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OXIDE BASED NON-VOLATILE RESISTANCE RANDOM ACCESS MEMORY

Zheng Ke

School of Electrical & Electronic Engineering

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Abstract

As one of the potential candidates for next generation non-volatile memory, resistance random access memory (RRAM) has attracted great attention recently. The study of resistive switching (RS) phenomenon could retrospect from 1960s and in nowadays various materials and structures have been gradually explored to fabricate RRAM devices. Transition metal oxides outstand in many aspects over other materials due to their relatively deposition process and stable RS performance. In this thesis, we firstly brief the history and development of RRAM research, including the material and fabrication issue, the operating mechanism and the industrial integration scheme. Then, our work focuses on several highly concerned issues of RRAM: developing transparent RRAM device based on economic and effective materials, reducing or avoiding Joule heating in filament based RRAM device to improve RS property and adjusting intrinsic defects in oxide to obtain more enduring and stable RS performance.

By depositing GZO and ZnO on glass wafer, transparent RRAM cells without indium were constructed. This device with bipolar resistive switching behavior performs well in both endurance and retention test. The switching process could be understood by applying the filament model. The two resistance states, HRS and LRS, correspond to the connecting filamentary paths and broken ones within the bulk materials, which is controlled by the migration of oxygen vacancies. Compliance current should be properly applied in set operation or the device will be unable to reset. Joule heating plays a dual role in resistive switching, which can both strengthen the formed filaments in set process and accelerates the annihilation of filaments in reset process.

A unidirectional bipolar RS was observed in the In/GaO_x/NiO_x/ITO heterostructure fabricated by magnetron sputtering at room temperature. The RS behavior could be concluded as the switching between rectifying and Ohmic behavior of the diode. The migration of intrinsic defects (oxygen vacancies in GaO_x and oxygen ions in NiO_x) alters the barrier, which accounts for the RS behavior observed. This design relies on interface type RS and offers an alternative scheme to reduce side effect in filament. The scaling potential is also examined by reducing the device size to 1 μm , where we observed that the switching current was reduced and switching windows was increased. The device shows good endurance and retention performance, manifesting the potential application of p-n junction structure in non-volatile memory.

ZnO, Ga₂O₃ and NiO were introduced into TaO_x to make a comparison on RS property. Among them, the ZnTaO_x sample exhibited evident improvement of RS performance, including better endurance, smaller operating voltage and more stable resistance distribution. The improved behavior mainly attributes to the introduction of more intrinsic defects such as oxygen vacancies by mixing TaO_x with ZnO_x, which facilitates the filament-based RS. The I-V characteristics were also investigated to further clarify the variation of conduction induced by different mixtures. This experiment offers an alternative way to engineer the intrinsic defects in oxide and enhance the RS performance.

In summary, the thesis addresses three parts of work on improving current RRAM subjects. ZnO and its variants were applied in transparent RRAM device. Interface type RS was constructed by utilizing p-n heterojunction stacks, which facilitate to reduce negative Joule heating effect. An effective way to adjust intrinsic defects of oxide and improve RS performance was demonstrated by mixing different oxide in certain ratio.

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Abbreviations

1D1R	1-Diode-1-Resistor
1T1M	1-Transistor-1-Memristor
3D	3 Dimensional
BE	Bottom Electrode
CC	Compliance Current
CC-NDR	Current-Controlled Negative Differential Resistance
CF	Conductive Filament
CMOS	Complementary Metal–Oxide–Semiconductor
CRS	Complementary Resistive Switching
DRAM	Dynamic Random Access Memory
EDX	Energy-dispersive X-ray spectroscopy
FeRAM	Ferroelectric Random Access Memory
FWHM	Full Width Half Maximum
GZO	Gallium doped Zinc Oxide
HDD	Hard-Disk Drive
HRS	High Resistive Status
HVS	High Voltage Switching
LRS	Low Resistive Status
LVS	Low Voltage Switching
MIM	Metal-Insulator-Metal
MIBM	Metal-Insulator-Base-Metal
MIIM	Metal-Insulator-Insulator-Metal
MOM	Metal-Oxide-Metal
MOCVD	Metal Organic Chemical Vapor Deposition
MRAM	Magnetoresistive Random Access Memory
O ²⁻	Oxygen Ion
PF	Poole-Frenkel
PCRAM	Phase-change Random Access Memory
RRAM	Resistive switching Random Access Memory
RS	Resistive Switching
SCLC	Space Charge Limited Conduction
SL	Sampling Length
TCO	Transparent Conductive Oxide
TC-SCLC	Trap-Controlled Space Charge Limited Conduction
TE	Top Electrode
TRRAM	Transparent Resistive switching Random Access Memory
XRD	X-ray diffraction
XPS	X-ray Photoelectron Spectroscopy
V _o ⁺	Oxygen Vacancy

Chapter 1 Introduction

1.1 Introduction

Memory device is one of the key enablers for computing. With the recent development in big data, cloud computing, mobile entertainment etc., it becomes more demanding for memory devices. Enormous efforts have been devoted to explore the next generation of memory devices which integrate the advantages of several current leading technologies. These novel memory devices should outperform the dynamic random access memory (DRAM) in operation speed, the hard-disk drives (HDDs) in endurance, and the Flash memory in non-volatility. In addition, it should be easily integrated and densely packed.

Figure 1-1 Moore's Law applied on integrated circuit¹

The current state-of-the-art memory devices have significant improvement since its invention though there are still some shortcomings. For example, the information stored in DRAM is volatile due to the discharge of capacitor, so it needs periodical refreshing power to prevent the information lost; the writing and reading time of Flash

memory is relatively longer, so it is not the right choice for the core memory or page storage in computer; HDD operates not that fast either (usually a few ms for seek time) and moreover, extra power is wasted in the disk rotation. Apparently, the new candidate should overcome these problems.

Thanks to the improvements in photolithography technology, modern non-volatile memories have been scaled down successfully to achieve ultra-large capacity for information storage. However, according to Gordon Moore's projection in 1965 as shown in Fig. 1-1,¹ the number of components in an integrated circuit would double every year and the scaling of conventional charge storage memory would be approaching the technical limit in the near future. Facing this challenge, expanding the integration with three dimensional (3D) crossbar structures maybe a good choice compared with the traditional scaling scheme.^{2,3}

Figure 1-2 Next generation memory

As described in Fig. 1-2, there are many candidates for the next generation memory, including ferroelectric random access memory (FeRAM), magnetoresistive RAM (MRAM) and phase-change RAM (PCRAM). FeRAM utilizes the different polarization of a ferroelectric material to represent information; MRAM uses a magnetic tunnel junction as the storage cell and PCRAM focuses on the change of resistance between crystalline and amorphous phase of the dielectric.³

Besides these novel types of memory, resistance random access memory (RRAM) as another powerful contestant has stood out. RRAM shows a similar resistive change phenomenon as PCRAM. However, the change of resistance does not originate from the crystalline phase change. Resistive switching (RS) is an essential physical effect which describes a distinguishable change of resistance in certain materials by an extrinsic electrical stimulation. The different resistance states are non-volatile. People have studied the resistance switching effect since 1960s; however, the RRAM devices have not attracted booming attention in both scientific and industrial field until the re-evaluation of the RS effect in the late 1990s.⁴ This new wave of exploration stimulated the idea that such RS effect has great potential to be applied in the next generation non-volatile memory.

Interestingly, as early as in 1971, Chua *et al.* predicted the existence of the fourth elementary circuit component - memristor, which is categorized with resistor, capacitor and inductor.⁵ The new element is deduced from investigating the relationship of four fundamental circuit variables: voltage (v), current (i), electric charge (q) and magnetic flux (φ). The memristor, defined by memristance “ M ”, decides the relationship between flux and charge as $M(q) = d\varphi/dq$ as shown in the Fig. 1-3. Memristor is nearly the same as resistor in linear circuit. However, if M varies as a function of q , the relation between φ and q , as well as the i - v characteristics, would

be nonlinear. In such a case, a memristor acts as a variable resistor which could store its previous state according to M value. No one realized the connection between Chua's theory and the RS device until 2008 when R. S. Williams' group from HP labs finally combined them and showed that these RS devices behave just like a memristor.⁶

Figure 1-3 Four fundamental circuit components and relationship between them⁶

As shown in Fig. 1-4a, the RRAM memory cell has a very simple structure, similar to a capacitor. It consists of an insulating or semiconducting film sandwiched by two electrodes. Based on such stacks, high density crossbar structures could be

achieved with regards to the scaling need.⁷ In the RS behavior, a significant change in resistance (usually >100%) is triggered by **applying an** external electric field. And the value of **the** resistance can be controlled in a wanted range by proper bias setup. The two different resistance states could be used as binary storage. **Reports** have shown that the RRAM operation time can reach 10 nanoseconds.⁸ **A fast switching of 100ns under $\pm 5V$ pulse with the resistance window > 10 is shown in Fig1-4b.**

Figure 1-4 a) Basic schematic of RRAM cell, b) resistance switching in pulse test and c) crossbar architecture³

Hope is placed on crossbar architectures to significantly **reduce energy consumption, by virtue of** the direct data access by locally combining selecting elements and memory cells. **Clusters of bottom electrodes (BE) and perpendicular top electrodes (TE) lines sandwiching the RS functional materials at the joints are the basis of a 3D crossbar structure as shown in Fig 1-4c.** The simplicity of the geometry without any transistor makes the scheme especially suitable for low power and high density non-volatile memory chips. And the size of each cell can be reduced to $4F^2$ (F

is feature size for cell patterning), which is the smallest cell size applicable in 2D memory structure. Supposing that if we stack n crossbars together,⁹ the integration density can further aggrandize to $4F^2/n$, and each cell will be accurately accessed without disturbance from neighbouring ones.

Even though many researchers have been pursuing the advanced non-volatile RRAM devices since the 1960s till nowadays,^{10,11} the road has not been that smooth. Actually until 2002, Zhuang *et al.* published a 64-b perovskite-oxide-based RRAM memory array, using a 0.5- μ m complementary metal–oxide–semiconductor (CMOS) process.¹² This was the first successful attempt on fabricating practical RRAM device. Another milestone was achieved in 2004 with the birth of binary transition-metal-oxide-based RRAM given by Samsung Advanced Institute of Technology. Their device largely improved the performance of single RRAM chip: 3 V operation voltage and 2 mA operation current, 10^6 set/reset endurance and 10^{12} reading endurance.¹³ Among various materials, oxide materials have been studied most intensively on RS characteristics. In the recent 10 years, all types of RS behaviors have been reported in a series of transition metal oxides, such as PCMO,¹⁰ Cr-doped SrZrO_3 ,¹¹ SrTiO_3 ,¹⁴ NiO ,¹³ TiO_2 ,¹⁵ Ta_2O_5 ¹⁶ and Cu_2O .¹⁷ Transition metal oxides outstand in many aspects in RRAM field. First, due to the elementary chemical composition, the fabrication method is relatively simple, including physical and chemical deposition. The RS phenomenon could exist in the polycrystalline or even amorphous metal oxide. Therefore, the requirement of film deposition is not that rigid as other materials. This also guarantees the uniformity of integrated cells. Second, the filaments could be controlled more easily in these oxide films by external bias. Last but not least, the designing flexibility could be achieved by manipulating the stoichiometric of metal oxide to obtain various wanted RS behavior. In this thesis, four oxide materials are

selected as main study objects. One of the most promising candidates suitable for RRAM is ZnO. ZnO and its derivatives have low growth temperature, and show controllable bipolar/unipolar RS behavior with good stability and reliability.¹⁸ Furthermore, wide-band-gap ZnO can be used to fabricate the transparent RRAM, which is favourable for the next-generation see-through electronic systems.¹⁹ NiO is an early-discovered material for RRAM which mainly functions on filament through the oxide film. Besides the research on matching different electrodes with p-type NiO,²⁰ some other n-type oxides were combined with it to construct selecting diode when integrating unipolar RRAM cell into crossbar structure.²¹ Ga₂O₃ is rarely reported as the main functional material in RRAM device although the phase change behavior (from insulator state to metal state) was observed in non-stoichiometric amorphous gallium oxide.²² In most cases, Ga was applied as doping element to form other functional compounds such as IGZO.²³ Until very recently, the qualified RS behavior in gallium oxide was reported;²⁴ however, it remains as non-mainstream material in RRAM because of its ultra wide band gap and highly insulative property. Ta₂O₅, another well-known excellent candidate, can be frequently seen in RRAM research. Famous for its superior endurance characteristics,^{25 26} TaO_x together with HfO_x lead the industrial development of RRAM.

The detected switching behavior looks more or less different from oxides to oxides. However, a common undergoing mechanism in oxide based RRAM devices, as widely accepted, lies in the migration of oxygen vacancies which alters the valence of metal ions and the conductance state. The control of such dynamic procedure directly determines how stable the RRAM parameters could be. This is the basic framework on which this thesis constructs. Every experimental chapter will show in details that how this theory affects the device performance.

1.2 Motivation

ZnO is emerging as a new material for the RRAM applications, due to its low cost, environmental friendliness, and controllable unipolar/bipolar resistance switching. In contrast to other transitional metal oxides, the ZnO based RRAM can be more easily integrated with the Si-CMOS to develop high density crossbar memory arrays. Meanwhile, the high transparency makes ZnO based RRAM promising for the future see-through electronic devices. The ZnO based materials have not attracted attention in the RRAM application until 2007.²⁷ Although so far quite a lot of ZnO RRAM devices have been reported, there is still large room for improving the program/erase characteristics and the reliability of ZnO based RRAM by optimizing the film microstructure, doping and alloying process, and the device design. ZnO based RRAM device with low leakage current, low power consumption ($<2V$), high speed ($<20ns$) and excellent retention ($>10yrs$) at high temperature ($120^{\circ}C$) is still challenging. However, with doping and alloying, we can increase the bandgap, thus reducing leakage, and obtaining good performance at high temperature. Moreover, it is not yet clear how RS works in the metal oxide films, which is the main obstacle for effective optimization of RRAM devices. It is a challenge to propose a clear physical model on the RS behavior and employ it to optimize the performance of RRAM.

With our experience on the doping behavior of ZnO, we believe that the RS in ZnO mainly relates to the oxygen vacancy. We intend to fabricate ZnO film under different conditions to study the RS behavior and the relationship between the RS and defects (oxygen vacancy). By these experiments we could possibly get some idea about the origin of the RS.

In this thesis, we systematically studied the RS behaviour of the ZnO based thin films with different elements doping and alloying. We also proposed a model to describe the resistance switching physics in ZnO thin films and its dependence on the doping and alloying. Some ZnO based RRAM devices are developed for high density storage and transparent electronics. The ZnO based RRAM technologies developed here will have the potential for applications in (1) memory chips for the mobile, MP4, computer, digital camera etc., (2) high capacity solid state storage discs, and (3) transparent non-volatile memory, memory integrated on the display panel, and other transparent electronic products. As shown in Fig 1-5, Seo *et al.* reported the transparent RRAM structure by sandwiching ZnO with ITO electrodes with the transmittance > 80% including the glass substrate. The letter “KAIST” could be clearly seen through the device.

Figure 1-5 See-through electronic systems and transparent RRAM based on ZnO¹⁹

High integration density, as one of the major advantages of RRAM, is achieved by employing the 1-diode-1-resistor (1D1R) structure which was proposed as the most popular scheme and kept being discussed for many years.^{21,28} In this scheme, the RRAM must work in unipolar mode (set and reset with same polarity of voltage). Moreover, a single unipolar RRAM cell requires a selecting diode with high forward

current for accessing accuracy. So far as we know, the filament based resistive switching model dominates in almost all the unipolar mode RRAM devices. One of the most serious problems in filament based devices is the Joule Heating which would produce negative effects in the operation, such as shortening the endurance, varying operating voltage and leading to slow switching time. Generally speaking, the RESET power in a unipolar device is relatively higher than a bipolar one (set and reset with opposite polarity of voltage). This can be explained that in unipolar RRAM, the Joule heating plays the leading role to break the filaments. As illustrated in Fig. 1-6, a thermally assisted process was used to describe the dissolution of filaments. Φ is the initial diameter of filament in the RESET process. With the increasing of Joule heating (A), the dissolution firstly happens in the middle region of filament (B). Such phenomenon enhances the electric field and current density locally and further accelerates the dissolution (C) until the fully rupture (D). The hot spot corresponds to the shrinkage of the filament diameter. To finally integrating the unipolar cells into one chip with high density 1D1R scheme, reducing the inevitable thermal effect is the primary task.

Figure 1-6 Joule Heating assistant dissolution of filament²⁹

To overcome these shortcomings, great efforts were devoted to explore the non-filament based RRAM. Interface-type switching, different from filament-type, have attracted higher attentions, in which the RS behavior occurs near the interface of

insulating layer and electrode or between insulating multilayers, instead of filaments all through the bulk films.

Interface-type switching are usually related to the bipolar RS behavior and often observed in perovskite oxides and some other binary metal oxides. It offers solution to avoid or at least reduce the thermal effect in filament based RRAM device.³ Moreover, a new scheme of complementary resistive switching (CRS) passive crossbar was recently proposed to effectively integrate the bipolar RRAM cells in high density. Therefore, the interface-type RRAM would induce another research fever in the near future. ZnO and Ga₂O₃, as intrinsic n-type semiconductors, could be utilized to construct proper interface-type RS between them and other p-type semiconductors, such as NiO, Cu₂O and MoO₃. The p-n heterojunction is able to be used not only as rectifying diode in 1D1R scheme, but also as an interface-type RRAM cell in CRS scheme, depending on the materials and fabrication. Based on this consideration, different combination of n-type and p-type semiconductor materials or organic materials could also be studied by using such p-n heterojunction structure. In this thesis, GaO_x and NiO_x are selected to construct the p-n heterojunction RRAM devices.

As mentioned in the introduction part, the crucial mechanism in oxide based RRAM is the dynamic of oxygen vacancies. To achieve more stable performance, how well we operate the oxygen vacancies is the key. While people are exploring the RS potentiality of various oxide materials, another dimension of study on the oxygen vacancy engineering is also intensively conducted. Ways to manipulate the concentration or distribution of oxygen vacancies in oxide film have been developed. For oxide film synthesized by physical deposition, the ratio of oxygen in the gas ambient has been adjusted to simply affect the concentration of oxygen vacancies in as-prepared film. On the structure design of RRAM, matching certain electrode with

oxide film could create an effective interface to generate and reserve more oxygen vacancies. In the similar way, different combination of two different oxide films is also considered to produce such interface. Besides the material and structure design issue, varied external electrical operation, such as voltage and current intensity could also be utilized to control the agglomeration of oxygen vacancies during the RS behavior. These methods are proved to be successful in different occasions and we would like to develop some other effective and simple ways to enrich the choices in improving the device performance.

1.3 Objective

The main objective begins with the exploration of transparent RRAM (TRRAM) device based on ZnO and its alloying oxides. Different from the traditional ITO as electrode, we intend to employ conductive Ga doped ZnO (GZO) instead. From the economic point of view, GZO can not only compete with ITO on conductivity, but also reduce the cost due to the indium-free composition. The stacks of GZO/Ga₂O₃/ZnO/Ga₂O₃/GZO were all fabricated by metal organic chemical vapor deposition (MOCVD) method. The transmittance of the whole device and the regular endurance and retention performance were measured to prove its suitability for TRRAM. To know the RS mechanism, the area dependence of cell resistance and XPS spectra were studied. After the confirmation of filament model, we further figured out the effect of different fabrication temperature, compliance current and voltage bias on RS behavior of TRRAM device. With these data and analysis, we would like to clarify the role of Joule-heating in filament mode based RS.

In order to reduce or avoid the negative thermal effect in filament based RS, another objective is to construct a RRAM device which mainly operates on the interface between thin films, but not fully relies on filaments throughout the oxide film. N-type GaO_x and p-type NiO_x were selected in our experiment to form a p-n heterojunction. By manipulating the intrinsic defects inside both films near interface, we have obtained desirable RS behavior and finally proved a feasible device structure of $\text{In}/\text{GaO}_x/\text{NiO}_x/\text{ITO}$ by magnetron sputtering at room temperature. The device with only GaO_x or NiO_x as functional film was also fabricated to further confirm that the RS occurs at the interface between the two oxide films rather than throughout the bulk materials. As usual, the good endurance and retention performance accompanying with multi-cycle data were also obtained. After the study of conduction mechanism in both LRS and HRS, the procedure of RS based on interface was illustrated in detail with the schematic and we have successfully combined interface and filaments factors together. Oxide films with different doping extent were also combined to exhibit different RS curves and testified the effect of concentration of intrinsic defects on RS behavior. The potential of scaling down such RS device was studied by fabricating 1- μm cell, which revealed the importance of interface factor.

Another objective of this thesis is to find out an effective way to engineer the oxygen vacancies in oxide film, further to improve the filament based RS behavior. NiO_x , ZnO_x and GaO_x were selected respectively to mix with TaO_x by magnetron sputtering as the functional layer for RRAM device. Different RS phenomenon were observed and analysed to explore the relationship between the concentration of oxygen vacancies and switching characteristics. By introducing ZnO into TaO_x , the best improvement of resistance distribution, threshold voltage distribution and endurance property were realized, which was coincident with our prediction. The

conduction mechanism of HRS and LRS were also studied by fitting I-V curves to different conduction models. The transition of conduction property corresponds to the varied concentration of oxygen vacancies in oxide films.

1.4 Contribution

An indium-free transparent RRAM was fabricated by MOCVD. GZO instead of ITO was utilized as transparent electrode and the device showed fair endurance and retention performance. Local filamentary conduction was shown to dominate the RS behavior. The electrochemical migration of oxygen vacancies and oxygen ions in ZnO film mainly accounts for the formation and rupture of filament which leads to switching between HRS and LRS. Moreover, Joule heating was found to play different roles which strengthened the formation of filaments while simultaneously facilitated the dissolution of filaments.

A unidirectional bipolar RS was observed in the $\text{GaO}_x\text{-NiO}_x$ heterostructure fabricated by magnetron sputtering at room temperature. The RS behavior could be concluded as the switching between rectifying and Ohmic behavior of the diode. The alteration of junction barrier and the migration of intrinsic defects (oxygen vacancies in GaO_x and oxygen ions in NiO_x) by the electric field control the filamentary paths passing through the interface and account for the RS behavior observed. The device showed good endurance and retention performance, manifesting the potential application of p-n junction structure in non-volatile memory.

TaO_x based RRAM device was improved by introducing ZnO which effectively adjusted the intrinsic defects concentration. By co-sputtering ZnO and Ta_2O_5 , the In/ZnTaO_x/ITO device showed more uniform distribution of LRS resistance, HRS

resistance, SET voltage and RESET voltage, as well as better endurance performance. The improvement mechanism was investigated through the I-V curve analysis incorporated with the intrinsic defects dynamics. The significant role of oxygen vacancies in filament based RS behavior was emphasized again in this part of work. This experiment also offered an alternative point of view in engineering oxygen vacancies in oxide film and enhancing the RS property of filament based RRAM devices.

1.5 Organization

This thesis is divided into six major chapters of which the organization is list as follows:

Chapter 1 briefs the background and significance of RRAM development, including the basic design of RRAM cell and integrating structure, advantage of RRAM over other non-volatile memory candidates, materials issue of electrodes and functional films and fundamental operation mechanism. The motivation, main objectives and contribution of this thesis are also presented in this chapter.

Chapter 2 presents a thorough literature review. The outstanding research results are highlighted on RS type with related physic mechanism, RRAM thin film device design, the strategies to integrate single RRAM cell into crossbar structure, RS characteristics of different oxide materials and key performance parameters of RRAM devices.

Chapter 3 reports an indium-free transparent RRAM based on ZnO and GZO. The fabrication process with device structure is described in detail. The endurance and

retention data is shown to rate the device performance. RS mechanism is also discussed as well as the role of Joule heating in switching process.

Chapter 4 addresses a RRAM device designed on $\text{NiO}_x/\text{GaO}_x$ p-n heterojunction. Besides introducing the material selection and structure schematic, the advantage of this interface-type RS over filament-type one is presented with the study on switching mechanism. In addition, the scaling property of such RRAM cell is investigated by using more industrial techniques.

Chapter 5 demonstrates an effective way to improve the performance of oxide based RRAM device which acts on filament-type RS. Different oxide materials are mixed with TaO_x and a series of RRAM parameters are compared to illustrate the improvement. The enhancement mechanism is analyzed based on the adjustment of intrinsic defects in different oxide mixtures.

Chapter 6 summarizes all the work above and lists out relevant future works.

Chapter 2 Literature review

2.1 Structure and mechanism of RRAM

2.1.1 Basic scheme of resistive switching and crossbar structure of RRAM

To classify the RS phenomenon, the field-induced resistance variation of a metal–insulator–metal (MIM) stack as shown in Fig. 1-4 is studied in detail. The ‘M’ in MIM represents any desirable conductor for bottom and top electrodes, while the ‘I’ denotes an insulator or semiconductor which is the core material of RRAM. In many cases, an initial electroforming step (1st SET step) is required to softly breakdown the as-prepared device. The forming voltage is usually larger than subsequent SET voltages. After this “warms up” step, the device can be arbitrarily switched between a low resistive state (LRS) and a high resistive state (HRS). Whether this forming process is required is basically decided by the materials and switching type. Generally, the ‘I’ in MIM could adopt one of large group of oxides or organic compounds, and the ‘M’ often refers to various metal or some conductive non-metals, such as transparent conductive oxide (TCO).

Figure 2-1 two switching scheme of (a) unipolar switching (b) bipolar switching³⁰

Unipolar (or symmetric) switching will take place when the procedure has no relationship with the polarity of the external bias. The cell in the HRS is SET by a threshold voltage to the LRS as sketched in Fig. 2-1a. Compliance current (CC) should be applied along the SET operation to avoid the permanent break down of the insulating layer. Then a lower voltage (below the SET voltage) without CC will reset the cell from LRS to HRS. In contrast, the switching behavior is called bipolar (or antisymmetric) type when the SET and RESET process should be operated with opposite voltage polarity (Fig. 2-1b). Moreover, the structure of such system is usually designed with asymmetry, such as using different materials as top electrode and bottom electrode. A proper polarity of voltage is applied during the forming step in order to produce the bipolar switching behavior. In both two schemes of resistive switching, two resistance states could be switched repeatedly, which corresponds to the performance parameter of “endurance”. Without maintaining the external electrical signal, both two states should keep for a long period, which refers to the performance parameter of “retention”. Reading operation is implemented with very small voltage which would not affect its present state.

1D1R scheme for unipolar RRAM crossbar array

Integrating memory cells with crossbar structure is one of the advantages of RRAM. Low power and high density non-volatile memory chips could be achieved by this strategy. When unipolar RRAM cells are integrated into crossbar structure, a particular selective element should be attached to every cell for accurate accessing. The necessity of one-diode-one-resistor (1D1R) scheme for integrating unipolar RRAM cell is discussed as follows (Fig. 2-2): if the RRAM array is supposed to be

randomly accessed, every single memory cell must be combined with a selector in order to avoid reading disturbance among neighbouring cells.

Figure 2-2 a) Generalized crossbar array in which each bit cell is composed of a memory cell and a switch between conductive lines on top (word line) and bottom (bit line). b) Reading error in an array consisting of 2 by 2 cells without switches. c) Rectified reading operation in an array consisting of 2 by 2 cells with switches. d) Detailed structure of a single cell consisting of a Pt/NiO/Pt memory element and a Pt/VO₂/Pt switch element²⁸

Without the selector, a typical erroneous access of a cell in a simple 2×2 array will occur as shown in Figure 2-2b. Although we would like to access the “0” state of certain cell in HRS which is surrounded by other three LRS (“1”) cells, the current will prefer the way along the serial 3 LRS cells and finally the incorrect “1” is read instead. After connecting a selecting diode with rectifying characteristic, the bypass current will be prohibited effectively because the resistance state of all unwanted cells

are HRS and the reading current can only run through the right one, as shown in Figure 2-2c.

At the early age, silicon-based transistors came firstly to people's mind as a switch element for each RRAM cell. However, due to their high fabrication temperatures and the difficulty of depositing high-quality silicon epitaxially on metals, silicon-based transistors cannot be used for three-dimensional (3D) high-density, non-volatile memories stack. Therefore, many alternatives were taken into consideration. Lee *et al.* improved their work and reported a simplified switch element of Pt/VO₂/Pt with self-rectifying behavior in 2007.²⁸ Park *et al.* also fabricated Pt/TiO₂/Ti Schottky type selecting diode for alleviating the sneak current in RRAM arrays in 2010.³¹ For ZnO based RRAM, in 2011, J. W. Seo's group presented two types of heterojunction diodes, a NiO/ZnO p-n junction and a WO₃/ZnO tunnel barrier with feasible rectifying behaviors and high forward current density to successfully suppress the sneak current path.³²

Complementary resistive switching scheme for bipolar RRAM crossbar array

The 1D1R scheme crossbar architecture is only suitable for integrating unipolar RRAM cell which needs higher current to thermally dissolve the filament. For bipolar RRAM cell, there has been no desirable solution for long time. To avoid the higher power consumption of the unipolar RRAM cell and search a way to integrate the bipolar RRAM cell, Linn *et al.* proposed a scheme of complementary resistive switching (CRS) in 2010 as shown in Fig.2-3.³³ It consists of two back-to-back bipolar RS elements and enables constructing large passive crossbar arrays with a much lower consumption of power, without considering the bypass current issue. The details of operating such CRS cell will not be discussed in details here. In brief, The

CRS adopts essentially the similar principle as a CMOS inverter, which has successfully contributed to the amazing achievement of the CMOS technology in past 30 years.

Figure 2-3 Sweep property and possible states of the CRS³³

The total resistance of the RRAM chip based on CRS scheme is unaffected no matter how the storage pattern is like, which is a totally different case as previous 1D1R crossbar concept. Which one of the two serial RS elements is in the LRS will decide whether '0' or a '1' is stored in the whole CRS cell (As shown in the inset table of Fig. 2-3). And no matter '0' or '1' is written, the CRS cell will always be the same HRS ($LRS + HRS \approx HRS$ with $HRS \gg LRS$). This property effectively prohibits the sneak path current. Some calculations have predicted that with such scheme, 10^{10} memory cells are available to be integrated into crossbar structure with nano size.³⁴

2.1.2 Resistance switching mechanism of RRAM

The resistive switching mechanism has been the most controversial field in RRAM research for many years. RS phenomenon could be induced by a few physical mechanism, such as thermochemical effect, valence change effect, electrochemical metallization or electrostatic effects.²⁹ As illustrated in Fig. 2-4, among various origins of switching, filament model and interface model are widely discussed. The unipolar switching of Pt/NiO/Pt (Fig. 2-4a) belongs to typical filament model (Fig. 2-4c), while the bipolar switching of Ti/La₂CuO₄/La_{1.65}Sr_{0.35}CuO₄ (Fig. 2-4b) corresponds to the interface model (Fig. 2-4d).

Figure 2-4 (a) unipolar switching (b) bipolar switching (c) filament model (d) interface model³

Filament-type RS

As for filament-type switching, the formation and rupture of conductive filaments in the insulating layer account for the resistive switching. Both unipolar and bipolar switching behavior can be somewhat related to this model. Fig.2-5 shows a possible dynamic of one filament in the unipolar RS. In the initial forming process (“warm up” as we describe in section 2.1.1), a soft breakdown (reversible) in the dielectric material takes place when conductive filamentary paths pass through the insulating layer and change the cell from HRS to LRS. During the next RESET process, rupture of the filament turns the cell back to HRS and the following SET process reconnects the ruptured filament near one side of the insulating layer, changing the cell to LRS again. Usually the forming voltage is larger than all following SET voltages.

Figure 2-5 Unipolar resistive switching behavior and schematics of the initial state (as-prepared sample) and (1) forming, (2) reset, and (3) set processes³

Thermal redox process initialized from interface area between the oxide and electrode into the bulk is usually accepted as the driving force behind the filaments dynamic.³⁵

In bipolar RS, the migration of oxygen vacancies or oxygen ions under the field is considered to be the mechanism.³⁶

Interface-type RS

As illustrated in Fig. 2-4d, the RS occurring at the interface between the electrode and the insulating layer is so-called interface-type RS. Baikalov *et al.* have tested the perovskite oxide cells, showing that the contact resistance between the metal electrode and the perovskite oxide will change under the voltage bias.³⁷ In semiconducting perovskite oxides, interface-type RS is often detected. Several models have been proposed to explain the mechanism behind, including conducting paths cross the interface due to electrochemical migration of oxygen vacancies,³⁷ charge carriers captured or released by the traps,³⁸ and a Mott phase change aroused by carriers near the interface.³⁹

Figure 2-6 C–V curves under reverse bias for a Ti/PCMO/SRO cell show hysteretic behavior. This indicates that the depletion layer width at the Ti/PCMO interface is altered by an electric field³

The RRAM cell is usually composed of insulating or semiconducting oxides sandwiched by two electrodes, like a capacitor, so the contact resistance may be controlled by a changing Schottky barrier. Some studies had shown that the barrier width in LRS is much narrower than in HRS.³ Thus, with the depiction in Fig. 2-6, in LRS electrons will have certain probability to penetrate the thinner interface barrier with a tunneling process, whereas in HRS the electrons are prevented from tunnelling through the thicker barrier. **Electrochemical migration of oxygen vacancies near the interface which adjusts the self-doping concentration is considered to be the main force for the variation of barrier width.**

It seems that filament-type and interface-type RS are irreconcilable, however, recently a unified model combining both these two was proposed by Akinaga *et al.*⁴⁰, corresponding to oxide based MIM structure. In this model, as illustrated in Fig. 2-7, the filamentary paths will firstly form in the raw material as forming step we usually comprehended.

Figure 2-7 Unified model of resistive switching in oxide based MIM structure⁴⁰

But during the subsequent switching, the existing filaments in oxide will act as virtual electrode because the resistance change only occurs near the interface region due to the diffusion of oxygen ions or vacancies between the electrode and oxide depending on the polarity of electric field. In other words, the redox process in the thin oxide layer formed at the interface decides the resistance state of the MIM structure. As for the interface barrier, the migration of oxygen ions or vacancies not only varies the barrier shape but also leads to the penetration of filaments (usually by tunneling process) through the barrier.⁴¹ Similar studies were also reported by some other groups.^{42,43}

2.1.3 Conduction models in resistive switching process

Conduction property is a significant object of study when we look into the RS mechanism in oxide based device. Usually I-V characteristic is investigated to clarify what type of conduction dominates the switching process, helping to understand how the RS occurs in certain material. Generally speaking, all the conduction models found in oxide RRAM could be classified in Table 2-1. In this table, J is current density, E is electric field, ϵ_i is insulator permittivity, μ is electron mobility, V is voltage, d is insulator thickness, A^* is effective Richardson constant, ϕ_B is barrier height, k is Boltzmann's constant, T is temperature.

Table 2-1 Four conduction models in RS behavior

Conduction model	Equation
Ohmic conduction	$J \propto E$
Space-charge-limited-Conduction (SCLC)	$J = \frac{9\varepsilon_i \mu V^2}{8d^3}$
Schottky emission	$J \propto A^* T^2 \exp\left(\frac{-q(\phi_B - \sqrt{qE/4\pi\varepsilon_i})}{kT}\right)$
Poole-Frenkel (PF) emission	$J \propto E \exp\left(\frac{-q(\phi_B - \sqrt{qE/\pi\varepsilon_i})}{kT}\right)$

▪ Ohmic conduction

The Ohmic conduction describes the normal linear relationship between voltage and current. In this model, the resistance will not change with the intensity of voltage or current in constant temperature. However, the conductivity of materials will vary when the temperature changes. In our experiment, all electrical tests are implemented at room temperature with low current intensity. Thus, the I-V curve exhibits linear characteristic in Ohmic region as we usually see. When the device works in LRS, the Ohmic I-V behavior relates to the high conductive filaments, while in some case of HRS, especially under low voltage, Ohmic curve is also observed which corresponds to small current of thermal generated charges.⁴⁴

▪ **Space-charge-limited-conduction (SCLC)**

Space charges represent those excessive electric charges which spread continuously in the material bulk. In some cases, the injected charges from one contact will not 100% transmit to the other end due to the saturation of charge carriers within the material. The series of charged atoms or molecules will construct a space charge region. This region will suppress the electron injection and limit the intensity of current, which is called space-charge-limited-current. SCLC is a very common and important mechanism in many vacuum and solid-state electronic devices. It usually occurs in dielectric media such as semiconductor oxides but not in the metal because in the metal the injected charges will be promptly neutralized or transmit through the whole bulk.

In the oxide we discussed in this thesis, the space charge limited current is determined by the density and distribution of traps within the materials, which is called trap-controlled space charge limited conduction (TC-SCLC). The traps usually relate to the defect states which could trap the electron and profoundly influence the electrical property. TC-SCLC often plays a significant role in transition metal oxide because the density of free carriers is relatively low in these materials, and with the ohmic contact with the metal, it is easy to inject excess charges into oxide and cause the trap-filled limited current.⁴⁵ TC-SCLC is frequently reported in many oxide RRAM devices in which the defects related filaments accounts for the switching.^{45,46}

▪ **Schottky emission**

Comparing with SCLC which occurs in a relatively thicker film, Schottky emission is another current transfer mechanism related to the interface between metal and insulator.⁴⁷ It represents the high-field emission of hot electron from metal

contact into the conduction band of insulator and the process is illustrated in Fig. 2-8. The system is composed by an insulating layer sandwiched by two metals. The electrons in the metal should gain enough energy under external bias to overcome potential barrier and be injected into the insulator. High temperature dependence is the major characteristic of Schottky emission and the process is metal/electrode-limited.⁴⁷ At room temperature and regarding film thinner than 10 nm, the magnitude of Schottky emission is of the same order as tunnelling current. When we consider thicker film with higher work function, Schottky emission current is much more prominent. A number of RRAM devices were reported that the conduction in HRS follows Schottky emission model, especially there forms Schottky barrier between electrode and oxide.^{48 49}

Figure 2-8 Energy level diagram of MIM structure⁴⁷

▪ Poole-Frenkel (PF) emission

Although the mathematical expression of PF emission looks similar to Schottky emission, the process of PF emission is bulk/insulator-limited. PF effect, actually referring to the field-assisted thermal ionization, describes the lowering of Coulombic barrier under the electric field (Fig. 2-9). As for oxide materials, this process usually associates with reduction of traps barrier in the bulk.^{50 51}

Figure 2-9 Lowering of Coulombic barrier under electric field⁵⁰

Therefore, in Table 2-1, the ϕ_B in the equation of PF emission represents the Coulombic barrier raised by the interaction of positive traps and negative electrons, which is different from the ϕ_B in Schottky emission. Generally, the positive traps (usually oxygen vacancies) in oxides are necessary to initiate PF emission. In some cases, PF emission and Schottky emission coexist in a competitive way.^{49 52} When the metal/oxide barrier is lower than the trap barrier, Schottky emission will dominate the conduction; while in the opposite case, Schottky emission will be masked by PF emission. Moreover, PF emission tends to happen under relatively higher electric field than Schottky emission⁵³ and Schottky emission occurs more probably in the forming step of RRAM device.⁵⁴ One method to distinguish these two models is fitting the I-V curve in different scale according to their equation.

2.2 Materials and fabrication of RRAM device

The RS phenomena have been observed in all kinds of materials, such as solid electrolytes (GeSe and Ag_2S), perovskites (SrZrO_3 and $\text{Pr}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$), binary transition metal oxides (NiO , TiO_2 , Cu_2O and ZnO)³. Particularly, binary metal oxide based materials displaying the non-volatile RS have been a hot topic for a long time. From material point of view, the advantage of oxide is obvious. Metal-oxide-metal (MOM) structure could be fabricated according to traditional semiconductor industry. Low-current RS operation was discovered in the CuO_x -based MOM structure. The CuO_x layer was deposited by the thermal oxidation of the 0.18 μm Cu via.⁵⁵ CoO and NiO are also listed as study objects for RRAM since early period due to the phase transformation and stoichiometric variation, respectively.⁵⁶ In recent years, remarkable scaling ability has been certified in a $\text{TiN}/\text{Ti}/\text{HfO}_x/\text{TiN}$ RRAM device, of which each cell is of 30 nm in size.⁵⁷ This 1-kb array showed a high device yield ($\sim 100\%$) and excellent endurance ($>10^6$) with the switching time of 40 ns. At the same time, TiO_2 has also been selected as a typical RS oxide for many years.⁵⁸ Both unipolar and bipolar switching has been observed in these reports and TiO_2 based RRAM devices are good objects for device physics study, for example, the forming step, filament or interface dynamics and other conduction mechanism.

▪ Zinc Oxide

As one of binary transition metal oxides mentioned in chapter 1, ZnO is a promising candidate of RRAM material and it has been reported in various aspects of device performances such as unipolar RS properties,²⁷ high resistance ratio characteristic¹⁸ and transparent RRAM.¹⁹ As shown in Fig. 2-10, Yang *et al.* developed a simple

bipolar RRAM device consisting of Ag/ZnO: Mn/Pt with ultrafast switching speed of 5 ns, an ultralarge $R_{\text{OFF}}/R_{\text{ON}}$ window of 10^7 , desirable retention time of over 10^7 s, excellent endurance and high stability at varied temperatures.¹⁸ The device fabrication was fully accomplished by magnetron sputtering method at room temperature.

Figure 2-10 Structure schematic and endurance and retention performance of Ag/ZnO: Mn/Pt device¹⁸

N. Xu's group also published their work on TiN/ZnO/ Pt bipolar RRAM device based on filament dynamics (Fig. 2-11). Low voltage (± 1.2 V), fast switching time of 20-60 ns, and uniform repeating cycles with resistance window > 10 showed the excellent operation of this device among several competitive materials.^{59,60}

Figure 2-11 I-V curve and endurance performance of TiN/ZnO/ Pt RRAM cell⁵⁹

There are many other work exploring the potential of ZnO based RRAM device such as doped ZnO films,^{61 62} single crystalline ZnO nanowires and nanorods layer,⁶³ ⁶⁴ multiple layers combining ZnO with other materials.⁶⁵ Table 2-2 gives the comparison of RS performance between ZnO and other oxide materials.

Table 2-2 Comparison of resistive switching performance between different RRAM device⁵⁹

Oxide	Electrode	Switching mode	SET	RESET	Voltage
ZnO	TiN/Pt	Bipolar	20 ns	60 ns	-1.2 V/+1.2 V
ZnO	Si-sub	Bipolar	40 ms	40 ms	-40 V/+40 V
NiO	Pt/Pt	Unipolar	10 ns	5 μ s	0.5 V/1.0 V
TiON	TiN/Pt	Bipolar/Unipolar	50 ns	50 ns	-2.5 V/+4.5 V
TiO ₂	Pt/Pt	Bipolar	100 μ s	1 ms	-0.2 V/+0.5 V
Cu ₂ O	Cu/Ni	Unipolar	300 ns	300 ns	
Cu-MoO _x	Pt/Cu	Bipolar	1 μ s	1 μ s	-1.5 V/+1 V

Transparent RRAM (TRRAM) device is potentially valuable in the futuristic transparent electronics. By combining with other transparent electronic elements, the see-through system-on-glass will come true, for example, large transparent display,⁶⁶ which belongs to the macroelectronics. A fully TRRAM device based on ZnO was also realized and could be implemented in various electronic systems. Since J. W. Seo *et al.* firstly reported a ITO/ZnO/ITO TRRAM in 2008 (shown in Chapter 1),¹⁹ some other group also contributed to this smart concept, such as replacing the insulating

layer and electrode with different materials⁶⁷ and building up the RRAM cell on a flexible substrate.⁶⁸

▪ Nickel Oxide

NiO, another main role in this thesis, has also been intensively explored as one of the best candidates since the very beginning of oxide RRAM research. The non-stoichiometric NiO_x deposited by magnetic sputtering showed reproducible RS behavior as reported by J. W. Park *et al.* in 2005.⁶⁹

Figure 2-12 Improving of endurance of NiO device by pressure controlling in deposition⁷⁰

Although the term “filament” was not adopted in this paper, the conductive path which consists of intrinsic defects in NiO_x has already been revealed to describe the RS behavior. Soon afterwards, great amount of endeavour has been devoted into improving the RS property of NiO based device. R. Jung *et al.* enhanced the

endurance of unipolar RS in NiO_x through process controlling on deposition which is described in Fig. 2-12. The magnitude of switching voltage reduced (Fig. 2-12a) and the uniformity was enhanced (Fig. 2-12b&c) when the deposition pressure is decreased from 5 mTorr to 1.5 mTorr. The formation of more Ni-Pt phase near interface area under lower pressure produces much more defects and facilitates the formation of filaments.⁷⁰

Figure 2-13 Enhancement of several key parameters of RS through scaling down the memory cell size⁷¹

M. J. Lee's group from Samsung also carried on their work to scale down the size of RRAM cell, expecting to test the potential of nanofilaments based memory in low-power application.⁷¹ With the cell size decreasing, not only the switching power decreased dramatically, the switching speed was also elevated to <10 ns as depicted in

the Figure 2-13a. The HRS and LRS resistance increased due to the narrower filaments (Fig. 2-13b). Switching energy and operating voltage both reduced (Fig. 2-13c&d) because the filaments dynamic was facilitated as the cell size decreases. The nanofilaments were testified to be composed of nickel and form along the grain boundaries. This result manifested NiO to be one of the ideal materials in ultra-fast, high-density RRAM industry.

J. S. Choi *et al* compared unipolar and bipolar RS behavior via depositing NiO on Pt and SRO, respectively.⁷² By carefully studying the conduction characteristics during the switching process, they proved again that unipolar switching undoubtedly relates to the conductive filaments while the bipolar switching could be induced by introducing the interface Schottky barrier. In fact, this conclusion has been well acknowledged and applied to many oxide materials.

▪ Tantalum Oxide

TaO_x appeared active recently as an amazing competitor in oxide RRAM field. The research on unipolar and bipolar switching in common TaO_x MIM structure started in 2008.^{5,73} The high endurance property aroused pretty much attention at the early stage because of its high potential in memory industry. A lot of work also adopted TaO_x as an assistant layer in other RRAM devices, such as inserting TaO_x ultrathin layer into Pt/TiO₂ interface⁷⁴ and W/GeSe_x interface.⁷⁵

An important breakthrough was made in 2011, when M. J. Lee *et al.* demonstrated a fast, high-endurance and scalable non-volatile memory device based on TaO_x with extreme cycling endurance of over 10¹² and 10 ns switching times, which showed most outstanding performance among various materials.⁷⁶ From Fig. 2-14a, we could

Figure 2-14 The Pt/Ta₂O_{5-x}/TaO_{2-x}/Pt stacks with high endurance and scalability⁷⁶

see that this memory cell was designed according to Metal-Insulator-Base-Metal (MIBM) stacks, in which a medium resistive TaO_{2-x} film was employed as the base layer, and a thin high resistive Ta₂O_{5-x} film acted as the insulating layer. The oxygen ions injected or ejected at the interface between the insulating and base layers controlled the formation and rupture of filaments in insulating layer. Such stack was successfully integrated into crossbar structure (Fig. 2-14b). The resistance of the base layer (TaO_{2-x}) and insulator layer (Ta₂O_{5-x}) was accurately controlled by plasma

during deposition. As the cell size reduced to 30nm×30nm, the nanofilaments could still be well localized in insulator layer, leading to highly reproductive and retentive RS with fast speed and low power consumption. The endurance performance for the samples deposited under different oxygen partial-pressure conditions was excellent as described in Fig. 2-14c. This scheme opened up another way for the oxide based RRAM design, as long as the stoichiometric of certain oxide could be properly adjusted.

Figure 2-15 Endurance and switching stability advantage of TaO_x over TiO_x²⁵

The remarkable performance of TaO_x based device was seen in other work, too.^{77 78} And such ultrahigh endurance quality was majorly observed in TaO_x and HfO_x, which make them more eye-catching over TiO₂, NiO and ZnO which

previously dominated the RRAM research. In Fig. 2-15a&b, the comparison of endurance performance between TiO_x and TaO_x was made and TaO_x maintained a more stable resistance window with longer endurance than TiO_x . Moreover, the resistance change under 1 μs voltage pulse of different magnitude was also much stable in TaO_x than TiO_x as shown in Fig. 2-15c&d.

With respect to this trend, J. J. Yang summarized the critical features shared by TaO_x and HfO_x that there exist only two stable chemical compositions in these two oxides: near stoichiometric insulating phase and conducting metallic phase²⁵. Therefore the dynamic of filaments is very regular in such oxide which is not easily affected by external condition, for example, the overdriving of electric bias⁷⁹ and the need of gradually increased refreshing voltage.⁸ However, like TiO_x or WO_x , the stoichiometric composition is much more sophisticated. There are several metastable states in them instead of two, leading to the relatively irregular filaments activity and poorer endurance.

2.3 Performance requirements of RRAM

Based on the working requirements of three main leading memory technology (DRAM, Flash and HDD) today and to predict the scaling tendency in the near future, a series of parameters for RRAM cells are discussed and listed in table 2.3.^{2,29}

Table 2-3 The requirement of key parameters of RRAM

Write Time	< 100ns	Resistance Ratio	> 10
Write Voltage	< 5V	Endurance	> 10 ⁷
Read Time	< 100ns	Retention	> 10 years
Read Voltage	< 1V	Power consumption	< 1nJ/bit

Write operation

One of the shortcomings of Flash is that a relatively long time (usually a programming speed of around 10 ms) is needed to rewrite data into the memory chip. Therefore, for RRAM, the length of writing signal is supposed to be <100 ns so as to comply with DRAM requirement. In order to approach the speed of SRAM, <10 ns writing is required. In addition, the writing voltages of RRAM should be limited from a few hundred mV to a few V, so as to be compatible with the current CMOS industry and to precede Flash which suffers from high operating voltages.

Read operation

Usually applying a voltage to the selected word-line and coupling a signal amplifier to the bit-line could read out the resistance status of an RRAM cell. It is well accepted that the reading voltage should be much smaller than the writing voltage in order not to disturb existing storage state. Due to the circuit design constraints, reading voltage

cannot be less than approximately one tenth of writing voltage. Moreover, the minimum reading current should not be less than around 1 mA for an easy sensing of present state with the use of signal amplifiers. Lastly, the reading time must be equivalent as writing time or shorter.

Resistance ratio

The resistance ratio (also called resistance window) determines whether the electronic circuit can distinguish the states of memory cell between 0 and 1. Due to the high density of integration in crossbar structure, a large amount of elements will produce a distribution of on and off states. Therefore, the on-off ratio in a single cycle of a single cell is not sufficient to define the resistance windows of the whole device. Although for MRAM, an R_{OFF}/R_{ON} ratio of more than 1 is acceptable by special circuit setup, a statistic R_{OFF}/R_{ON} ratios of at least 10 is required to match the highly efficient sense amplifiers within RRAM devices.

Endurance

As one of the most important qualification, endurance performance refers to how many times the RRAM could be rewritten. One advantage of HDD is that it can be written and erased at least 10^{12} times. In contrast, currently Flash memory shows a limited quantity of repeating cycles between 10^3 and 10^7 . This is the reason why Flash memory could not be used as core memory or page storage in computer, but be used in some removable applications. Thus, RRAM should at least possess better endurance quality than Flash. 10^8 rewriting cycles or above would be applicable.

Retention

Another major incentive to develop a fast non-volatile memory lies in that DRAM requires continuous data refresh during work, otherwise it will lose all the data in typically a few milliseconds. Flash and HDD could stably retain their information for several years without power supply, and this is also required by next generation non-volatile memory. For archival data storage, retention of more than a hundred years would be desirable. A kind of write once read many (WORM) RRAM could be competent in this case. But for general application, A retention time >10 years at temperature up to 85 °C and under frequent reading electrical stress is required for universal RRAM.

Power consumption

A weakness of both DRAM and HDD is that more energy is wasted to maintain the device active even there is no operation at all, and the power is statistically a few mW per GB. In this aspect, Flash shows its superiority, consuming theoretically no power when standby. Only a few μW is needed to get the supporting electronics ready. To be the potential candidate of next generation non-volatile memory, RRAM should have similar low standby power as Flash. Of course, the main power consumption comes from the read and write operation. 1 pJ/bit which leads to mW consumption in a single write operation would be applicable to compete with Flash memory or HDD.

2.4 Conclusion

In this chapter, we start the literature review from some elementary topics about RRAM, such as the basic structure of RRAM device, the scheme of crossbar integration, the switching type and related physics. The filament type and interface type RS, as the two well-known mechanisms, are the important objects we studied in this thesis. The chronological review of RRAM research based on ZnO, NiO and TaO_x are given, respectively. Some critical breakthroughs in these fields are also listed and the related parameters are highlighted as reference. Lastly, the performance requirements of RRAM devices are discussed compared with other memory technologies.

Chapter 3 Indium free ZnO based transparent RRAM

3.1 Introduction

Transparent devices are potentially useful in the futuristic transparent electronics. For example, Samsung has produced the transparent OLED display, and Apple and Nokia both introduced the transparent mobile phone concept. Thus there is trend of commercial systems based on transparent electronics. TRRAM is to be integrated with other transparent electronic devices to produce the so-called system-on-glass. ZnO has been treated as an ideal candidate for TRRAM device by virtue of its natural abundance, relatively developed fabrication technologies and well compatibility with CMOS industry. ZnO has a wide bandgap of 3.37eV under room temperature and its conductivity can be regulated in a broad range from insulator like to metal like by extrinsic and intrinsic doping. So the concept of TTRAM could be well realized by using ZnO and its derivatives, such as GZO and IGZO. Some literatures have reported the RS behavior in transparent IGZO and studied the related influential factors.^{80 81} Flexible ZnO or IGZO based devices were also seen in some papers.^{82 83} However, these transparent devices were all achieved by sandwiching insulator layer with traditional ITO or conductive IGZO⁸⁴ as electrodes. With consideration to the limited resources and high cost of indium, indium-free transparent conductive oxide (TCO) has its significant economic advantage in application.

The transparent Ga doped ZnO (GZO) thin films we fabricated could reach a desirable low resistivity of $3 \times 10^{-4} \Omega \cdot \text{cm}$, which is comparable with commercial ITO.⁸⁵ Moreover, it could be well assembled with high resistive ZnO layer without interface barrier, assuring high current injecting efficiency^{86 87}. Thus, here we introduce the fabrication of both electrode and functional layers by applying ZnO with different

concentration of Ga doping, in order to construct indium free TRRAM stacks. The resistive switching characteristics are investigated and the conduction mechanism is discussed in detail.

3.2 Fabrication of TRRAM

Our research group has designed and built up a plasma enhanced MOCVD system for ZnO and Ga₂O₃ growth (Fig. 3-1).

Figure 3-1 Photos of the ZnO-MOCVD system, (a) an overview of the whole system, (b) the showerhead nozzle, (c) the heating halogen lamps, and (d) the plasma ignition.

In this system, we designed a special showerhead nozzle to separate the O₂ with metal-organic vapour. This design effectively eliminates the pre-reaction of the precursors, which is the general problem in ZnO growth by MOCVD. Employing this special designed MOCVD system, high quality epitaxial ZnO films and nanostructures has been obtained. Using such an in-house MOCVD system, multilayers of conductive GZO, resistive ZnO and higher resistive Ga₂O₃ were deposited successively on 2.5cm × 3.5 cm glass substrate to construct the GZO/Ga₂O₃/ZnO/ Ga₂O₃/ZnO stacks.

The chamber was first pumped down by a mechanical pump to a vacuum of around 2.5×10^{-2} Torr before deposition. Then the 500 standard cubic centimeters per minute (sccm) N_2 combining with 150 sccm O_2 was introduced into the chamber as carrier and reacting gas until the pressure arrives at 25 Torr. After that, 2.0 sccm Trimethylgallium (TMGa) and 2.0 sccm Dimethylzinc (DMZn) as precursors entered the chamber from the shower head which is 10cm above the depositing plate. The pyrolysis of TMGa and DMZn at high temperature lead to the directly reaction of Ga, Zn with O_2 to form crystalline ZnO and Ga_2O_3 layers on the substrate. And the by-products, such as CO_2 and H_2O left the chamber with the pumping flow. The reaction equations are listed as below:

In the subsequent growth, a 200 nm of GZO as transparent bottom electrode (BE) was deposited on the glass wafer as the temperature of plate was heated up by filaments to $300^\circ C$. Then the flow O_2 was increased to 500 sccm and a gas valve between pump and chamber was used to adjust the chamber pressure to 40 Torr. As the temperature further increased to $400^\circ C$, the multiple layers consisting of 120nm ZnO (DMZn at 2 sccm) sandwiched by 50nm Ga_2O_3 (TMGa at 20 sccm) were subsequently deposited on the GZO film, respectively. At last, with a shadow mask, a 200 nm patterned GZO array as top electrode (TE) was deposited, of which the condition was same as BE. As we can see in Fig. 3-2, by adjusting the ratio of ZnO and Ga_2O_3 , three types of oxide films with different resistivity could be achieved.⁸⁵ The most conductive GZO was employed as BE and TE and the most resistive Ga_2O_3 was used as blocking layers sandwiching the moderate resistive ZnO as RS functional layer.

Figure 3-2 The device structure schematic and the resistivity to which each layer corresponds ⁸⁵

In order to make a comparison, the ZnO film was also fabricated at 350°C and 300°C with other condition unchanged. A semiconductor parameter analyzer was utilized to measure the RS characteristics in DC sweep mode. The chemical bonding states of ZnO film were investigated by x-ray photoelectron spectroscopy (XPS). The crystal structure of ZnO and GZO was examined by X-ray diffraction (XRD) measurement.

3.3 Characterization and device performance

The XRD spectrum of ZnO film and conductive GZO film deposited is shown in Fig. 3-3a. The ZnO film shows a polycrystalline structure with mainly c-axis growth orientation. With a lower doping of Ga and lower growth temperature of 300°C, the conductive GZO film displays peaks at same position but with lower intensity and a slightly wider full width at half maximum (FWHM). The inset shows the whole device transmittance. Through the sample, we can clearly see the logo underlying, proving the excellent transparency of whole device. Including the glass substrate, the device transmittance is above 85% in the visible region.

Figure 3-3 (a) XRD spectra of ZnO and GZO films in our TRRAM device. Inset is transmittance of our TRRAM device with the inset showing seen-through device; the inset shows the device structure⁸⁸ (b) bipolar switching in log scale; the inset shows the I-V curve of GZO/ZnO/GZO device

According to the traditional metal-insulator-metal (MIM) structure, the resistance of insulating layer varying between high and low states fulfills the binary storage. We firstly attempted to fabricate GZO/ZnO/GZO device. Although the resistivity of ZnO thin film by MOCVD was high, such device exhibited large current

in I-V curve with very low resistance as shown in the inset of Fig. 3-3b. ZnO is often used as a buffer layer for GZO growth and GZO/ZnO stacks work as transparent electrodes. Therefore, the GZO grown on ZnO will increase the oxygen vacancies and reduce the resistivity of ZnO⁸⁶⁻⁸⁹. To suppress the reduction of ZnO resistivity, we inserted Ga₂O₃ between GZO and ZnO because Ga₂O₃ has a different crystal structure from wurtzite ZnO and its oxygen vacancies concentration is really low⁹⁰. Such structure successfully resulted in the RS behavior as we report above. To exclude the possible RS occurs in Ga₂O₃, we also fabricated GZO/Ga₂O₃/GZO device. It permanently broke down by a voltage bias and no resistive switching happened. Therefore, we define the Ga₂O₃ as a blocking layer to maintain the high resistivity of ZnO during fabrication. Ga₂O₃ permanently broke down to conductive state at initial SET step and the subsequent RS behavior took place in ZnO layer. Such multilayer structure aims to not only ensure a highly resistive and switchable ZnO as prepared, but also maintain the necessary resistance window. Fig. 3-3b shows the typical bipolar RS of our TRRAM device. Applying a positive sweeping bias of ~14 V with the protection of 20 mA compliance current (CC), an abrupt increase of current was observed and the device drastically switched to LRS. Even if bias voltage swept back, the device maintained the LRS, which confirmed the nonvolatility. When the negative bias proceeded till another threshold value of ~12V, the device was reset back to HRS. The SET and RESET process requires opposite polarity of external bias. The steady repeating of such operation leads to the bipolar switching in the TRRAM. Although during the subsequent operation, the resistance reduced slightly, the resistance ratio still remained over 10², which meets the criteria we mention in the introduction. We applied the same polarity of bias in SET and RESET on the device, but failed to

trigger the unipolar RS. As introduced in Chapter 2, the dynamics of oxygen vacancies possibly dominates the switching behavior.

The resistances of HRS and LRS in 50 switching cycles are shown in Fig. 3-4a to evaluate the reliability of our TRRAM device. Despite of the fluctuation of resistance in HRS and LRS, the ratio of HRS/LRS is around 10^2 , exhibiting a desirable resistance window for distinguishing 0 and 1. The retention characteristic was measured to test the nonvolatility of our device. **Actually, the endurance test in DC sweep mode will result in poorer performance than in pulse test mode due to the thermal effect by Joule heating. Our device is not good enough to take the pulse test yet. Moreover, the device is not packaged. This will also degrade the device performance.** As shown in Fig. 3-4b, both HRS and LRS resistances vary in a very small range without significant decay after 10^5 s, which could be expected to perform highly stable storage. **The variation of switching voltage is in an acceptable range as shown in Fig 3-4c.**

TRRAM is meant to be integrated with other transparent electronic devices to produces of the so-called system-on-glass, which belongs to the macroelectronics (large scale electronics). Macroelectronics refers to lower density integrated circuits on a larger area. Therefore, some trade-offs are inevitable, such as slower operation speed or higher operating voltage. Based on analysis of some parameters above, there is still much room to improve the performance of our TRRAM devices, such as reducing the switching voltage and enhancing the endurance.

Figure 3-4 (a) R_{ON} and R_{OFF} in 50 switching cycles at room temperature; (b) Retention characteristic at room temperature⁸⁸; (c) SET and RESET voltage distribution in 50 cycles

3.4 Study of mechanism

To primarily confirm filament mechanism in our RRAM devices, the study of area dependence of the cell resistance was applied. As shown in Fig. 3-5, the HRS and LRS resistances of all three devices are independent of device area. Only when the memory cell is scaled **down to similar order** as nanofilaments, the dependence of resistance on cell size will occur, because the cell area then decides the amount or diameter of filament clusters connecting BE and TE.^{76 71} **Our TE size is of 0.1-2 μm in diameter which is much larger than the filaments size. Therefore, the independence of resistance on cell size indicates that the local filamentary conduction takes place in our case.**^{18,91}

Figure 3-5 Cell area dependence of R_{on} and R_{off} for three devices

In a filament model, the dielectric material will be softly broken down to LRS with the formation of filamentary paths, and will return to HRS due to the annihilation

of these paths. As for the MIM structure with certain metal electrode contacting with electrolyte-like oxide film, thermal redox or anodization starting near the interface and spreading through the bulk is usually considered as the main **mechanism** in filament dynamics.^{92 93}

Figure 3-6 XPS spectra of ZnO film for (a) Zn 2p and (b) O 1s⁸⁸

And the electrochemical migration of oxygen vacancies with positive charges (V_o^+) and oxygen ions (O^{2-}) with negative charges in oxide film is widely regarded as the driving force in structures with other combination of metal or non-metal electrodes

and oxides.^{81 94} To quantitatively analyse the filament in our device, the XPS spectra of ZnO film for Zn 2p and O 1s core levels were taken (Fig. 3-6).

We can see from Fig. 3-6a that the energy interval between Zn 2p_{1/2} and Zn 2p_{3/2} peaks is 23.0 eV, which indicates there is no metallic Zn in the film because of the full oxidization of Zn.⁹⁵ However, that does not exclude the existence of oxygen vacancies in the ZnO film. In Fig. 3-6b, the 529.3 eV peak of O 1s is attributed to the O-Zn bonding while the 531.0 eV peak corresponds to the O-H bonding due to the chemisorbed oxygen in the film.⁹⁶ This indicates there is a large amount of nonlattice oxygen ions in the ZnO film. These nonlattice oxygen ions and intrinsic oxygen vacancies play key roles in the filament mechanism.

The conducting property study would also help to understand the RS mechanism in our device. The log-log I-V plots of both HRS and LRS are drawn in Fig. 3-7.

Figure 3-7 I-V characteristic of HRS and LRS in SET process with the inset shows PF mission fitting at high voltage region with $\text{Ln}(I/V)\text{-}V^{1/2}$ scale.

It can be seen that the LRS curve has a slope of ~ 1.00 , indicating that the conduction behavior obeys the Ohmic transport. The approximate linear part of HRS curve with a slope of 1.01 under low field region also follows Ohm's Law. However, when it comes to higher voltage region, the nonlinear I-V curve of HRS shows totally different conduction behavior. As we introduced in the literature review chapter, there are three typical model used to fit the nonlinearity of I-V relation in higher voltage region of HRS: SCLC, Schottky emission and PF emission. According to the SCLC mechanism, there are three steps of conduction: Ohmic behavior ($I \propto V$), Child's law ($I \propto V^2$) and drastic increase of current. The slope of nonlinear region is 4.86, which firstly rules the SCLC model out (in SCLC the slope should be ~ 2 according to Child's law). We also exclude the electron emission through interface barrier after permanent breakdown of Ga_2O_3 blocking layer, so Schottky emission model could also be ruled out. The $\ln(I/V)$ - $V^{1/2}$ plot at high field region in the inset shows the linear fitting of PF emission model, so the conduction in HRS at high voltage region follows PF emission mechanism. At the low voltage region, the injected carrier density is lower than the thermal generated carrier density and the conduction follows the Ohm's law. With the increasing of voltage, the electrons are excited from the traps into conduction band which correspond to PF emission. In the ZnO film deposited by MOCVD, the oxygen vacancies act as traps and the excitation of electrons from these traps dominates the HRS conduction behavior of the device.

Considering the study above, we could relate the oxygen vacancies and filaments as follows: at the initial forming step, the V_o^+ and O^{2-} in as-prepared film will migrate in opposite direction under the bias sweeping and prefer to softly breakdown the dielectric near the interface between the electrode and the insulator. The subsequent dielectric breakdown results in the formation of complete conductive filamentary

paths all through the insulating layer and the device is set to LRS. The electrons are hopping among the intrinsic defects (traps) which compose the filaments and this behavior dominates the conduction in LRS.⁹⁷ During the reset process, the negative bias repels the V_o^+ and O^{2-} from two ends respectively, which leads to the primary fracture of filament near ZnO/Ga₂O₃ interface and the resistance increases to HRS. In the next writing cycle, reconnecting the ruptured part of filaments at the interface area instead of rebuilding up completely new ones can switch the device to LRS again.⁹⁸ Taking such incomplete dissolution and reconnection of filaments into account, the lower resistance of HRS than as-prepared material could be explained by the incomplete conduction paths in ZnO film. Moreover, the independence of HRS and LRS resistance to cell size in Fig. 3-4 can also be interpreted that the cell area is far larger than the dimension of filaments and relatively constant number of filaments (complete or incomplete ones) directly decide the resistance of device.

The RS curves in log (I) -V scale were compared as shown in Fig. 3-8a. With the decrease of growth temperature, the threshold voltage in both set and reset steps reduce. However, by further examining, the resistance of HRS decreases drastically as the temperature decreases.

Figure 3-8(a) set behavior of devices fabricated at 300 °C, 350 °C and 400 °C; (b) The change of HRS and LRS resistance with the ZnO growing temperature; the complete RS cycle of device fabricated at (c) 400 °C (d) 350 °C (e) 300 °C

And meantime, by calculating R_{ON} and R_{OFF} , the resistance window of the three devices also become narrower (from $> 10^2$ to < 10) as the temperature decreases (Fig. 3-8b). This degradation will bring difficulty in distinguishing the binary information in practical application. If the temperature is less than 300°C, the case was even worse that the resistive switching behavior disappeared and the stacks showed near Ohmic behavior. This phenomenon probably attributes to gradually more conductive ZnO film grown at lower temperature with more intrinsic defects such as oxygen vacancies.⁹⁹ The reversible dielectric breakdown could not be effectively triggered if

the oxide film is not resistive enough. The complete RS cycles of these three devices are displayed in Fig 3.8c, d and e for reference. Despite all the three devices display similar bipolar switching, the one synthesized at 400°C exhibits the best performance, for example, better endurance and larger resistance window. The other two devices cannot produce more than 10 robust switching cycles.

Compliance current is also a critical factor which affects the RRAM operation significantly. In our experiment, different values of CC were imposed in SET process to study the characteristic of the filaments.

Figure 3-9 Different RESET behaviors based on CC in SET process from 10mA to 40 mA

With the increase of CC (Fig. 3-9), the current of LRS and the reset threshold voltage both increase slightly. When the CC exceeds 40mA, the device cannot be switched back to HRS and the I-V curve exhibits near Ohmic characteristic. The proper range of compliance current may be attributed to the property of filament. In

our device, larger CC fastens the electromigration of oxygen vacancies and this would help to strengthen the filaments, resulting in a more conductive LRS. Meanwhile, the thicker filaments also require higher voltage and more Joule heating induced by current to be ruptured.¹⁰⁰ When the CC exceeds a limited range, “hard breakdown” will occur in the ZnO film irreversibly and the device could not be switched back to HRS. To summarize, a suitable CC between 20mA and 30mA guarantees good switching performance in our TRRAM device.

As discussed in previous chapter, Joule heating effect always exists in filament dynamic, typically assisting the rupture of filament in reset process.¹⁰¹ The reset current produces much Joule heating and severely repel the V_o^+ and O^{2-} to middle region of film and annihilates the filament from interface region.¹⁰² Here, to investigate the function of Joule heating in filament dynamic, sweeping bias with different sampling length (SL) of 320 ms, 20 ms and 640 μ s was applied on the same memory cell. The longer the SL is applied, the more Joule heat will be produced due to the longer sampling time for each single plot. Judging from Fig. 3-10, SL of three different values in SET (SL_{SET}) and RESET (SL_{RESET}) measurement give rise to obvious impact on the RESET threshold voltage and LRS resistance. Firstly, when we increased the SL_{RESET} , the RESET voltage gradually reduced (Fig 3-10a, b and c), and the LRS resistance increased (Fig 3-10d). Secondly, with the SL_{SET} increased, the resistance in LRS decreased slightly (Fig 3-10d). Another observation is that, when the device was set with 20ms and 320ms SL bias, it could not be reset by 640 μ s bias though it could still be reset by 20ms and 320ms SL bias (Fig. 3-10a and b). This entire phenomenon demonstrates the important role of Joule heating in the activity of filament.

Figure 3-10 the effect of different SL_{SET} and SL_{RESET} on reset behavior, basing on the device with ZnO fabricated at 400°C. The reset sweeping was applied with different SL_{RESET} after (a) 320 ms , (b) 20 ms (b) and (c) 640 us SL_{SET} in last set cycle; (d) The resistance of LRS versus SL_{SET} and SL_{RESET}

In RESET process, Joule heating helps to accelerate the rupture of existing filaments as we mentioned above. Therefore the residual thinner conductive paths due to imposed high SL RESET bias result in the higher resistance in LRS. In contrast, in SET process, the Joule heating will also help the electromigration of V_o^+ and O^{2-} to interface region and promptly assemble thicker cluster of filaments. Just like the CC analysis, the thicker filaments will lead to low resistance in LRS.

3.5 Summary

A transparent indium-free RRAM device based on GZO and ZnO was fabricated by MOCVD. This TRRAM device shows bipolar switching behavior with fair cycle endurance and retention time. The conductivity of GZO film by MOCVD is as excellent as commercial ITO; however, the ZnO film deposited by MOCVD in our device is not defective enough to produce more endurable switching, and the operating voltage is relatively high. Thus, such device has large room for improvement. In this thesis, the main objective is to offer an alternative indium-free design. The dependence of resistance on cell size and conduction properties were both investigated to prove that local filamentary conduction probably dominates the RS behavior. The electrochemical migration of oxygen vacancies and ions in ZnO film mainly accounts for the formation and rupture of filament, which leads to switching between HRS and LRS. The RS behavior deteriorates as the deposition temperature of ZnO decreases from 400°C to 300°C, mainly due to the excessive amount of intrinsic defects and less resistive film. CC should be properly applied in SET operation or the device will be unable to reset. Joule heating plays a dual role in resistive switching, which can both strengthen the formed filaments in SET process and accelerates the annihilation of filaments in RESET process.

Chapter 4 Resistive Switching in a GaOx-NiOx p-n heterojunction

4.1 Introduction

As introduced in Chapter 2, the RS behavior could be classified as filament-type and interface-type. It is generally accepted that the interface-type RS usually originates from the redox process based on the transport of oxygen vacancies and change in Schottky barrier height or width by trapping/detrapping effects near interface region.³ When there is potential barrier between the electrode and oxide, the electrons penetrate the thinner barrier via a tunneling process in LRS, while the thicker barrier in HRS prevents the electrons from tunneling in HRS.¹⁰³ Usually the Schottky barrier was constructed by contacting n-type oxide with metal of larger work function or contacting p-type oxide with metal of smaller work function.¹⁰⁴ By studying the Sm/LCMO interface, Hasan *et al.* discovered that it is the uniform interface rather than filaments accounting for the conduction in RS.¹⁰⁵ Shono's group also employed Ti and Ta as TE on PCMO, and indicated that the RS occurred due to the redox process near interface.^{106 107} In addition, Wang *et al.* found that the In/PCMO and Ag/PCMO exhibited opposite switching direction because of different interface barrier properties.¹⁰⁸ We can see most interface-type RS was discussed relating with the Schottky barrier between perovskite oxides and various metal electrodes. In 2009, Li *et al.* further explored the RS by contacting Au, Ag, Cu and Al on PCMO, showing that the thin metal oxide formed at the interface also vary the nature of interface barrier.¹⁰⁹ Therefore, similar to barrier engineering in perovskite oxide based RRAM devices above, adjusting the interface between p-type and n-type binary oxide films in metal/insulator/insulator/metal (MIIM) structure could also

result in RS phenomenon. According to the initial rectifying characteristic of p-n junction (HRS under reverse bias, LRS under forward bias), the reproducible resistance change could be obtained by an opposite operation: the proper soft breakdown under reverse bias switches the device from to LRS, whereas the forward bias will recover the device back to HRS (preferably in low voltage region).

Transition from stable rectifying behavior to RS behavior has been reported in MIM structure with a Schottky junction,¹¹⁰ however, there is little report on such transition for p-n junctions⁴³. In this chapter, we will report a stable RS phenomenon in a p-n junction based on a $\text{GaO}_x/\text{NiO}_x$ heterostructure, which offers an alternative design of RRAM device. We will show that migration of oxygen vacancies near interface of p-n junction plays an important role in the switching process.

4.2 Fabrication details

To fabricate simple MIIM stacks, commercial ITO glass was employed as the substrate with ITO as the BE in our device. The whole process was carried out in our RF magnetron sputtering system as the overall image shown in Fig 4-1a. The mechanical pump works with molecular pump (Fig 4-1b) to guarantee the high vacuum of the chamber. There are three sputtering sources inside the chamber, one DC source, one RF source and one DC & RF source (Fig. 4-1c). The sputtering parameters are displayed and could be manually controlled on the panel (Fig. 4-1d). The sample holder beneath the sputtering source is rotatable to improve the uniformity of deposited thin film (Fig. 4-1e). Before being put into magnetron sputtering chamber, part of ITO glass was covered with high-temperature tape, remaining as BE area. A NiO_x and GaO_x film with a thickness of 90 nm and 70 nm

respectively were deposited successively on the ITO substrate. The pressure of chamber was firstly controlled below 10^{-7} Torr, then 28 sccm Ar was transferred into the chamber till the pressure arrives at 6×10^{-3} Torr. A pre-sputtering process was required for both NiO and Ga₂O₃ targets, in which both target power supply were set to 100 W. The shutters were closed to avoid any deposition on substrate. The pre-sputtering lasting for 10 minutes helps clean the surface of targets which possibly suffers from contamination in previous process. The sputtering process started when the shutters opened and the process was carried out in Ar ambient at room temperature. To fabricate NiO_x and GaO_x of different defects concentration for comparison, 1 sccm O₂ was also introduced into Ar background during sputtering. Finally, indium shots were used as a simple top electrode for test.

Figure 4-1 RF sputtering system (a) overall view (b) mechanical pump and molecular pump (c) three sputtering sources (d) control panel (e) deposition plate and target installation.

The schematic structure of the device is shown in the inset of Fig. 4-2a. The I-V characteristics were measured by a semiconductor parameter analyzer in a diode I-V sweeping mode at room temperature. During the test, the bottom ITO electrode was always grounded while different biases were applied on top electrode (In). After confirming the feasibility, 1 μm single test cells with Ti/W-GaO_x-NiO_x-ITO stacks were fabricated on 4-inch silicon wafer to further explore the scaling ability of the heterojunction RRAM cell. All the layers were deposited by magnetron sputtering at room temperature and patterned by standard lithography process.

4.3 Device performance

Fig. 4-2a shows the current-voltage (IV) characteristics of the as-fabricated stack of In/GaO_x/NiO_x/ITO and we can see a typical rectifying curve with a turn-on voltage of about -2 V for In/GaO_x/NiO_x/ITO stack. It is worth mentioning that here the positive voltage applied on In cannot be too high, otherwise it will trigger break down and RS behavior. For our In/GaO_x/NiO_x/ITO structure, the RS behavior could possibly happen in the following five regions: within the GaO_x bulk, within the NiO_x bulk or at the interface between GaO_x/NiO_x, In/GaO_x and NiO_x/ITO. Here we prepared the stacks of In/GaO_x/In and ITO/NiO_x/ITO for comparison to figure out where the RS takes place. As shown in Fig. 4-2a, the In/GaO_x/In and ITO/NiO_x/ITO structures display near Ohmic behavior with low resistance and are unable to induce RS phenomenon by applying bias of any polarity or intensity. Thus, we can exclude the possibility of RS in the oxide bulk or their interfaces with electrodes.

Figure 4-2 (a) I-V curve of initial behavior in In/GaO_x/NiO_x/ITO, In/GaO_x/In and ITO/NiO_x/ITO structure; inset is schematic of In/GaO_x/NiO_x/ITO device. (b) RS behavior in In/GaO_x/NiO_x/ITO structure; inset is RS performance in 50 cycles¹¹¹

As reported previously, non-stoichiometric NiO_x ($x > 1$) is a p-type semiconductor due to the excess oxygen ions (Ni-deficient) as acceptors for generating holes,¹¹² and non-stoichiometric GaO_x ($x < 1.5$) is an n-type semiconductor due to the oxygen vacancies (oxygen-deficient) as donors for generating electrons.²² With Hall Effect

measurement in Table 4-1, the sheet carrier concentration of GaO_x and NiO_x is - 8.603×10¹¹/cm² and +2.012×10¹⁴/cm², respectively, which proves the type of both films.

Accordingly, the as-prepared GaO_x and NiO_x layers in Ar ambient at room temperature were relatively conductive due to the existence of intrinsic defects (Oxygen vacancies/Oxygen ions). On the other hand, from the curves in Fig. 4-1a, the contact of NiO_x/ITO and GaO_x/In are close to ideal Ohmic, thus there is no Schottky barrier between the semiconductor and electrode. Summarizing from all the analysis above, the rectifying and RS behaviors should come from the p-n junction formed by GaO_x and NiO_x; under external excitation, the alteration of the potential barrier at the junction between n-type GaO_x and p-type NiO_x would be responsible for RS.

Table 4-1 Hall measurement of as-prepared NiO_x and GaO_x film

Oxide	Sheet Resistivity	Hall Coefficient	Hall Mobility	Sheet Concentration
NiO _x	-5.46×10 ⁴ Ω/sq	-7.26×10 ⁴ m ² /C	1.18×10 ⁴ cm ² /Vs	-8.6×10 ¹¹ /cm ²
GaO _x	2.83×10 ³ Ω/sq	3.1 m ² /C	11 cm ² /Vs	2.01×10 ¹⁴ /cm ²

Fig. 4-2b demonstrates a typical bipolar RS behavior of the In/GaO_x/NiO_x/ITO stack. The RS phenomenon was based on the intrinsic rectifying characteristics shown in Fig. 4-2a. When a positive bias applied on In TE sweeps to a critical value of about

3 V, the current suddenly increases due to a restorable breakdown and the device is set from HRS to LRS. A nearly ohmic behavior is detected as the bias sweeps back to negative (within -1 V). When the negative voltage increases further to another threshold, an abrupt decrease of current occurs and the device is reset from LRS to HRS. With further increase of the negative voltage, the current climbs up again with non-linear behavior. As a matter of fact, after RESET process, the device returns to rectifying behavior again and the HRS state **only** exists in a narrow voltage window at negative region (-1 ~ 0V). It is worth mentioning that, the device could only be set by applying positive voltage and reset by applying negative voltage on In, which also provides the evidence that RS behavior originates from p-n interface in asymmetric metal/n-type semiconductor/p-type semiconductor/metal structure, rather than the interface of In/n-type GaO_x or p-type NiO_x/ITO. Supposing that there is any barrier at either of these two interfaces, the device should be set from HRS to LRS when negative voltage was applied on the In (equivalent to reverse bias on metal/n-type oxide Schottky barrier), or when positive voltage was applied on ITO (equivalent to reverse bias on p-type oxide/metal Schottky barrier). **Therefore, we confirm the RS comes from the p-n interface.**

The inset of Fig. 4-2b shows the I-V curves of RS performance in 50 cycles, from which we can see that the SET voltages distribute randomly in a relatively larger range (2~5V) compared to RESET ones (-2~0V). As is widely accepted, the forming process and compliance current (CC) are two important factors for RS operation. In our measurement, there exists no forming process. Similar phenomenon could be found in other literatures^{113 114} and it is well accepted that certain amount of defects (oxygen vacancies) near interface area or even pre-existing of some scattered filaments in the pristine oxide is important prerequisite for forming-free RRAM

device.¹¹⁵ As we mention in previous paragraph, the as-prepared NiO_x and GaO_x by sputtering were both defective (oxygen vacancies in GaO_x and Ni vacancies in NiO_x), which coincided with the result. In addition, a CC of 5mA was applied on the SET operation to prevent the device from permanent breakdown. When the CC exceeded 15mA, the repeatable RS behavior disappeared due to hard breakdown and was replaced by Ohmic behavior.

Figure 4-3 (a) Endurance performance in 100 repeating cycles; (b) Retention characteristic at room 25 °C and 85 °C¹¹¹

Fig. 4-3a shows the endurance characteristics of the In/GaO_x/NiO_x/ITO memory cell in DC sweep mode at room temperature. We can see that although there is a relatively larger fluctuation in HRS resistance in the first 30 cycles, the resistance ratio of HRS/LRS maintains $\sim 10^2$ and the resistance distribution gradually becomes stable as the cycle increases. The initially fluctuating distribution of HRS resistance may be ascribed to the self-adjusting of conductive paths in oxides.^{27 116} The retention performance of our device at both 25 °C and 85 °C are shown in Fig. 4-3b. Both resistance in HRS and LRS display little decay in 10⁶ s, showing good non-volatility for RRAM applications. As the temperature increases, the LRS resistance increases slightly according with the characteristic of metallic filament, while the HRS resistance declines which corresponds to the transport property of semiconductor.

4.4 Study of mechanism

To study the switching behavior of p-n heterojunction, the conduction property during whole resistive switching is investigated. As illustrated in Fig. 4-4, typical I-V curve of both SET and RESET are both redrawn in positive log-log scale. In these two processes, the device exhibits Ohmic behavior in LRS, representing the existing of filamentary path as widely accepted.^{82 117} However, the case is more complicated in HRS region. Under low electric field, the device also obeys the Ohmic behavior, while the I-V curve shows nonlinearity under higher electric field. Three main conduction models, including SCLC, Schottky emission and PF emission were employed respectively to fit the nonlinear region before abrupt inflecting point.

Figure 4-4 The I-V curve of (a) SET and (b) RESET process drawn in log-log scale; fitting the nonlinear region with Schottky emission and PF emission models in (c) SET and (d) RESET process¹¹¹

Firstly, the slope in log-log curves was 3.18 in SET process and 3.09 in RESET process, which excludes the SCLC mechanism (slope should be around 2 according to Child's Law) in our case. For Schottky emission, the relationship between current and voltage could be expressed as follows:⁷²

$$I \propto T^2 \exp \left[\frac{e \sqrt{(eV)/(4\pi\epsilon_i \epsilon_0 d)}}{kT} \right]$$

And PF emission can be depicted as:⁷²

$$I/V \propto \exp \left[\frac{e \sqrt{(eV)/(\pi\epsilon_i \epsilon_0 d)}}{kT} \right]$$

Where I is the current, V is the voltage, e is the electron charge, ϵ_0 is the permittivity of free space, ϵ_i is the dielectric constant, d is the thickness of film, k is the Boltzmann's constant and T is the temperature. After comparison, the PF emission better fits the nonlinear region than Schottky emission as shown in the Fig 4-4c&d. The curves in $\ln(J/T^2) - 1000/T$ scale according to Schottky emission characteristics are also plotted as shown in Fig. 4-5. This group of curves shows poor linearity and it excludes the Schottky emission dominating in our case. PF emission usually refers to electric-field-enhanced thermal excitation of electrons from defect-related trapped states into conduction band. According to previous reports, it usually occurs at higher electric field region compared with Schottky emission in RS behavior.¹¹⁸ The PF model was also been modified by Ieda *et al.* that at low electric field the current can follow the Ohm's Law, while at high field it will obey the usual PF equation.⁵¹ To summarize, the conduction mechanism relates to filamentary property in LRS while be dominated by PF emission in HRS in our device. The decline of HRS resistance at 85 °C in Fig. 4-3b corresponds to the higher emission rate from traps.

Figure 4-5 The curves in $\ln(J/T^2) - 1000/T$ scale according to Schottky emission model

As for the RS mechanism, a controversy between the filament and interface models has lasted for a long period. Unlike the irreconcilable discussion in early time, recently more people would like to believe that these two mechanisms can exist simultaneously and affect each other in some types of RS behaviors. Akinaga *et al.* also offered a unified model of RS based on such combination.⁴⁰ Considering the conduction analysis above, the RS process in the p-n heterojunction could be illustrated with the energy band diagram as Fig. 4-6 shows. The process is divided into four steps:

a) When a positive bias is applied on the In top electrode, **the p-n junction is reverse-biased**. External electric field will enlarge the depletion region and elevate the interface barrier, which suppresses the diffusion current passing through the junction as a usual diode behaves. Although some filamentary paths due to the pre-existing oxygen vacancies spread at both sides according to the direction of electric field, they were intercepted by the p-n interface barrier and the device is in HRS. Thus the Ohmic behavior in the low voltage region of HRS **comes from the small current by thermal excited electrons**.⁴⁴

b) Oxygen vacancies (V_o^+) are known to be positively charged and mobile.¹¹⁹ Further increasing the positive bias leads to accumulation of positive oxygen vacancies (from inside GaO_x) at the p-n junction on GaO_x side, forming a high-doping region. At the same time, there also forms a negatively charged high-doping region on NiO_x side near the interface due to the accumulation of negative oxygen ions (O^{2-}). Thus, a significant reduction of effective barrier height and depletion region width could be expected.^{119,120} In such abundant V_o^+ or O^{2-} region (trap region), a current gain

produced by the excitation of electron from the traps into conduction band could be realized, which is presented as PF emission characteristics. Beyond a critical value, large amount of electrons could tunnel through the narrower barrier between two high-doping regions and the filamentary paths are able to connect both oxide film,¹²¹ which bring the device to LRS. The Ohmic behavior of LRS reflects the property of filament, and the process corresponds to the so-called soft breakdown of insulator because the pierced barrier could restore as we show later.

c) Because of the stable filaments crossing the interface, the junction behaves like a normal resistor with high current and the LRS is non-volatile. Until a high enough negative bias on In electrode is applied to repel these defects (V_o^+ or O^{2-}) away from interface region, the barrier recovers back, cutting off the connected filaments. The current suddenly drops and the device returns to HRS. The small drift current is mainly due to the electron transporting along the residue filament and over the p-n barrier (like diode).

d) With further increase of negative bias, the height of barrier reduces and enables an increasing current passing through the interface, tracing back the rectifying behavior of heterojunction.

Figure 4-6 The illustration of RS behavior in p-n heterojunction: (a) low current due to the barrier (b) high current due to the soft breakdown of barrier (c) low current due to the recovery of barrier (d) increasing current under forward bias of diode¹¹¹

Summarizing from above description, the RS can be interpreted as a switching between rectifying and Ohmic behavior. The filaments in both NiO_x and GaO_x away from interface just serve as virtual cathode and anode, while the junction barrier engineered by defects migration controls the connection and dissolution of filaments near interface, triggering the RS behavior. There exists only a unidirectional bipolar RS in p-n heterojunction (set in reverse bias, reset in forward bias) due to the rectifying characteristics.

The distribution of operating voltages was also investigated as shown in Fig. 4-7. We can see that, the RESET voltage (V_{reset}) distributes randomly in a smaller range (-

0.7V ~ -3.5V) compared to the SET voltage (V_{set}) (0.9V ~ 7.8V), which can be seen from the inset in Fig. 4-1b as well. The dynamics of defects under applied electric field may be responsible for such distribution. When a certain amount of oxygen vacancies accumulate near the interface, the device could be set to LRS due to the barrier variation. To reset the device, a relatively fixed power is required to drive these oxygen vacancies away from interface, resulting in a relatively small-range distribution of V_{reset} . However, each RESET sweeping will redistribute these oxygen vacancies into the oxide bulk randomly.¹²² As a result, the power needed for attracting the same amount of oxygen vacancies to the interface region in the next set cycle will be much more different, resulting in a much more random distribution of V_{set} than V_{reset} . The phenomenon was also often observed in those filament based device because of the relatively random generated filaments in SET process and rupture at relatively fixed region in RESET process.¹²³

Figure 4-7 Distribution of set and reset voltage in 150 repeating cycles¹²⁴

Figure 4-8 XPS spectra of (a) NiO_x film for Ni 2p and (b) GaO_x film for O 1s¹²⁴

The influence of intrinsic defects concentration on p-n heterojunction resistive switching behavior was further investigated by fabricating the GaO_x and NiO_x films with different extent of self-doping. As we introduced above, NiO_x ($x > 1$) is a p-type semiconductor due to the Ni vacancies as acceptors for generating holes and GaO_x ($x < 1.5$) is an n-type semiconductor due to the oxygen vacancies as donors for generating electrons. Therefore, introducing O_2 during sputtering will increase the self-doping concentration in NiO_x while reduce the self-doping concentration in GaO_x . Hence we label the NiO_x deposited under $\text{Ar}+\text{O}_2$ atmosphere as p+ NiO_x and the one

without O₂ as p NiO_x. In the same way, the GaO_x deposited Ar+O₂ atmosphere is n GaO_x and the one without O₂ is n+ GaO_x.

The XPS measurement was first adopted to investigate the chemical composition of the four films (Fig 4-8). The Referring to Ni 2p spectrum of NiO_x shown in Fig 4-8a, the main peak at binding energy of 852eV corresponds to the metallic Ni⁰ while the relatively broader peak at around 856 eV attributes to the Ni³⁺ state.¹²⁵ After we introduce O₂ to fabricate p+ NiO_x, both two peaks decay manifesting more Ni deficiency. As for the O 1s spectrum for GaO_x film in Fig. 4-8b, with O₂ during deposition the tiny peak at round 527eV disappear and only a peak of 526eV maintains. As reported in other work, the peak at around 526eV refers to the O-Ga bond of Ga₂O₃ while the one of 527eV relates to the O-H bond which mainly comes from the surface absorbed oxygen.¹²⁶ Therefore, we could expect the reduction of oxygen vacancies from n+ GaO_x to n GaO_x.

Table 4-2 Atomic concentration of Ga and O in two GaO_x devices, and Ni and O in two NiO_x devices

Oxide	Atomic Concentration (%)		
	Ga3d	Ni2p	O1s
n GaO _x	24.22		49.39
n+ GaO _x	25.8		47.87
p NiO _x		15.33	39.67
p+ NiO _x		11.48	39.97

The atomic concentration of elements is listed out in Table 4-2. The higher oxygen deficiency in n+ GaO_x than n GaO_x, and higher Ni deficiency in p+ NiO_x than p NiO_x can be clearly seen in this table, which is consistent with the XPS spectra above.

Different combinations of these four type oxides would lead to interfaces of different properties. As shown in Fig. 4-9, the RS of n GaO_x/p NiO_x heterojunction exhibits lower HRS resistance (1.5k ~ 5kΩ) than n+ GaO_x/p+ NiO_x stacks (5k ~ 35kΩ). This difference probably attributes to that the p+/n+ junction will form higher barrier than p-n junction which lead to the higher resistance in HRS, and this also enlarges the resistance window of RRAM device.

Figure 4-9 The resistive switching in two devices (a) lightly-doped GaO_x/NiO_x (b) heavily doped

GaO_x/NiO_x¹²⁴

We also fabricate a 1-μm testing cell with the same thickness of GaO_x and NiO_x to explore the scaling property of p-n heterojunction RRAM. As presented in Fig. 4-

10a, the whole device was deposited by magnetron sputtering on silicon wafer and patterned by photolithography. Ti/W alloy instead of indium spots is employed as n-contact top electrode on GaO_x film.

Figure 4-10 (a) structure 1 μm single testing cell; (b) the SEM image of one cell with cell pattern on the wafer at the right side (6 cells in one group); (c) RS curves of single test cell and large size device¹¹¹

As a low work function metal alloy, there is no Schottky barrier between Ti/W and GaO_x , either. SiO_2 wrapped around the stack is to isolate the cell from being interfered by neighbour ones. Compared with previous device, an apparent decreasing of current (increasing of resistance) in both LRS and HRS was observed in the 1-μm testing cell as Fig. 4-10b shows. According to the resistance dependence on cell area reported by many other works,^{127 128} the interface factor should play a significant role

in the RS in the $\text{GaO}_x\text{-NiO}_x$ heterojunction. The reducing cell area directly decreases the amount of effective conductive paths crossing over the interface, further increases the resistance.

4.5 Summary

In conclusion, a unidirectional bipolar RS was observed in the $\text{GaO}_x\text{-NiO}_x$ heterostructure deposited by magnetron sputtering at room temperature. The RS behavior could be interpreted as the shift between rectifying and Ohmic behavior of the heterojunction diode. Under the electric field, the migration of intrinsic defects (oxygen vacancies in GaO_x and oxygen ions in NiO_x) controls the filamentary paths passing through or block by the interface barrier, which correspond to the LRS and HRS. The device showed good endurance and retention performance, suggesting an alternative design of bipolar RRAM cell. By fabricating the cell arrays with photolithography techniques, the scaling potential was examined and it proved that such heterojunction RRAM cell is suitable for high density integration.

Chapter 5 A ZnTaO_x based resistive switching random access memory

5.1 Introduction

Among various non-volatile memory devices, the resistance switching random access memory (RRAM) is outstanding for its high-density storage capability, low operation voltage/current and fast switching speed. Besides those intensively studied oxide materials for the RRAM fabrication, such as TiO₂,¹²⁹ NiO,¹³⁰ ZnO,¹³¹ HfO_x¹³² and ZrO₂,¹³³ recently Ta₂O₅ or TaO_x based RRAM device has been frequently investigated due to its excellent endurance performance and switching speed. Based on the filament dynamic mechanism, both unipolar and bipolar resistive switching (RS) behaviour were reported with amazing endurance and retention properties.^{73,134}

¹³⁵ Similar to other oxide-based devices, the formation and rupture of conductive filament (CF) which is related to the chemical composition of oxygen determine the RS behavior in TaO_x RRAM. One of the effective ways to obtain better RS performance in TaO_x RRAM is to better control the oxygen ion or oxygen vacancy concentration. Therefore, quite some work has been carried out to understand the behavior of oxygen vacancies in resistance switching. For example, Kurnia *et al.* investigated the evolution of oxygen vacancies based CF and achieve the forming-free RS in Pt/TaO_x/Pt structure.¹¹⁴ By applying different voltage on the 1-transistor-1-memoristor (1T1M) device, Miao *et al.* successively tuned the conduction channel in TaO_x which related to the oxygen concentration, and obtained varied switching behaviour.¹³⁶ Moreover, Ta was used instead of Pt as top electrode on TaO_x by J. S. Chen's group to form an oxygen vacancy reservoir of supplying or storing the oxygen vacancies at the Ta/TaO_x interface, and further realized the multilevel switching

property.¹⁶ Here we demonstrate another way to engineer the oxygen vacancies in TaO_x and improve the RS performance. By mixing various oxides with TaO_x, the concentration of oxygen vacancies could be adjusted, and among them, ZnO shows the best improvement of operation parameters.

5.2 Device fabrication and characterization

The simplest metal-insulator-metal (MIM) structure was applied to fabricate the RRAM testing cell. The commercial ITO glass was employed as the substrate and bottom electrode. All the oxide films were deposited by RF magnetron sputtering system as introduced in Chapter 4. Indium shots pressed on top of the sample were used as the top electrodes. The sputtering power for all oxides (Ta₂O₅, ZnO, Ga₂O₃ and NiO) were accurately controlled and the sputtering chamber was kept in the Ar atmosphere (flow rate 30 sccm) with the pressure of 6×10^{-3} Torr at room temperature. Besides the pure TaO_x device, the TaO_x was co-sputtered with other 3 targets respectively to deposited ZnTaO_x, GaTaO_x and NiTaO_x films for comparison. The thickness of all four films was ~100nm. The components of oxide films were examined by EDX measurement and the crystalline state were studied by XRD measurement. The I-V characteristics were measured by a semiconductor parameter analyser in diode mode. The ITO bottom electrode was always grounded while biases with different polarity and intensity were applied on In top electrode during test.

It is well known that non-stoichiometric TaO_x ($x < 2.5$),¹³⁷ ZnO_x ($x < 1$)¹³⁸ and GaO_x ($x < 1.5$)¹³⁹ are all n-type semiconductor due to the existence of oxygen vacancies acting as donors for generating electrons, while non-stoichiometric NiO_x ($x > 1$)¹⁴⁰ is a p-type semiconductor because of the excess oxygen ions acting as acceptor for

generating holes. The dynamics of these intrinsic defects directly relate to the conduction mechanism of oxide film. Except the pure TaO_x film, all other three compound oxide films were characterized by EDX measurement as shown in Fig. 5-1 in order to examine the chemical composition. The EDX measurement was done with SEM scanning the surface of all samples. The observed strongest O, Ta, Zn, Ga and Ni signals correspond to the energy of 0.525, 1.964, 1.012, 1.051, 0.851 keV, respectively. The composition statistics shows the atomic ratio of Ta : Zn/Ga/Ni is approximately 4:1. Thus, the TaO_x was confirmed mixed with other 3 types of oxides by co-sputtering to form new compounds but not doped by Zn, Ga or Ni.

Figure 5-1 EDX spectrum of ZnTaO_x , GaTaO_x and NiTaO_x

The XRD spectrum of TaO_x , ZnTaO_x , GaTaO_x and NiTaO_x are listed in Fig 5-2 for reference. The two weak peaks correspond to Ta_2O_5 in the as-prepared polycrystalline TaO_x but most of other featured peaks of Ta_2O_5 could not be detected.

The mixing of ZnO_x , NiO_x and GaO_x by sputtering shows no apparent change to the XRD spectrum because they didn't change the crystalline property of TaO_x much.

Figure 5-2 XRD spectrum of TaO_x , GaTaO_x , NiTaO_x and ZnTaO_x polycrystalline film

Fig. 5-3a shows the I-V characteristics of all 4 devices in V-log (I) scale. The TaO_x , ZnTaO_x and GaTaO_x all exhibit similar bipolar RS behavior except NiTaO_x which only presents the nonlinear conduction with a small hysteresis lag. The SET process in positive voltage region and RESET process in negative voltage region are clearly illustrated in this figure. The as-prepared stacks are initially at HRS and no forming process is required to initialize the devices. During one complete switching cycle, when the bias firstly sweeps to a positive threshold value, an abrupt increasing of current occurs corresponding to the SET operation and the device is switched to LRS. A CC of 1 mA is imposed during the sweeping to prevent device from permanent breakdown. In the next step, sweeping to another negative threshold

voltage will bring the device to HRS, referring to RESET operation. Both the HRS and LRS will maintain without any sustaining bias, manifesting the non-volatility of the RRAM device. The information could be read out by applying a small reading voltage ($\sim 0.1\text{V}$)

Figure 5-3 (a) Bipolar RS under DC sweep mode of TaO_x, ZnTaO_x and GaTaO_x devices; no RS in NiTaO_x (b) multiple switching cycles of ZnTaO_x device; the insets show multiple switching cycles of TaO_x and GaTaO_x devices.

Among the three RRAM devices, the TaO_x shows the largest average HRS resistance and SET voltage and the ZnTaO_x gives the lowest ones, although their range of distribution does overlap with each other to some extent. Therefore we select the typical RS curves of each device in Fig 5-3a for a better comparison. Here we also could get some clues from the curves about the mixing behavior among these oxides instead of doping one. If the Zn was doped into n-type TaO_x , from stoichiometric point, the replacement of Ta atom by Zn will lead to less conductive samples. However, the phenomenon is opposite as observed in Fig. 5-3a (The ZnTaO_x and GaTaO_x compound are both more conductive than TaO_x). The multiple-cycle data of ZnTaO_x device is shown in Fig 5-3b. More than 200 stable bipolar switching cycles could be achieved. The SET and RESET voltage fluctuate in 0.4~0.8V and -0.1~1.4V, respectively. The cycle data of TaO_x and GaTaO_x are shown in the inset for comparison. **The original TaO_x device performs worse switching endurance** under DC sweep mode (50-100 cycles) and the largest distribution of SET (0.5~4.8V) and RESET (-0.3~ -1.9V) voltages. Introducing GaO_x into TaO_x brings some improvement on the distribution of SET voltage (0.5-2.8V) but degrades the endurance much (~20 cycles). Thus, the ZnTaO_x device shows improvement in both switching stability and endurance, which will be discussed in details below.

5.3 Device parameter comparison

Fig. 5-4a shows the endurance characteristic of In/ ZnTaO_x /ITO device under DC sweep mode at room temperature. In 200 repeating cycles, the resistance of both HRS and LRS distribute within a small range of voltage, which is suitable for practical use. Although initially the HRS resistance is slightly high due to the filament stabilizing

process, the resistance window maintain well >10 in during the repeating operation.¹⁴¹

In our three main parts of work, TaO_x based RRAM exhibit best endurance performance than ZnO and p-n heterojunction ones in Chapter 3 and 4, which exactly proves the advantage of TaO_x as we introduced above.

Figure 5-4 (a) Endurance performance of ZnTaO_x device in 200 repeating cycles; (b) Retention characteristic of ZnTaO_x device at 25 °C and 85 °C; (c) Endurance performance of TaO_x and GaTaO_x devices; (d) Retention characteristic of ZnTaO_x device at 85 °C of ZnTaO_x device

The retention property of ZnTaO_x device at 25 °C and 85 °C is also given in Fig. 5-4b to rate the non-volatility. By continuously sampling at different time, the resistances of both HRS and LRS remained almost unchanged in 10^6 s, based on

which a desirable retention performance could be expected in RRAM application. The endurance and 85 °C retention performance of TaO_x and GaTaO_x devices are also shown in Fig 5-4c&d. Although the retention of these three TaO_x based devices shows no apparent difference, the ZnTaO_x exhibits the best endurance and GaTaO_x shows the worst.

Figure 5-5 (a) Cumulative probability statistic of (a) SET voltage (b) RESET voltage (c) HRS resistance and (d) LRS resistance in TaO_x ZnTaO_x and GaTaO_x devices

To further reveal the improvement of TaO_x based RRAM by introducing ZnO, more detail comparison of parameters among the TaO_x, ZnTaO_x and GaTaO_x devices were exhibited in Fig. 5-5. According to the cumulative probability statistics, ZnTaO_x

with best endurance has much smaller distributing range of SET voltage (0.4~1.8V), RESET voltage (-0.1~ -1.4V), HRS resistance (10~30k Ω) and LRS resistance (200~500 Ω) than TaO_x. GaTaO_x shows slightly better LRS resistance distribution than ZnTaO_x, however, the poor endurance undoubtedly rules it out of competition. The overall evaluation of three devices is also listed in the Table 5-1. Of these parameters, the major improvement of ZnTaO_x device lies in SET voltage and HRS resistance. The differences in RESET voltage and LRS resistance with other two devices are relatively smaller. The reason will be revealed in the following switching mechanism study.

Table 5-1 The overall comparison of SET voltage (V_{SET}), RESET voltage (V_{RESET}), resistance of HRS (R_{HRS}), resistance of LRS (R_{LRS}) and endurance.

Oxide	V_{SET} (V)	V_{RESET} (V)	R_{HRS} (Ohm)	R_{LRS} (Ohm)	Endurance (n)
TaO _x	0.5~4.8	-0.3~-1.9	60k~1.3M	200~1.2k	50~100
GaTaO _x	0.5~2.8	-0.2~-1.6	17k~170k	200~350	~20
ZnTaO _x	0.4 ~ 1.8	-0.1 ~ -1.4	10k ~30k	200~500	>200

5.4 Study of improvement mechanism

To further study the RS behavior in these devices, the conduction property in SET process was investigated by plotting the I-V curve in log-log scale as shown in Fig. 5-6. Two different types of conduction mechanism were found co-existing in all three RRAM devices, which could be classified according to low voltage switching

(LVS) (SET voltage usually $<2V$) and high voltage switching (HVS) (SET voltage usually $>2V$). Based on the parameter comparison in section 5.3, obviously the LVS frequently occurs in $ZnTaO_x$ device while the HVS mainly takes place in TaO_x and $GaTaO_x$ ones. In this figure, the HVS curve is collected from TaO_x sample and the LVS one corresponds to $ZnTaO_x$ sample for reference. Both this two types of conduction display Ohmic behavior (slope ~ 1.0) in LRS, while the difference rises in the HRS part. Initially, under low external electrical field in HRS, both LVS and HVS show near Ohmic feature, although the HVS one shows a bit larger deviation from the Ohmic behavior (slope ~ 1.32).

Figure 5-6 The I-V curve of set process drawn in log-log scale (the HVS curve refers to TaO_x sample and the LVS one corresponds to $ZnTaO_x$ sample); the inset shows the fitting curve of Schottky emission with $\ln(I)-V^{1/2}$ and PF emission fitting with $\ln(I/V)-V^{1/2}$ scale.

As the bias further increases approaching the switching threshold value, the slope of LVS becomes ~ 2 , which can be well explained by space charge limited conduction (SCLC). According to the SCLC mechanism, there are three steps of conduction: Ohmic behavior ($I \propto V$), Child's law ($I \propto V^2$) and drastic increase of current,¹⁴² which accurately fits our LVS case.

However, the I-V nonlinearity in HVS under high electric field is much different (slope = 5.27). To further investigate this region, Schottky emission and Poole-Frenkel emission (PF emission) modes are applied, respectively. The equations of these models could be found in last chapter. After fitting the curve of this region to both two modes, PF emission better coincides with our case as shown in the inset of Fig. 5-6, in which the I-V curve is plotted in $\ln(I/V)-V^{1/2}$ and $\ln(I)-V^{1/2}$ scale, respectively.

As we discussed in the previous part, the Ohmic behavior in LRS directly relates to the formed filamentary paths consisting of oxygen vacancies in the oxide film.¹⁴³ **Filament conduction is also responsible for the LRS in both LVS & HVS cases.** As for HRS, before the formation of filaments; the SCLC mechanism in LVS probably works on the defect-related shallow traps (oxygen vacancies) in the oxide films. At lower applied bias, the thermally generated carrier density is higher than the injected carrier density and the conduction follows Ohm's law. With the increasing bias, the injected carriers gradually fill all the traps and become dominated, inducing a higher current gain depicted in Child's law.¹⁴⁴ As for the PF emission (corresponds to HRS of HVS in our case here), it is well attributed to thermal excitation of electrons from defect-related traps (oxygen vacancies) into conduction band by electric field enhancement.¹⁴⁵ And usually, the electric field should be high enough (higher than

SCLC mode) to activate the trapped electrons so as to dominate in conduction. It is worth mentioning that, between the Ohmic and PF emission region in HVS case, there exist a fluctuating “transition” region, including the current-controlled negative differential resistance (CC-NDR) phenomenon. In some part of this region, the current decreases as the voltage increases. The NDR behavior could be sometimes observed as precursor of reversible switching (both unipolar and bipolar switching) and is responsible for Joule heating that assists generating large concentration of oxygen vacancies to form metallic suboxide conductive filaments (described as CFs) in oxide film.¹⁴⁶ The NDR only exists right before the soft breakdown (SET) and is not reversible.

For our devices, the HRS conduction in ZnTaO_x sample's switching cycles mainly belongs to SCLC mode (not exclude a few PF emission cycles), while the SCLC and PF emission modes co-exist in TaO_x and GaTaO_x ones as we see the broader distribution of switching voltage (PF emission is more probably found in TaO_x which has larger switching threshold than GaTaO_x). Based on the conduction analysis above, the different switching behaviors could be interpreted as varied concentration of intrinsic defects by mixing different oxides with TaO_x . The lower density of defects in pure TaO_x leads to a larger initial or HRS resistance. Higher voltage, as well as more Joule heat is required not only to excite electrons from defects for HRS conduction (PF emission), but also to generate enough oxygen vacancies to form reliable CFs for LRS conduction. Introducing GaO_x somewhat helps to increase the defects in TaO_x but it is still not desirable. The GaO_x is also n-type oxide as ZnO_x , but the as-prepared GaO_x is much more highly resistive than ZnO_x due to its wider bandgap and less intrinsic defects. Moreover, GaO_x is seldom used as single RS layer because of its undesirable endurance performance. Therefore,

mixing GaO_x with TaO_x may not be that effective as adopting ZnO_x (GaTaO_x shows worst endurance). The as-prepared ZnTaO_x cell has the lowest HRS resistance, suggesting enhancing conduction through defect-abundant region (including grain boundaries, oxygen vacancies and dislocation). The CF also forms most easily under relatively lower electric field due to the richest content of defects in ZnTaO_x , directly leading to the low switching threshold. The most probable HRS conduction is also transformed from HVS PF emission mode to LVS SCLC mode. The varied concentration of intrinsic defects determines the larger difference in resistance of HRS and the SET voltage; while attributing to the similar property of existing CFs in three devices, the resistance of LRS and RESET voltage show not that significant differences. These conclusions also coincide with the parameters comparison in Fig. 5-5. As for p-type NiO_x , there should be a reduction of oxygen vacancies after combining it with n-type TaO_x , leading to an unswitchable oxide compound. The mixing behavior will also introduce some structural defects such as grain boundary or dislocation. This can assist the formation of conductive filamentary path and improve the switching property as well; however, those do not play the key roles here.

Different ratio of ZnO and TaO_x were mixed to figure out the optimal composition for RS performance. The sputtering power of ZnO target during deposition was set to four different values of 30W, 50W, 70W and 100W, while the power of Ta_2O_5 target was kept constant 100W. Other fabrication conditions such as chamber pressure and temperature were all unchanged. After deposition, the chemical composition of these four samples was characterized by EDX firstly. As labeled in Fig 5-7, from sample 1 to 4, the sputtering power of ZnO target increases, leading to the larger ratio which Zn accounts in ZnTaO_x film (the ratio of $\text{Zn}/(\text{Ta}+\text{Zn})$ from 8.5%

~ 26.1%). We can also see the feature peak of Zn gradually enhance as the ratio of Zn increases.

Figure 5-7 EDX spectrum of ZnTaO_x films with different ratio of Zn and Ta

The same bias sweeping setup was applied on the four $\text{In/ZnTaO}_x/\text{ITO}$ devices to compare the I-V characteristics. All devices except sample 4 exhibited similar bipolar RS behavior and the typical I-V curve of SET processes were portrayed in Fig 5-8. Judging from this figure, the resistance of HRS as well as the resistance window reduced as the Zn weight increased in ZnTaO_x . With the lightest blending of Zn, the SET behavior resembled as TaO_x , including the NDR region before approaching the switching threshold. However, the resistance still reduced a bit compared with TaO_x shown in Fig 5-3a because the introduction of even small amount of ZnO also added more oxygen vacancies into TaO_x . Increasing the ratio of Zn will further optimize the concentration and distribution of these intrinsic defects, leading to better RS

performance, such as lower switching voltage and resistance. Nevertheless, when the proportion of Zn reached over certain limit, no RS will occur in the ZnTaO_x film, just as the case of sample 4. The reason may be the heavy blending of ZnO into TaO_x , which deteriorates the polycrystalline state of TaO_x . When the structural defects aggravate, the film would be permanently broke down due to large leakage current, failing to obtain restorable RS.

Figure 5-8 SET process of ZnTaO_x sample 1-3

Knowing that oxygen vacancies play the critical role in oxide RS operation, varied amount of O_2 was imported with Ar during sputtering ZnTaO_x film. In section 5.3, all the depositions were carried out at full Ar ambient. Here we added 1 sccm and 2 sccm O_2 to Ar respectively during **sputtering while keeping** the total gas flow at 28

sccm. After that the two samples were compared with the previous one which is fabricated without O₂.

Figure 5-9 Effect of O₂ pressure in depositing on the RS behavior of ZnTaO_x

From Fig 5-9, three typical RS loops selected from these three devices show apparent differences. Our previous ZnTaO_x device displays the smallest loop in SET process with largest loop in RESET process. The sample with 27 sccm Ar + 1 sccm O₂ shows moderate loops in both SET and RESET processes while the one with 26 sccm Ar + 2 sccm O₂ exhibits largest SET loop and smallest RESET loop. Actually the competition mechanism between SET and RESET loops was already discussed by some groups that the property of filaments majorly decides the characteristics of switching loop.¹⁴⁷ The as-prepared ZnTaO_x without O₂ possesses the largest oxygen vacancies concentration, which directly gives rise to easiest formation of thicker filaments, lower switching threshold in SET step and lower HRS resistance. Obviously, the power required to dissolve such strong filaments should be highest, corresponding to the largest RESET threshold. As the increasing of O₂ partial

pressure, the concentration of oxygen vacancies in ZnTaO_x reduces, resulting in higher HRS resistance and SET voltage. Meanwhile the filaments formed are also not that robust as the previous device, directly resulting in the faster rupture of filaments with lower RESET voltage. Here, the sample with 27 sccm Ar + 1 sccm O_2 seems to own ideal RS loops, but the poorer endurance than previous one do not bring real improvement for the device. After all, the concentration of oxygen vacancies should be high enough to maintain great numbers of repeating operation.

5.5 Summary

To summarize, TaO_x , ZnTaO_x , GaTaO_x and NiTaO_x films were deposited by magnetron sputtering system to fabricate RRAM cells. Among them, the ZnTaO_x sample exhibited evident improvement of RS performance, including better endurance, smaller operating voltage and more stable resistance distribution. The improved behavior mainly attributes to the introducing of more intrinsic defects such as oxygen vacancies by mixing TaO_x with ZnO_x which facilitates the filament based RS. The SCLC mechanism dominates the HRS conduction in LVS of ZnTaO_x ; while for some HVS in TaO_x and GaTaO_x , the HRS conduction could be understood by PF emission mechanism accompanied with CC-NDR phenomenon. The mixing of ZnO with TaO_x should be controlled in certain ratio, or the crystalline state will decay, failing to produce desirable RS. The introduction of O_2 during film deposition affected the RS behavior as well, which proved the filament essentiality. Although this helped to optimize the switching loop, the best endurance still belonged to the device deposited without O_2 .

Chapter 6 Conclusion and future work

6.1 Conclusion

The work of this thesis consists of three parts, investigating RRAM from different aspects. The transparent RRAM application was attempted by adopting ZnO and GZO as functional layer and electrode, respectively. The $\text{GaO}_x\text{-NiO}_x$ heterojunction was also applied as functional layer instead of traditional single oxide layer, aiming to construct interface-type RS device. TaO_x mixed with ZnO was testified to effectively improve the RS parameters.

An indium-free TRRAM with structured mainly on ZnO and GZO was fabricated by MOCVD. The conductive GZO shows excellent transmittance and conductivity, acting as good replacement of traditional ITO for the RRAM electrode. The device performs well in endurance and retention test, while the operating voltage still needs to be improved. With the measurement of XPS and the resistance dependence on cell size, the oxygen vacancies related filaments dynamics dominate the bipolar switching of our TRRAM. To obtain best performance of our device, the temperature in fabrication, CC during SET process and bias IT should be properly set. The underlining reasons are all connected with the filament properties. Also, we discuss an inevitable factor in filament based RS, the Joule Heating. According to our experiment, the Joule Heating plays dual roles in RS, strengthening the existing filaments in SET process and facilitating the rupture of filaments in RESET process. As we all know, the Joule Heating is generally a negative factor in RRAM because it reduces the endurance of device. Thus, our second part work follows and aims to deal with it.

GaO_x-NiO_x p-n heterojunction was synthesized by sputtering at room temperature as RS functional layers. The purpose of such design is to localize the RS near the interface barrier instead of producing and breaking filaments throughout the bulk layer with Joule heating. The In/GaO_x/NiO_x/ITO device exhibits well endurance and retention performance, better than the ZnO based TRRAM. The alteration of interface barrier under external electric field not only decides the ON and OFF status of device, but also determine the polarity to the bipolar RS. The variation of barrier is also proved to relate with migrating oxygen vacancies or oxygen ions in the oxide films. To further approach the application, we scale down the device size and effectively reduce the operating current. These results offer alternative design scheme of RRAM cell integrated into high density crossbar structure. After this work, we find that the oxygen vacancies play such a crucial role in oxide based RRAM, and also realize that better control the oxygen vacancies in oxide should bring improvement to the device performance. **Therefore, in the third part of work, we mainly focus on manipulating the oxygen vacancies in oxide films.**

By co-sputtering different oxide targets, ZnO, Ga₂O₃ and NiO were blended with Ta₂O₅ to form ZnTaO_x, GaTaO_x and NiTaO_x as functional layers. With electrical test, the introduction of NiO disables the TaO_x from the RS and Ga₂O₃ improves the RS of TaO_x a bit. After comparison, ZnTaO_x demonstrates the best enhancement in endurance, operation voltage and resistance. The conduction property and the EDX spectrum of the devices are investigated and reveal that the improvement originated from the effectively introduction of more oxygen vacancies into TaO_x. This experiment offers an alternative way to engineer the oxygen vacancies in certain oxide, obtaining the high switchable and more stable RS property. However, the mixing of different type of oxides should be controlled in certain ratio. Improper

mixing behavior will degrade the crystalline states of the polycrystalline oxide film and lead to large leakage current, unable to trigger RS.

6.2 Future work

6.2.1 Improving the ZnO and TaO_x based RRAM

The ZnO based TRRAM could be improved in many aspects, such as simplifying the fabrication, lowering the operating voltage, reducing the switching current and increasing the repeating cycles. Furthermore, the TRRAM can also be fabricated on flexible substrate such as plastic sheet to construct full transparent and flexible memory (Fig. 6-1). Some groups recently reported the simplified structure of GZO-ZnO-GZO and fully GZO based TRRAM on PEN substrate,^{148,149} but the endurance and retention performance are not desirable. Therefore, more efforts are needed to improve the ZnO TRRAM. Besides MOCVD, other equipment would be used to fabricate the GZO electrode and ZnO film, such as magnetron sputtering. Compared with MOCVD, sputtering deposition at room temperature will produce more defects in the film, which plays critical role in resistive switching in ZnO RRAM. The thinner stacks could be synthesized to obtain lower voltage operation.

Figure 6-1 Flexible and transparent RRAM based on GZO¹⁴⁸

The TaO_x based RRAM, as one of the best candidates for RRAM industry, should also be further intensively studied to improve its performance. After all, our results are just based from a mechanism viewpoint and the performance is still not competent for practical application. Some other oxides will be taken into consideration, either to be combined with TaO_x or to solely act as functional materials.

6.2.2 Metal-Insulator-Base-Metal (MIBM) structure

To reduce the programming current, the RRAM device based on MIBM structure instead of conventional MIM structure would be taken into consideration.⁷⁶ Lee *et al.* had demonstrated the high-endurance bipolar resistive switching in $\text{Ta}_2\text{O}_{5-x}/\text{TaO}_{2-x}$ bilayer structures as shown in Fig. 6-2. A thick TaO_{2-x} film with resistivity of $\sim 10^7$ - $10^8 \Omega \text{ cm}$ was employed as the base layer, while a thin $\text{Ta}_2\text{O}_{5-x}$ film with resistivity of $\sim 10^{13} \Omega \text{ cm}$ acted as insulating layer. The medium resistive base layer in series could effectively reduce the resistance of whole cell even it is in LRS, and it plays roles of both oxygen supplier and reservoir. This MIBM structure also combines the filament and interface factors in resistive switching because the oxygen ions injected or ejected at the interface between insulating and base layers control the formation and rupture of filaments in insulating layer.

Figure 6-2 A typical MIBM structure of Pt/ $\text{Ta}_2\text{O}_{5-x}$ / TaO_{2-x} /Pt⁷⁶

Similarly, this concept could also be used in ZnO and other binary oxides as long as the oxygen vacancies are the main controllable defects in the film. For example, the ZnO_x layer will be intentionally fabricated containing far less oxygen vacancies than ZnO_y . Therefore, the resistance of ZnO_y is lower than ZnO_x and act as base layer, which could offer and receive oxygen vacancies under opposite bias and reduce the LRS current (extra resistor in series). The ZnO_x will act as insulating layer and the migration of oxygen vacancies will lead to the resistive switching.

6.2.3 Exploring other heterojunction for interface-type RRAM

The bipolar switching will domain the RRAM research interest in the near future due to its less thermal effect in operation than unipolar one. The $\text{GaO}_x/\text{NiO}_x$ based device should be improved in operating voltage, switching current and endurance performance. Till now, resistive switching performance in all our devices are measured by DC sweep mode and no pulse test is carried out. Because the operating voltage is still a bit higher, the measuring voltage from pulse generator is not able to trigger the switching. After improving DC sweep behavior, the pulse test must be applied as displayed in Fig. 6-3, in order to investigate the switching speed of our devices which is a necessary parameter in next generation nonvolatile memory. Moreover, many other materials could be taken into account to fabricate p-n heterojunction based RRAM, for example, p-type Cu_2O , SnO , MoO_3 , n-type ZnO , MgO , TiO_2 or even the organic materials.

Figure 6-3 Pulse test of Pt/ Ta₂O_{5-x}/ TaO_{2-x}/Pt RRAM cell⁷⁶

As for unipolar RRAM crossbar integration, a rectifying diode is necessary to connect with each resistor according to 1D1R scheme we discussed before. To replace silicon based transistor, many oxide based diode were fabricated with rectifying characteristics and large forward current to be equipped with unipolar RRAM cell, for example, CuO_x/InZnO_x (Fig. 6-4), NiO_x/TiO_x and Pt/TiO_x (Fig. 6-5) Schottky type diode.^{21,31,150} We can not only explore new type of oxide based diode, but also move forwards to transparent diode to construct the whole transparent 3D system.

Figure 6-4 n-IZO_x/p-CuO_x selecting diode for RRAM¹⁵⁰

Figure 6-5 Pt/TiO₂/Ti Schottky type diode³¹

6.2.4 CRS structure for the integration of bipolar RRAM cells

After obtaining stable performance of one bipolar switching cell, two antiseriial (back to back) cells could be combined to study the non-linear CRS behavior and the potential in crossbar structure. For example, based on NiO_x/GaO_x bipolar switching cell, a NiO_x/GaO_x/NiO_x or GaO_x/ NiO_x/GaO_x can be attempted as CRS structure. However, no CRS behavior was detected by the author so far, probably related to the issues of operating voltage, film thickness and the density of defects. More work need to be conducted on the oxide based CRS behavior.

Author's Publication

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2. **K. Zheng**, X. W. Sun and K. L. Teo, "The Effect of Intrinsic Defects on Resistive Switching Based on p-n Heterojunction", Nanoscience and Nanotechnology Letters, **5**, 868-871 (2013)
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