particularly, it is indispensable for the characterization of FLASH memory devices in order to obtain the charge trapping properties. Moreover, such a technique is also extensively used to measure other devices, such as bipolar junction transistors, microelectromechanical systems (MEMS) devices,

carbon nanotubes, and photovoltaic cells. For interface-type ReRAM device, C-V measurement is frequently used to determine the interface barrier properties³⁵. On the other hand, it is also reported that the occurrence of negative capacitance can be associated with the presence of conducting filament formation in filament type ReRAM³⁶.

§ 2.5.3 Retention and Endurance Testing

Endurance is the parameter that indicates the cumulative write/erase cycling capability of a logic or memory device. Each write/erase operation may potentially introduce defects into the memory cell material matrix, which may further accumulate over time. At certain point, these accumulated defects may cause the failure of a cell by preventing a cell from programming, erasing or reading.

For a nonvolatile memory device, the first critical end-of-life parameter is the ability to maintain and retain the written state of any data bit over a proper period. Retention is the parameter that refers to the maximum value of such a period of time that one can retrieve the data from the cell after programming. Although the ability for a cell to hold the data bit is essentially determined by the devices intrinsic properties, it is also affected by a lot of factors, including temperature, reading voltage, accumulated operation cycles (endurance), electrostatic influence, and radiation exposure, etc.

Chapter 3 RS Characteristics of ReRAM

§ 3.1 Introduction

To describe the different RS characteristics, we need to distinguish between two operation modes with respect to the polarity of electrical field applied to RS cell. There are two modes of switching: unipolar and bipolar, depending on whether both positive and negative electrical field are required for the write/erase operations (Figure 3-1).³⁷ In this Chapter, both of the unipolar and bipolar switching characteristics and related mechanism will be introduced in detail. It should be noted that the separation of unipolar and bipolar modes is an oversimplified picture based on phenomenological observation of the current-voltage curves, which does not imply that the underlying mechanism of one is essentially differentiated from that of the other.

Figure 3-1 Two types of RS: (a) unipolar and (b) bipolar

§ 3.2 Unipolar RS

§ 3.2.1 Current-Voltage Characteristics

In unipolar RS, the switching procedure does not depend on the polarity of the applied electric field. All the write, erase and read processes can be realized in either positive or negative bias regions. In some cases of unipolar switching, the write and erase

process can happen on both positive and negative bias regions, which was named as nonpolar RS. In this thesis, we still treated it as unipolar RS as they have the same characteristics: the reset voltage (transition from low resistance state (LRS) to high resistance state (HRS)) voltage is always smaller than the set voltage and the reset current is always larger than the set current, which is limited by the so-called compliance current (CC). The switching direction may depend on greatly depending on different material systems, including not only the insulators in the middle but also the bottom and top electrodes. It should be noted that most of the as-prepared devices do not show a unipolar RS, unless a larger voltage (usually larger than the set and reset voltages) is applied to activate the device. Such a process is called the “forming” process, which is the first step to initiate a device before it can function. Although CC is also used, the larger transient current accompanying the forming process may cause physical damage to the device, or at least lead to degradation of the device stability. Regarding this problem, recently, Y. M. Lu *et al.* offered a solution by utilizing as optimized circuit design.³⁸

§ 3.2.2 Basic Physical Mechanism

The mechanism of unipolar RS is generally associated with the conducting filament formation and rupture. The main challenge is to identify the phase of the conducting filament and the place where the formation and rupture happen.

An early work on the typical unipolar RS was done regarding the Pt/NiO/Pt configuration.⁹ Polycrystalline NiO films were deposited on Pt bottom electrode by magnetron sputtering. The ON/OFF ratio of about two orders of magnitude and retention more than 20 hours were achieved. As the bottom and top Pt electrodes were chemical

inert, the migration of electrode ions could be excluded. By changing the compliance current, the reset current also changed, which implies that there was still some filament-like paths formed in the insulator that controlled by the setting of compliance current. Hence, it was suggested that the paths were formed by the Ni defects in the polycrystalline films for the switching from HRS to LRS when applying an electric field.⁹ And if the compliance current was removed, as the device was at LRS, the current would dramatically increase and then abruptly drop to HRS due to the filament rupture caused by the Joule heat.¹³

In the past a few years, a lot of efforts was spent on the unipolar RS in binary transition metal oxide, such as TiO_2 ²², MnO_x ³⁹, SnO_2 ⁴⁰, ZrO_2 ⁴¹, and ZnO ¹¹. Recently, we reported the unipolar RS in ternary metal oxides ZnMnO_3 and ZnMn_2O_4 sandwiched by Au top electrodes and Pt bottom electrodes.¹⁹ By comparing these two similar compounds, we suggested that formation and rupture of conducting filaments are universal in certain ternary oxides, even though they may possess distinct crystalline structures. For most of these systems, the mechanism is still far from clear. It is generally accepted that the switching from HRS to LRS originates from the formation the tiny filaments in the insulator, which may be formed by the oxygen vacancies along the grain boundaries in metal oxides by applying external electric field. The switching from LRS to HRS is supposed to be caused by the Joule heat. The unipolar RS was well stimulated by Chae *et al.* via a percolation model involving a random circuit breakers network.⁴² Based on the modified model from the same group, they showed that the reset process were governed by the thermal stability of the filaments and a competition between Joule heating and thermal dissipation.⁴³ Recently, by using a pulse-forming method instead of the traditional

DC voltage sweeping, M. Noman *et al.* showed that the Joule heating and thermal dissipation dynamics also play a vital role in term of the electroforming process.⁴⁴ Moreover, local heating enhances the mobility of oxygen vacancies, giving rise to the high switching speed. The simulation of W. Jiang *et al.* showed that using the mobility of oxygen vacancies at room temperature, the switching time in SrTiO_{3-x} is about 8 orders of magnitude lower than the nanosecond ReRAM.⁴⁵

One significant characteristic of the filamentary based RS is that the filaments tend to form locally in the insulator. The study on the area dependence of the LRS showed that the ON state current did not sensitively depend on the area, which supports the local nature of the filament.³⁷ If a large electrode was put on NiO thin films and switched into the ON state or the OFF state, the density of conducting filaments could drastically change. Experiments suggested that the filaments are mainly localized at the regions related to extended defects, presumably along the grain boundaries of the NiO thin films⁴⁶⁻⁴⁹.

§ 3.3 Bipolar RS

§ 3.3.1 Current-Voltage Characteristics

On the other hand, for the bipolar RS, the operation procedure must involve both positive and negative bias regions. That is, if the turning on process happens under a positive bias, it can only be turned off by applying a negative bias. As this operation is slightly complicated, such devices seem to be less favorable compared to the unipolar ones, at first glance. However, unlike unipolar ones, some of the bipolar ReRAM does not

require a forming process. Moreover, some of the bipolar ReRAMs can operate under an extremely low current condition, thus, they show great potentials in terms of low power consumption.

§ 3.3.2 Basic Physical Mechanism

The interface effect of the junction between the insulator and the electrode, or between the bilayer oxides structure, can induce significant bipolar RS. Sawa *et al.* reported the vertical transport properties of epitaxial layered structures composed of $\text{Pr}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ sandwiched between SrRuO_3 bottom electrode and several kinds of top electrodes, such as SrRuO_3 , Pt, Au, Ag, and Ti. Devices with Ti top electrode showed larger hysteresis.⁵⁰ They proposed that by applying an electric field, the charge carriers were trapped at the interface and the height and width of the Schottky-like barriers was changed, which modulates the conducting state of the interface. T. Fujii *et al.* investigated the electrical properties of heteroepitaxial oxide Schottky junctions, $\text{SrRuO}_3/\text{SrTi}_{1-x}\text{Nb}_x\text{O}_3$ ($0.0002 \leq x \leq 0.02$).²⁶ They concluded that the RS in Schottky junctions came from the change in conductance through additional tunneling paths rather than the change in barrier potential. But they also suggested that electron charging in, or discharging from, the interface depended on the bias polarity and may account for the colossal electroresistance effect. Recently, D. B. Strukov studied bipolar RS in nanoscale systems in which solid-state electronic and ionic transport were coupled under an external bias voltage, and gave a definition of the “missing” memristors as the forth fundamental circuit elements predicted by Leon Chua in 1971.^{51,52}

Figure 3-2 Filamentary conduction model in Cu/SiO₂/Pt

On the other hand, electrical field driven ionic migration can also trigger the bipolar switching. Such a device usually adopts a chemical active metal as one of the electrodes, such as Cu and Ag, while the other end is a chemically inert metal, such as Pt, Au and Ir. The insulator in the middle can be a chalcogenide or a metal oxide, such as AgS, SeGe, or SiO₂. By applying an electric field, the chemically active metal will readily diffuse into the insulator, forming a tiny conducting filament connected to the opposite electrode, setting the device into the LRS or ON state. The forming of this metallic filament allows this high conducting state to be maintained for a long time until another sufficient reverse bias is applied, which causes the eletrochemical dissolution of the metallic filament and the device to reset into the initial HRS or OFF state.³⁷

Taking Cu/SiO₂/Pt (or Ir) as an example, it showed typical bipolar RS and as exponential dependence of the operation speed on the operation voltage (Figure 3-2).¹⁵ The operation voltage was about 2 V and the on state current was only around 200 nA, which had a great advantage of low power consumption. While the forming voltage had a linear dependence on the thickness of the SiO₂, the set voltage did not. These results were explained using the typical filamentary model. Specifically, it was believed that the

filaments in Cu/SiO₂/Pt (or Ir) configuration were formed by the Cu ions. Another example of this kind of cation-based filamentary conduction is Ag/ZnO:Mn/Pt, where only 5 ns voltage pulse was needed to set or reset the device. Retention of more than 10⁷ s (about 4 months) had also been achieved.⁵³ But the shortcoming was that the cycling endurance was still far from the commercial requirement. The mechanism behind it was attributed to the migration of the Ag ions into the insulator. It should be pointed here that the Mn doping was to increase the resistance of the OFF state.⁵³

§ 3.4 Summary

In terms of device geometry, unipolar switching is frequently observed in devices which use inert metals for both of the bottom and top electrodes. Bipolar switching usually occurs in device where one of the electrodes is chemically active, such as Ag or Cu, and the other one chemically stable. Particularly, bipolar switching also frequently observed at the interface between two oxides.

From a circuit point of view, the unipolar switching is more preferable, since only one diode is needed to be used as a selector to block sneak currents. However, bipolar switching shows superior advantages in terms of power consumption. In fact, nowadays, most of the major memory manufacturers are focusing their research and development on the bipolar switching devices.

In order to explore the potential of the ReRAM further and to exploit their limits, a considerable amount of research is still needed with respect to a deeper understanding of the microscopic mechanism of the switching processes.

Chapter 4 Unipolar RS in Ternary Metal Oxides

§ 4.1 Introduction

Various RS phenomena with different performance characteristics have been observed in lots of materials systems, such as binary metal oxides,^{54,55} perovskites,^{7,25,56,57} and chemically active Ag- or Cu-doped chalcogenides glass.⁵⁸ ZnO is one of most studied wide band gap semiconductors, and recently steady RS behaviors have been observed in devices based on ZnO thin films.^{59,60} Mn-doped ZnO, as one of ZnO doped phases, also show good performances as ReRAM material.⁵³ Mn-doped ZnO has attracted a lot of research interest also because it has been suggested to be one of the room-temperature diluted magnetic semiconductors theoretically,⁶¹ which was later verified by experiments.^{62,63} Nevertheless, the origin of the ferromagnetism in Mn-doped ZnO is still puzzling and may involve more than one mechanism simultaneously.⁶⁴ Thus the Mn-Zn-O ternary oxides systems are of interest in terms of both the electrical and magnetic properties.

However, compared with the binary ones, the RS behaviors in ternary oxides have been less studied. Szot *et al.* demonstrated the RS regarding individual dislocations in single-crystalline SrTiO₃, in which the occurrence of switching was related to an intrinsic feature of the dislocations.¹⁸ Garbarino *et al.* further verified this model and suggested that the current-induced Na⁺ ion migration results in the RS in Na_{0.5-δ}CoO₂.⁶⁵ The charge-order state breakdown is another frequently reported switching mechanism, which

was used to be used to explain the colossal electroresistance phenomena in charge-ordered LuFeO_4 .⁴² The versatile electrical and magnetic properties, which can be tuned by external parameters, especially electric and magnetic fields, of manganites make them stand out from the oxides family. Indeed, a lot of attention has been put on the RS in manganites, for example, $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$,⁶⁶ $\text{Bi}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$,⁶⁷ and $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$.^{7,16,68,69} As intensified research efforts are spent on the optimization of ReRAM devices and the elucidation of the underlying physics, it is urgent to interrogate a wider range of oxides materials to search for candidates with better performances and to get deeper understanding of the underlying mechanism. In this work, we studied two zinc manganese oxides, ZnMn_2O_4 with spinel structure and ZnMnO_3 with ilmenite structure, which correspond to Zn/Mn atomic ratio of 1:2 and 1:1, respectively. We observe stable switching behaviors in both of these zinc manganese oxides, which enable them to find potential applications in ReRAM devices

§ 4.2 Nonvolatile RS in spinel ZnMn_2O_4 and ilmenite ZnMnO_3

§ 4.2.1 Fabrication of ZnMn_2O_4 and ZnMnO_3 ReRAM

In our experiments, the sol gel technique is used to fabricate the zinc manganese oxide thin films on top of commercially available Pt/Ti/SiO₂/Si substrates. The source was the mixture of $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ and $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ powder, and the solvent and the stabilizer are 2-methoxyethanol and 2-ethanolamine, respectively. Oxide thin films were synthesized by spin coating the clear and homogeneous solution on the

substrate at 4000 rpm for 30s, followed by a preheating step at 300 °C for 15 minutes. To obtain the film with the desired thickness (~200nm), the above process was repeated several times. Finally, in order to enhance the crystalline quality, thin films were post annealed at 650 °C for 1 hour in air.

Figure 4-1 XRD datas and SEM images (insets) of (a) spinel ZnMn_2O_4 , and (b) ilmenite ZnMnO_3 thin films. The scale bars in the insets are 300 nm.

The crystalline quality of the zinc manganese oxide films was characterized by using x-ray diffraction (XRD). Because of the limited solubility, when the Mn precursor concentration in the sol gel source is larger than ~10 at. %, besides the wurtzite ZnO-related phase, the manganese oxides impurity phases were consistently observed, which is in line with the previous reports.^{70,71} At higher Mn concentrations, however, we found that single phase oxides can be reproducibly achieved by carefully adjusting the Zn/Mn ratio in the source precursor. Figure 4-1 shows the XRD patterns taken on two samples synthesized from precursors with different Zn/Mn molar ratios (1:2 and 1:1). All

the XRD diffraction peaks in Figure 4-1 (a) and Figure 4-1 (b) can be related to the spinel ZnMn_2O_4 and the ilmenite ZnMnO_3 , respectively,⁷² and no secondary impurity phase was detected. Scanning electron microscopy (SEM) was used to characterize the surface morphology of the thin films, and typical surface morphology are shown in the insets of Figure 4-1.

§ 4.2.2 Electrical Characterization and Performance Testing

To carry out the electrical measurements, Au top electrodes were deposited on top of the thin films by using magnetron sputtering system. A shadow mask as used for the electrode patterning, and the thickness of electrode is around 50nm. After the electrodes deposition, the devices were post annealed at 150 °C for 30 minutes in air to improve the contact quality. In our RS experiments, the current flowing from the top electrode through the thin film to the bottom electrode is defined as the forwards (positive) bias direction. Keithley 4200 semiconductor characterization system was used to obtain the I-V curves. Initially, both the ZnMn_2O_4 and the ZnMnO_3 devices were at the high resistance states (HRS). After the forming process the devices were switched to the low resistance states (LRS). A compliance current was set to protect the devices from being permanently damaged by the huge leakage current. Figure 4-2 (a) and (b) show the typical RS characteristic of $\text{Au/ZnMn}_2\text{O}_4/\text{Pt}$ and $\text{Au/ZnMnO}_3/\text{Pt}$ in log-log scale. Steady and reproducible RS behaviors were observed in both cases, and the reset voltages are consistently lower than 2 V. The ON/OFF ratios are at the range of 10^5 – 10^7 for $\text{Au/ZnMn}_2\text{O}_4/\text{Pt}$ and 10^4 – 10^5 for $\text{Au/ZnMnO}_3/\text{Pt}$. We carried out set and reset operations for 150 times, and for both devices there are clear separation between the set voltages and

the reset voltages, which indicates robust programming and erasing operations. Using the van der Pauw method, we determined the room temperature resistivities of ZnMn_2O_4 and ZnMnO_3 to be around 9.52 and 0.12 $\text{M}\Omega\cdot\text{cm}$, respectively, which could be correlated with the higher resistance in HRS and the larger ON/OFF ratio observed in ZnMn_2O_4 based devices.

Figure 4-2 Typical RS characteristics of (a) $\text{Au/ZnMn}_2\text{O}_4/\text{Pt}$ and (b) $\text{Au/ZnMnO}_3/\text{Pt}$ devices in log-log scale. “0” and “1” denote the OFF and ON states, respectively.

§ 4.2.3 Conduction Mechanism Analysis

The log-log scale curves in Figure 4-2 also allow us to investigate the conduction mechanisms in low and high bias regimes. LRS in both devices follow a linear Ohmic behavior and the slopes are 1.05 for ZnMn_2O_4 and 1.01 for ZnMnO_3 . This is consistent with the generally discussed metallic conducting filamentary model in transition metal oxides⁷³, particularly, the Zn-Mn-O systems, including ZnO ,⁶⁰ Mn doped ZnO ,⁵³ and MnO_x .⁷⁴ For HRS, at lower electric fields, both devices show approximately Ohmic

behavior, and then the relationship between the leakage current and the applied voltage becomes highly nonlinear at higher electrical field. As shown in Figure 4-2 (a) and (b), the slopes of the current vs. voltage curves change to 2.02 for ZnMn_2O_4 and 2.00 for ZnMnO_3 . At even higher fields, the slopes increase continuously until the devices are set to LRS. This behavior coincides with the typical space-charge-limited current (SCLC) conduction mechanism, where the conduction obeys the Ohmic law at low field, then the Child's Law, and finally reaches a traps-filled-limit regime when the traps in the crystals are completely filled.⁷⁵ This model was also adopted by other authors previously to interpret the conduction mechanism in ZrO_2 and Mn-doped ZnO thin films.^{53,76}

The Ohmic behavior in LRS is in line with a filamentary conduction mechanism, which has been frequently accounted for the RS in oxide thin films.^{53,60} Herein the set and reset operations in the zinc manganese oxide thin films appear to be dictated by the creation and annihilation of conducting filaments. According to the filamentary model, charged defects in metal oxides, in particular, oxygen vacancies, tend to align into metallic filaments under a high electric field in the forming process.^{25,56,58,77} Sol-gel derived zinc manganese oxides thin films often contain high-density oxygen vacancies. Such oxygen vacancies are presumably formed along the grain boundaries, and may serve as the building blocks for the formation of metallic filaments. Substantial Joule heating results from the large current flowing through the filament during the reset process, which leads to the avalanche breakdown of filaments and transition to HRS.^{78,79} A higher electric field can reestablish the conducting filaments by realigning the charged defects, which constitutes the set process. During the set process at the high electrical field, the carrier traps are completely filled, resulting in the high-field SCLC conduction as

delineated above.

§ 4.2.4 Endurance and Retention Comparison

Figure 4-3 (a) Read endurance of the Au/ZnMn₂O₄/Pt device and the Au/ZnMnO₃/Pt device. Each state was read out for 1000 times at 0.1V after a set or reset operation. (b) Retention of the Au/ZnMn₂O₄/Pt device and the Au/ZnMnO₃/Pt device. Each state was read out at 0.1V every 20 minutes.

Figure 4-3(a) shows the performance testing in terms of the reading endurance of the Au/ZnMn₂O₄/Pt and the Au/ZnMnO₃/Pt devices. Electric pulses of 23V and 3V are applied to obtain the ON and OFF states, respectively, then the resistance of each state was read out with a voltage pulse of 0.1 V with a pulse width of 5 ms up to 1000 times. Good stability was observed. In order to test the retention, after setting the device to the ON state, we retrieved the resistance by applying a voltage pulse of 0.1 V every 20 minutes. After 40000s (about 11 hours), another voltage pulse was applied to reset the

device to the OFF state. Consequently, the resistance was read out again at 0.1 V every 20 minutes. As shown in Figure 4-3(b), both LRS and HRS can be maintained for more than 10 hours without consuming external power.

§ 4.3 Summary

We synthesized ZnMn_2O_4 and ZnMnO_3 thin films by using a simple sol-gel method, and demonstrated that both of them are promising candidates for next generation nonvolatile memory devices. Both HRS and LRS exhibit good performance, in terms of retention and reading endurance. The Ohmic behavior in LRS is suggestive a metallic filamentary conduction mechanism, while SCLC is dominating the HRS during the reset process. Our work suggests that both of these two ternary oxides, ZnMn_2O_4 and ZnMnO_3 , may find potential applications in next generation nonvolatile memory devices. Further research on the related functional ternary oxides is highly encouraged for the advancing of high performance ReRAM devices.

Chapter 5 Electrode dependence of RS

§ 5.1 Electrode dependence of RS in Mn-doped ZnO: filamentary vs. interfacial mechanisms

§ 5.1.1 Introduction

In the operation of ReRAM devices, electrodes play a critical role in terms of switching characteristics (unipolar or bipolar). The majority of studies in the literature focused on either unipolar or bipolar switching; observation of both behaviors in a single material has been sparsely documented, so far. On the other hand, to shed light on the underlying mechanisms, more thorough understanding of the relationship between these two switching modes and the associated operation characteristics is imperative.

The coexistence of bipolar and unipolar RS has been observed in TiO_2 and Cu doped SiO_2 .^{22,80} The set process in both cases was attributed to the formation of conducting pathways due to the electrochemical reactions under electric field. However, the reset process in unipolar RS was thought to be thermally assisted.⁸⁰ In a very recent report, different RS mechanisms of NiO thin films were explored by altering the bottom electrodes; Pt and SrRuO_3 electrodes led to the filamentary conduction and the formation of interfacial Schottky barrier, respectively.⁸¹

In the first part of this Chapter, we report that unipolar and bipolar RS can be obtained in Mn-doped ZnO thin films grown on Pt and Si, respectively. By nonlinear fitting, we interpret the unipolar RS by filamentary conduction and the bipolar RS by an

interfacial effect. A broader distribution of operation voltages was observed in unipolar RS, corresponding to the random formation of conducting filaments. In contrast, the bipolar RS is more stable and its switching characteristics can be modulated by reverse biases. We also observed distinct resistance evolutions – filament type RS exhibited good retentions for both HRS and LRS; on the other hand, the LRS in interface type RS relaxed quickly towards HRS.⁸² Mn-doped ZnO was selected as the switching material due to its potential applications in ReRAM and its reported room temperature ferromagnetism.^{53,61}

§ 5.1.2 Preparations of Mn:ZnO ReRAM

In this work, we used sol-gel spin coating for the thin film synthesis considering that the oxide thin films grown by this method usually contain sufficient extended defects, especially along grain boundaries. $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ was used as the doping source and mixed with $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ at a molar ratio of Mn:Zn=1:99, which corresponds to a nominal doping concentration of $\sim$ at.1%. The mixture was dissolved in 2-methoxyethanol and 2-ethanolamine which were used as solvent and stabilizer, respectively. After 3 hours stirring, clear and homogeneous light-brown solutions were obtained. Thin films with desired thicknesses ($\sim$ 50nm) were prepared by solution spin coating followed by annealing in air ambient at 650 °C for 1 hour.

The crystalline structure of the Mn-doped ZnO thin films was characterized by using X-ray diffraction (XRD). As shown in Figure 5-1, the samples exhibit a highly c-axis orientation with no detectable secondary phase. The absence of the (002) peak shifts may due to the low doping concentration (inset of Figure 5-1).⁸³ In order to conduct the electrical measurements, 50 nm Pt top electrodes with a typical dimension of 150×350

μm^2 were sputtered on the thin films through a shadow mask.

Figure 5-1 XRD patterns of Mn-doped ZnO and undoped ZnO thin films. Inset shows the enlarged view of (002) peaks.

A Keithley 4200 Semiconductor Characterization System was used to conduct the transport measurements at room temperature. A forward (positive) bias applied to the device is defined as the current flowing from the top Pt electrode into the thin film.

§ 5.1.3 Unipolar RS in Pt/Mn:ZnO/Pt

A typical unipolar RS was observed in the Pt/Mn:ZnO/Pt configuration, as shown in Figure 5-2(a). A compliance current of 5 mA was used during the set process, while a larger current was always required to accomplish the reset operation. Survey of dozens of devices suggests an ON/OFF ratio larger than 2×10^2 . As demonstrated in the inset of Figure 5-2(a), the set voltages had a relatively wide distribution, which is a general feature in unipolar RS.⁸⁴ Nevertheless, there is no overlap between the set and reset voltages, which warrants reliable device operations. Recent studies have suggested that transition metal doping can reduce the intrinsic carrier density and create deep levels in wide band gap semiconductors.^{53,85} Since the dominant carrier is oxygen vacancies, the estimation of carrier concentration is de factor an estimation of the concentration of

oxygen vacancies.⁸⁶ From the linear region of the current-voltage curves, we calculated the resistivity of our Mn-ZnO and then estimated the carrier concentration, which is $\sim 10^{11} \text{ cm}^{-3}$. Corroborating the previous results, these optimal RS properties delineated above rationalize our usage of Mn:ZnO.

Figure 5-2 (a) I-V characteristics of the Pt/Mn:ZnO/Pt device. The inset shows the distribution of the set and reset voltages. (b) Log-log plot showing the Ohmic behavior in LRS. Inset is the device configuration. (c) I-V characteristics of the Pt/Mn:ZnO/Si device in semilog scale showing 20 consecutive sweepings. Inset is the device configuration. (d)

Resistance hysteresis modulated by different reverse biases. Inset summarizes the correlation between the positive threshold voltage (V_{th}) and the negative reverse bias (V_{rel}).

§ 5.1.4 Bipolar RS in Pt/Mn:ZnO/Si

To investigate the electrode effect, we also grew Mn:ZnO thin films directly on the Si substrates. Instead of Pt, Si with a resistivity of $1\sim 100 \Omega\cdot\text{cm}$ was used as the bottom electrode. Interestingly, Pt/Mn:ZnO/Si exhibited bipolar RS without a forming process, as shown in Figure 5-2(c). A reverse bias sweep is needed to drive the device to HRS. Another sufficiently high forwards voltage sweep switches it back to LRS. These RS behaviors were extremely stable within dozens of consecutive voltage sweepings. We

applied various negative biases from 0 to -20 V to investigate the dependence of the resistance hysteresis on the amplitude of the reverse bias (V_{re}). As illustrated in Figure 5-2(d), the hysteresis in the positive region became less and less prominent with decreasing V_{re} . The correlation between the positive threshold voltage (V_{th}) and V_{re} was summarized in the inset of Figure 5-2(d). This reverse bias modulation is suggestive of the interfacial effects.^{87,88}

§ 5.1.5 Filamentary vs. Interfacial Mechanisms Analysis

To investigate the conduction and RS mechanisms in these two kinds of devices, we measured dozens of devices with different electrode areas. As demonstrated in Figure 5-3 (a), the resistance of Pt/Mn:ZnO/Si devices exhibits an inverse linear area dependence, indicating that the RS take places over the entire interface area. In contrast, the resistance of Pt/Mn:ZnO/Pt devices is almost independent of the electrode area, suggesting local filamentary conduction.

Figure 5-3 (e) Area-dependent resistance of Pt/Mn:ZnO/Pt and Pt/Mn:ZnO/Si. (f) Linear fittings for Pt/Mn:ZnO/Si: Ohmic behavior and SCL conduction at LRS; Schottky emission and P–F emission at HRS.

To corroborate the different origins of these two switching behaviors, we also studied their conducting mechanisms from the perspective of nonlinear fittings to the transport characteristics. For nonlinear current-voltage curves, we have considered three

leakage mechanisms: space-charge-limited (SCL) conduction, Schottky emission, and Poole-Frenkel (P-F) emission. For SCL conduction, the I-V curve starts from Ohm's law and then follows Child's law:⁷⁵

$$J \propto \frac{8}{9} \epsilon_r \epsilon_0 \mu \frac{E^2}{d}$$

where, J is the current density, ϵ_r is the relative dielectric constant, ϵ_0 is the permittivity of free space, μ is the mobility of charge carriers, E is the electric field and d is the film thickness. For Schottky emission:

$$\ln I \propto \sqrt{\frac{e^3}{4\pi\epsilon_r\epsilon_0 d}} / kT \cdot \sqrt{V}$$

where, I is the current, V is the applied voltage, e is the electronic charge, k is the Boltzmann's constant, and T is the temperature. If the leakage is controlled by P-F emission, the relationship of the current density and electric field can be expressed as:

$$\ln(J/E) \propto \sqrt{\frac{e^3}{\pi\epsilon_r\epsilon_0}} / rkT \cdot \sqrt{E}$$

where, r is a coefficient ranging between 1 and 2, depending on the exact position of the Fermi level.⁸⁹ For $r = 1$, the conduction mechanism is referred as normal P-F emission. If the insulator contains substantial carrier traps, $1 \leq r \leq 2$ and the conduction mechanism is called modified P-F emission. The validity of the fitting is determined by the derived refractive index.

The I-V curve of Pt/Mn:ZnO/Pt was drawn in log-log scale in Figure 5-2(b). The HRS is dominated by the SCL conduction and the LRS follows the Ohmic behavior, coincident with the typical filamentary model, which has been extensively discussed.^{37,53,81,90} The RS in Pt/Mn:ZnO/Si, however, is related to the interfacial effect.

While the HRS was dominated by the Schottky emission at low electric field and by modified P-F emission at high electric field (Figure 5-3(b)), the LRS exhibited the SCL conduction (Figure 5-3(b)). This behavior is consistent with previous reports on the interfacial effects.^{81,91} The migration of oxygen vacancies in the vicinity of the interface drives RS in various heterojunctions.³⁵ Under a negative electric field, oxygen vacancies with positive charges migrate and are trapped at the Schottky-like interface between Mn-doped ZnO and Si, which widens the interface barrier, resulting in the HRS. When applying a positive voltage, the oxygen vacancies are de-trapped from the interface, which lowers the interface barrier and increases the emission current, corresponding to the Schottky emission at low electric field. At high electric field, the PF emission is dominating, which means that the electrons can move into the conduction band and the device is set to LRS. The modulation of resistance hysteresis by the reverse bias shown in the inset of Figure 5-2(d) is in line with this scenario of defects migration: as the reverse bias decreases, the migration of oxygen vacancies from the interface into the bulk is also weakened, thus a smaller positive voltage is needed to switch the resistance state.

§ 5.1.6 Influence on Device Retention Performance

The different RS mechanisms delineated above also lead to distinct resistance evolutions. For Pt/Mn:ZnO/Pt, as shown in Figure 5-4(a), both HRS and LRS have good retention, and no obvious decay was observed within 5000 s. Each resistance state also shows good reading endurance (inset of Figure 5-4(a)). In the case of Pt/Mn:ZnO/Si, after a negative voltage sweeping, the LRS was obtained, but it readily relaxed towards HRS. This relaxation is very similar to the resistive hysteresis recently observed in BaTiO₃-ZnO

heterostructures, which was attributed to the ferroelectricity of BaTiO₃.⁸⁸ We found that the time dependence of the LRS current can be well fitted with a double-exponential decay function: $I(t) = I_0 + A_1 e^{(-t/\tau_1)} + A_2 e^{(-t/\tau_2)}$, where, I_0 , A_1 and A_2 are constants, τ_1 and τ_2 are time constants, as shown in Figure 5-4(b). This fitting yields time constants of $\tau_1 = (2.99 \pm 0.10)$ s for the faster decay and $\tau_2 = (16.10 \pm 0.04)$ s for the slower decay. The faster decay can be attributed to the oxygen vacancies migration,^{25,92} while the slower one may originate from the thermal effect.⁹³ The inset of Figure 5-4(b) depicts the current relaxations of successive HRS and LRS in Pt/Mn:ZnO/Si.

Figure 5-4(a) Retention in Pt/Mn:ZnO/Pt. Inset shows the read endurance. (b) Double exponential decay fitting for LRS in Pt/Mn:ZnO/Si. Inset depicts the current relaxations of HRS and LRS.

The distinct resistance evolutions in the filament type and interface type RS may result from the different characteristics of the oxygen vacancies migration. In filament type RS, the oxygen vacancies are aligned in conducting channels, which is nonvolatile during data retrieval with small bias. The good retention may be related to the particular electronic structure of the grain boundaries in the thin films, which serve as reservoir for

charged oxygen vacancies. On the other hand, for interface type RS, the oxygen vacancies are trapped or de-trapped at the Schottky-like interface, modulating the conduction current by changing the barrier width. The stored oxygen vacancies tend to escape from the interface to the thin films along the grain boundaries at the vicinity of the interface, which could be responsible for the fast resistance relaxation and poor data retention.

To summarize, we carried out a comparative study of two types of RS in Mn-doped ZnO thin films by altering the bottom electrodes. The formation and rupture of conducting filament indicate the unipolar RS in Pt/Mn:ZnO/Pt, while bipolar RS was observed in Pt/Mn:ZnO/Si due to the field-induced change of the Schottky-like interfacial barrier. Only filament type RS gives good retention, while fast resistance relaxation was observed in interface type RS. Our studies of the diverse RS behaviors suggest that different modes of oxygen vacancies migration dictate the switching characteristics and electrode engineering is a viable approach to render reliable ReRAM devices.

§ 5.2 Electrode dependence memory and threshold switching in a single device

§ 5.2.1 Introduction

RS can be categorized into two types according to the volatility: nonvolatile memory switching and threshold switching. For memory switching, both the low resistance state (LRS) and the high resistance state (HRS) can be retained even after the external voltage is shut off. In threshold switching, however, only the HRS is stable at low bias voltages and an external voltage is needed to maintain the LRS.⁹⁴ It is critical to understand exactly the conditions that trigger the onset of memory and threshold RS as well as the

underlying mechanisms. Unintentionally incorporating threshold switching devices into nonvolatile memory cells can be detrimental to the reliable operation of integrated circuits due to the volatile nature of threshold switching. On the other hand, however, controllable conversion between memory and threshold switching in the same device can offer the industry technological benefits: While the former is the key component for the nonvolatile information storage, the later can actually be used as a selector in series with a memory cell to block the sneak current in cross-point geometry or multistack structures^{95,96}. Compared to the conventional methods where either transistors or diodes are used as the selectors, this scheme offers advantages in terms of scalability and simple processing technique. However, the difference between memory and threshold RS is quite subtle, and it remains a challenge for individual memory devices to controllably switch between the two modes. In the second half of Chapter 5, the conversion between memory and threshold switching in a single device is demonstrated.

§ 5.2.2 Preparations of Pt/NiO/ITO transparent ReRAM

NiO thin films were deposited on tin-doped indium (ITO)-coated glass substrates or Pt-coated Si wafers at 450 °C using pulsed laser deposition (PLD) system equipped with a solid state Nd:YAG laser ($\lambda = 532$ nm). The crystalline structural information was obtained by using high-resolution x-ray diffraction (XRD). Thin films grown on both substrates show good crystalline structures (Figure 5-5 (a) and (b)). Using the cross-sectional SEM technique, the thickness of NiO films is estimated to be about 200 nm.

Figure 5-5 XRD patterns of NiO on (a) ITO and (b) Pt, respectively. A photograph of the transparent NiO film is shown in the inset. (c) Ohmic I - V curve of the tungsten (W)-ITO-W junction, which forms by touching the ITO substrate with tungsten probes. This suggests that the threshold switching does not originate from the ITO layer. (d) Although the NiO samples grown on different substrates exhibit different crystalline orientations, the resistance values of their junctions is similar. (e) and (f) show the unipolar memory switching in the Pt/NiO/Pt device with $CC=1\text{mA}$ and $CC=10\text{mA}$, respectively. No threshold switching was observed.

Pt top electrodes were deposited on NiO thin films by magnetron sputtering. The electrodes are patterned by using a shadow mask, and the electrode area is of $150\text{ }\mu\text{m}\times 150\text{ }\mu\text{m}$ with a separation distance of $150\text{ }\mu\text{m}$ between electrodes. The deposited electrodes were post annealed at $200\text{ }^{\circ}\text{C}$ in air to improve the contact quality. The I - V curves of the ReRAM devices were obtained using a Keithley 4200 Semiconductor Characterization System. In order to prevent permanent dielectric breakdown of the device, a compliance current (CC) was implemented during all measurements.

§ 5.2.3 Conversion between memory and threshold switching

In NiO thin films prepared on ITO coated glass substrates, we observed the typical unipolar memory switching with a compliance current (CC) of 1 mA being used during the set operation (Figure 5-7 (a)). As shown in Figure 5-6, this memory switching in the NiO/ITO device is stable and reproducible with good endurance and retention.

Figure 5-6 Stability testing of the memory and threshold switching in Pt/NiO/ITO. (a) 50 cycles of the unipolar memory switching. (b) Reading endurance of the OFF and ON in memory switching. The resistance states were read out using a DC bias of 0.1 V. (c) Retention of the OFF and ON states is more than 10 hours. (d) Once stable threshold switching is achieved, it can be retained for more than 15 hours.

The threshold switching can be obtained if the CC increased to 10 mA, which corresponds to a current density of 44.4 A/cm^2 (Figure 5-7 (b)). Such threshold switching persists, even after the CC returns back to 1 mA, as shown in Figure 5-7 (c). On the other hand, the reference NiO devices fabricated on a Pt layer ($\sim 200 \text{ nm}$) coated Si wafer show only memory switching as the CC varies between 1 and 10 mA (Figure 5-5 (e) and (f)). This strong contrast underscores the critical role of the bottom electrode.

Figure 5-7 Conversions between memory and threshold switching modes. (a) Memory switching was observed in the Pt/NiO/ITO device when a compliance current (CC) of 1 mA was used. The blue and red lines represent ten set and reset cycles, respectively. (b) Threshold switching was achieved when CC was increased to 10 mA. Ten cycles of operation are shown. Inset: Polarity dependence of the forming process, and only the positive bias leads to the threshold switching. (c) Threshold switching was retained even after CC was reduced to 1 mA, while the hysteresis loop became smaller. (d) After annealing in vacuum at 300 °C for 30 minutes, the threshold switching was converted back to the memory switching which resembles (a). (e) Current-controlled memory switching. A compliance voltage of 2 V was used during the reset operation. (f) Current-controlled sweeping curve corresponding to the voltage-controlled threshold switching mode, exhibiting negative differential resistance.

In RS, the existence and migration of oxygen vacancies under electrical field often play important roles.³⁷ In NiO, the extended defects can even lead to the formation of nanoscale Ni filaments⁴⁶. Therefore, it is reasonable to speculate that the transition between two types of volatility may be related to the film stoichiometry, in particular the oxygen concentration. To verify our hypothesis, the device showing the threshold switching (Figure 5-7 (c)) is annealed in vacuum (0.01Pa) at 300 °C for 30 minutes. Interestingly, the threshold switching is converted back to the memory switching, as shown in Figure 5-7 (d). And if we increase the CC to 10 mA, we can achieve the threshold switching again. This indicates that increasing CC has the opposite effect of annealing in vacuum, which presumably modulates the stoichiometry of the films.

The memory and the threshold switching modes correspond to different current-controlled sweeping behaviors. As shown in Figure 5-7 (e), expected memory switching was observed in the Pt/NiO/ITO device. During the current sweeping, voltage was monitored and a compliance voltage of 2 V was adopted to avoid the high voltage breakdown during the reset process. On the other hand, no sharp RS was observed under the current controlled mode (Figure 5-7 (f)) for the device with the threshold switching (Figure 5-7 (b)). Instead, a smooth current controlled negative differential resistance (CC-NDR) was observed at the voltages ranging from 2.4 to 3.7 V, which is exactly equal to the two threshold voltages under the voltage controlled mode (Figure 5-7 (b)). Although the voltage controlled threshold switching and CC-NDR are often reported separately,^{94,97,98} here we show that they can manifest in the same device.

§ 5.2.4 The Effect of Oxygen Concentration

In order to obtain the stoichiometry information of devices showing different switching behaviors, we performed the time-of-flight secondary ion mass spectroscopy (TOF-SIMS) measurements on devices on four kinds of states, pristine, memory ON, memory OFF, and threshold OFF states, respectively. Firstly, the top electrode Pt will be removed by the bombardment, then the NiO thin films, and finally the ITO substrate. Devices with larger top electrode sizes of 500 μm ×500 μm were used to make sure that the sputtered area, which is around 200 μm ×200 μm , is within the area covered by the electrodes. In the SIMS depth profiling, there are many artifacts related to instrumental factors, as described in detail by Klaus Wittmaack⁹⁹. In our experiment, as the purpose is to evaluate the relative variation of the ratio of Ni and O elements, we used the normalized

distribution curves. For the device at its pristine state, we assume the Ni to O ratio is 1:1 at the interface between the NiO thin films and the top electrode Pt. The SIMS profiles of normalized O/Ni ratios for different switching states are shown in Figure 5-8 (a). In general, the O/Ni ratio is higher near the interface of NiO/ITO because ITO bottom electrode serves as an oxygen ions reservoir. The O/Ni ratio is the lowest in the memory ON state, and the highest in threshold OFF state. This is consistent with the previous reports where Ni-deficient NiO films show threshold switching⁹. Since in NiO the formation energy of vacancies is much lower than interstitials,¹⁰⁰ the off stoichiometry in different switching states can be attributed to the presence of either oxygen or nickel vacancies. The estimated average concentrations of oxygen vacancies in the memory OFF and ON state are 6.3 at.% and 7.7 at.%, respectively, while the average concentration of nickel vacancies in the threshold OFF state is 1.5 at.%.

Figure 5-8 Determination of compositions in various RS states. (a) SIMS profiles for different RS states. The estimated average concentrations of oxygen vacancies are 7.7% and 6.3% for the memory ON and OFF states, respectively. The average concentration of nickel vacancies is 1.5% for the threshold OFF state. (b) PF emission fittings to the pristine and the threshold OFF states. The derived dielectric constant of the threshold OFF state is larger than that of pristine state, in line with the SIMS result that the O/Ni ratio is higher in the threshold OFF state. (c) Schematic of the Ni-rich metallic filament in NiO whose formation and rupture is the result of dynamic competition between the oxygen-gradient-induced drift and the field-induced diffusion motions of the oxygen ions.

Compared to the pristine state, the enhanced O/Ni ratio in the threshold OFF state has implications on the transport mechanisms. The I - V curves of both states follow the Poole-Frenkel (PF) mechanism⁹⁶. The PF mechanism describes the

high-electric-field-assisted conduction in insulators, which can be quantitatively expressed as follows:

$$\ln(J/E) \propto q \left(\sqrt{\frac{qE}{\pi \epsilon_0 \epsilon_i}} - \phi_B \right) / kT$$

where, E is the applied electrical field, J is the current density, T is the temperature, q is the electronic charge, ϵ_0 is the permittivity of free space, ϵ_i is the dielectric constant, ϕ_B is barrier height, and k is the Boltzmann constant. As shown in Figure 5-8 (b), both the I - V curves of the pristine state and the threshold OFF state can be well fitted by using the PF conduction model. The dielectric constants (ϵ_i) extracted from our fitting are 10.9 and 11.9 for the pristine state and the threshold OFF state, respectively. As a higher ϵ corresponds a higher oxygen concentration,^{96,101,102} our data confirm that the oxygen concentration of the threshold OFF state is higher than that of the pristine state. To further verify our model, NiO thin films were directly deposited under different oxygen pressures, and indeed the sample grown in high pressure grown sample shows the threshold switching while the one in lower pressure shows the memory switching (Figure 5-9).

Figure 5-9 (a) Memory switching in NiO prepared at an oxygen pressure of 0.01 Pa. (b) Threshold switching in NiO prepared at an oxygen pressure of 0.5 Pa. The CC is 2 mA for both cases.

§ 5.3 Summary

As presented, electrodes indeed play a vital role that determines whether the ReRAM device is bipolar or unipolar; whether the binary states are volatile or nonvolatile. In both cases, the variation may result from the modulation of the dynamics of oxygen migration. The RS behaviors may be observed due to formation of conducting filament, when sufficient amount of oxygen ions are drifted away along with the direction of electrical field. To stabilize the formed filament, the migrated oxygen should be stored at the interface until next operational external electrical stimulus is applied to intentionally change the state. On the other hand, when conducting oxides are used as one of the electrodes, the device performance becomes very sensitive to the operation temperature due to the potential undesirable diffusion of oxygen, which can hinder the formation of stable conducting filaments.¹⁰³ The above model is supported by our experimental observation.

Chapter 6 Deterministic conversion between memory and threshold RS via tuning the strong electron correlation

§ 6.1 Introduction

Notably, many ReRAM materials are strongly correlated electron systems. For example, although NiO is a prototypical Mott insulator that is predicted to be a metal by the conventional band theory, experimentally, it is an insulator as a result of the strong Coulomb repulsion between electrons¹⁰⁴⁻¹⁰⁶. On the other hand, RS in NiO was first reported in the 1960s¹⁰⁷, and to interpret the unipolar RS in NiO, mechanisms involving thermochemical formation and annihilation of conducting filaments are often adopted³⁷. In transition metal oxides, it is well known that the strong electron correlation can split the energy bands, affecting electronic band structures and transport properties. Furthermore, the correlated interaction between electrons can be modulated by tuning various factors like sample stoichiometry, strain and external fields, which renders lots of flexibility in rational material designs. As RS is an electronic (ionic) phenomenon by nature, the many-body mutual interactions among electrons should play important roles. Indeed, it was recently proposed that, in some ternary chalcogenides, Mott insulator-to-metal transition is responsible for the nonvolatile RS^{108,109}. However, in general, it is not clear how the strong correlation between electrons influences the switching characteristics in ReRAM devices.

§ 6.1.1 Mott-Hubbard Insulator

Most of TMOs are Mott insulators, which are predicted to be conducting under conventional one electron approximation band theories, but are insulators according to the experiments. To address this question, Peierls suggested that the gap opening is due to the Coulomb interaction between the electrons.¹⁰⁴ Mott and Hubbard further formulated the concept of the Mott-Hubbard insulator, which can be used to describe the electronic properties of the early TMOs decently.^{105,106} The charge fluctuation of the Mott-Hubbard insulator is of the type $d_i^n + d_j^n \leftrightarrow d_i^{n-1} + d_j^{n+1}$, which is suppressed by the d-d Coulomb and exchange interactions (U). Generally speaking, Mott metal-insulator-transition (MIT) can be triggered by the temperature or pressure. Besides, the MIT of some of these Mott insulators can be also induced by electrical field, although it is still controversial whether this RS originates from typical Mott transition or the Peierls transition driven by electron-phonon interactions, such as charge density waves, which induce a structural phase transition. One extensively studied example is VO_2 , whose resistance can be changed over several orders of magnitude by applying electrical field.^{110,111}

§ 6.1.2 Charge-Transfer Insulator

The charge fluctuation of the charge-transfer insulator is determined by the charge transfer energy (Δ) $d_i^n \rightarrow d_i^{n+1} \underline{L}$, where $\underline{L}$ denotes a hole in the anion valence band.

Figure 6-1 Zaanen-Sawatzky-Allen diagram

In 1985, J. Zaanen *et al* formulated the Zaanen-Sawatzky-Allen (ZSA) diagram (Figure 6-1) to categorize the Mott insulators.¹¹² According to this diagram, both of the Coulomb repulsion between 3d electrons and the charge-transfer energy between metal-3d and anion-*p* states are critical to determine the fundamental electronic structure. The categories of Mott-Hubbard insulator and charge-transfer insulator are defined by comparing the value of Coulomb repulsion energy, U_{dd} , and the charge-transfer energy, Δ . In ZSA diagram, NiO is placed in the intermediate region of the Mott-Hubbard insulator and the charge-transfer insulator.¹¹² However, as later calculated by Fujimori *et al*¹¹³ and experimentally proved by Shen *et al* using ARPES¹¹⁴, the charge fluctuation in single crystal NiO is determined by the interaction between the nickel 3d electron and the oxygen *p* electron, thus stoichiometric NiO is categorized as a charge-transfer insulator.

§ 6.1.3 Negative-Charge-Transfer Insulator

Decreasing the Δ shifts the Mott insulators from charge transfer insulator region towards the negative-charge-transfer insulator region, in which the band gap is not of the *p*-to-*d* nor *d*-to-*d* but *p*-*p* type, with a considerable mixture of *d* character into *p* states. In the ground state of a negative charge transfer insulator with small Δ , the strong hybridization interaction opens the gap, and the insulating state is stabilized by the

formation of a chemical bond between the d^{n+1} configuration and a ligand hole in a way analogous to the formation of a Heitler-London state.¹⁰⁴ In case of Ni^{3+} oxides, the $d7$ and $d8L$ are nearly degenerate and are strong hybridized with each other, leading to the formation of the split-off state in the ground state. In this sense, this kind of insulator is a “valence-bond insulator” or “covalent insulator”, which is contrasted with the basically ionic Mott-Hubbard and charge-transfer insulators.^{104,115}

§ 6.2 Correlation between nonvolatility and insulator type: NiO as an example

§ 6.2.1 The correlation between the band structure and the RS volatility in NiO

As shown in Figure 6-2 (a), NiO is a charge-transfer insulator, with the band gap determined by the oxygen $2p$ band related to the nickel $3d$ upper Hubbard band¹⁰⁴. The intra-atomic $d-d$ Coulomb energy U results from the strong electron correlation. Since the first ionization state is of primarily oxygen $2p$ character rather than of nickel $3d$ character, the charge-fluctuation energy in NiO is determined by the charge transfer gap (Δ) $d^8 \rightarrow d^9 \underline{L}$, where $\underline{L}$ denotes a hole in the oxygen valence band. This charge transfer process is analogous to the redox reaction, involving electron transfer between oxygen and nickel, which is believed to play the pivotal role in memory switching³⁷. As a charge-transfer insulator, NiO exhibits the memory RS behavior (Figure 6-2 (b)).

Figure 6-2 Schematics illustrating the correlation between the band structure and the RS volatility. (a) Energy diagram of NiO as a charge-transfer insulator. Δ denotes the energy of the ligand-to-metal charge-transfer, $d^8 \rightarrow d^9 \underline{L}$ ($\underline{L}$: ligand hole). U represents the intra-atomic $d-d$ Coulomb energy. Correspondingly, we observed (b) voltage-controlled memory switching. (c) Energy diagram of non-stoichiometric Ni_{1-x}O which can be classified as a negative-charge-transfer insulator, where the band gap is determined by the split oxygen $2p$ bands. Correspondingly, we observed (d) voltage-controlled threshold switching.

On the other hand, tuning the oxygen concentration and hence the chemical stoichiometry in NiO can effectively modify the electron correlation and the electronic structure. As shown in Figure 6-2 (c), the charge transfer gap Δ is decreased by introducing the nickel deficiency, which shifts NiO toward the negative-charge-transfer insulator type,¹⁰⁴ in which the band gap is not of the p -to- d nor d -to- d but p - p type, $d^8 \underline{L} + d^8 \underline{L} \leftrightarrow d^8 + d^8 \underline{L}^2$, with a considerable mixture of d character into the p states. Our key hypothesis is that this alteration of the band structure will drastically affect the switching characteristics and give rise to the threshold switching (Figure 6-2 (d)).

§ 6.2.2 First Principle Calculation and X-ray Absorption

Spectroscopy

In order to further analyze the relationship between the nickel deficiency and the modulation of band structure, we performed first-principles calculations on NiO with different chemical stoichiometry by using a supercell of $\text{Ni}_{32}\text{O}_{32}$ ($2 \times 2 \times 2$ unit cells). The spin-polarized DOS calculations were carried out using the frozen-core projector-augmented wave (PAW) method^{116,117} within the frame of density functional theory (DFT) as implemented in the VASP codes^{118,119}. The generalized gradient approximation (GGA) for electron exchange and correlation were performed^{116,120}. Furthermore, on-site Coulomb repulsion U was taken into account as a result of the strong correlation effect of Ni 3d states at the Hartree Fock level ($U=6.3$ eV and $J=1$ eV)¹⁰⁰. The cutoff energy for the plane-wave basis set was 400 eV. A rock-salt structural NiO supercell with 64 atoms was employed, and for the Ni vacancy calculation a Ni atom was removed from the supercell. All the atoms were allowed to relax until the Hellmann–Feynman forces become less than 0.01 eV/Å. The calculated lattice constant of the perfect NiO is 4.17 Å, which is in good agreement with the experimental value¹²¹. Figure 6-3 (a) and (b) show the density of states (DOS) for ideal $\text{Ni}_{32}\text{O}_{32}$ and Ni-deficient $\text{Ni}_{31}\text{O}_{32}$, respectively. As expected, the electronic band structure of $\text{Ni}_{32}\text{O}_{32}$ exhibits the feature of a typical charger-transfer insulator, where the valence band shows primarily the oxygen 2p character and the conduction band mainly the nickel 3d character^{112,113}. In contrast, for the supercell of $\text{Ni}_{31}\text{O}_{32}$ containing one nickel vacancy, the Fermi level enters the oxygen 2p band and the Coulomb repulsion results in the band splitting, in a way analogous to the cases in some formally Ni^{3+} oxides.¹⁰⁴ The charge transfer energy Δ

becomes smaller and even negative. In this sense, NiO with nickel vacancies is a negative-charge-transfer insulator, in which both of the conduction band maximum and valence band minimum are primarily of the oxygen 2*p* band character. Although other defects besides Ni vacancies and their complexes may exist in NiO, the calculation here captures the basic physical picture regarding the electronic band structure of Ni-deficient NiO, and more sophisticated models can be developed in the future to shed light on the various physical states during RS operations.

Figure 6-3 Calculated band structures of stoichiometric and Ni-deficient NiO. (a) Calculated density of states (DOS) of NiO. A supercell of Ni₃₂O₃₂ was used. In addition to the total DOS (black lines), partial contributions from O 2*p* and Ni 3*d* are also shown. Inset is the enlarged view of the region near the Fermi level. The band gap is determined by the charge-transfer gap. (b) Calculated DOS of Ni-deficient NiO as simulated by Ni₃₁O₃₂. Inset is the enlarged view of the DOS near Fermi level. As a result of the Ni deficiency, the oxygen band expands across the Fermi level and splits due to the Coulomb repulsion between electrons. In this case, the band gap is determined by the negative-charge-transfer gap.

In order to corroborate the calculation result of electronic structure of the Ni-deficient

NiO as a negative-charge-transfer insulator, we performed the x-ray absorption spectroscopy (XAS) measurements on NiO samples grown at two different oxygen pressures. The XAS measurements were carried out at the SINS beamline (SINS) of the Singapore Synchrotron Light Source. The spectra were measured in the total electron yield (TEY) mode with the p-polarized light, and the photon energy resolution $E/\Delta E$ was set at about 1000. As shown in Figure 6-4, for both samples, peak B at 530.5 eV in the O K-edge spectra can be attributed to the transition from the O 1s level to the states with O 2p character in the upper Hubbard band.¹²² The peaks C and D can be assigned to the Ni 4p bands¹²³. Notably, for NiO with high oxygen concentration (grown at the higher oxygen pressure), a new peak A centered at 527.3 eV was observed (inset of Figure 6-4), which can be attributed to the transition from O 1s to the nickel vacancies induced O 2p states right above the Fermi level^{123,124}. This result coincides with the first principle calculation that this high-pressure NiO sample is a negative-charge-transfer insulator. At the Ni L-edge, the peaks E and F can be assigned to Ni 2p_{3/2} and Ni 2p_{1/2} to Ni 3d transitions, respectively¹²⁵. In addition, the absence of any shift in peaks E and F at the Ni L-edge suggests that the nickel-deficiency-induced holes have more O 2p character than Ni 3d character,^{122,126} which is consistent with the our first-principles computational results (Figure 6-3 (b)).

Figure 6-4 X-ray absorption spectra of NiO. Oxygen *K*-edge (left) and Ni *L*-edge (right) XAS spectra for NiO prepared in different oxygen ambient, 0.01 Pa (black line) and 30 Pa (red line). The inset highlights the onset of peak A in the sample grown at the higher oxygen pressure.

The modification of band structure is significantly related to the volatility of RS. In stoichiometric NiO, a high electric field can facilitate transferring electrons from the valence band (primarily oxygen *2p* character) into the conduction band (primarily nickel *3d* character). Such charge transfer process is reminiscent of the redox reaction,^{37,49} and the resulting solid metallic Ni filament is responsible for the stable LRS in the memory switching of NiO. On the other hand, in NiO with nickel vacancies, which is a negative-charge-transfer insulator, such a redox reaction is more difficult as the Fermi level is lying between the lower and the higher oxygen *2p* bands. A low electric field mainly excite charge fluctuations between two oxygen *2p* bands, resulting in the switching from HRS to LRS. However, a stable metallic filament cannot be maintained, giving rise to the threshold switching with unstable LRS state.

§ 6.3 Summary

Using NiO, the prototypical Mott insulator, as an example, we investigated the

intricate characteristics of RS from the perspective of strong electron correlation effect. We found that the strong electron correlation effects can not only result in the complex band structures, but also have significant impact on various aspects of transport properties in TMOs including the RS phenomena. The electron correlation and the associated band structure can be tailored by modifying the chemical stoichiometry. Specifically, stoichiometric NiO is a charge-transfer insulator with the p - d type charge fluctuation giving rise to the general memory switching. On the other hand, the oxygen-rich NiO is a negative-charge-transfer insulator, with the p - p type charge fluctuation, and tends to exhibit the threshold switching. The above findings are evidenced by our first-principles calculations as well as XAS measurements. Among the various factors considered so far in literature, the strong electrons correlation effect has been largely ignored during the interpretation of RS mechanisms. Our study suggests that such correlation effect between electrons does profoundly affect the characteristics and performance of RS, and its general role in the operation of memory devices made of transition metal oxides clearly warrants further investigations

Chapter 7 Conclusions and Future Works

§ 7.1 Conclusions

This dissertation is mainly focused on our research on the fabrication and characterization of ReRAM device. The purpose is to interpret the underlying physics governing the resistive switching and to optimize the device performance, through new material exploration, defects and electrode engineering, and proposed physical models.

While binary metal oxides have been extensively investigated for unipolar ReRAM applications, in Chapter 4, we narrated our discovery of two new ternary oxides, ZnMnO_3 and ZnMn_2O_4 , from Zn-Mn-O materials system. Both show excellent switching performance, in terms of more than four orders of magnitudes ON/OFF ratios, good endurance and retention, and thus may find potential application in ReRAM. The ON state conduction is attributed to the metallic filamentary conduction model, while the OFF state conduction is interpreted by using the space charge limited conduction model. Although these two compounds possesses distinct crystalline structures, their switching characteristics and performances are similar to each other, which is suggestive of the common filamentary conduction in the unipolar ReRAM based on transition metal oxides.

The filament formation is closely related to the migration of oxygen vacancies, whose dynamics are greatly influenced by the electrodes. In the first part of chapter 5, we

demonstrated that the bottom electrode significantly affects the switching polarity and the conducting mechanism. In the Pt/Mn:ZnO/Pt device, resistive switching originates from the formation and annihilation of conducting filament. On the other hand, replacing bottom electrode from Pt to Si essentially changes the unipolar switching to bipolar switching. And, the modulation of a Schottky like interfacial barrier results in the resistive switching in that case. These two types of devices are governed by different conducting mechanisms and this exhibit significantly different retention behaviors, with filament type RS giving good retention, and interface type RS showing fast resistance relaxation.

Oxide based ReRAM is believed to use the electrical field induced migration of oxygen ions, however, when a conducting oxide is used as the electrode, the diffusion of the oxygen ions from the oxide electrode can be serious enough to disturb the ReRAM operation. In the second part of Chapter 5, we illustrated the diffusion effect of the conducting oxides electrode when the device is working in high current condition. The oxygen ions diffuse from the ITO substrate into the NiO thin films, which changes the switching mode from memory switching into threshold switching. The device can be restored to the one showing memory switching simple by annealing in vacuum to rebel the redundant oxygen. Alternatively, such diffusion can be restrained by reducing the operation current.

Many transition metal oxides fall into the category of strong correlated oxides system. The strong correlation effect significantly affects the physical properties of the material, including the switching characteristics of resistive switching. In Chapter 6, we used NiO as an example to describe our hypothesis on the relationship between the insulating type of switching media and the switching mode. Stoichiometric NiO is a

charge-transfer insulator, where the charge fluctuation is the p-d type, giving rise to the commonly reported memory switching. On the other hand, the oxygen-rich NiO, namely Ni_{1-x}O , is a negative-charge-transfer insulator, where the charge fluctuation is mainly the p-p type, which tends to exhibit the threshold switching. Such conclusion is supported by our first-principles calculations coupled with XAS measurements. Our study suggests that the strong electron correlation effect does profoundly affect the characteristics of RS, and its general role in the operation of memory devices made of transition metal oxides clearly warrants further investigations

§ 7.2 Future Works

To continue the work in this field, optimized device fabrication method and characterization technique is indispensable. ReRAM has shown its great potential as next generation high speed, good scalability, and low power consumption nonvolatile memory. It is thus very urgent to search for design and fabrication methods of ReRAM with better performance and lower cost. The factors that limit the reliability as well as the guideline of scaling need to be addressed.

The recommended directions include: (i) To fabricate high resistivity materials based ReRAM. The high resistivity potentially enables the ReRAM to operate under a ultra low current, and thus low power consumption. Nowadays, high-k materials can be a good point to start with. (ii) Electrode engineering. Pt and Au are usually used in ReRAM as the oxygen reservoirs. Electrodes that can serve for the same purpose but with lower cost are always desirable. (iii) Further investigation on the correlation effect. The electrons transfer process essentially determines the characteristics of redox based resistive

switching. What is the driving force of the electron transfer? How the electrons are transfer? What is the maximum transfer speed? What is the maximum amount that can be transfer?.....the answer to above questions will help to understand the factors that limit the reliability and catch the guide line for the further development of ReRAM.

In a wider perspective, the research of ReRAM may be extended to other disciplines: neural network and reconfigurable computing, for example. (1) The circuit based on ReRAM is subjected to a series of electrical pulses, store the information, and wait for another series of pulses, in a way analogous to the synapse behaviors in a human brain. Therefore, ReRAM circuit is promising for the design and construction of artificial neural network. (2) Conventional field programmable gate array (FPGA) is based on static random-access memory (SRAM) which consumes six transistors for the storage of only one bit. Replacing the SRAM with ReRAM can significantly reduce the circuit area. In addition, the nonvolatile nature of ReRAM also offers a superior advantage in terms of low power consumption.

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