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**DEVICE APPLICATIONS OF TRANSITION METAL
OXIDE THIN FILMS**

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SCHOOL OF ELECTRICAL AND ELECTRONIC ENGINEERING

2016

DEVICE APPLICATIONS OF TRANSITION METAL OXIDE THIN FILMS

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This thesis is dedicated to my parents.

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ABSTRACT

The transition metal oxide thin films are technologically important materials in many fields due to their various properties. The objective of this thesis is to study the electrical and optoelectronic characteristics of the transition metal oxide thin films, including the Hafnium oxide (HfO_x), Nickel oxide (NiO), and Indium gallium zinc oxide (IGZO) and their potential applications in non-volatile memory, p - n junction, ultraviolet (UV) photodetector, and artificial synapse. All the transition metal oxide thin films in this work are deposited with sputtering or atomic layer deposition techniques, which are fully compatible with the modern complementary-metal-oxide-semiconductor technology. Both the transition metal oxide thin films and the related devices have been characterized by the techniques of transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), and current-voltage (I - V) measurement.

The HfO_x -based resistive switching random access memory (RRAM) device has been successfully fabricated with stable bipolar resistive switching behavior. The resistive switching performance of the RRAM device has been investigated at both room temperature and elevated temperature up to 200 °C. Through the temperature dependent I - V characteristics, the current conduction mechanisms of both the low resistance state (LRS) and high resistance state (HRS) have been studied. The LRS follows the ohmic conduction with little temperature dependence. In contrast, the HRS follows the ohmic conduction at low electric field, and Poole-Frenkel emission at high electric field. Multibit storage in one RRAM cell is realized by controlling either the compliance current in the set process or reset stop voltage in the reset process. Multilevel high resistance states have been studied by impedance spectroscopy. The analysis of complex impedance suggests that the redox reaction

at the TiN/HfO_x interface and the modulation of the leakage gap should be responsible for the changes in the parameters of the equivalent circuit of the RRAM device. The leakage gap widening effect is shown to be the main reason for the higher resistance value associated with a larger reset stop voltage. Both the constant voltage stress (CVS) and ramped voltage stress (RVS) methods are used to study the set speed-disturb dilemma. The RVS is proved to be an effective method with faster speed and low cost. The HfO_x-based RRAM device is also integrated with 180 nm Cu back end of line (BEOL) process platform.

The *p*-type nickel oxide/*n*-type indium gallium zinc oxide (*p*-NiO/*n*-IGZO) thin film heterojunction structure has been fabricated for resistive switching memory application. The as-fabricated structure exhibits the normal *p-n* junction behaviors with a good rectification characteristic. The structure is turned into a bipolar resistive switching memory by a forming process in which the *p-n* junction is reversely biased. The device shows good memory performances; and it has the capability of multibit storage, which can be realized by controlling the compliance current or reset stop voltage during the switching operation. The mechanisms for both the forming process and bipolar resistive switching are discussed; and the current conduction at the low- and high-resistance states are examined in terms of temperature dependence of the current-voltage characteristic of the structure.

The *p*-NiO/*n*-IGZO thin film heterojunction structure has been fabricated for both the diode and UV photodetector applications. The conductivity of both the NiO and IGZO thin films has a strong influence on the performance of the heterojunction diode. The best diode performance can be obtained with both the high conductivity NiO and IGZO thin films. The *p*-NiO/*n*-IGZO heterojunction structure can also be used for the UV light detecting application. The performance of the photodetector is largely affected by the conductivity of the *p*-NiO thin film, which can be controlled by varying the oxygen partial pressure during the deposition of the *p*-NiO thin film. A highly spectrum-selective ultraviolet photodetector

has been achieved with the p -NiO layer with a high conductivity. The results can be explained in terms of the “optically-filtering” function of the NiO layer.

The synaptic transistor based on the IGZO - Al_2O_3 thin film structure, which uses UV light pulses as the pre-synaptic stimulus, has been demonstrated. The synaptic transistor exhibits the synaptic plasticity behavior like the paired-pulse facilitation. In addition, it also shows the brain’s memory behaviors including the transition from short-term memory to long-term memory and the Ebbinghaus forgetting curve. The synapse-like behavior and memory behaviors of the transistor are due to the trapping and detrapping photo-generated holes at the IGZO/ Al_2O_3 interface and/or in the Al_2O_3 layer.

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LIST OF ABBREVIATIONS

ALD	atomic layer deposition
CBRAM	conductive bridging random access memory
CC	compliance current
CMOS	complementary metal-oxide-semiconductor
CVS	constant voltage stress
DRAM	dynamic random access memory
EEPROM	electrical erasable/programmable read only memory
EPROM	erasable and programmable read only memory
FeRAM	ferroelectric random access memory
FIB	focused ion beam
FN	Fowler-Nordheim
FWHM	full width at half maximum
HfO _x	hafnium oxide
HRS	high resistance state
HRTEM	high-resolution transmission electron microscopy
IGZO	indium gallium zinc oxide
I-V	current-voltage
LRS	low resistance state
LTM	long-term memory
LTP	long-term plasticity
MIM	metal-insulator-metal
MIS	metal-insulator-semiconductor
MOSFET	metal-oxide-semiconductor field-effect transistor
MRAM	magneto-resistive random access memory
MSM	metal-semiconductor-metal
NiO	nickel oxide
PF	Poole-Frenkel

PCRAM	phase-change random access memory
PPF	paired-pulse facilitation
RF	radio frequency
RRAM	resistive switching random access memory
RVS	ramped voltage stress
SCLC	space charge limited current
STM	short-term memory
STP	short-term plasticity
TMO	transition metal oxide
TEM	transmission electron microscopy
TFTs	thin film transistors
TSOs	transparent semiconductor oxides
UV	ultraviolet
VLSI	very-large-scale integration
XPS	X-ray photoelectron spectroscopy
XRD	X-ray power diffraction
1T1R	one-transistor/one-resistor

LIST OF SYMBOLS

A	device size
A^*	effective Richardson constant
A_1	magnitude of the first post-synaptic current
A_2	magnitude of the second post-synaptic current
c_1	initial facilitation magnitude of the rapid phase
c_2	initial facilitation magnitude of the slow phase
E_a	activation energy
E_B	binding energy of the electron
E_g	bandgap
ϵ_0	vacuum permittivity
ϵ_i or ϵ	dynamic permittivity
$G(t)$	channel conductance at time t
G_0	channel conductance recorded immediately after the last pulse of a pulse series
G_{init}	channel conductance before any UV light stimulus
$h\nu$	photon energy
I	current
I_D	drain current
k	Boltzmann constant
M^{z+}	metal cations
N_c	effective density states in the conduction band
O_o	oxygen atoms in the regular lattice
O_i^{2-}	oxygen atoms out the regular lattice
ρ_s	sheet resistivity
ρ	bulk resistivity
q	electron charge
$q\Phi$	Schottky barrier height

$q\Phi_{PF}$	depth of potential well
$S.S$	subthreshold swing
T	absolute temperature
Δt	UV light pulse interval
τ	characteristic relaxation time
τ_1	characteristic relaxation time of the rapid phase
τ_2	characteristic relaxation time of the slow phase
μ	mobility
V	voltage
V_D	drain voltage
V_G	gate voltage
V_{Ni}	nickel vacancy
V_o	oxygen vacancy
V_{reset}	reset voltage
V_{set}	set voltage
V_{stop}	reset stop voltage
ω	angular frequency
Z	complex impedance
Z'	real part of the complex impedance
Z''	imaginary part of the complex impedance
β	an index between 0 to 1
λ	wavelength of the beam

Chapter 1 INTRODUCTION

This thesis presents the studies in the electrical and optoelectronic properties of the transition metal oxide thin films synthesized using reactive sputtering and atomic layer deposition techniques. Specifically, hafnium oxide, nickel oxide, and indium gallium zinc oxide thin films have been explored for their applications in non-volatile memory, p - n junction diode, ultraviolet photodetector, and synaptic transistor. This chapter introduces the background, motivations, objectives and major contributions of this thesis. Details of this study are presented in the following chapters.

1.1 Background

1.1.1 Brief introduction to transition metal oxides

The transition metal elements are those elements having a partially filled d subshell in the oxidation state, which includes a wide range of elements in the element periodic table, as shown in Fig. 1.1. By bounding these transition metal elements to the oxygen atoms, transition metal oxides can be formed. The ternary or more complex compounds can be synthesized by introducing additional elements from pre-transition, transition, or post-transition groups [1], which further enrich the range of transition metal oxides. Transition metal oxides are technologically important materials in many fields, including the inorganic and materials chemistry, geology, condensed matter physics, and mechanical and electrical engineering [2]. They can be found everywhere such as the catalysts in chemical industry,

electrode materials in electrochemical processes, conductors in electronic industry and so on. The wide application of the transition metal oxides mainly lies on their various properties. Due to the differences in the electronic structures, transition metal oxides can be insulators (e.g. TiO_2 , BaTiO_3), semiconductors (e.g. CuO , ZnO), metals (e.g. ReO_3), and superconductors (e.g. $\text{YBa}_2\text{Cu}_3\text{O}_7$). In addition, the transition between the metallic state and non-metallic state can be realized by changing the temperate, pressure, or composition. Diverse magnetic properties such as ferromagnetism or antiferromagnetism can also be found in transition metal oxide materials [3]. Due to these various properties, transition metal oxides have been studied and commercialized for years, which helps to establish the mature systems from material synthesis to device fabrication. Thus, utilizing the existing transition metal oxides to realize new functions, such as the non-volatile memories, diodes, ultraviolet photodetectors, and artificial synapses, has attracted much attention.

Main-group Elements		Transition Metals										Main-group Elements					
H																	
Li	Be															H	He
Na	Mg											B	C	N	O	F	Ne
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Al	Si	P	S	Cl	Ar
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	Ga	Ge	As	Se	Br	Kr
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	In	Sn	Sb	Te	I	Xe
Fr	Ra	Ac	Rf	Ha	106	107	108	109				Tl	Pb	Bi	Po	At	Rn
Lanthanides		Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu		
Actinides		Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr		

Fig. 1.1. The transition metal elements in the element periodic table [4].

1.1.2 Brief introduction to non-volatile memory

Semiconductor device technology has experienced a fast development in the last twenty years. Among the various semiconductor devices, the memory device is considered to be one essential core component for the electronic system. There are two types of memory devices, namely the volatile and non-volatile memory devices, which are categorized with the retention time of the stored data. For the volatile memory device, the stored data is lost immediately after the power supply is turned off, which is represented by the dynamic random access memory (DRAM). In contrast, the stored data in non-volatile memory can be kept for years even the power supply is turned off. The first non-volatile memory device was proposed by Kahng and Size in 1960's [5]. Since then, more types of non-volatile memory devices have been invented, including the erasable and programmable read only memory (EPROM) [6], the electrical erasable/programmable read only memory (EEPROM) [7], and the Flash memory [8]. In recent years, the Flash memory is the dominated non-volatile memory devices in the memory market.

The Flash memory is essentially a metal-oxide-semiconductor field-effect transistor (MOSFET) with a floating gate buried within the gate oxide, as shown in Fig. 1.2(a). The floating gate, which is used for charge storage, is electrically and physically isolated from both the control gate and channel. By applying a writing bias to the control gate, electrons can be injected and be trapped inside the floating gate, which causes the change of threshold voltage of the MOSFET, as shown in Fig. 1.2(b). The trapping electrons can be removed by applying a reverse bias, leading to the threshold voltage back to the initial state. The amplitude of the shift of the threshold voltage is largely dependent on the amount of trapping electrons. Thus, multibit storage can be achieved in one Flash memory cell, which makes the high density storage without scaling the cell size possible.

In recent years, further scaling of the Flash memory has shown profound limitation. When the channel is smaller than 20 nm, great deterioration can be observed for the device performance like the endurance and retention properties. Though 3D stack is considered to be a possible solution for high density data storage in Flash memory, the memory cell performance in 3D stack is poorer than it in planar Flash memory arrays, which may cause the increased complexity and cost for the controller and system. To solve this, several potential candidates have been proposed for the next-generation non-volatile memory applications, including the magneto-resistive random access memory (MRAM), ferroelectric random access memory (FeRAM), phase-change random access memory (PCRAM), and resistive switching random access memory (RRAM).

Fig. 1.2. (a) Schematic of a floating gate Flash memory cell. (b) Drain-source current versus gate voltage bias, threshold voltage shift caused by change in electronic charge on storage element [9].

1.1.3 Brief introduction to ultraviolet photodetector

The photodetector is essentially a device that can convert the optical signals to electrical signals (e.g. voltage or current), which is based on the photoelectric effect [14]. It can be seen everywhere from the simply automatic doors, to the photodiodes in the fiber-optic connection,

to the far-infrared cell on the astronomical satellites, which make it one of the most ubiquitous technologies in use today [10]. The photodetectors can fall into different types, like the infrared photodetector, visible light photodetector, and ultraviolet (UV) photodetector, based on the sensing light wavelength range, as shown in Fig. 1.3. Among them, the photodetector operating in the UV light range has attracted much attention due to its various applications in the civil and military areas, such as flame detection, space-to-space communication, missile plume detection, astronomy and biological researches [11,12]. In general, the UV photodetectors can be categorized into two types, namely the thermal detector and the photon detector. For the thermal detector, the incident light radiation is absorbed to increase the temperature of the material. The final output signal can be measured in forms of some material properties that are highly dependent on the temperature. The photon detector can be divided into three types based on different structures including the photoconductive detector [13], *p-n* junction detector [14], and Schottky barrier detector [15]. Each of them has their own merits and drawbacks. In this work, we try to fabricate a *p-n* heterojunction type UV photodetector using the transition metal oxide thin films.

Fig. 1.3. The electromagnetic spectrum [16].

1.1.4 Brief introduction to neuromorphic system

The neuromorphic system, also known as neuromorphic computing, was firstly proposed by Carver Mead in 1980s [17], to define the use of the very-large-scale integration (VLSI) systems to mimic nervous system [18]. The concept of the neuromorphic itself was even earlier. Back to 1960s, the researchers already used the discrete components to build a fairly detailed model of pigeon retina [19]. However, this approach was largely limited by its complexity and cost, which makes it only suitable for research purpose. In the recent years, due to the great improvement of the CMOS technology and high speed digital computers, the neuromorphic system can be physically implemented by complicated VLSI systems or emulated at the software stage. However, both of the two methods will occupy large areas and consume much energy than human brain. To solve these problems, the researchers have proposed to use a single device to mimic the components in the human brain. In this work, we try to emulate the synapse, which is responsible for the interconnection between neurons in the human brain, using metal oxide-based thin film transistor.

1.2 Motivations

In view of the important roles of the transition metal oxides in the business and research fields, the utilization of transition metal oxide thin films to fabricate electronic and photoelectric devices, such as non-volatile memory, p - n junction diode, UV photodetector, and artificial synapse, deserves much investigation. The Flash memory, which dominated the non-volatile memory market in the last few years, is approaching to its limitation. The RRAM device shows potential applications for the non-volatile memories. Currently, RRAM devices with transition metal oxide thin films show great memory performance, like large

memory window, fast reading/writing speed, low power consumption, and good compatibility with the CMOS technology. Thus, a detailed study on the resistive switching performance and mechanism of the RRAM devices based on transition metal oxide (TMO) thin films is conducted. The UV photodetector plays an important role in both the civil and military fields. Among the various kinds of UV photodetectors, the p - n heterojunction type UV photodetector has many advantages. Due to this, a study on the p - n heterojunction type photodetector using TMO thin films is conducted. The neuromorphic system, which can mimic the human brain, is believed to be a useful solution to break the limitation of the conventional digital computer with von Neumann architecture. The artificial synapse, as one key component in the realization of the neuromorphic computation, has been emulated either by the software-based method with von Neumann computers or hardware-based method with large amount of transistors and capacitors. Both of the two methods occupy large areas and consume much energy than human brain. Thus, the realization of a single device based on transition metal oxide thin films with the synaptic functions has been studied in this work.

1.3 Objectives and scope of research

In this thesis, TMO thin films including hafnium oxide (HfO_x), nickel oxide (NiO), and indium gallium zinc oxide (IGZO) thin films have been fabricated using radio frequency (RF) magnetron sputtering or atomic layer deposition (ALD) technology. The main objective of this thesis is to investigate the electrical and optoelectronic properties of these TMO thin films for applications in non-volatile memory, p - n junction diode, ultraviolet photodetector, and artificial synapse.

The scope of the research and the approach are as follow:

- (1) Fabrication of the HfO_x -based RRAM devices with metal-insulator-metal structure.

- (2) Investigation of the resistive switching behaviors of the HfO_x -based RRAM device with current-voltage characteristics under different temperatures.
- (3) Investigation of the current conduction mechanisms of different resistance states of HfO_x -based RRAM device.
- (4) Realization of multibit storage in one HfO_x -based RRAM cell by changing the resistive switching operation conditions. Study of the multilevel high resistance states by impedance spectroscopy.
- (5) Study of the set speed-disturb dilemma in HfO_x -based RRAM device with both the constant voltage stress and ramped voltage stress methods.
- (6) Fabrication of the HfO_x -based RRAM device with the 180 nm Cu BEOL process platform.
- (7) Fabrication of the $p\text{-NiO}/n\text{-IGZO}$ heterojunction structure for resistive switching memory application. Study of the resistive switching mechanism of the heterojunction structure.
- (8) Study of the current conduction mechanisms of the low- and high-resistance states of the $p\text{-NiO}/n\text{-IGZO}$ heterojunction structure.
- (9) Realization of the multibit storage in $p\text{-NiO}/n\text{-IGZO}$ heterojunction structure by changing the resistive switching operation conditions.
- (10) Fabrication of the $p\text{-NiO}/n\text{-IGZO}$ heterojunction structure for diode and UV photodetector applications.
- (11) Investigation of the influence of the conductivity of both the NiO and IGZO thin films on the performance of the $p\text{-NiO}/n\text{-IGZO}$ heterojunction diode.
- (12) Study of the $p\text{-NiO}/n\text{-IGZO}$ heterojunction UV photodetector with highly spectrum-selective property.

- (13) Fabrication of a UV light stimulated synaptic transistor based on InGaZnO-Al₂O₃ thin film structure.
- (14) Emulate the synaptic plasticity and memory functions with UV light stimulus in the IGZO-based synaptic transistor.

1.4 Major contributions of the thesis

The major contributions of the thesis are listed as follows:

- (1) The bipolar resistive switching properties of the HfO_x-based RRAM device have been investigated.
 - a) The HfO_x thin film has been deposited by ALD technology to fabricate the metal-insulator-metal structured RRAM device.
 - b) The temperature dependences of the switching parameters such as the set/reset voltages and high/low resistance states have been investigated. Current conduction mechanisms of different resistance states are studied with the temperature dependent current-voltage characteristics.
 - c) Multibit storage in one memory cell has been realized by controlling the switching parameters during the resistive switching operation. Multilevel high resistance states have been studied by impedance spectroscopy.
 - d) The set speed-disturb dilemma has been studied with both the constant voltage stress and ramped voltage stress methods.
 - e) The HfO_x-based RRAM device has been integrated with the 180 nm Cu BEOL process platform.
- (2) The bipolar resistive switching properties of the *p*-NiO/*n*-IGZO heterojunction structure have been investigated.

- a) The p -NiO/ n -IGZO heterojunction structure has been fabricated for resistive switching memory application.
 - b) Both the forming and bipolar resistive switching processes have been investigated. The as-fabricated structure shows good rectification characteristic. After the forming process, stable bipolar resistive switching behavior can be observed. The transition between low and high resistance states can be attributed to the connection and rupture of the oxygen vacancy based conductive filament.
 - c) The current conduction mechanisms of both the low- and high-resistance states have been investigated through the temperature dependent current-voltage measurement.
 - d) The endurance characteristic of the RRAM device has been studied. Multibit storage has been realized in one memory cell by changing the resistive switching operation conditions.
- (3) The p - n junction diode and ultraviolet photodetector applications of p -NiO/ n -IGZO heterojunction structure have been investigated.
- a) The conductivity of the p -NiO thin film can be controlled by introducing different amount of oxygen gas during the sputtering deposition. The n -IGZO thin films with different conductivities can achieved by the O₂ plasma treatment with different durations. The electrical and optical properties of the thin films have been characterized by Hall effect measurement and UV-Vis spectrophotometer, respectively.
 - b) The p -NiO/ n -IGZO heterojunction structure has been fabricated for the diode and UV photodetector applications.
 - c) The influence of the conductivity of the p -NiO and n -IGZO thin films on the rectifying property of the diode has been investigated.

- d) The influence of the conductivity of the p -NiO thin film on the performance of the UV photodetector has been investigated.
- (4) A light-stimulated synaptic transistor with synaptic plasticity and memory functions based on InGaZnO_x-Al₂O₃ thin film structure has been investigated.
 - a) The bottom-gate IGZO thin film transistor with Al₂O₃ as the gate oxide was fabricated for synaptic transistor application.
 - b) Both the synaptic plasticity and memory functions have been emulated in the synaptic transistor with UV light stimulus.

1.5 Organization of the thesis

This thesis is mainly focused on the applications of the TMO thin films in the RRAM, diode, ultraviolet photodetector, and artificial synapse fields.

Chapter 1 briefly introduces the concepts of the non-volatile memory, ultraviolet photodetector, and neuromorphic system. The motivation, objective and scope of the research and the major contributions of this thesis are also given in this chapter.

Chapter 2 presents a literature review on the TMO thin films. Firstly, some common technologies used to characterize the structural, composition, and electrical properties of the TMO thin films are reviewed. Then, the applications of the TMO thin films in RRAM, ultraviolet photodetector, and artificial synapse fields are discussed in detail.

In **chapter 3**, the bipolar resistive switching behavior of HfO_x-based RRAM device has been investigated. The temperature dependent current-voltage measurement has been conducted to study the resistive switching performance of the RRAM device under different temperatures, as well as the current conduction mechanisms of different resistance states. Both the constant voltage stress and ramped voltage stress methods have been used to study

the set speed-disturb dilemma of the RRAM device. Multibit storage is realized in one RRAM cell by changing the resistive switching operation conditions. In addition, the multilevel high resistance states have been studied by impedance spectroscopy. Finally, the HfO_x -based RRAM device is integrated with the 180 nm Cu BEOL process platform.

In **chapter 4**, the bipolar resistive switching behavior of the $p\text{-NiO}/n\text{-IGZO}$ thin film heterojunction structure has been investigated. Typical $p\text{-}n$ junction behavior with rectifying property can be observed for the as-fabricated heterojunction structure. After the forming process, stable bipolar resistive switching behavior can be achieved. Both the resistive switching mechanism and current conduction mechanisms for different resistance states have been studied. Multibit storage in one RRAM cell has been realized by changing the resistive switching operation conditions.

In **chapter 5**, the applications of $p\text{-NiO}/n\text{-IGZO}$ heterojunction structure in diode and UV photodetector have been investigated. The influence of the conductivity of both the NiO and IGZO thin films on the rectifying property of the heterojunction has been studied. The UV photodetector with highly spectrum-selective property is achieved. The effect of the conductivity of the $p\text{-NiO}$ thin film on the performance of the UV photodetector has been investigated.

In **chapter 6**, the synaptic transistor based on $\text{IGZO-Al}_2\text{O}_3$ thin film structure has been investigated. The UV light is used as the pre-synaptic stimulus for the first time. Both the synaptic plasticity and memory functions have been emulated in this synaptic transistor with UV light stimulus.

Lastly, **chapter 7** summarizes the research works in the thesis and give the recommendations for the future work.

Chapter 2 LITERATURE REVIEW

2.1 Introduction

The transition metal oxide thin films have attracted much interest because of the electrical and optoelectronic characteristics and various applications. Nowadays, the limitation of the Flash memory on the device scaling makes it unsuitable for high density data storage. To solve this, many new types of non-volatile memories have been invented. Among them, the resistive switching random access memory based on transition metal oxide thin films has attracted much attention due to its simple structure, low-power consumption, high read/write speed, good reliability, and great scalability. For the ultraviolet light detecting application, a filter is usually needed to filter out the visible light for conventional Si-based ultraviolet photodetector, which may increase the complexity and cost of the device fabrication. To overcome this, the ultraviolet photodetector based on wide bandgap metal oxide thin films is widely studied. The TMO thin films can also be used to fabricate the two- or three-terminal electronic synapse, which is the key component in the implementation of the neuromorphic system. In this chapter, we briefly introduce the characterizations and device applications of the TMO thin films.

2.2 Characterization of transition metal oxide thin films

2.2.1 Chemical and structural characterization techniques

Transmission electron microscopy

The transmission electron microscopy (TEM) was firstly invented by Max Knoll and Ernst Ruska in 1931. Since then, it became a major analysis method in physical, chemical, and biological research work [20]. Though the basic principle for the TEM is the same as the optical microscopy, it uses a beam of electrons instead of light as the “light source” [21]. The de Broglie wavelength of the electron is much smaller than light, so a much higher resolution can be obtained for TEM system. For the conventional optical microscopy, the limit of the resolution is about hundred nanometers. In contrast, in most of the top high-resolution TEM (HRTEM) system, the spatial resolution even can be smaller than 1 nm. In addition, the electron diffraction pattern which reflects the scattering of electrons by atoms can also be obtained from a TEM measurement, which provides additional information about the crystal structures, like the dots pattern for the single crystal, and rings pattern for the polycrystalline or amorphous solid materials.

Fig. 2.1 shows a schematic diagram of a TEM system. The electron gun, which is made of tungsten filament or lanthanum hexaboride source, can emit electrons. The emitted electrons can be focused into a beam by adjustment of the electromagnetic lenses, corresponding to the glass lenses in the optical microscopy. The electron beam can travel through the specimen we want to test and hit the fluorescent screen, which gives us the image of the specimen. The amount of the electrons that arrive at the fluorescent screen is dependent on the density of target material. Due to the operational principle of the TEM system, the specimen must be thin enough for the electrons to pass through. Thus, sample preparation is extremely important for the TEM measurement. The focused ion beam (FIB) is widely used for the TEM sample preparation.

Fig. 2.1. Schematic diagram of a TEM system.

X-ray photoelectron spectroscopy

The X-ray photoelectron spectroscopy (XPS) is a useful chemical characterization tool, which can be used to analyze the elemental composition, empirical formula, chemical state and electronic state of the elements inside the materials [22]. It can be used to analyze the TMO thin film based electronic devices, like the RRAM or the thin film transistor devices [23-34]. The XPS system was firstly invented in 1960s at Hewlett-Packard in the USA. The XPS system was based on the photoelectric effect, which was discovered by Heinrich Rudolf Hertz in 1887 and explained by Albert Einstein in 1905. Fig. 2.2 shows the basic components of a typical XPS system. In the XPS measurement, when the surface of the material is irradiated by the X-ray beam, the core electrons inside the atoms can be ionized and emit from the material due to the absorption of the photon inside the X-ray beam. Both the kinetic energy and the number of electrons can be collected with the electron collection lens and analyzed by the combination of the electron energy analyzer and electron detector, as shown in Fig. 2.2. The electron binding energy is written as [35]:

$$E_B = h\nu - E_K - W \quad (2.1)$$

where E_B is the binding energy of the electron, $h\nu$ is the photon energy of the X-ray photons being used, E_K is the kinetic energy of the photoelectron, and W is the spectrometer work function dependent on the spectrometer and the material. All the three variables in the right side of the equation are already known or can be measured by the system, so the binding energy can be calculated. The XPS spectrum can be obtained with the photoelectron intensity versus the binding energy. The XPS system can only detect the electrons that are emitted from the surface of sample (about 1 ~ 10 nm). Beyond this range, no electrons can escape and reach the electron detector. So the XPS is essentially a surface sensitive equipment. To get the information inside the material, focused ion beam system must be integrated into the XPS instrument, which helps to get the depth-profiling XPS spectrum.

Fig. 2.2. Basic components of a monochromatic XPS system [35].

X-ray diffraction

X-rays were firstly discovered by Wilhelm Rontgen in 1895, and used to image the inside of objects in the medical radiography or airport security fields, due to its great penetrating

ability. With the development of the study on X-rays, people found that its wavelength was quite close to the size of an atom. Thus, a new prediction was proposed by Max Von Laue in 1912 that the X-rays could be used to identify the structure of the crystal. After Von Laue's pioneering research, the field developed rapidly, most notably by William Lawrence Bragg and his father William Henry Bragg. In 1912-1913, the younger Bragg developed Bragg's law, which connects the observed scattering with reflections from evenly spaced planes within the crystal. With the development of the X-ray diffraction (XRD) technology, the XRD gradually becomes a powerful analytical technique that can identify the composition of the material, and the structures of the atoms or molecular inside the material. For the XRD measurement, the monochromatic X-rays that are emitted from a cathode ray tube are scattered by the atoms inside the target crystal. The crystal here can serve as the grating, which can produce both constructive and destructive interference for X-rays. The constructive interference happens when the diffraction of X-rays by crystals meets the Bragg's law [36]:

$$2d \sin \theta = n \lambda \quad (2.2)$$

where d is the spacing between the diffracting planes, θ is the incident angle, n is an integer, and λ is the wavelength of the beam. The measured diffraction pattern can be compared with the standard reference patterns in the database, which helps us to identify the crystalline forms of the target material. Besides the typical phase analysis, the XRD measurement can also be used to calculate the size of the sub-micrometer particles or crystallites inside the target material by using the Scherrer equation, which can be written as [37]:

$$D = \frac{K \lambda}{\Delta \theta \cos(\theta_B)} \quad (2.3)$$

where λ is the wavelength of the X-ray, $\Delta \theta$ is the full width at half maximum of the Bragg peak, θ_B is the Bragg angle, and K is a dimensionless shape factor, with a value close to unity. The shape factor has a typical value of about 0.9, but varies with the actual shape of the

crystallite . This non-destructive analytical technique has been widely used to characterize the TMO thin films [38-48].

2.2.2 Electrical characterization techniques

Four-point probe measurement

The four-point probe measurement is a simple method to accurately measure the resistivity of the semiconductor materials. Compared with the two-point probe method, no calibration is needed for the testing result of the four-point probe measurement due to the separation of the current and voltage electrodes, which greatly eliminates the lead and contact resistance from the measurement [49]. Even some other resistance measurement techniques should be calibrated by four-point probe method. The current flow is supplied by the outer probes and the induced voltage can be read from the inner voltage probes, as shown in Fig. 2.3. Using the voltage and current value reading from the probes, the sheet resistance of the material can be calculated as [50]:

$$\rho_s = \frac{\pi}{\ln(2)} \frac{V}{I} \quad (2.4)$$

where ρ_s is the sheet resistivity of the sample, V is the voltage reading from the inner probes, and I is the current reading from the outer probes. To measure the bulk resistivity of the material, the sample thickness must be added into the formula, as shown below:

$$\rho = t \frac{\pi}{\ln(2)} \frac{V}{I} \quad (2.5)$$

where ρ and t are the bulk resistivity and the thickness of the sample, respectively. The above formulas works for when the sample thickness less than half of the probe spacing. For thicker samples the equation becomes:

$$\rho = \frac{V}{I} \frac{\pi t}{\frac{\sinh(\frac{t}{s})}{\ln(\frac{s}{\sinh(\frac{t}{2s})})}} \quad (2.6)$$

where s is the probe spacing.

Fig. 2.3. Schematic of the four-point probe configuration.

Hall effect measurement

With the development of the times, the understanding on the electrical characterization of the material has gone through three stages. In 1800s, resistance (or conductance) was used to describe the electrical property of the materials. Soon, people found that only resistance could not well reflect the material property due to the large geometry dependence of the resistance. Later, resistivity (or conductivity) was proposed to describe the current-carrying capability of the material [51]. However, it was still not the fundamental material parameter, since different materials may have the same resistivity value. With the development of the quantum theory, the carrier concentration and carrier mobility were proposed as the intrinsic material properties, which could be measured through the Hall effect measurement. The Hall effect

was firstly discovered by Edwin Hall in 1879. It describes a phenomenon that a voltage difference can be produced when a magnetic field is perpendicularly added to a current flow, and the induced electric field is perpendicular to both the current flow and magnetic field following the right hand rule, as shown in Fig. 2.4. The Hall effect measurement system is essentially consisted of two parts, namely the resistivity measurement and Hall measurement. Through the resistivity measurement, which can be realized by the van der Pauw technique, the sheet resistance and resistivity can be obtained. Through the Hall measurement, the Hall coefficient can be obtained. With the combination of the resistivity and Hall coefficient, the material parameters such as the carrier concentration, carrier mobility, and conductivity type can be decided.

Fig. 2.4. Illustration of Hall effect [52].

Current-voltage measurement

The current-voltage measurement equipment used in this thesis is Keithley 4200 semiconductor characterization system connected to a switching matrix, as shown in Fig. 2.5. The device performance of both the two-terminal devices, like the resistive switching random access memory [53-56], *p-n* heterojunction [57-61], and the three-terminal devices, like the

thin film transistor [62-66] can be evaluated by current-voltage measurement. By equipped with the TRIO-TECH TC1000 temperature controller, the study of the temperature dependence of the device performance can be realized. With the current-voltage measurements at different temperatures, the current conduction mechanisms for the transition metal oxide thin films can be studied.

Fig. 2.5. Keithley 4200 Semiconductor Characterization System.

2.3 Introduction to resistive switching random access memory

The fast development of the information technology escalates the demands for high-speed and large-capacity non-volatile memories. Today, Flash memory dominates the non-volatile market because of its high density and low cost. However, obvious disadvantages cannot be ignored for it, like the poor endurance, low write speed, and high operating voltages [67]. In addition, the limitation of the Flash memory on the device scaling also makes it not satisfy the large-capacity requirement. In recent years, further scaling of the Flash memory has shown profound limitation. It is widely accepted that with the scaling below 20 nm, great deterioration can be observed for the device performance like the endurance and retention

properties. To overcome this, various memory concepts have been proposed, like the ferroelectric random access memory (FeRAM), in which the polarization of a ferroelectric material is reversed; or magnetoresistive random access memory (MRAM), in which a magnetic field is involved in the resistance switching [68]. However, both of the techniques cannot solve the scalability problem as the Flash memory. Nowadays, resistive switching random access memory (RRAM) has attracted much attention due to its simple structure, low-power consumption, high read/write speed, good reliability, and great scalability [69]. The study of the RRAM device started from 1962, when Hickmott firstly reported the hysteretic resistive switching phenomenon in aluminum oxide thin film with metal-insulator-metal (MIM) structure [70]. Since then, a huge variety of materials from binary or multinary metal oxides to organic compounds have been proved to be suitable for RRAM application.

2.3.1 Classification of device operation

A general resistive switching memory cell is based on a capacitor-like structure, in which an insulating or semiconducting material is sandwiched between two metal electrodes, as shown in Fig. 2.6. In this MIM structure, the switching layer “I” can be metal oxides, chalcogenides or organic materials. The top and bottom electrodes can be the same or different metallic and electron-conducting non-metallic materials [71]. These MIM cells can be electrically switched between high resistance state (HRS) and low resistance state (LRS), which corresponds to the “1” and “0” states in the digital information technology. The transition process that changes the device from HRS to LRS is called “set” process. In contrast, the reverse transition process that changes the device from LRS to HRS is called “reset” process. For the fresh RRAM device, a relatively high voltage is needed to trigger the device from initial state to switching state, which is called “forming” process. However, this forming process is not necessary for all the RRAM devices.

Fig. 2.6. The typical MIM capacitor structure of a resistive switching memory cell.

Fig. 2.7. Two types of resistive switching behavior: (a) unipolar resistive switching and (b) bipolar resistive switching [71].

To better distinguish the resistive switching behaviors, the RRAM devices can be distinguished into two modes based on the electrical polarity required for resistance state transition. For the unipolar resistive switching device, as shown in Fig. 2.7(a), the transition between the HRS and LRS depends not on the polarity but on the magnitude of the applied voltages. Both the set and reset process occur in the same polarity. For set process, a compliance current supplied by the control system or series resistor is used to prevent the hard-breakdown of the device. For reset process, a higher reset current with a smaller voltage than the set process is usually needed to reset the device from LRS to HRS. In contrast, for

the bipolar RRAM device, the set process occurs at one polarity and the reset process occurs at the reverse polarity, as shown in Fig. 2.7(b). A compliance current is usually needed to prevent the hard-breakdown of the device during the set process. To realize the bipolar resistive switching, different electrode materials are usually needed for the MIM structure.

With about 20 years' development, the performance of Flash memory almost approaches to its upper limit, which cannot fulfill the requirement for the high-density data storage. To replace the Flash memory, the RRAM devices must have good performance in some basic indexes of the non-volatile memories.

Write/erase operation

The set/reset voltages are required to be smaller than 1 V to overcome the disadvantage of the high programming voltages in Flash memory. The set/reset pulse width should be smaller than 100 ns, which is comparable with that of the DRAM devices. The set/reset current during the write/erase operation should be as small as possible.

Read operation

The read voltage should be smaller than the set and reset voltages to prevent the misoperation during the read process. The read pulse width should be smaller or comparable with the write/erase pulses.

HRS/LRS ratio

The HRS/LRS ratio is an essential parameter that is used to distinguish the different resistance states in RRAM device. Larger HRS/LRS ratio can greatly reduce the complexity and cost of the peripheral circuit. HRS/LRS ratio larger than $\times 10$ is needed for small and highly efficient sense amplifiers [67]. Larger HRS/LRS ratio also provides the possibility for multibit storage in one RRAM cell, which is an efficient method to increase the data storage density without scaling the device.

Endurance property

The endurance is the maximum number of cycles that one RRAM cell can endure transition between the HRS and LRS. The commercial Flash memory in today's market generally can bear $10^3 \sim 10^7$ cycles depending on the type. So the RRAM device should have a similar or better endurance property.

Retention property

For the non-volatile memory applications, the data must be kept at least for 10 years after the power supply is cut off. The RRAM device must have the capacity to keep the data unlost even with the working temperature up to 85 °C.

2.3.2 Classification of resistive switching mechanism

Besides the classification based on the device operation, the RRAM device can also be categorized into different types based on its resistive switching mechanism. Though it was already decades since the first resistive switching phenomenon was observed, the physical mechanism of resistive switching behavior was still unclear. There are several hypotheses to explain the resistive switching phenomenon, including the conductive filament-type resistive switching and homogeneous interface-type resistive switching. In the conductive filament theory, the transition between the LRS and HRS is attributed to the formation and rupture of the conductive filament, which can be made of metal ions or oxygen vacancies. For the homogeneous interface-type resistive switching, the transition between the different resistance states can be attributed to the field-induced change of the Schottky-barrier at the interface over the entire electrode area [67]. The causes for the both types of resistive switching can be categorized into three types, including the thermochemical effect, electrochemical metallization effect, and valence change effect.

Thermochemical effect

The RRAM devices that are based on the thermochemical effect typically show the unipolar resistive switching behavior. The most famous resistive switching material that shows unipolar resistive switching behavior is NiO thin film, which was firstly reported in 1960s in the Pt/NiO/Pt structure [72]. Since then, various materials were reported with unipolar resistive switching phenomenon, like the ZrO_2 [25], Sb_2O_5 [28], ZnO [73], and Al_2O_3 [74]. Fig. 2.8 shows the I - V characteristics of the NiO-based RRAM device. Both the set and reset processes are triggered by the positive bias. For the set process, the compliance current is added to prevent hard-breakdown of the NiO thin film. For the reset process, the compliance current is released to generate high level reset current to change the device back to HRS.

Fig. 2.8. The unipolar I - V characteristic of a Ni/NiO/Ni MIM structure RRAM device [75].

As shown in Fig. 2.9, the transition between the HRS and LRS can be attributed to the formation and rupture of the conductive filament. The initial resistance of the fresh device is quite high. When a forming voltage is applied to the device, a soft-breakdown occurs in the insulator layer, which is caused by Joule heating effect. Due to the negative free energy of

formation for metal oxides, a little increase of the temperature always leads to a stable oxide with a lower valence metal, which means the oxide ion binding to the metal ions will runaway from the lattice to form the metal oxide with low valence state. When the added compliance current is small, the localized thermal runaway effect will cause a temporal low resistance state, so called threshold switching. When the compliance current is high, more oxygen ions will drift out of the localized high temperature region leading to the local redox reaction. So a conductive filament is formed to connect the top and bottom electrodes, as shown in Fig. 2.9, corresponding to the set process. This conductive filament may be composed of the electrode metal ions transported into the insulator, carbon from residual organics, or decomposed insulator material such as sub-oxides [71]. For the reset process, the conductive filament is thermally ruptured due to the local high power density, which analogies to the traditional household fuse.

Fig. 2.9. Schematics of fresh state and (1) forming, (2) reset, and (3) set process, respectively [68].

Fig. 2.10. A series of *in situ* TEM images (a-e) and the corresponding *I-V* characteristics (f-j) during the forming process [76].

With the development of the microscopic measurement technique, the direct observation of the thermal growth of the conductive filament becomes possible. Chen *et al.* [76], have used the HRTEM technique to observe the dynamic evolution of the conductive filament in the ZnO-based RRAM device, as shown in Fig. 2.10. Starting from top electrode, the filament grows towards to the bottom electrode with the increase of the forming voltage. After the filament touching the bottom electrode, the device is changed to LRS.

Electrochemical metallization effect

The RRAM devices that are based on electrochemical metallization effect are also called conductive bridging random access memory (CBRAM) in the literature, in which the transition between the HRS and LRS can be attributed to the connection and rupture of the metallic conductive filament. The CBRAM is typically based on MIM structure with the anode electrode made of active materials, such as Ag [77] or Cu [78] with high mobility in the solid electrolytes; the cathode electrode made of inert materials like Pt [79], W [80], or Ir [81]. A variety of chalcogenides, such as Cu₂S [82], GeSe [83], or oxides, such as SiO₂ [81], CuO_x [84], or even organic materials [85,86] were reported as the insulating layer in CBRAM devices.

For the CBRAM devices, the electrochemical metallization is related to the cation-migration induced redox reaction. The RRAM devices that are based on electrochemical metallization effect typically show the bipolar resistive switching behavior, as shown in Fig. 2.11. The overall set process involves the following steps:

- 1) By applying a positive voltage to the anode electrode, the metal atoms inside the active metal electrode can be oxidized and dissolved into the insulator layer

where M^{z+} is the metal cations in the solid insulator layer;

- 2) Under the positive electric field, the M^{z+} cations migrate across the insulator layer.
- 3) The M^{2+} cations reduce at the cathode electrode through the cathodic deposition reaction

The metallic filament is grown from the cathode electrode towards the anode electrode until a conductive path is formed across the whole insulator layer. Fig. 2.11 shows a device with Ag and Pt as the active and inert electrode, respectively. The initial resistance of the fresh device is quite high. When a positive voltage is applied, the oxidized Ag⁺ can migrate

into the insulator layer, as shown in Fig. 2.11(B). After the Ag^+ reaching the cathode electrode, it can be reduced to Ag again and grow towards to anode electrode, as shown in Fig. 2.11(C). When a complete Ag-based conductive filament connects the top and bottom electrode, as shown in Fig. 2.11(D), the device can be switched to LRS. When a reversed voltage is applied, the metal atoms dissolve at the edge of the metal filament, which ruptures the conductive path inside the insulator layer, as shown in Fig. 2.11(E). Thus, the device is changed back to HRS. Yang. *et al*, has used the in-situ TEM technology to directly observe the growth of Ag based conductive filament in CBRAM device, as shown in Fig. 2.12, which provides the solid evidence to the correctness of the electrochemical metallization theory.

Fig. 2.11. Sketch of the steps of the set (A-D) and reset (E) operations of an electrochemical metallization memory cell [87].

Fig. 2.12. *In-situ* TEM observation of Ag-based conductive filament growth in vertical Ag/ a-Si/W memories. (a) Experimental set-up. The Ag/a-Si/W resistive memory device was fabricated on a W probe. Scale bar, 100 nm. (b) Current-time characteristics recorded during the forming process at a voltage of 12 V. (c-g) TEM images of the device corresponding to data points c-g in (b) recorded during the forming process. Scale bar, 20 nm [88].

Valence change effect

The third type resistive switching mechanism for RRAM devices is the valence change effect. Being different from the electrochemical metallization effect, the anions with negative charges instead of cations with positive charges migrate inside the insulator layer to control the resistive switching of the valence change type RRAM device. For the valence change type RRAM device, the materials for the insulator layer could be various, such as the TiO_2 [89], ZrO_2 [90], TaO_x [91], HfO_x [92], CeO_x [93], Sb_2O_5 [94], SrTiO_3 [95], and so on. Within this valence change system, two different types of resistive switching behaviors can be observed, namely filament-type and homogeneous interface-type resistive switching, respectively, which are classified based on the area dependence of the LRS. For filament-type RRAM devices, the conductive filament is localized in a small area, thus the LRS is

independent on the electrode area. In contrast, for the homogeneous interface-type RRAM devices, the value of the LRS is proportional to the electrode area.

In the filament-type RRAM device with transition metal oxides as the switching layer, the oxygen ions or oxygen vacancies are much more mobile than the metal cations. When a forming voltage is applied to the device, the oxygen atoms that are bound to the metal atoms will be knocked out of the lattice due to the high electric field, leaving the oxygen vacancies, which can be described with [96]:

where O_o and O_i^{2-} are the oxygen atoms in and out the regular lattice, respectively; and V_o^{2+} is the oxygen vacancy. Under the positive electric field, the oxygen ions will migrate to the anode and oxidize the top metal electrode to form a thin metal oxide interface layer, which serves as the oxygen reservoir. The migration of the oxygen ions leaves the oxygen vacancies gathering at the cathode. Thus an oxygen deficient region can be built-up and grow towards near the anode. When this oxygen deficient region, which is referred to the oxygen vacancy based conductive filament, reaches the top electrode, the LRS can be achieved. Due to the lack of the oxygen atoms in the lattice, the valence state of the metal cations reduces, which changes the metal oxide into a highly conductive phase. Thus the oxygen vacancy based conductive filament is essentially a filament made of highly conductive low valence state metal oxide phase, as shown in Fig. 2.13. For the reset process, when a reverse voltage is applied, the oxygen ions inside oxygen reservoir will move back to the switching layer to passivate some of the oxygen vacancies inside the filament, which can be described as:

Thus, the conductive filament is ruptured, which changes the device from LRS to HRS.

Fig. 2.13. High-resolution TEM images of (a) a complete Ti_4O_7 conductive filament and (b) an incomplete Ti_4O_7 conductive filament [97].

Fig. 2.14. The capacitance-voltage curves under reverse bias for a $\text{Ti}/\text{PCMO}/\text{SRO}$ cell show hysteretic behavior. This indicates that the depletion layer width at the Ti/PCMO interface is altered by applying an electric field [68].

Besides the filament-type RRAM device, the homogeneous interface-type RRAM device, for which the LRS has area-dependence, was also reported [98]. The resistive switching for interface-type RRAM device can be attributed to the field-induced change of the Schottky-barrier width at the metal-oxide interface. When a setting voltage is applied, the V_o^{2+} will move towards the interface, which effectively reduces the width of the Schottky-barrier. Thus,

LRS can be achieved. When a resetting voltage is applied, the V_o^{2+} will move away from the metal-oxide interface, which will increase the barrier width. Thus, the HRS can be achieved. The change of the Schottky-barrier width between HRS and LRS has been confirmed by capacitance-voltage measurement, as shown in Fig. 2.14.

2.4 Introduction to ultraviolet photodetector

The research on the UV light began in the latter half of the 19th century, when this invisible electromagnetic wave beyond the blue end of the visible spectrum was discovered [99]. The UV light can be divided into three regions: UV-A (320 nm-400 nm), UV-B (280 nm-320 nm), and UV-C (10 nm-280 nm). Most of these UV lights that come from the sunshine are absorbed by the atmospheric ozone layer before reaching the earth surface. The UV lights in long (200 nm–300 nm) and short (110 nm-200 nm) region are absorbed by the ozone and molecular oxygen in the terrestrial atmosphere, respectively. An overexposure under UV light may lead to skin cancer to human [100]. Thus, the UV photodetectors can provide early warning signs for preventing overexposure. Since its invention, UV photodetectors have been widely used in the civil and military areas, such as flame detection, space-to-space communication, missile plume detection, astronomy and biological researches.

2.4.1 Photoconductive photodetector

Due to the simple structure and high responsivity, the photoconductive photodetector has attracted much attention in the low cost monitoring applications. The typical photoconductive photodetector is based on metal-semiconductor-metal (MSM) structure, as shown in Fig. 2.15. The photoconductive photodetector is essentially a light-sensitive resistor. In the operation of it, the incident light is shone on the semiconductor channel of the MSM structure. The photon

with energy ($h\nu$) that is larger than the bandgap of the semiconductor material will be absorbed by the photodetector. The electron-hole pairs will generate due to this photoelectric effect, which can increase the conductivity of the device to realize the detection of the UV light. Photodetectors based on narrow bandgap semiconductors, especially Si (bandgap $E_g = 1.1$ eV), have been commercialized for light detection for a long time. However, to realize the selective detection in the UV light range, an optical filter is usually needed to filter out the visible and infrared light, which greatly increases the complexity and cost of the photodetectors. To overcome this problem, wide bandgap semiconductors, like ZnO [101], ZnMgO [102], SnO₂ [103], ZnS [104], and Zn₂GeO₄ [105], have been investigated for UV light detecting application.

Fig. 2.15. Schematic of the photoconductive photodetector [99].

2.4.2 Schottky-barrier photodetector

The Schottky-barrier photodetector as another important type UV photodetector has been studied extensively. Compared with the p - n junction type photodetector, the Schottky-barrier photodetector has simple fabrication process and high response speed. The rectifying behavior of the metal-semiconductor contact rises from the different work functions of the metal and semiconductor material, as shown in Fig. 2.16. When the incident light is shone on

the device, the photon-generated electron-hole pairs can be separated by the built-in electric field. For the UV detecting application, to have a high signal to noise ratio, a low dark current is required. Thus, a thin insulator layer can be inserted between the metal and semiconductor material to form the metal-insulator-semiconductor (MIS) structure, which effectively decreases the dark current.

Fig. 2.16. Equilibrium energy band diagram of Schottky contacts: (a) metal-(*n*-type) semiconductor ($\Phi_m > \Phi_s$); (b) metal-(*p*-type) semiconductor ($\Phi_m < \Phi_s$) [99].

2.4.3 *p-n* junction photodetector

The third type photodetector is the *p-n* junction photodetector made of semiconductor materials. With the formation of the *p-n* junction, a built-in electric field can be obtained in the depletion region, which causes the electrons and holes to move to the opposite directions depending upon the external circuit. Fig. 2.17(a) shows the schematic diagram of a *p-n* junction photodetector. When the energy of the photons is larger than the bandgap of the semiconductor materials, electron-hole pairs will be generated in both sides of the junction. The minority carriers, as the holes in *n*-type side and electrons in *p*-type side, will diffuse to the depletion region and be separated by the built-in electric field immediately. Then, these

electrons and holes, acting as the minority carriers before, will become the majority carriers in the n - and p -region, respectively. The photo-generated current here will cause the shift of the current-voltage curve of the junction, as shown in Fig. 2.17(c). The p - n junction type photodetector usually works under the reversed bias operation, which is used for the high frequency applications. Compared with other two types photodetectors, the p - n junction type photodetector has many advantages, including the low bias current, high impedance, capability for high frequency operation, and compatibility of the fabrication technology with planar-processing techniques [99].

Fig. 2.17. Schematic representation of the operation of a p - n junction photodetector: (a) geometrical model of the structure, (b) equivalent circuit of an illuminated photodetector, (c) current-voltage characteristics for the illuminated and non-illuminated photodetector [99].

2.5 Introduction to artificial synapse

The von Neumann architecture, in which the memory and processor are separated, was firstly developed in 1940s [201]. Since then, almost all the modern computers are based on this stored program scheme. Recently, this conventional von Neumann architecture is becoming increasing inefficient for the further requirement for complicated computation or recognition due to the limited throughput of the shared data channel between the program memory and data memory, namely, the so-called “von Neumann bottleneck”. To solve this problem, many efforts have been made to build neuromorphic systems that can mimic the human brain, which is believed to be the most powerful information processor that can easily recognize various objects and visual information in complex world environment through complicated computation [203]. The human brain is composed of large amount of neurons ($\sim 10^{11}$) and synapses ($\sim 10^{15}$). Synapses are the connections between the neurons, as shown in Fig. 2.18. Thus the synapse emulation is a key step to realize the neuromorphic computation [204]. Though much work has been done to implement neuromorphic systems through software-based method by conventional von Neumann computers [205], or hardware-based methods by emulating the synapse with a large number of transistors and capacitors in CMOS integrated circuits [202], both of the two approaches occupy larger areas and consume much more energy than the human brain. Thus, the realization of a single device with synaptic functions has attracted much attention for the implementation of the neuromorphic system.

With the development of the artificial synapse, a variety of biological synapse functions have been demonstrated based on two-terminal memristors or three-terminal synaptic transistors [206-216]. The two-terminal memristor is essentially a resistive switching random access memory device, whose conductance can be modulated by the electrical inputs. The three-terminal synaptic transistor is generally based on a thin film transistor structure, in

which the channel conductance can be controlled by the trapped charges inside the gate oxide layer. The synaptic weight of the biological synapse corresponds to the conductance of the memristor for two-terminal devices and conductance of the channel for three-terminal devices, respectively. Through the electrical inputs, synaptic functions can be fully or partially realized, such as the paired-pulse facilitation, long-term potentiation, long-term depression, spike-time dependent plasticity, spike-rate-dependent plasticity, short-term memory to long-term memory transition, and Ebbinghaus forgetting behaviors.

Fig. 2.18. Schematic diagram of a synapse between two neurons [96].

2.6 Summary

In this chapter, a literature review on the characterization and applications of the TMO thin films has been presented. First of all, different characterization techniques that are used to study the structural, morphological, and electrical properties of the TMO thin films or related devices have been introduced. Then, the device applications of the TMO thin films in the RRAM, ultraviolet photodetector, and artificial synapse have been discussed in detail.

Chapter 3 RESISTIVE SWITCHING IN HfO_x-BASED RRAM DEVICE

3.1 Introduction

Due to the requirement for the high capacity data storage memories, much work has been done on the research of the next generation non-volatile memories. Among the various candidates, resistive switching random access memory (RRAM) has attracted much attention due to its simple structure, fast read/write speed, low power consumption, good reliability and great scalability potential. A variety of materials have been reported for RRAM application, such as Al₂O₃ [53], AlN [106], BaTiO₃ [55], CeO₂ [107], GaO_x [30], HfO_x [108], and so on. Among them, HfO_x thin film seems to be a good choice due to its low cost and high compatibility with conventional CMOS semiconductor fabrication process [109].

In this chapter, bipolar resistive switching behavior of TiN/HfO_x/Pt structured RRAM device has been investigated. The resistive switching behaviors of RRAM device under both room and elevated temperatures have been studied. To understand the physical mechanism of the resistive switching, current conductions at the LRS and HRS are examined in terms of temperature dependence of the current-voltage characteristics. Multibit storage is achieved in one RRAM cell by controlling the compliance current in the set process or controlling the reset stop voltage in the reset process. Multilevel high resistance states in the HfO_x-based RRAM have been studied by impedance spectroscopy. Both the constant voltage stress and ramped voltage stress methods have been used to study the set speed-disturb dilemma in the

HfO_x-based RRAM device. In the end, we try to fabricate the TiN/Ti/HfO_x/TiN structured RRAM device with the 180 nm Cu BEOL process platform.

3.2 Experiment and device fabrication

The TiN/HfO_x/Pt RRAM structure was fabricated with the following sequence. Firstly, a 500 nm SiO₂ film was deposited on an 8-inch *p*-type Si wafer by plasma-enhanced chemical vapor deposition to prevent the leakage during the switching operation of the RRAM device. Then, 50 nm Pt/ 20 nm Ti layer was deposited by electron-beam evaporation to form the bottom electrode on the SiO₂ film. Subsequently, a 10 nm HfO_x layer was deposited by atomic layer deposition on the bottom electrode. Finally, a 100 nm TiN layer was deposited on the HfO_x layer using DC sputtering and then patterned with lithography and metal etch process to form the top electrode with the area of about 4 μm². Fig. 3.1 shows the schematic illustration of the TiN/HfO_x/Pt RRAM cell. A Keithley 4200 semiconductor characterization system equipped with TRIO-TECH TC1000 temperature controller was used to characterize the switching properties of the device. Impedance measurement of different high resistance states was carried out with an Agilent E4980A Precision LCR Meter in the frequency range of 20 Hz to 2 MHz with a 30 mV AC signal.

Fig. 3.1. Schematic illustration of the TiN/HfO_x/Pt RRAM cell.

3.3 Bipolar resistive switching of the HfO_x-based RRAM device

Fig. 3.2. Bipolar current-voltage (I - V) characteristics of the TiN/HfO_x/Pt RRAM device after the forming process. The inset shows the forming process and the first reset process.

The initial resistance of the device is quite high. A forming process is needed to change the device to a relatively low resistance state, which is similar to the soft-breakdown phenomenon in the high- k dielectrics. As shown in the inset of Fig. 3.2, when the forming voltage applied to the device reaches about 3 V, a sharp increase of the current can be observed. After the forming process, the resistance of the structure drops drastically compared to the virgin resistance state before the forming process. As can be observed in Fig. 3.2, after the forming process, stable bipolar resistive switching behavior can be achieved. By applying a positive voltage with a compliance current of 0.5 mA, which is used to prevent the hard-breakdown during the set process, the device can be set from HRS to LRS; by applying a negative voltage without compliance current, the device can be reset from LRS to HRS.

To study the endurance characteristics of the RRAM device, consequent DC sweeping test was conducted. As shown in Fig. 3.2, no obvious cycle-to-cycle variation is observed in the I - V curves of different switching cycles, indicating good stability and repeatability of resi-

Fig. 3.3. (a) Distributions of the LRS/HRS resistance measured at 0.1 V for 100 switching cycles. (b) Distributions of the set/reset voltage for 100 switching cycles. (c) Retention test at room temperature (the resistance is measured at 0.1 V).

-stive switching behavior. The device exhibits narrow distributions of the switching parameters including the resistance of HRS and LRS, set voltages (V_{set}), and reset voltages (V_{reset}) within 100 switching cycles, as shown in Fig. 3.3. The resistance ratio of HRS/LRS is larger than 20 for all the switching cycles, which is large enough for practical memory device application. Both the magnitudes of V_{set} and V_{reset} are smaller than 1 V, yielding a low power consumption during the switching operation. Meanwhile, as shown in Fig. 3.3(c) for the retention test, there is no significant degradation for both HRS and LRS in the measurement duration up to 10^5 s, showing the non-volatile capability of the HfO_x-based RRAM device.

Fig. 3.4. Distributions of (a) HRS and LRS (b) V_{set} and V_{reset} for 100 resistive switching cycles from 10 randomly picked RRAM cells.

To prove the reliability of the HfO_x -based RRAM device, 100 consequent DC sweeping tests were conducted on 10 randomly picked RRAM cells. Fig. 3.4 shows the distributions of resistance states and transition voltages of the 10 randomly picked RRAM cells. As shown in Fig. 3.4 (a), the LRS shows a narrow distribution. The distribution for the HRS value is different from cell to cell. However, the HRS/LRS ratio is larger than 20 for all the RRAM cells. Both the set and reset voltages show tight distributions, as shown in Fig. 3.4 (b). Thus, the HfO_x -based RRAM device in this work shows a reliable resistive switching behavior.

As discussed in chapter 2, there are many theories to explain the resistive switching phenomenon in the RRAM device. For the HfO_x -based RRAM device in this work, the resistive switching between HRS and LRS can be explained by the conductive filament model, which is one kind of the valance change system. When the forming voltage is applied to the TiN top electrode, the oxygen atoms binding to the metal atoms can be knocked out of the lattice due to the high electric field. Under the positive electric field, the oxygen ions can move to the top electrode and react with TiN to form a TiON interface layer, which acts as the oxygen reservoir. The depletion of the oxygen ions will form an oxygen vacancy based conductive filament inside the HfO_x layer. When this oxygen vacancy filament connects the top and bottom electrode, the device will change from HRS to LRS. The conduction in LRS is dominated by electron hopping effect among the localized oxygen vacancies. For the reset process, when the reverse bias is applied to the top electrode, the oxygen ions inside the TiON interface layer will be driven back to the HfO_x layer. The oxygen vacancies inside the conductive filament can be passivated by these oxygen ions leading to the device changing back to HRS. Thus, the transition between the HRS and LRS for HfO_x -based RRAM device can be attributed to the connection and rupture of the oxygen vacancy based conductive filament.

3.4 Temperature dependence of the resistive switching behavior

The investigation of the resistive switching behavior of the RRAM device at an elevated temperature is quite meaningful for the practical application of the device. To study this, consequent DC sweeping test was conducted on the TiN/HfO_x/Pt RRAM device with the temperature ranging from 25 °C to 200 °C. Fig. 3.5 shows the distributions of the resistive switching parameters including the resistances of HRS and LRS, V_{set} , and V_{reset} , which are yielded from 40 DC sweeping cycles for each temperature point. As shown in Fig. 3.5(a), both the V_{set} and V_{reset} decrease with the increase of the temperature, which means that the conductive filament is easier to form and rupture at the elevated temperatures. As discussed in section 3.3, the positive electric field can knock the oxygen ions out of their original lattices to form an oxygen vacancy based conductive filament in the set process. In the reset process, the oxygen ions can migrate back to the HfO_x layer under the negative electric field to passivate the oxygen vacancies inside the conductive filament. So the generation rate of oxygen vacancies and the oxygen ion mobility dominate the rate of the creation and rupture of conductive filament. According to the crystal defect theory, both of oxygen vacancy generation and oxygen ion migration can be enhanced at higher temperature [110]. Due to this, the magnitudes of set and reset voltages will decrease with increase of the temperature. In contrast to the transition voltages, no temperature dependence is observed for both the HRS and LRS, as shown in Fig. 3.5(b). The HRS/LRS ratio is larger than 30 in the whole temperature range, which makes this HfO_x based RRAM device work well under high temperatures.

Fig. 3.5. Temperature dependence of (a) V_{set} and V_{reset} ; (b) HRS and LRS. The parameters were collected from 40 consequent DC sweep cycles at each temperature point. The trend lines are for guiding the eyes only.

3.5 Conduction mechanisms of LRS and HRS

In the previous part, much work has been done on the studies of the resistive switching behaviors and mechanisms of the HfO_x-based RRAM device. To better understand the physics behind the resistive switching phenomenon, the current conductions of both LRS and HRS are examined with the temperature dependent I - V measurements in this part.

Fig. 3.6(a) shows the I - V characteristics of the LRS under different temperatures. A linear I - V relationship with the slope of ~ 1 is observed for all the temperatures, showing the ohmic conduction of LRS for the oxygen vacancy based conductive filament. The overlap of these I - V curves indicates that the temperature has little effect on the LRS. This temperature independent behavior is also confirmed in Fig. 3.6(b), in which no obvious change for current (read at 0.1V) is observed. In general, the current transport for LRS can be attributed to electron hopping effect or ohmic conduction mechanism. For the electron hopping effect, there is no continuous filament formed between the top and bottom electrodes, and the electrons will hopping among the discrete oxygen vacancies [111]. In this situation, the thermal excitation process will be enhanced at higher temperature, so the resistance should decrease with the increase of the temperature. In contrast, when there is a strong enough filament connecting the top and bottom electrodes, ohmic conduction can be observed. And the conductive filament here is usually metallic with the resistance increasing with the temperature [112]. For the device in this work, the ohmic conduction with weak temperature dependence could be attributed to the very small activation energies of the carrier conduction in the oxygen vacancy based conductive filament.

Unlike the LRS, the current transport mechanism has electric field dependence for HRS. A linear relationship between the current and voltage is observed at low electric field for HRS, as shown in Fig. 3.7(a). Fig. 3.7(b) shows the ohmic conduction behavior of the HRS with the voltage ranging from 0 V to 0.2 V under different temperatures. In contrast to the temperature independent behavior of the LRS, the current here increases with the increase of the temperature, which is quite similar to the semiconductor's current-temperature property. For this ohmic conduction, the current can be written as:

$$I = AqN_c\mu\frac{V}{d}\exp\left(\frac{-E_a}{kT}\right) \quad (3.1)$$

Fig. 3.6. (a) I - V characteristics of the LRS under various temperatures. (b) The current read at 0.1 V versus temperature. The trend line is for guiding eyes only.

where I is the current, q is the electron charge, A is the device size, N_c is the effective density states in the conduction band, μ is the electronic mobility in insulator, V is the applied voltage, d is the film thickness, E_a is the activation energy, k is the Boltzmann constant, and T is the absolute temperature [113]. Fig. 3.7(c) shows the Arrhenius plot ($\ln(I)$ versus $1/kT$) of the HRS at the voltage of 0.1 V. The activation energy E_a , yielded from the slope of the Arrhenius plot, is about 0.286 eV. Based on the above discussion, the current conduction of the HRS at low electric field can be attributed to the electron hopping from one defect to

another by thermal excitation. This excitation process will be enhanced at higher temperature, which leads to a higher current level, as shown in Fig. 3.7(b).

Fig. 3.7. (a) I - V characteristic of the HRS under room temperatures. (b) I - V characteristics of the HRS at low electric field under the temperature ranging from 313 K to 413 K. (c) Arrhenius plot of the HRS current at a low electric field. The current was measured at 0.1 V.

When the applied voltage is high, the I - V curve departs from the ohmic conduction, as shown in Fig. 3.7(a). The current transport of HRS at high electric field can be explained by Poole-Frenkel emission model, which is a mechanism of bulk effect. For the HfO_x-based RRAM here, the Coulombic traps in Poole-Frenkel emission model should be oxygen vacancies, which are neutral when filled with electrons and positive charged when empty. The Poole-Frenkel emission I - V relationship can be described as [114]:

$$I = AC \frac{V}{d} \exp \left\{ -\frac{q}{kT} \left[\phi_{PF} - \sqrt{\frac{qV}{d\pi\epsilon_0\epsilon_i}} \right] \right\} \quad (3.2)$$

where A is the device area, C is a constant, d is the film thickness, q is the electron charge, $q\phi_{PF}$ is the depth of potential well, ϵ_0 is the vacuum permittivity and ϵ_i is the dynamic permittivity [114]. According to this equation, there should be a linear relationship between the $\ln(I/V)$ and $V^{1/2}$ for Poole-Frenkel emission model. And this relationship is confirmed for the HRS at high electric field under the temperatures ranging from 313 K to 413 K, as shown in Fig. 3.8(a). As shown in Fig. 3.8(a), the current increases with the temperature, and this is also due to the enhanced thermal excitation effect, which is the same as the situation in low

electric field. The activation energy of Poole-Frenkel emission, $q(\phi_{PF} - \sqrt{\frac{qV}{d\pi\epsilon_0\epsilon_i}})$ can be obtained from the Arrhenius plots ($\ln(I/V)$ versus $1000/T$), as shown in Fig. 3.8(b). The slope of every fitting line in Fig. 3.8(b) corresponds to the activation energy of HRS under different voltages. As can be seen in Fig. 3.8(c), the activation energy has a linear dependence on the square root of voltage and it has a decreasing trend with the applied voltage. In the typical Poole-Frenkel emission model, higher voltage results in more serious barrier lowering effect. Thus, less thermal activation energy is needed for the electrons to escape from the Coulombic traps, so the activation energy will decrease with the applied voltages. In addition, the depth of the potential well ($q\phi_{PF}$) that is extracted from the intercept of the fitting line in Fig. 3.8(c)

is about 0.328 eV. Based on the above discussion, the current transport of the HRS at high electric field can be described as Poole-Frenkel emission model. The oxygen vacancies act as Coulombic traps inside the HfO_x layer. When temperature increases, the probability for the trapped electrons to escape from the traps will increase, so the conductivity of the material will be increased. Meanwhile, when there is a larger voltage applied to the device, a smaller resistance can be expected due to the barrier lowering effect.

Fig. 3.8. Current conduction of the HRS at high electric field. (a) The Poole-Frenkel emission plots of $\ln(I/V)$ vs $V^{1/2}$ for the HRS under various temperatures. (b) The Arrhenius plots of $\ln(I/V)$ vs $1000/T$ for HRS under different voltages. (c) The activation energy as a function of the square of the voltage.

3.6 Multibit storage

High capacity storage is important for next-generation memory devices. Compared with the device scaling method, multibit storage realized by controlling the switching operation conditions is an easier way to increase the storage capacity in one RRAM cell. For the TiN/HfO_x/Pt RRAM cell in this work, the multibit storage can be achieved by changing the compliance current (CC) or reset stop voltage (V_{stop}). As shown in Fig. 3.9, the LRS can be tuned by changing the compliance current during the set process. With the increase of the compliance current, more oxygen ions will be knocked out of the lattice and react with the TiN top electrode, which strengthens the oxygen vacancy based conductive filament. Thus, a decreasing trend can be expected for the LRS with the increase of the compliance current, as shown in Fig. 3.9(b).

Fig. 3.9. (a) *I-V* characteristics of the HfO_x-based RRAM device obtained with different compliance currents. (b) Statistical distributions of HRS and LRS obtained from 20 switching cycles under different compliance currents.

As shown in Fig. 3.10, the HRS can be tuned by changing the reset stop voltage during the reset process. With the increase of the magnitude of the reset stop voltage, more oxygen ions move back to the HfO_x switching layer to eliminate the oxygen vacancies inside the conductive filament, which enhances the rupture of the conductive filament. Thus, an

increasing trend can be expected for the HRS with the increase of the reset stop voltage, as shown in Fig. 3.10(b).

Fig. 3.10. (a) I - V characteristics of the HfO_x-based RRAM device obtained with different reset stop voltages. (b) Statistical distributions of HRS and LRS obtained from 20 switching cycles under different reset stop voltages.

3.5 Study of the multilevel high-resistance states by impedance spectroscopy

Resistive switching random access memory based on metal oxides like Al₂O₃, ZnO, NiO_x, TiO₂, and Cu_xO is promising in the application of next-generation non-volatile memory due to its simple structure, low power consumption, high read/write speed, and good reliability [115-118]. Recently, multilevel resistance states in RRAM devices have been demonstrated to increase the storage density of an RRAM device [119,120]. Until now, most of the research studies were focused on the performance improvement and reliability of the multibit storage, there are relatively few studies on the mechanism for the multilevel resistance states of RRAM device. In this work, impedance spectroscopy is employed to investigate the multilevel high resistance states in TiN/HfO_x/Pt RRAM structure. Impedance spectroscopy is

a powerful tool to examine the conduction properties of dielectric thin films, making it suitable for resistive switching property study [121,122]. For the TiN/HfO_x/Pt RRAM structure used in this work, the multilevel high resistance states may be attributed to the different rupture degrees of the conductive filament, which is hard to be detected by the microscopic techniques such as transmission electron microscopy and scanning probe microscopy. However, through the analysis of the impedance measurement, we have been able to obtain the information about the redox reaction relating to the change of TiON interfacial layer and rupture of the conductive filament for different high resistance states.

Fig. 3.11(a) shows the typical bipolar resistive switching behavior of the TiN/HfO_x/Pt RRAM structure at different reset stop voltages (V_{stop}) ranging from -1.3 V to -2.0 V. Multilevel high resistance states can be achieved by varying V_{stop} . Fig. 3.11(b) shows the values of the high resistance states created with different V_{stop} (read at 0.1 V) and the corresponding set voltages (V_{set}). As observed in Fig. 3.11(b), the resistance of the device increases with $|V_{stop}|$. Based on the conductive filament model, when a positive voltage is applied to the TiN top electrode, the oxygen atoms inside the HfO_x layer will be knocked out of the lattice and become oxygen ions to react with the TiN electrode to form TiON [123]. The formation of TiON could result from the replacement of nitrogen by oxygen or defects that favor the incorporation of oxygen in the cation sub-lattice [124]. When the generated oxygen vacancies form a strong enough conductive filament to connect the top and bottom electrodes, the device will be set to a low resistance state. For the reset process, a negative voltage is applied to the top electrode, and the oxygen ions will move back to eliminate the oxygen vacancies, breaking the conductive filament; as a consequence, a leakage gap in the oxide is formed between the top electrode and the residual filament, as schematically illustrated in the inset of Fig. 3.12. When V_{stop} is of a larger magnitude, more oxygen ions will move back to the HfO_x layer to eliminate the oxygen vacancies, which will widen the

gap between the top electrode and the residual conductive filament, and thus the resistance value will increase due to the gap widening [125]. In this case, the V_{set} during the following set process also increases with the magnitude of V_{stop} , as demonstrated in the Fig. 3.11(b). It is because that a larger V_{set} is needed to rebuild the conductive filament for a wider leakage gap.

Fig. 3.11. (a) Bipolar $I-V$ curves of TiN/HfO_x/Pt RRAM device. Multilevel high resistance states can be achieved with different V_{stop} . (b) The values of the high resistance states created with different V_{stop} (read at 0.1 V) and the corresponding V_{set} .

The above arguments could be verified with the impedance measurement. The complex impedance measurement is conducted after the reset process by applying a 30 mV small AC signal in the frequency range of 20 Hz to 2 MHz without DC bias. The scatter plot in Fig. 3.12 shows the complex impedance spectra of the high resistance state after reset operation with the V_{stop} of -1.3 V. The approximately semicircle shape of the Nyquist plots ($-Z''$ VS Z') indicates that the high resistance state can be modelled as a parallel connection of a resistor and a capacitor in series with some resistors, as shown in the inset of Fig. 3.12. The RRAM devices with other sizes ($5 \times 5 \mu\text{m}^2$ and $8 \times 8 \mu\text{m}^2$) are also tested, and similar semicircle shapes of the Nyquist plots are observed (not shown here). This indicates that device size in the range has no influence on the equivalent circuit. The impedance of the equivalent circuit can be described with

$$Z = R_s + R_f + R_c + \frac{R}{1 + \omega^2 R^2 C^2} - j \frac{\omega R^2 C}{1 + \omega^2 R^2 C^2} \quad (3.3)$$

where Z is the complex impedance, ω is the angular frequency, R_s , R_f and R_c are the equivalent series resistance for the TiON interfacial layer, residual conductive filament and measurement connections, respectively, and R and C are the equivalent parallel resistance and capacitance of the leakage gap, respectively. As discussed above, the redox reaction between the TiN electrode and the oxygen ions during the set process results in a TiON interfacial layer, which is more resistive than the pure TiN electrode. Though the series resistance should be the sum of the resistance of the TiON interfacial layer, residual filaments and measurement connections, the last two items can be neglected because of their much lower values [126]. Therefore, Eq. 3.3 can be rewritten as

$$Z = Z' + jZ'' = R_s + \frac{R}{1 + \omega^2 R^2 C^2} + j \left(-\frac{\omega R^2 C}{1 + \omega^2 R^2 C^2} \right) \quad (3.4)$$

where Z' and Z'' are the real part and imaginary part of the complex impedance, respectively. The fitting with Eq. 3.4 to the measurement data is shown in Fig. 3.12. An excellent

agreement between the fitting and measurement is achieved, which indicates that the equivalent circuit shown in the inset of Fig. 3.12 can well describe the electrical characteristic of the RRAM structure. The fitting yields the values of 5336 Ω , 8741 Ω and 9.81 pF for R_s , R and C , respectively. With the obtained R_s value, one may estimate the resistivity ρ of the TiON interfacial layer with $\rho = (A/t_{\text{TiON}})R_s$, where t_{TiON} is the thickness of the interfacial layer, and the device area $A = 4 \mu\text{m}^2$. Under the assumption that t_{TiON} is 5 nm [127,128], the resistivity is estimated to be $\sim 400 \Omega\cdot\text{cm}$, which is within the reported resistivity range of TiON films [129].

Fig. 3.12. Complex impedance spectra of the high resistance state obtained with the V_{stop} of -1.3 V. The curve is the best fitting based on Eq. 3.4. The inset shows the schematic illustration of the conductive filament and the equivalent circuit for high resistance state.

To examine the behavior of different high resistance states, we conducted the complex impedance measurement after each reset process at different V_{stop} , and the result is shown in Fig. 3.13(a). The Nyquist plots of all V_{stop} can be well fitted with Eq. 3.4, which indicates that all the high resistance states can be modelled with the equivalent circuit shown in the inset of Fig. 3.12. The values of the components in the equivalent circuit are shown in Fig. 3.13(b).

The R_s value has an obvious decreasing trend when the V_{stop} changes from -1.3 V to -2.0 V. Since TiON is more resistive than pure TiN, the decrease of the R_s means more TiON is reduced to TiN for a larger $|V_{stop}|$. The parallel RC element represents the leakage gap between the top electrode and the residual conductive filament, and the modulation of the gap width is responsible for the changes in the R and C values. As shown in Fig. 3.13(b), the R value increases with the increase of $|V_{stop}|$, which means the width of the leakage gap gradual-

Fig. 3.13. (a) Complex impedance spectra of different high resistance states obtained with different $|V_{stop}|$. The inset in (a) shows the enlarged complex impedance spectra with the V_{stop} of -1.3 V, -1.6 V and -1.8 V. (b) The values of R_s , R and C as a function of $|V_{stop}|$.

-ly increases. It is reasonable to argue that the recombination of the oxygen vacancies with the oxygen ions supplied from the TiON layer or even the surrounding HfO_x layer is enhanced as the V_{stop} changes from -1.3 V to -2.0 V. It is worth noting that R_s and R have an opposite evolution tendency, while the change of the DC resistance, shown in Fig. 3.11(b), is consistent with the evolution of R because the R value is much larger than the R_s value. The capacitance of the RC element should be inversely proportional to the width of the leakage gap between the top electrode and the residual filament, being similar to the situation of a parallel plate capacitor; thus the decrease in the C value with $|V_{stop}|$ suggests that a larger $|V_{stop}|$ results in a wider leakage gap. Therefore, both dependence trends of R and C on $|V_{stop}|$ suggest that the leakage gap width increases with $|V_{stop}|$, which explains the increase of the DC resistance with $|V_{stop}|$ as shown in Fig. 3.11(b).

Fig. 3.14. $\ln(R)$ versus $1/C$.

C can be described with $C = \epsilon_r \epsilon_0 A / t_{ox}$, where ϵ_0 is the permittivity in vacuum, and ϵ_r and t_{ox} are the dielectric constant and thickness of the leakage gap, respectively; and R can be assumed to be $R = R_0 \exp(\alpha t_{ox})$, where R_0 and α are two constants as it has been suggested by Monte Carlo simulation that R has an exponential dependence on t_{ox} [130,131]. Under the above assumptions, one may find the simple relationship between R and C as follows

$$\ln R = \ln R_o + \frac{\varepsilon_o \varepsilon_r \alpha A}{C} \quad (3.5)$$

The linear relationship between $\ln(R)$ and $1/C$ predicted by Eq. 3.5 roughly agrees with the experimental result, as shown in Fig. 3.14.

To examine the influence of DC bias on the complex impedance measurement, a positive voltage ranging from 0 V to 0.25 V was superimposed to the AC signal during the impedance measurement, and the complex impedance spectra of the high resistance state under different positive DC biases are shown in Fig. 3.15(a). The semicircle shape of all the Nyquist plots indicates that the DC bias has little influence on the equivalent circuit of the high resistance state. The values of R_s , R and C obtained from the fitting as a function of the DC bias are shown in Fig. 3.15(b). Only the R has an obvious decreasing trend with the increase of DC bias. The little change of both R_s and C indicates that the redox reaction at the TiN/HfO_x interface is not significant under the influence of a small positive DC bias and the leakage gap should change little or remain unchanged. Therefore the change of the R value cannot originate from the leakage gap modulation effect. Previous studies on the current transport in HfO_x-based RRAM device show that Poole-Frenkel emission model can well describe the conduction of the high resistance state; and the oxygen vacancies inside the HfO_x layer could act as the Coulombic traps in the Poole-Frenkel emission model [132,133]. When a bias is applied to the switching layer, one side of the barrier height of the Coulombic traps will be reduced, and the probability for the electrons escaping from the trap well by thermal emission increases, thus the R value will decrease with increasing DC bias [114]. The decrease of R with DC bias is indeed observed in Fig. 3.15(b). This is also consistent with the experimental result shown in Fig. 3.15(c) that the DC resistance of the high resistance state decreases with the read voltage (V_{read}).

Fig. 3.15. (a) Complex impedance spectra of the high resistance state under different positive DC biases. (b) The values of R_s , R and C as a function of the DC bias. (c) The resistance value of the high resistance state as a function of V_{read} .

In conclusion, impedance spectroscopy is a useful technique to study multilevel high resistance states in HfO_x-based RRAM device. The analysis of complex impedance suggests that the redox reaction at the TiN/HfO_x interface and the modulation of the leakage gap should be responsible for the changes in the parameters of the equivalent circuit of the RRAM device. The leakage gap widening effect is shown to be the main reason for the higher resistance value associated with a larger $|V_{stop}|$. Both R_s and C show little change with DC bias; however, R decreases with the DC bias, which can be attributed to the barrier lowering effect of the Coulombic trap well in the Poole-Frenkel emission model.

3.6 Set speed-disturb dilemma and rapid statistical prediction methodology

Resistive switching random access memory has been studied for years due to its excellent performance as the non-volatile memory. However, some problem still restricts its practical application, one of which is the HRS disturbance. The HRS disturbance happens when a read process is executed. Generally, the read voltage is with same polarity but smaller magnitude as the set voltage in a bipolar RRAM device. To avoid the mis-operation during the read process for the HRS, a small read voltage is preferred to achieve a long disturb time. In contrast, for the set/read process, a large voltage is desirable for a high speed operation. The different requirement between disturb time and set speed for the magnitude of voltage is called the set speed-disturb dilemma.

The set behavior is quite similar to the breakdown phenomenon in the dielectric thin films, which can be explained with the analytical percolation model [134]. Both the constant voltage stress (CVS) and ramped voltage stress (RVS) methods are used to study this set speed-disturb dilemma.

3.6.1 Sample fabrication and device structure

To study the speed-disturb dilemma, the TiN/Ti/HfO_x/TiN structured RRAM device was fabricated with the following sequence. Firstly, a 500 nm SiO₂ film was deposited on an 8-inch *p*-type Si wafer by plasma-enhanced chemical vapor deposition to prevent the leakage during the switching operation. Then, a 100 nm TiN layer was deposited by DC sputtering to form the bottom electrode on the SiO₂ film. Subsequently, a 10 nm HfO_x layer was deposited by atomic layer deposition on the bottom electrode. Finally, a 100 nm TiN/10 nm Ti layer was deposited onto the HfO_x layer using DC sputtering and patterned to form the top electrode with the area of about 4 μm². Fig. 3.16 shows the diagram of the TiN/Ti/HfO_x/TiN RRAM cell. A Keithley 4200 semiconductor characterization system was used to characterize the resistive switching properties of the device.

Fig. 3.16. The schematic illustration of the TiN/Ti/HfO_x/TiN structured RRAM cell.

3.6.2 CVS prediction method

In this report, TiN/Ti/HfO_x/TiN RRAM cell, as shown in Fig. 3.16, is chosen to conduct the CVS and RVS test. In the CVS test, a constant voltage is applied to the RRAM cell to change device from HRS to LRS. To prevent the hard breakdown during the operation, a compliance current of 1 mA is applied. Fig. 3.17 shows the current-time traces of the

TiN/Ti/HfO_x/TiN RRAM cell with the constant bias of 0.38 V. After each CVS set process, the device is reset back to HRS with the same reset stop voltage to promise all the CVS set operation begins from the same HRS.

Fig. 3.17. The current-time traces for CVS method at 0.38 V.

According to the analytical percolation model, the set time from CVS method and set voltage from RVS method have the statistical Weibull distribution. For the CVS method, the relationship between the set time and constant stress voltage follows the power law dependence [135]. The cumulative failure probability (F_{CVS}) after stress time (t_{SET}) at a constant voltage (V_{CVS}) is defined as [134]:

$$F_{CVS}(t_{SET}, V_{CVS}) = 1 - \exp\left[-\left(\frac{t_{SET}}{t_{63\%}}\right)^\beta\right] \quad (3.6)$$

$$t_{63\%} = aV_{CVS}^{-n} \quad (3.7)$$

$$W_{SET} = \ln[-\ln(1-F)] = \beta[\ln(t_{SET}) - \ln(t_{63\%})] \quad (3.8)$$

where $t_{63\%}$ is the characteristic time at the 63rd failure percentile and β is the Weibull curve slope. The Eq. 3.7 shows the power law model in dielectric breakdown theory, and a is constant and n is the acceleration factor.

To investigate the statistical distribution of t_{SET} , 160 switching cycles are conducted for each constant voltage. Fig. 3.18(a) shows the t_{SET} distribution measured at the constant

voltages ranging from 0.36 V to 0.41 V. All the t_{SET} shows well Weibull distribution, which is in agreement with the Eq. 3.8. The β value extracted from the slope of Weibull plots is 0.63. According to the power law model, as shown in Eq. 3.7, $t_{63\%}$ and V_{CVS} should have a linear relationship in log scale as:

$$\ln(t_{63\%}) = -n \ln(V_{CVS}) \quad (3.9)$$

the $\ln(t_{63\%})$ values can be extracted from the intercepts of the Weibull distribution curves in Fig. 3.18(a). Fig. 3.18(b) shows the linear relationship between the $\ln(t_{63\%})$ and $\ln(V_{CVS})$, and acceleration factor n of 31 can be extracted from the slope of this curve.

Fig. 3.18. (a) The t_{SET} Weibull distribution measured at different constant voltages. (b) Power-law $\ln(t_{63\%})$ vs $\ln(V_{CVS})$ relationship obtained from CVS tests.

3.6.3 RVS prediction method

The set time obtained from CVS prediction method lies in a wide range from 10^{-1} s to 10^2 s, as shown in Fig. 3.17. This high time-cost testing method severely restricts the research on the HRS disturbance especially at low CVS voltage. Compared with the CVS method, the RVS is an equivalent prediction method with quite fast speed. Fig. 3.19 shows the typical current-voltage traces for RVS method with a ramp rate of 1 V/s, which is essentially a bipolar resistive switching curve with an accurately controlled ramped rate.

Fig. 3.19. The current-voltage traces for RVS method with a ramp rate of 1 V/s.

The RVS essentially is the sum of linearly ascending stress voltages with the same duration. The relationship between the CVS and RVS method can be described with:

$$t_{SET} = \frac{V_{CVS}}{RR(n+1)} \left(\frac{V_{SET}}{V_{CVS}} \right)^{n+1} \quad (3.10)$$

$$\ln[-\ln(1-F)] = \beta_{RVS} [\ln(V_{SET}) - \ln(V_{63\%})] \quad (3.11)$$

where V_{SET} is the set voltage of RVS method, RR is the ramp rate, β_{RVS} is the Weibull distribution slope, $V_{63\%}$ is the characteristic voltage at the 63rd failure percentile [134]. By substituting the t_{SET} in Eq. 3.8 by Eq. 3.10, we can get an expression as:

$$\ln[-\ln(1-F)] = \beta(n+1)[\ln(V_{SET}) - \ln(V_{63\%})] \quad (3.12)$$

Compared the Eq. 3.12 with Eq. 3.11, we can get:

$$\beta_{RVS} = \beta(n+1) \quad (3.13)$$

$$V_{63\%} = [t_{63\%} RR(n+1) V_{CVS}^n]^{\frac{1}{n+1}} \quad (3.14)$$

To investigate the statistical distribution of V_{SET} , more than 160 DC sweep cycles are conducted with four different ramp rates. Fig. 3.20(a) shows the Weibull distribution of set voltage with different ramp rates, which is consistent with the Eq. 3.12. The β_{RVS} value obtained from the slope of the Weibull curves is about 21. According to Eq. 3.13 and the β value obtained from the CVS method, $n+1$ should be around 33.33. To prove the accuracy of $n+1$ value, we try to collect this value from Eq. 3.14. Fig. 3.20(b) shows the linear relationship between $\ln(V_{63\%})$ and $\ln(RR)$, and the $n+1$ value extracted from the slope is about 33, which is in agreement with the $n+1$ value calculated from Eq. 3.13.

Fig. 3.20. (a) V_{SET} Weibull distribution measured with different ramp rates. (b) $\ln(V_{63\%})$ versus $\ln(RR)$.

According to Eq. 3.10, the t_{SET} distribution can be converted from the parameters obtained from the RVS method. Excellent agreement between converted t_{SET} distribution and measured CVS data at 0.42 V can be seen in Fig. 3.21, which indicates that the RVS method is equivalent to the CVS method with fast speed and low cost.

Fig. 3.21. t_{SET} Weibull distribution measured at 0.42V (symbol) and the converted t_{SET} Weibull distribution from RVS method with different ramp rates (line).

3.6.4 Set speed-disturb dilemma

As discussed in the beginning of chapter 3.6, a relatively high voltage is preferred for both set and read operations in RRAM devices to improve the operation speed and reduce the sensing noise [135]. However, high read voltage may cause the HRS disturbance problem, as shown in Fig. 3.17. So a dilemma exists between the set speed and the disturbance of HRS. Both CVS and RVS methods can be used to estimate the disturb time and set time of the RRAM device under a constant voltage. The 1 ppm failure probability (FP) is chosen as the criteria to study the set speed-disturb dilemma, but it has different meanings for these two situations. For disturb time, 1 ppm FP means that the probability for the RRAM device to be changed from HRS to LRS under a read voltage is only 1 ppm, so the cumulative failure probability (CDF) for this event is 1 ppm. On the other hand, for set time, 1 ppm FP means the probability for the RRAM device unable to be changed from HRS to LRS under a constant stress voltage is only 1ppm, so the CDF for this event is 1 - 1 ppm.

For the CVS method, the relationship between disturb time (t_{DIS}) and disturb voltage (V_{DIS}) or set time (t_{PRO}) and set voltage (V_{PRO}), shown as symbols in Fig. 3.22, can be obtained

through Eq. 3.7 and 3.8. For RVS method, substituting the V_{SET} of Eq. 3.10 into Eq. 3.11, we can get the expressions as follows [134]:

$$V_{DIS} = V_{63\%} \left[\ln \left(\frac{1}{1-FP} \right) \right]^{\frac{1}{\beta_{RVS}}} \left(\frac{1}{RRt_{DIS}} \right)^{\frac{1}{n}} \left(\frac{1}{n+1} \right)^{\frac{1}{n}} \quad (3.15)$$

$$V_{PRO} = V_{63\%} \left[\ln \left(\frac{1}{1-FP} \right) \right]^{\frac{1}{\beta_{RVS}}} \left(\frac{1}{RRt_{PRO}} \right)^{\frac{1}{n}} \left(\frac{1}{n+1} \right)^{\frac{1}{n}} \quad (3.16)$$

According to Eq. 3.15 and 3.16, the relationship for t_{DIS} versus V_{DIS} and t_{PRO} versus V_{PRO} are shown as lines in Fig. 3.22(a) and (b), respectively. With Fig. 3.22(a), we can find the disturb time under any voltage with 1 ppm FP. Meanwhile, we can get the set time under any voltage with 1ppm FP from Fig. 3.22(b). The overlap of symbols and lines in Fig. 3.22(a) and (b) indicates the feasibility to use rapid RVS prediction method to replace the conventional CVS method.

Due to the requirement for high speed read/write operation and high level stability, set speed-disturb time dilemma is studied in this work. Compared with the CVS method, RVS is proved to be an equivalent method with faster speed and low cost. And both the disturb time and set time under a specific voltage with a decided failure probability can be estimated by this fast prediction methodology.

Fig. 3.22. (a) t_{DIS} versus V_{DIS} (b) t_{PRO} versus V_{PRO} at 1ppm failure probability. Symbols represent the CVS prediction method. Lines represent the RVS prediction method.

3.7 HfO_x-based RRAM device integrated with the 180 nm Cu BEOL process platform

Resistive switching random access memory based on metal oxides like Al₂O₃, ZnO, NiO_x, TiO₂, IGZO, TaO_x and Cu_xO is one promising candidate for the next-generation non-volatile memory due to its simple structure, low power consumption, high read/write speed and good reliability. Much work has been done on the study of the switching mechanism or

optimization of the switching performance of the RRAM devices. However, most of the RRAM devices are fabricated with traditional aluminum (Al) interconnect technology, which greatly restricts the circuit performance due to its large resistance-capacitance effect. To overcome this problem, copper (Cu) as an interconnecting material came to the forefront and gained much attention due to its lower bulk resistivity, better heat dissipation, lower electromigration failure, and better thermomechanical properties [136]. So in this work, we try to integrate the RRAM device with the 180 nm copper BEOL process platform. Regarding to the good switching performance and high compatibility with CMOS process, TiN/Ti/HfO_x/TiN stack is chosen as the switching cell in this work.

Fig. 3.23 shows the evolution of the device cross-sections during the fabrication of the HfO_x-based RRAM device in Cu BEOL process platform. Firstly, a 500 nm Cu layer was deposited on 8-inch Si wafer by electrochemical plating (ECP) and chemical mechanical polishing (CMP) processes, as shown in Fig. 3.23(a). Then, the hole for bottom via was defined by lithography and etched by dry etching process. Cu as the contact material was grown by ECP and CMP processes, as shown in Fig. 3.23(b). Subsequently, TiN/Ti/HfO_x/TiN RRAM cell was deposited by physical vapor deposition and patterned through lithography and dry etching processes, as shown in Fig. 3.23(c). Fig. 3.23(d) shows the open of contact holes for top via and bottom Cu layer. Finally, ECP and CMP processes were carried out to fill the contact holes with Cu, as shown in Fig. 3.23(e). The electrical properties of the RRAM devices were carried out using a Keithley 4200 semiconductor characterization system.

Fig. 3.23. Schematic diagrams showing the evolution of the device cross-sections during the fabrication of the HfO_x-based RRAM device in Cu BEOL process platform.

To study the resistive switching behaviors of the HfO_x-based RRAM device, *I-V* characteristics were carried out by DC sweep. At the beginning, a forming voltage is applied to change the device from fresh state to high conductive state, as shown in Fig. 3.24. After this, stable bipolar resistive switching behaviors can be obtained. To change the device from HRS to LRS, positive voltage is applied to the top Cu via with 1 mA compliance current, which is used to prevent the hard breakdown during the switching operation. In contrast, negative voltage can change the device from LRS to HRS without compliance current. To

study the reliability of the device, 80 consequent DC sweeping cycles are conducted, and no obvious change is observed for the I - V curves of different switching cycles, as shown in Fig. 3.24.

Fig. 3.24. Bipolar I - V curves of TiN/Ti/HfO_x/TiN RRAM device fabricated in the Cu BEOL process platform.

Fig. 3.25 shows the distribution of the transition voltages and resistance states of the 80 switching cycles. No obvious variation is observed for both HRS and LRS, as shown in Fig. 3.25(a), and the HRS/LRS ratio is stable at around $\times 10$, which is large enough to distinguish HRS and LRS in practical memory application. Moreover, the set voltages and reset voltages also show little fluctuation and small magnitude corresponding to low power consumption during the switching operation. Fig. 3.26 shows the retention behaviors of the HRS and LRS at 25 °C. Both the HRS and LRS exhibit little change within the time limit (10^5 s), which can prove the non-volatile property of the RRAM device. Based on the above discussion, the HfO_x-based RRAM device fabricated in Cu BEOL process platform shows good reliability and stability, which makes it a good choice for memory application.

In this work, we successfully fabricated the HfO_x-based RRAM device in Cu BEOL process platform, which gradually replaces the traditional aluminum interconnect technology

in semiconductor industry. With good switching performance of the RRAM device, the Cu BEOL process is proved to be a reliable technology for the fabrication of this next-generation memory device.

Fig. 3.25. (a) Distribution of HRS and LRS (read at 0.1 V). (b) Distribution of V_{set} and V_{reset} .

Fig. 3.26. Retention behaviors of the HRS and LRS at 25°C.

3.8 Summary

In summary, HfO_x-based RRAM device has been fabricated for non-volatile memory application in this work. Stable bipolar resistive switching behaviors with tight distributions for resistance states and transition voltages are observed under both room temperature and elevated temperature. The transition between HRS and LRS can be attributed to the connection and rupture of the oxygen vacancy based conductive filament. Both the current conduction mechanisms for LRS and HRS have been studied by *I-V* characteristics under different temperatures. The LRS shows ohmic conduction with little temperature dependence, which could be attributed to the very small activation energies of the carrier conduction in the oxygen vacancy based conductive filament. For HRS, when the applied electric field is low, the current transport follows the ohmic conduction; when the applied electric field is high, Poole-Frenkel emission model can be used to describe the current conduction. Multibit storage is realized in one RRAM cell by controlling either the compliance current in the set process or reset stop voltage in the reset process. Impedance spectroscopy has been used to study the multilevel high resistance states in the HfO_x-based RRAM device. It is shown that

the high resistance states can be described with an equivalent circuit consisting of the major components R_s , R , and C corresponding to the series resistance of the TiON interfacial layer, the equivalent parallel resistance and capacitance of the leakage gap between the TiON layer and the residual conductive filament, respectively. These components show a strong dependence on the stop voltage, which can be explained in the framework of oxygen vacancy model and conductive filament concept. Both the CVS and RVS methods have been used to study the speed-disturb time dilemma. Compared with CVS, RVS is proved to be an equivalent method with faster speed and low cost. The HfO_x-based RRAM device was also successfully fabricated with 180 nm Cu BEOL process platform. The RRAM device in this Cu interconnection technology shows the similar bipolar resistive switching performance as in the conventional Al interconnection technology.

Chapter 4 RESISTIVE SWITCHING IN P-TYPE NICKEL OXIDE/N-TYPE INDIUM GALLIUM ZINC OXIDE THIN FILM HETEROJUNCTION STRUCTURE

4.1 Introduction

Resistive switching random access memory is promising in the application of next-generation non-volatile memory due to its simple structure, low power consumption, high read/write speed and good reliability [137]. In the last few years, most of the studies were focused on the RRAM devices with metal-insulator-metal structure, in which resistive switching mainly occurred at the interfaces between the insulator layer and the metal electrodes. Despite of the achievements made so far, challenges like switching speed, energy, and cycling endurance still exist in the RRAM devices based on a single oxide layer [138]. Recent studies indicate that constructing a heterojunction composing of two oxide layers can improve the device performance such as cycling and scaling potential [138-141]. In addition, the properties like carrier concentration or thickness of each layer in the heterojunction can be tuned during the device fabrication, which offers more freedom for the device optimization compared to the single layer RRAM devices. As demonstrated by Yang *et al.*, the resistive switching characteristics of the RRAM devices based on multilayer oxide structures can be systematically controlled by tailoring each layer, thus greatly improving the degrees of

control and flexibility for optimized device performance [138]. Up to now, the reports on the heterojunction RRAM devices made of oxides with different carrier types are limited, and most of the reported devices are based on the perovskite oxides or ferroelectric materials, not the simple transition metal oxides [142-145]. Resistive switching in *p*-NiO/*n*-GaO and *p*-NiO/*n*-Mg_{0.6}Zn_{0.4}O heterojunction structures have been demonstrated, showing the good potential in non-volatile memory applications [146,147].

In this chapter, we have fabricated a *p-n* heterojunction RRAM device based on *p*-type nickel oxide (*p*-NiO) and *n*-type indium gallium zinc oxide (*n*-IGZO) thin films. The as-fabricated device works as a normal *p-n* junction. After the forming process with a reverse bias applied to the *p-n* junction, stable bipolar resistive switching is observed. Multibit storage is achieved by controlling the compliance current or reset stop voltage during the resistive switching operation. As the *n*-IGZO thin film is widely used as the channel material for thin film transistors (TFTs), there is a potential that the RRAM device can be integrated with the IGZO TFT to form the “one-transistor/one-resistor” (1T1R) RRAM structure, which could be suitable for NOR flash-like and embedded nonvolatile memory applications where high reliability and short latency are important [148]. In this work, a study of the current conduction at the different resistance states of the heterojunction structure at elevated temperatures has been conducted also.

4.2 Experiment and device fabrication

The *p*-NiO/*n*-IGZO heterojunction RRAM device was fabricated with the following sequence. Firstly, IGZO thin film with the thickness of 16 nm was deposited on a commercial ITO glass by radio frequency (RF) magnetron sputtering of an IGZO target in mixed Ar/O₂ ambient. Circular patterns with the diameter of 100 μm were defined by lithography process.

Then, a 23 nm NiO thin film was deposited by RF sputtering of a NiO target in mixed Ar/O₂ ambient. Different levels of carrier concentrations in the NiO and IGZO layers can be achieved by introducing different amount of O₂ gas during the sputtering deposition [149,150]. With more O₂ gas introduced during the sputtering deposition, more nickel vacancies, which act as the acceptors, are created in the *p*-NiO thin films [149]; however, less oxygen vacancies, which act as the donors, are created in the *n*-IGZO thin films [150]. For examples, with the Ar partial pressure fixed at 3×10^{-3} Torr, a low carrier concentration in the order of $10^{16} - 10^{17} \text{ cm}^{-3}$ (the actual value of the carrier concentration is hard to be measured accurately from the Hall effect measurement due to the relatively low conductivity of the oxide thin film) and a high carrier concentration in the order of 10^{19} cm^{-3} can be achieved for the *n*-IGZO thin film at the O₂ partial pressure of 3×10^{-4} and 0 Torr, respectively; the similar levels of low and high carrier concentrations can be achieved for the *p*-NiO thin film at the O₂ partial pressure of 0 and 2×10^{-4} Torr, respectively. The present study focuses on the low carrier concentration in the order of $10^{16} - 10^{17} \text{ cm}^{-3}$ for both the *p*-NiO and *n*-IGZO layers. After the growth of NiO layer, 15 nm Ni/100 nm Au layer was deposited by electron-beam evaporation to form the top electrode. The 15 nm Ni layer acts as the top electrode. The 100 nm Au layer acts as the protecting layer to prevent the oxidation of the Ni layer. Finally, lift-off process was carried out. The schematic structure of the device is illustrated in the inset of Fig. 4.1(a). Transmission electron microscopy (TEM) was used to examine the morphology of the heterojunction structure and measure the thicknesses of the deposited layers as well, as shown in Fig. 4.1(b). The forming process and electrical characterization were conducted with the Keithley 4200 semiconductor characterization system equipped with TRIO-TECH TC1000 temperature controller.

Fig. 4.1. (a) Schematic illustration of the heterojunction structure. (b) Cross-sectional TEM image of the heterojunction structure.

4.3 Bipolar resistive switching in the *p*-NiO/*n*-IGZO thin film heterojunction structure

We first examined whether there is resistive switching in the NiO and IGZO layers themselves using a simple MIM structure with a single oxide layer (i.e., either the NiO layer or IGZO layer) prior to the study on the resistive switching in the *p*-NiO/*n*-IGZO heterojunct-

Fig. 4.2. *I-V* characteristics of (a) Au/Ni/NiO/ITO, (b) Au/Ni/IGZO/ITO, and (c) Au/Ni/*p*-NiO/*n*-IGZO/ITO structures.

-ion. As shown in Fig. 4.2(a) and (b), for the Au/Ni/NiO/ITO and Au/Ni/IGZO/ITO structures, respectively, both structures exhibit symmetric *I-V* characteristic and no resistive switching behavior. Both structures exhibit a stable low resistance; e.g., the resistance at 1.5 V is 33 Ω and 49 Ω for the Au/Ni/NiO/ITO and Au/Ni/IGZO/ITO structures, respectively. The stable low resistance of the structures, which is due to the low resistivity and the thin thickness of the NiO or IGZO layer, makes it difficult to trigger a resistive switching. Thus, the situation here is different from that of the NiO or IGZO-based RRAM devices in other reports [151-153]. With the formation of the *p*-NiO/*n*-IGZO heterojunction, however, the Au/Ni/*p*-NiO/*n*-IGZO/ITO structure shows an obvious *p-n* junction behavior with the

rectification ratio of 10^3 at the bias voltage of ± 1.5 V, as shown in Fig. 4.2(c). The resistance of the structure is $5 \times 10^9 \Omega$ at -1.5 V and $3.3 \times 10^6 \Omega$ at +1.5 V. In the voltage range of -1.5 - +1.5 V, the structure exhibits no resistive switching; and its *I-V* characteristic is repeatable in the repeated *I-V* measurements.

The Au/Ni/*p*-NiO/*n*-IGZO/ITO structure with the *p-n* junction behavior can be turned to a resistive switching device by the forming process, i.e., applying a sufficiently large reverse bias to the device to cause a “breakdown” in the *p-n* junction. As shown in Fig. 4.3(a), when the voltage applied to the *p-n* junction reaches about -5 V, a sharp increase in the reverse bias current is observed. After the forming process, the resistance of the structure measured at a reverse bias drops drastically; e.g., at the measuring voltage of -0.1 V, the resistance after the forming process is about 6 orders lower compared to the virgin resistance state (VRS) before the forming process. As can be observed in Fig. 4.3(b), after the forming process, stable bipolar resistive switching behavior can be achieved in the heterojunction. By applying a positive voltage with a compliance current of 0.8 mA, the device can be set from a HRS to a LRS; by applying a negative voltage without compliance current, the device can be reset from LRS to HRS. In contrast to the structure before the forming process, the device shows no rectification behavior for both HRS and LRS. The average values of the set voltage (V_{set}), reset voltage (V_{reset}), and resistances of the HRS and LRS for the first 100 resistive switching cycles are 0.73 V, -0.48 V, $\sim 5 \times 10^4 \Omega$, and $\sim 600 \Omega$, respectively. It should be pointed out that the above switching parameters are affected by the carrier concentrations of the NiO and IGZO layers, which may offer more freedom for tailoring the device for a specific application. For example, the corresponding V_{set} , V_{reset} , and resistances of the HRS and LRS are 0.88 V, -0.73 V, $\sim 3.5 \times 10^3 \Omega$, and $\sim 1.7 \times 10^3 \Omega$, respectively, for the RRAM structure with the higher carrier concentration in both the NiO and IGZO layers (both in the order of 10^{19} cm^{-3}), as shown in Fig. 4.3(c).

Fig. 4.3. (a) The forming process and first reset/set process. (b) Bipolar *I*-*V* characteristics of the Au/Ni/*p*-NiO/*n*-IGZO/ITO resistive switching device after a forming process. (c) Bipolar *I*-*V* characteristics of the Au/Ni/*p*-NiO/*n*-IGZO/ITO resistive switching device with a higher carrier concentration in both the NiO and IGZO layers (both in the order of 10^{19} cm^{-3}).

To study the endurance characteristics of the RRAM device, consequent DC sweeping test was conducted. As shown in Fig. 4.3(b), no obvious cycle-to-cycle variation is observed in the *I*-*V* curves of different switching cycles, indicating good stability and repeatability of resistive switching. The device exhibits tight distributions of the switching parameters including the resistance of HRS and LRS, V_{set} , and V_{reset} within 5000 switching cycles, as shown in Fig. 4.4. The resistance ratio of HRS/LRS is larger than 20 for all the switching cycles, which is large enough for practical memory application. Both the magnitudes of V_{set} and V_{reset} are smaller than 1 V yielding a low power consumption during the switching

operation. Meanwhile, as shown in Fig. 4.4(c) for the retention test, there is no significant degradation for both HRS and LRS in the measurement duration of up to 10^5 s, showing the non-volatile capability of the heterojunction RRAM device.

Fig. 4.4. (a) Distributions of the LRS/HRS resistance measured at 0.1 V for 5000 switching cycles. (b) Distributions of the set/reset voltage for 5000 switching cycles. (c) Retention test at room temperature (the resistance is measured at 0.1 V).

4.4 Resistive switching mechanism of the heterojunction structure

Our experiment shows that the resistive switching is observed only after a *p*-NiO/*n*-IGZO junction is formed and the junction is reversely biased with a sufficiently large voltage (i.e., the forming process). This suggests that the resistive switching is related to some processes occurring in the depletion region of the *p-n* junction. The estimated width of the depletion region [221] under the reverse bias (~ -5 V) in the forming process is larger than the total thickness of the NiO and IGZO layers (~ 40 nm). This means that the depletion region touches both the top electrode and the bottom electrode under the reverse bias condition in the forming process. It has been proposed that oxygen vacancies (V_O) and Ni vacancies (V_{Ni}) (equivalent to excess oxygen ions O^{2-}) act as donors and acceptors in the *n*-IGZO and *p*-NiO thin films, respectively [154]. The depletion region is formed in the heterojunction with negatively charged acceptors (equivalent to O^{2-}) in the NiO side and positively charged donors (V_O^{2+}) in the IGZO side (Fig. 4.5(a)). It is known that the difference of oxide semiconductors from the conventional semiconductors is that the space charges like oxygen vacancies and excess oxygen ions are mobile under an electric field [146, 154-156]. When a negative forming voltage is applied, under the influence of the strong electric field ($\sim 10^6$ V/cm), the V_O^{2+} migrates across the NiO/IGZO interface into the NiO side [157]. As a result, a V_O^{2+} based conductive filament (CF) connecting the two electrodes is formed, as shown in Fig. 4.5(b), which makes the device into LRS with non-rectification. The reset process in our device occurs under the bias with the same polarity as the forming process, as shown in Fig. 4.3(a), being different from the conventional bipolar RRAM devices. A plausible explanation is given in the following. There is a high concentration of V_{Ni} (equivalent to excess oxygen

ion O^{2-}), which acts as acceptors in the *p*-NiO layer. As pointed out early, these excess oxygen ions are mobile under an electric field. It is believed that resistive switching may come from a thermal effect, an electronic effect, or an ionic effect [71]; and it has been also proposed that an electric field directs negative oxygen ions towards/away from a CF tip, thus favoring bipolar operation [158,159]. The bipolar switching observed in this work highlights the role of electric field. In the reset process, under the influence of the negative bias, the oxygen ions migrate in the *p*-NiO layer to passivate some of the V_O^{2+} in the filament ($V_O^{2+} + O^{2-} \rightarrow O_O$), breaking the conductive filament [160,161]; therefore, the device is reset from LRS to HRS, as shown in Fig. 4.5(c). In the set process under a positive bias, the O^{2-} trapped in the V_O^{2+} site in the *p*-NiO layer is detrapped, leading to the recovery of the conductive filament and thus the switching from HRS to LRS.

Fig. 4.5. Proposed mechanisms for forming, reset, and set processes.

4.5 Conduction mechanisms of LRS and HRS

To understand the physics behind the resistive switching phenomena, the current conduction of both LRS and HRS are examined with temperature dependent *I-V* measurement. The *I-V*

characteristic of the LRS was measured at various temperatures, as shown in Fig. 4.6. A linear I - V relationship with the slope of ~ 1.02 is observed, showing the ohmic conduction of LRS for the oxygen vacancy based conductive filament. Typically, metallic behavior, i.e., the LRS resistance increased with the increase of the temperature, was observed for the LRS with ohmic conduction [162,163]. However, there is no obvious temperature dependence for the LRS in our work, as shown in Fig. 4.6. Such weak temperature dependence was also observed in other studies [111,132]; and it could be attributed to the very small activation energies of the carrier conduction in the oxygen vacancy based conductive filament [132].

Fig. 4.6. I - V characteristics of the LRS under various measurement temperatures.

Fig. 4.7. I - V characteristic (in linear scale) of the HRS at 298 K.

In contrast to the ohmic conduction of the LRS, the I - V curve of the HRS exhibits nonlinear behavior, as shown in Fig. 4.7. The conduction mechanisms including the Fowler-Nordheim (FN) tunneling [164], space charge limited current (SCLC) [165], Poole-Frenkel (PF) emission [166], and Schottky emission [120,163] can be used to fit this nonlinear current conduction. However, FN tunneling is ruled out since it cannot explain the strong temperature dependence observed in Fig. 4.8(a); and the SCLC model cannot adequately describe our experiment data either. Although the PF emission and Schottky emission have similar behaviors, our analysis shows that the Schottky emission best describes the current transport of the HRS in our work (note that the electric field is low due to the small voltages in the I - V measurements). The I - V relationship of the Schottky emission can be written as [120,163]

$$I = AA^*T^2 \exp\left\{-\frac{q}{kT}\left[\Phi - \sqrt{\frac{qV}{4\pi d\epsilon}}\right]\right\} \quad (4.1)$$

where I is the current, A is the device size, A^* is the effective Richardson constant, T is the absolute temperature, q is the electron charge, k is the Boltzmann constant, V is the applied voltage, d is the film thickness, $q\Phi$ is the Schottky barrier height, and ϵ is the dynamic dielectric permittivity. Based on Eq. 4.1, a linear relationship between $\ln(I)$ and $V^{1/2}$ is obtained for the HRS under all temperatures, as shown in Fig. 4.8(a). To further investigate the characteristics of the conduction mechanism, the activation energy, $E_a = q(\Phi - \sqrt{\frac{qV}{4\pi d\epsilon}})$, for Schottky emission is obtained from the Richardson plot ($\ln(I/T^2)$ vs $1000/T$) for a given voltage, as shown in Fig. 4.8(b). The Schottky barrier height extracted from the voltage dependence of E_a is ~ 0.31 eV, as shown in Fig. 4.8(c). The conduction mechanism of Schottky emission is consistent with the above analysis of the resistive switching behavior. For the reset process, the conductive filament is oxidized and ruptured, making the conductive path blocked by the NiO layer. Due to the low conductivity of the NiO layer, the

device is switched to HRS. Therefore, under the positive bias, the electrons injected from the bottom electrode must overcome a barrier between the conductive filament and NiO film by an emission process, which can be described by the Schottky emission [167].

Fig. 4.8. (a) The Schottky emission plots of $\ln(I)$ vs $V^{1/2}$ for the HRS under various temperatures. (b) The Richardson plots of $\ln(I/T^2)$ vs $1000/T$ for HRS under different voltages. The dotted line is the best fitting based on Eq. 4.1. (c) The activation energy as a function of the square root of the voltage.

4.6 Multibit storage

Large storage capacity is one important requirement for next-generation memories. Multibit storage realized by controlling the switching operation conditions is a useful way to increase the storage capacity. As shown in Fig. 4.9(a) and Fig. 4.10(a), the LRS and HRS

resistance can be tuned by varying the compliance current and reset stop voltage, respectively. With the increase of the compliance current, more V_O^{2+} will migrate into the NiO side, which strengthens the conductive filament, and thus the LRS resistance decreases, as shown in Fig. 4.9(b). In contrast, with the increase of the magnitude of the reset stop voltage, more O^{2-} will move to eliminate the V_O^{2+} , which enhances the rupture of the conductive filament, and thus the HRS resistance increases, as shown in Fig. 4.10(b). It is worthy to mention that the difference in the LRS resistance (in the scenario of compliance-current control) or in the HRS resistance (in the scenario of reset-stop voltage control) between two bits corresponding to two compliance currents or two reset-stop voltages can be increased by tuning the carrier concentration or thickness of the NiO or IGZO layers.

Fig. 4.9. (a) Bipolar *I-V* characteristics of the Au/Ni/*p*-NiO/*n*-IGZO/ITO resistive switching device under different compliance currents. (b) Statistical distributions of HRS and LRS obtained from 20 switching cycles under different compliance currents.

Fig. 4.10. (a) Bipolar *I-V* characteristics of the Au/Ni/*p*-NiO/*n*-IGZO/ITO resistive switching device under different reset stop voltages. (b) Statistical distributions of HRS and LRS obtained from 20 switching cycles under different reset stop voltages.

4.7 Summary

In conclusion, stable bipolar resistive switching behaviors have been observed in the *p*-NiO/*n*-IGZO heterojunction structure. The forming process occurs when the *p-n* junction is reversely biased with a large voltage, possibly due to the migration of the V_{O}^{2+} from the IGZO side into the NiO side. The switching between the LRS and HRS can be explained with the formation and rupture of the V_{O}^{2+} based conductive filament. Multibit storage is achieved by controlling either the compliance current in the set process or the reset stop voltage in the reset process. The LRS shows ohmic conduction with little temperature dependence; while the conduction in HRS can be described by the Schottky emission with the Schottky barrier height of ~ 0.31 eV.

Chapter 5 STUDY OF THE DIODE AND ULTRAVIOLET PHOTODETECTOR APPLICATIONS OF P-NIO/N-IGZO THIN FILM HETEROJUNCTION STRUCTURE

5.1 Introduction

Semiconductor diode, one of the extremely important components in modern electronics, has been studied for years due to its various applications such as rectifier, detector, photovoltaic devices, or luminescent devices. In general, the rectifying characteristic exists in three kinds of structures, namely point-contact diode, p - n junction diode, and Schottky diode [168-174]. Among them, p - n heterojunction diode made of transparent semiconductor oxides (TSOs) has attracted much attention due to its good electrical property and optical transparency.

Besides the electronic diode application, the p - n junction can also be used for the light detection. The photodetectors operating in the ultraviolet (UV) light range have many applications in the civil and military areas, such as flame detection, space-to-space communication, missile plume detection, astronomy and biological researches [11, 12]. Photodetectors based on narrow bandgap semiconductors, especially Si (bandgap $E_g = 1.1$ eV), have been commercialized for light detection for a long time. However, to realize the selective detection in the UV light range, an optical filter is usually needed to filter out the visible and infrared light, which greatly increases the complexity and cost of the

photodetectors. To overcome this problem, wide bandgap semiconductors like ZnO, GaN, ZnMgO, $\text{In}_2\text{Ge}_2\text{O}_7$, Zn_2GeO_4 , and ZnS have been investigated for UV light detecting application. Compared with the Si-based photodetector, the photodetectors with wide bandgap semiconductors have many advantages like high breakdown field, filter-free UV light detection, high radiation-resistance, and highly chemical and thermal stabilities [175, 176]. There are three types of photodetectors, including the photoconductive detector, Schottky barrier photodetector, and p - n junction photodetector. Among them, photoconductive detector has attracted much attention due to its simple structure and high responsivity from photoconductive gain; unfortunately, the high photoconductive gain is usually accompanied by the slow recovery speed, which can be attributed to the persistent photoconductive effect [177]. To avoid this problem, p - n junction photodetector is employed to realize fast response to the light. As compared to the photoconductive detector, the p - n junction photodetector has many advantages like low dark current, high impedance, capability for high-frequency operation, and good compatibility with planar-processing techniques; meanwhile, its low saturation current and high built-in voltage make it also superior to the Schottky barrier photodetector [99].

Up to now, a variety of n -type TSOs has been investigated for p - n junction diode or UV photodetector applications. Among them, amorphous indium gallium zinc oxide (a-IGZO) has been widely studied because of its high mobility, good uniformity, low temperature process, and high optical transparency [178]. The amorphous nature of the IGZO thin film makes it a good choice for multi-layer devices due to the smooth interface, which is quite helpful to device performance [179]. Not like the n -type materials, p -type TSOs do not widely exist in the nature. Among the available p -type TSOs, nickel oxide (NiO) has been highlighted for its p -type property and transparency [180-182].

In this chapter, we have fabricated a p - n heterojunction structure based on n -IGZO and p -NiO thin films. The influence of the resistivity of both the n -IGZO and p -NiO thin films on the rectifying property of the heterojunction diode has been investigated. The current conduction mechanism for the forward current has been studied. A highly spectrum-selective UV photodetector has also been fabricated based on this p -NiO/ n -IGZO heterojunction structure. The influence of the conductivity of the p -NiO thin film on the performance of the photodetector is studied in this chapter.

5.2 Study of the rectifying characteristics of p -NiO/ n -IGZO thin film heterojunction structure

5.2.1 Experiment and device fabrication

The p -NiO/ n -IGZO heterojunction diode was fabricated with the following sequence. Firstly, IGZO thin film with the thickness of 170 nm was deposited on a commercial ITO coated glass by radio frequency (RF) magnetron sputtering with an IGZO target in Ar ambient. After the deposition, the IGZO thin films were put into Tepla O₂ Plasma Asher for 60 s, 90 s, and 300 s O₂ plasma treatment, respectively. The IGZO thin films with different conductivities can be achieved with this O₂ plasma treatment. Circular patterns with the diameter of 300 μ m were defined by lithography process. Then, a 130 nm NiO thin film was deposited by RF sputtering with a NiO target in a mixed Ar/O₂ ambient. Low conductivity (L-NiO) and high conductivity (H-NiO) of the NiO thin films were achieved by sputtering at the oxygen partial pressure of 0 and 1×10^{-4} Torr, respectively. After the growth of NiO, 100 nm Au/15 nm Ni layer was deposited by electron-beam evaporation to form the top electrode. Finally, lift-off process was carried out. The crystallinity and orientation of the thin films

were estimated by X-ray diffraction (XRD, Shimadzu, Kyoyo, Japan) with Cu $K\alpha$ radiation. The chemical states of the NiO thin films were analyzed by a Kratos AXIS X-ray photoelectron spectroscopy (XPS) equipped with monochromatic Al $K\alpha$ (1486.71 eV) X-ray radiation (15 kV and 15 mA). Carrier concentrations and resistivity of the IGZO and NiO thin films were measured with a Hall effect measurement system (Nanometrics HL5500PC). The electrical characteristics of the heterojunction diodes were carried out with a Keithley 4200 semiconductor characterization system.

Fig. 5.1. X-ray diffraction spectra of the IGZO without O_2 plasma treatment, H-NiO, and L-NiO thin films.

Fig. 5.1 shows the XRD rocking curves of the IGZO thin film without O_2 plasma treatment and NiO thin films with different conductivities. For the IGZO thin film, no obvious diffraction peaks are observed in the whole testing range, indicating the amorphous nature of the room-temperature sputtered IGZO thin film, which is consistent with the previous reports [150]. For the NiO thin films, both the H-NiO and L-NiO thin films show a crystalline structure with three diffraction peaks located at $2\theta = 36.8^\circ$, 43.3° , and 62.9° ,

respectively, which are consistent with standard ICDD data (ICCD File: 78-0643) of NiO thin film. The (111) preferred orientation is also observed in other report about the room-temperature sputtered NiO thin film [180].

Fig. 5.2. Ni 2p_{3/2} XPS spectrum of (a) L-NiO and (b) H-NiO thin films.

The electrical properties of the NiO and IGZO thin films were measured with the Hall effect measurement system in the Van der Pauw configuration at room temperature. The

resistivity and hole concentration of the H-NiO film obtained from the Hall effect measurement are $0.083 \text{ } \Omega \cdot \text{cm}$ and $2.8 \times 10^{19} \text{ cm}^{-3}$, respectively. Due to the quite high resistivity, reliable data cannot be obtained for the L-NiO thin film. To confirm the effect of the O_2 gas during the reactive sputtering deposition on the NiO thin films, XPS measurement was conducted on the L-NiO and H-NiO films, respectively. Fig. 5.2 shows the XPS results. The Ni $2p_{3/2}$ spectrum can be deconvoluted into three component peaks centered at 852.2 eV, 853.7 eV, and 855.8 eV, corresponding to the binding energy for Ni^0 of metallic Ni, Ni^{2+} of NiO, and Ni^{3+} of Ni_2O_3 , respectively [181,182]. Not like the purely stoichiometric NiO, which is excellent insulator with resistivity larger than $10^{13} \text{ } \Omega \cdot \text{cm}$ [183], the sputtered NiO thin film is usually non-stoichiometric and made of Ni, NiO, and Ni_2O_3 , as shown in Fig. 5.2. The metallic Ni, acting as donors, can release electrons. In contrast, the nickel vacancies (V_{Ni}) created in Ni_2O_3 phase, acting as acceptors, can release holes. So the competition between the Ni and V_{Ni} decides the carrier concentration in the NiO thin film. For L-NiO thin film, as shown in Fig. 5.2(a), both the content of Ni^0 and Ni^{3+} are high, so the compensation between electrons and holes results in the low conductivity of NiO thin film. By introducing amount of O_2 gas during the sputtering, most of the Ni^0 will be oxidized to Ni^{2+} and Ni^{3+} , as shown in Fig. 5.2(b). Thus, the decrease of Ni^0 and increase of Ni^{3+} result in the high conductivity of the NiO thin film, which is consistent with the Hall effect measurement results.

Based on our previous study, O_2 plasma treatment can cause the increase of the resistivity of the IGZO thin film [184]. As an *n*-type semiconductor material, the electrons in the IGZO thin film mainly origin from the interstitial metal ions and oxygen vacancies. The O_2 plasma treatment can obviously decrease the oxygen vacancy concentration in the IGZO thin film, which finally causes the increase of the resistivity. In this work, after 30 s O_2 plasma treatment, the electron concentration of the IGZO thin film decreases from $4.43 \times 10^{19} \text{ cm}^{-3}$ to

$4.68 \times 10^{18} \text{ cm}^{-3}$ with the resistivity increased from $0.004 \text{ } \Omega \cdot \text{cm}$ to $0.02 \text{ } \Omega \cdot \text{cm}$. For longer treatment time, reliable data cannot be obtained due to the high resistivity.

5.2.2 Effects of the thin film conductivity on the rectifying characteristic of the heterojunction diode

To examine the influence of the thin film resistivity on the rectifying characteristics of the heterojunction diode, IGZO thin films underwent O_2 plasma treatment for different durations before the deposition of the NiO thin film. As shown in Fig. 5.3(a), an obvious decreasing trend can be observed for the forward current of the heterojunction diode with the increase of the O_2 plasma treatment time. As discussed in the last section, the O_2 plasma treatment can cause the increase of the resistivity of the IGZO thin film, and the longer the treatment time, the more resistive the IGZO thin film is. When a forward bias is applied to the diode, besides of the voltage falling across the depletion region, part of the voltage will drop across the high resistive IGZO region. In this case, the more resistive the IGZO thin film is, the less partial bias will fall across the depletion region, so a smaller forward current can be expected. In addition, the high resistive IGZO region itself also restricts the current passing through the whole device. Thus, a decreasing trend can be expected for the forward current with the increase of the resistivity of the IGZO thin film. To study the influence of conductivity of the NiO thin film on the diode performance, L-NiO thin film is deposited to form L-NiO/IGZO heterojunction diode. The reverse currents measured at -2 V for the devices with L-NiO and H-NiO thin films are $8.3 \times 10^{-10} \text{ A}$ and $3.4 \times 10^{-12} \text{ A}$, respectively. The reverse current of the diode is mainly attributed to the drift current that are made of the minority carriers from both sides of the heterojunction. When the conductivity of the NiO and IGZO thin films is high, the minority carrier concentrations as the electrons in NiO film and holes in IGZO films are

quite low, which causes a low level drift current under reverse bias. The electron concentration of the L-NiO film is higher than that of H-NiO film, so the minority carrier drift current of the L-NiO/IGZO device under reverse bias is also higher, as shown in Fig. 5.3(b). Base on the above discussion, the best rectifying performance with the rectification ratio of 4.4×10^8 at ± 2 V and small threshold voltage of 1.7 V, can be obtained for the heterojunction diode consisting of H-NiO thin film and IGZO thin film without O₂ plasma treatment.

Fig. 5.3. (a) *I*-*V* characteristics of the H-NiO/IGZO heterojunction diode with IGZO thin film undergoing O₂ plasma treatment for 0 s, 60 s, 90 s, and 300 s, respectively. (b) *I*-*V* characteristic of the L-NiO/IGZO heterojunction diode.

Fig. 5.4(a) shows the I - V characteristics of the H-NiO/IGZO heterojunction diode under different temperatures. Both the forward and reverse currents show an increasing trend with the temperature, which can be attributed to the enhancement of the intrinsic excitation. With the increase of the temperature, more electron-hole pairs are created, which results in the increase for both the forward and reverse currents. Though the current of the diode is sensitive to the temperature, the rectification ratio is at a high level under all the temperatures, as shown in Fig. 5.4(b), indicating the potential application of the heterojunction diode at high temperature atmosphere.

Fig. 5.4. (a) I - V characteristics of the H-NiO/IGZO heterojunction diode under different temperatures. (b) The rectification ratio of the heterojunction diode read at ± 1.5 V as a function of the temperature.

Fig. 5.5. Plot of $\ln I$ versus V of the H-NiO/IGZO heterojunction diode.

Fig. 5.5 shows the plot of the $\ln I$ versus V of the H-NiO/IGZO heterojunction diode. The linear relationship between $\ln I$ and V below 0.4 V indicates that the I - V characteristic follows the conventional Schottky barrier thermionic emission model, which can be described with [185]

$$I = I_o \exp\left(\frac{qV}{nkT}\right) \quad (5.1)$$

where I_o is the saturation current, k is the Boltzman constant, T is the absolute temperature, q is the electronic charge, V is the applied voltage and n is the ideality factor. So the ideality factor n can be calculated with [186]

$$n = \left(\frac{q}{kT}\right) \cdot \left(\frac{dV}{d(\ln I)}\right) \quad (5.2)$$

Based on Eq. 5.2, the ideality factor of the heterojunction diode n is calculated to be 1.25 at the voltage ranging from 0.1 V to 0.4 V. According to the Sah-Noyce-Shockley theory, when the forward current is dominated by the diffusion current, which is caused by the recombination of minority carriers injected into the neutral regions of the junction, the

ideality factor should be equal to 1.0. In contrast, when the forward current is dominated by the recombination current, which is caused by the recombination of carriers in the space charge region, the ideality factor should be equal to 2.0 [186]. The ideality factor of 1.25 here suggests that the current transport is not purely diffusion limited or recombination limited [187]. When the forward bias is larger than 0.4 V, the higher ideality factor of 4.6 indicates a weak voltage dependence of the current. This early saturation phenomenon can be attributed to the single-carrier injection behavior in space charge limited conduction [188].

Fig. 5.6. *I*-*V* characteristic of the H-NiO/IGZO heterojunction diode in log-log scale.

To understand the current conduction of the heterojunction diode, the *I*-*V* characteristic of the H-NiO/IGZO structure is presented in log-log scale, as shown in Fig. 5.6. Two distinct regions are observed for the forward *I*-*V* characteristic. When the voltage is smaller than 0.1 V, a linear *I*-*V* relationship with the slope of ~ 1 is observed, showing the ohmic conduction behavior. Under this low bias, the injected effective carrier concentration is negligible compared to the intrinsic carrier concentration, so the ohmic conduction mainly arises from the existing background doping or thermally generated carriers [188]. As the voltage

increases, the current rises rapidly from about 0.2 V. In this case, the injected carriers are predominant over the intrinsic carries, which changes the current transport from ohmic conduction to space charge limited conduction. In the typical trap-free space charge limited conduction, the current has a square-law dependence on the voltage. However, the exponential index above 0.2 V is quite large in our structure, as shown in Fig. 5.6. This large slope indicates the existence of the traps distributed in the trap-level energies, which is related to the trap-filled space charge limited conduction [189].

5.3 A highly spectrum-selective ultraviolet photodetector based on *p*-NiO/*n*-IGZO thin film heterojunction structure

5.3.1 Experiment and device fabrication

The *p*-NiO/*n*-IGZO heterojunction photodetector was fabricated with the following sequence. Firstly, IGZO thin film with the thickness of 170 nm was deposited on a commercial ITO glass by radio frequency (RF) magnetron sputtering of an IGZO target in Ar ambient. Circular patterns with the diameter of 300 μm were defined by lithographic process. Then, a 130 nm NiO thin film was deposited by RF sputtering of a NiO target in a mixed Ar/O₂ ambient. Low conductivity (L-NiO), medium conductivity (M-NiO), and high conductivity (H-NiO) of the NiO thin films were achieved by sputtering at the oxygen partial pressure of 0, 6×10^{-5} , and 1×10^{-4} Torr, respectively. After the deposition of the NiO layer, ITO thin film as the top electrode layer was deposited by RF sputtering. Finally, lift-off process was carried out. Carrier concentrations of the IGZO and NiO thin films were measured with a Hall effect measurement system (Nanometrics HL5500PC). Optical transmittance of the thin films was measured with an UV-Vis spectrophotometer (Perkin-Elmer 950) in the wavelength range of 250 - 900 nm. Electrical characteristics and

photoresponse spectra of the as-fabricated photodetectors were measured with a Keithley 4200 semiconductor characterization system, a 300 W Xenon light source and an UV-Vis-IR monochromator.

Fig. 5.7. (a) Optical transmittance spectra of the L-NiO, M-NiO, and H-NiO thin films; (b) Plots of $(\alpha h\nu)^2$ versus $h\nu$ for the L-NiO, M-NiO and H-NiO thin films.

Electrical properties of the IGZO and NiO thin films were measured with the Hall effect measurement system in the Van der Pauw configuration at room temperature. The carrier concentrations of the IGZO, H-NiO, and M-NiO thin films obtained from the Hall effect measurement are $4.4 \times 10^{19} \text{ cm}^{-3}$ (electrons), $2.8 \times 10^{19} \text{ cm}^{-3}$ (holes), and $3.1 \times 10^{17} \text{ cm}^{-3}$ (holes),

respectively. Due to the high resistivity, reliable data cannot be obtained for the L-NiO thin film. To examine the optical properties of the NiO thin films, 80 nm NiO thin films with different conductivities were deposited on quartz glass substrates, respectively. The optical transmittance was measured in the wavelength range of 250 - 900 nm. As observed in Fig. 5.7(a), the average transmittance of the L-NiO, M-NiO, and H-NiO thin films in the visible range (400 - 700 nm) are 63.25%, 61.62%, and 35.98%, respectively, indicating a decreasing trend of the transmittance with the conductivity of the NiO thin film, which can be attributed to the increasing concentration of the intrinsic defects in the films. With the increase of the oxygen partial pressure during the sputtering deposition, more nickel vacancies, acting as acceptors in the *p*-NiO films, are created accompanying the formation of Ni³⁺ ions, which exhibit charge transfer transitions in the oxide matrix resulting in a strong, broad absorption band in the visible range [190, 191]. Meanwhile, stress field induced by the intrinsic defects may cause the light scattering effect [192]. In addition, free-carrier absorption may also occur in the long-wavelength region (e.g., the near infrared region) [193]. Thus, the transmittance will decrease with the conductivity of the NiO thin film. The optical bandgap of the NiO thin film can be estimated with

$$\alpha h\nu = A(h\nu - E_g)^m \quad (5.3)$$

where α is the optical absorption coefficient, A is a constant, E_g is the optical bandgap, $h\nu$ is the photon energy, and m is 1/2 for direct bandgap [194]. The absorption coefficient α is calculated with

$$\alpha \approx \ln(1/T)/d \quad (5.4)$$

where T is the transmittance and d is the thin film thickness [195]. As shown in Fig. 5.7(b), the direct bandgaps for the L-NiO, M-NiO, and H-NiO films are 3.60 eV, 3.57 eV, and 3.43 eV, respectively, which are within the reported bandgap range for *p*-NiO film (3.4 - 3.8 eV) [39]. The decreasing trend of the bandgap, which is also observed in other reports, can be

attributed to the effect of free carriers as well as the change in stoichiometry and crystallinity of the oxide films [191]. The bandgap of IGZO thin film determined with spectroscopic ellipsometry is ~ 3.45 eV as reported in our previous work [196]. The wide bandgaps of both IGZO and NiO films promise a low response of the photodetector to visible and infrared light.

5.3.2 Effects of the p -NiO conductivity on the performance of the UV photodetector

Fig. 5.8. I - V characteristics of the ITO/IGZO/ITO, ITO/L-NiO/ITO, ITO/M-NiO/ITO, and ITO/H-NiO/ITO thin film structures in the dark or under 365 nm UV light illumination. The inset shows the schematic illustration of the thin film structures.

To examine the photoelectric response to UV light of the IGZO (or L-NiO, M-NiO, H-NiO) thin film itself, a simple ITO/IGZO (or L-NiO, M-NiO, H-NiO)/ITO thin film structure was also fabricated, as schematically illustrated in the inset of Fig. 5.8. Symmetric current-voltage (I - V) curve is observed for the IGZO-based structure due to the high conductivity of the IGZO thin film itself. The asymmetric I - V curves of the NiO-based structures mainly originate from the difference in the quality between the top sputtered ITO electrode and bottom commercial ITO electrode. As can be seen in Fig. 5.8, the UV illumination doesn't

produce a significant influence on the I - V curves of all the four structures. This indicates that the UV-induced relative change in the carrier concentration of the IGZO (or L-NiO, M-NiO, H-NiO) thin film is insignificant and the thin film structures do not have the capability of UV light detection.

Fig. 5.9. I - V characteristics of (a) ITO/L-NiO/IGZO/ITO, (b) ITO/M-NiO/IGZO/ITO, and (c) ITO/H-NiO/IGZO/ITO structures measured under the following sequent conditions: dark, 365 nm UV light illumination, and UV light off. The inset in (a) shows the schematic illustration of the ITO/ p -NiO/ n -IGZO/ITO structures.

In contrast to the above simple thin film structures, with the formation of the p -NiO/ n -IGZO heterojunction, the ITO/ p -NiO (L-NiO, M-NiO, or H-NiO)/ n -IGZO/ITO structures show an obvious electrical rectification behavior and a large photoelectric response to the UV illumination, as shown in Fig. 5.9(a)-(c). The reverse dark current measured at -3 V for the structures with L-NiO, M-NiO, and H-NiO thin films are 1.23×10^{-9} A, 2.47×10^{-10} A, and

6.15×10^{-12} A, respectively. This shows the typical behavior of a *p-n* junction, i.e., a higher acceptor concentration in *p*-NiO layer leads to a lower reverse current. Obviously, to have a high signal to noise ratio, a low dark current is required; thus the H-NiO layer is more suitable for UV light detection. For all the three structures with different *p*-NiO layers (i.e., L-NiO, M-NiO, or H-NiO), the UV illumination causes an increase in the reverse current by about two orders, showing a promising application in UV light detection.

As shown in Fig. 5.9, the reverse currents of the structures with L-NiO or M-NiO cannot fully recover back to their original levels after the UV light is off; in contrast, the reverse current of the structure with H-NiO is fully recovered after the UV light is off. The phenomena could be attributed to the effect of the UV-induced hole trapping in the *p*-NiO layer. UV illumination produces electron-hole pairs in both *p*-NiO and *n*-IGZO layers. If some of the UV-generated holes are trapped in the deep-levels in the *p*-NiO layer, the *I-V* characteristic of the *p-n* junction would be affected by the hole trapping. The hole trapping would partially compensate the negative space charge in the *p*-NiO side of the depletion region of the *p-n* junction, reducing the built-in electric field as well as the barrier height of the *p-n* junction. This would have a more significant impact on the small reverse current than on the large forward current. Compared to H-NiO, L-NiO and M-NiO have a lower concentration of acceptors, thus their densities of the negative space charge are lower and the widths of the depletion region in the *p*-NiO are larger. Therefore, the charge compensation and its effect on the reverse current are more significant for L-NiO and M-NiO than for H-NiO. This explains the difference in the recovery of the *I-V* characteristic (in particular the reverse current) after UV light is off among the photodetector structures with different *p*-NiO conductivities. Obviously, the full recovery of the structure based on H-NiO as shown in Fig. 5.9(c) makes the structure suitable as an UV photodetector.

Fig. 5.10. (a) Spectral responsivity of the ITO/H-NiO/IGZO/ITO photodetector under the bias of -3 V. The inset shows the responsivity as a function of the reverse bias; (b) Normalized spectral responsivities of the ITO/L-NiO/IGZO/ITO, ITO/M-NiO/IGZO/ITO, and ITO/H-NiO/IGZO/ITO photodetector structures under the bias of -3 V.

Fig. 5.10(a) shows the spectral responsivity of the photodetector structure based on H-NiO at -3 V bias. A peak responsivity of 0.016 A/W is observed at the wavelength of ~ 370 nm with the full width at half maximum (FWHM) of smaller than 30 nm, showing a high spectrum selectivity. The peak responsivity of 0.016 A/W is comparable or better than that of some of the metal-oxide-based p - n junction UV detectors reported in literature [197-199]. Note that the responsivity of the photodetector in this work can be further improved by

optimizing the thicknesses of the ITO top electrode, p -NiO and n -IGZO layers. Fig. 5.10(b) shows the normalized responsivity of the photodetectors with L-NiO, M-NiO, and H-NiO thin films. It can be concluded from the figure that the photodetector based on the H-NiO thin film has the best spectral selectivity, which is explained in the following. The transmittance of the ITO top electrode decreases sharply when the wavelength is shorter than ~ 400 nm, which should be partially responsible for the falling of the responsivity at the wavelengths shorter than ~ 370 nm. However, the ITO top electrode with the same thickness was used in all the three structures. This suggests that the difference in the spectral responsivity among the structures is related to the difference in the transmittance of the NiO thin film. For the light with the wavelengths shorter than ~ 360 nm, the photon energy is larger than the bandgap of the NiO film; thus most of the photons arriving in the NiO film are absorbed in the neutral region of the top NiO layer instead of reaching the depletion region [199]. In this way, the top NiO layer works as a “filter” to filter out the light with short wavelengths. For the visible and infrared light, though the photons can reach the depletion region, they cannot excite electron-hole pairs due to their energies smaller than the bandgap of NiO and IGZO films; thus low responsivity is obtained. As H-NiO film has the lowest near UV-visible-near infrared transmittance, as shown in Fig. 5.7(a), the photodetector based on H-NiO thus has the best spectral selectivity. As can be observed in Fig. 5.10(b), among the three photodetector structures, the H-NiO/IGZO photodetector has the highest UV to visible rejection ratio (e.g., the ratio of responsivity at the wavelength of 370 nm to the responsivity at 500 nm is 1030 for the H-NiO/IGZO photodetector, while it is only 60 for the L-NiO/IGZO photodetector) due to the lowest visible transmittance of H-NiO film, showing the best visible blindness. This is important for the application of an UV photodetector in a visible light background [200]. It can be also observed from Fig. 5.10(b) that the wavelength of the peak responsivity shifts from ~ 370 nm (H-NiO) to ~ 360 nm (L-NiO) (blue shift) with

the decrease of the conductivity of NiO film. The blue shift is due to the bandgap increase of the *p*-NiO films (note that the direct bandgaps for L-NiO, M-NiO, and H-NiO films are 3.60 eV, 3.57 eV, and 3.43 eV, respectively), as shown in Fig. 5.7(b). On the other hand, the influence of the reverse bias on the responsivity of the H-NiO/IGZO photodetector has been examined, and the result is shown in the inset of Fig. 5.10(a). With the increase of the reverse bias, a larger photocurrent is produced due to the widening of the depletion region, and thus the responsivity increases.

Fig. 5.11. Experiment on the repeatability and photocurrent response of the H-NiO/IGZO photodetector under the bias of -0.2 V, at the wavelength of 365 nm and with various UV light intensities.

Good repeatability and fast response are critical to the detection of a quickly varying UV signal. An experiment on the repeatability and photocurrent response was carried out on the H-NiO/IGZO photodetector at the wavelength of 365 nm with various UV light intensities. The UV light was mechanically switched on for 10 s and off for 20 s alternatively. The result is shown in Fig. 5.11. As can be observed in the figure, good repeatability and fast response have been achieved, in a wide light intensity range of 0.7 - 10.2 mWcm⁻².

5.4 Summary

In conclusion, the p -NiO/ n -IGZO thin film heterojunction has been fabricated for both the diode and UV photodetector applications. For the diode application, both the conductivities of the NiO and IGZO thin films have a strong influence on the rectifying characteristic of the heterojunction diode. The best rectifying performance can be obtained for the diode with both high conductive NiO and IGZO thin films. The forward current shows ohmic conduction under low voltage bias; while the conduction under high voltage bias can be described as trap-filled space-charge limited conduction. For the UV photodetector application, the performance of the photodetector is largely affected by the concentration of acceptors in the p -NiO layer, which can be controlled by varying the oxygen partial pressure during the sputtering deposition of the p -NiO layer. A highly spectrum-selective UV photodetector has been achieved with the p -NiO layer with a high concentration of acceptors. The photodetector has a good repeatability and fast response.

Chapter 6 A LIGHT-STIMULATED SYNAPTIC TRANSISTOR WITH SYNAPTIC PLASTICITY AND MEMORY FUNCTIONS BASED ON IGZO_x-AL₂O₃ THIN FILM STRUCTURE

6.1 Introduction

A modern digital computer is based on the von Neumann architecture [201], in which the memory and processor are physically separated. Despite of the achievements made so far, the von Neumann architecture is becoming increasing inefficient for the further requirement for complicated computation or recognition due to the physical separation of computing parts and memories. In contrast, the human brain deals with information in parallel, enabling the brain to efficiently process information with low power consumption [202]. Therefore, many efforts have been made to build neuromorphic systems that can mimic the human brain, which is believed to be the most powerful information processor that can easily recognize various objects and visual information in complex world environment through complicated computation [203]. The human brain is composed of $\sim 10^{15}$ synapses, which have signal processing, memory, and learning functions; thus the synapse emulation is a key step to realize the neuromorphic computation [204]. Though many works have been done to implement neuromorphic systems through software-based method by conventional von Neumann computers [205], or hardware-based methods by emulating the synapse with a large number of transistors and capacitors in complementary metal-oxide-semiconductor

integrated circuits [202], both of the two approaches occupy larger areas and consume much more energy than the human brain. Thus, the realization of a single device with synaptic functions has attracted much attention for the implementation of the neuromorphic system.

Nowadays, a variety of electronic synapses based on two-terminal memristors or three-terminal synaptic transistors has been demonstrated [206-216]. However, to the best of our knowledge, almost all the reported electronic synapses were stimulated with electrical stimulus; and no artificial synapse based on light stimulus has been reported. Compared with the electrical stimulus, the light stimulus may offer some advantages, e.g., a much wider bandwidth and no RC delay for signal transmission. Thus, the demonstration of a synapse operated with light stimulus provides an alternative way for the emulation of biological synapse.

In this work, a light-stimulated synaptic transistor has been fabricated based on the indium gallium zinc oxide (IGZO) - aluminum oxide (Al₂O₃) thin film structure. Synaptic plasticity and memory behaviors including paired-pulse facilitation (PPF), short-term memory (STM) to long-term memory (LTM) transition, and Ebbinghaus forgetting curve were successfully mimicked in this synaptic transistor with light stimulus.

6.2 Experiment and device fabrication

The synaptic transistor based on the IGZO - Al₂O₃ thin film structure was fabricated with the following sequence. Firstly, a 30 nm Al₂O₃ thin film was deposited on a heavily doped *n*-type Si substrate with atomic layer deposition process at the temperature of 250 °C. Then, a IGZO thin film with the thickness of ~50 nm was deposited onto the Al₂O₃ thin film by radio frequency magnetron sputtering of an IGZO target in a mixed Ar/O₂ ambient with the Ar partial pressure of 3×10⁻³ Torr and O₂ partial pressure of 2×10⁻⁴ Torr. In the device structure

of the synaptic transistor shown in the inset of Fig. 6.1(a), the Al₂O₃ thin film, IGZO thin film and heavily doped *n*-type Si substrate serve as the gate dielectric, channel layer, and bottom gate of the transistor, respectively. The pattern of the IGZO channel with the length of 20 μm and width of 40 μm was formed with lithography and a wet etching process. Finally, 100 nm Au/20 nm Ti layer was deposited by electron-beam evaporation at room temperature to form the source and drain electrodes of the transistor. Electrical characterization of the synaptic transistor was conducted with a Keithley 4200 semiconductor characterization system at room temperature. In the experiments of synaptic plasticity and memory behaviors of the synaptic transistor, the light stimulus was supplied with a UV spot light source with the wavelength of 365 nm (HAMAMATSU-LC8 spot light source).

6.3 Electrical characteristic of the bottom gate IGZO transistor

We firstly investigated the electrical characteristics of the bottom-gate IGZO synaptic transistor. Fig. 6.1(a) shows the transfer characteristics of the transistor with the gate voltage (V_G) sweeping from -5 V to 10 V at the drain voltage (V_D) of 0.1 V. The on/off ratio of the drain current (I_D), field-effect mobility (μ), and subthreshold swing ($S.S$) that are obtained from the transfer curve are 5×10^5 , $15.8 \text{ cm}^2/\text{V}\cdot\text{s}$, and 0.36 V/dec, respectively. The typical output characteristic of an *n*-type field effect transistor is observed from the synaptic transistor as shown in Fig. 6.1(b). After 1 s UV light illumination, an obvious negative shift of the transfer curve can be observed in Fig. 6.1(a), indicating the decrease of the threshold voltage (V_{th}) of the transistor. According to our previous work, the negative shift of V_{th} is due to the photo-generated holes trapped at the IGZO/Al₂O₃ interface and/or in the Al₂O₃ layer [217].

Fig. 6.1. (a) Transfer characteristics (I_D versus V_G) of the bottom-gate IGZO synaptic transistor at $V_D = 0.1$ V before and after 1 s UV light illumination. The inset shows the schematic cross-sectional diagram of the transistor. (b) Output characteristics (I_D versus V_D) of the bottom-gate IGZO synaptic transistor.

6.4 Emulating the synaptic plasticity in synaptic transistor with UV light stimulus

Fig. 6.2. Analogy between the IGZO-based synaptic transistor and a biological synapse. (a) Electron-hole pair generation in the transistor by UV stimulus and the post-stimulus distribution of the photo-generated electrons and holes. (b) Schematic illustration of a biological synapse. (c) The drain current (the post-synaptic current) of the synaptic transistor recorded in response to the UV pulse train. The intensity, width, and interval of the UV pulse train are 3 mW/cm², 100 ms, and 5 s, respectively; and the post-synaptic current was recorded at $V_D = 0.5$ V.

Fig. 6.2(a) shows the schematic diagram of the IGZO-based synaptic transistor, which can be used to mimic the biological synapse shown in Fig. 6.2(b). In the operation of the

synaptic transistor, UV light pulses, which act as the pre-synaptic input, are shone onto the IGZO channel of the transistor, as shown in Fig. 6.2(a). The drain current and the channel conductance (measured at the drain voltage V_D of 0.5 V in this work) of the transistor are analogous to the post-synaptic current and synaptic weight, respectively. The trapping and detrapping of the photo-generated holes at the IGZO/Al₂O₃ interface and/or in the Al₂O₃ layer under the stimulation of the UV pulses play a role similar to that of a neuro-transmitter in the modulation of the strength of the synaptic connection in a biological synapse [218]. As the bandgap of the IGZO thin film is ~3.36 eV [196], the UV light with the photon energy of 3.4 eV generates many electron-hole pairs in the IGZO channel as shown in the inset of Fig. 6.2(a). A photocurrent flowing between the source and drain in the transistor is thus produced under the influence of the drain voltage, leading to an increase of the post-synaptic current. Some of the photo-generated holes are trapped at the IGZO/Al₂O₃ interface and/or in the Al₂O₃ layer and are gradually released during the off-periods of the UV light pulses. The trapped holes induce conduction electrons in the IGZO channel layer, as shown in the inset of Fig. 6.2(a). As a result, the post-synaptic current does not disappear immediately when the UV light illumination is turned off. Instead, a decay of the post-synaptic current is observed during the off-periods of the UV light pulses, as shown in Fig. 6.2(c). The decay of the post-synaptic current is analogous to the memory loss in biological system. On the other hand, as not all of the photo-generated holes are released during the off-periods of the UV light pulses, there is an accumulation of the trapped holes, leading to a continuous increase in the post-synaptic current with time or number of the UV light pulses, as shown in Fig. 6.2(c).

Fig. 6.3. (a) Post-synaptic currents of the synaptic transistor triggered by a pair of UV light pluses. The pulse intensity, pulse width, and pulse interval are 3 mW/cm², 100 ms, and 2 s, respectively. The post-synaptic current was measured with V_D of 0.5 V. A1 and A2 are the magnitudes of the first and second post-synaptic currents, respectively. (b) PPF decays with the pulse interval (Δt). The pulse intensity and width are fixed at 3 mW/cm² and 100 ms, respectively. The experimental data are the average values of the PPF obtained from 10 independent tests.

Synaptic plasticity is an important characteristic of biological synapses, which can be categorized into two types, short-term plasticity (STP) and long-term plasticity (LTP), based on the retention time [207]. The STP is a temporal potentiation of the synaptic connection, which lasts for a few minutes or less; the LTP is a permanent change of the synaptic connection, which lasts for a longer time from hours to years [204]. The paired-pulse

facilitation (PPF), which is a form of STP, is a phenomenon in which the post-synaptic response evoked by the spike is increased when the second spike closely follows the previous one [203]. The PPF, which is believed to play an important role in decoding temporal information in auditory or visual signals [208], can be mimicked in our synaptic transistor with UV light stimulus. As shown in Fig. 6.3(a), two successive UV light pulses with fixed intensity and pulse width were applied to the IGZO channel with the pulse interval (Δt) of 2 s, and the post-synaptic current was read with V_D of 0.5 V. The post-synaptic current that is triggered by the second UV light pulse is larger than the first one, which is similar to the PPF behavior in the biological synapse. The PPF of the synaptic transistor can be described with [219]

$$PPF = 100\% \cdot (A_2 - A_1) / A_1 \quad (6.1)$$

where A_1 and A_2 are the magnitudes of the first and second post-synaptic current, respectively. The PPF decreases with the increase of the UV light pulse interval, as shown in Fig. 6.3(b). After the first UV light pulse, some of the photo-generated holes are trapped at the IGZO/Al₂O₃ interface and/or in the Al₂O₃ layer. If the interval is small enough, the trapped holes that are generated during the first UV light pulse will not be completely released before the second light pulse arrives. Correspondingly, the conduction electrons in the IGZO channel induced by the trapped holes will not disappear completely, and thus the post-synaptic current that triggered by the second UV light pulse is larger than the first one. With a longer pulse interval, more trapped holes are released, resulting in a smaller second post-synaptic current and thus a smaller PPF as shown in Fig. 6.3(b). The PPF decay with the pulse interval can be divided into a rapid phase and a slow phase, which is analogous to the PPF decay observed in a biological synapse. The PPF decay can be described as [219]

$$PPF = c_1 \cdot \exp(-\Delta t / \tau_1) + c_2 \cdot \exp(-\Delta t / \tau_2) \quad (6.2)$$

where Δt is the UV light pulse interval, c_1 and c_2 are the initial facilitation magnitudes of the rapid and slow phases, respectively; and τ_1 and τ_2 are the characteristic relaxation time of the rapid and slow phases, respectively. The experimental PPF decay with the UV light pulse interval is well fitted by Eq. 6.2, as shown in Fig. 6.3(b). The values of c_1 , c_2 , τ_1 , and τ_2 yielded from the fitting are 35.9%, 35.5%, 3.1 s, and 839 s, respectively.

6.5 Emulating the memory functions in synaptic transistor with UV light stimulus

The memory behavior in psychology, which can also be categorized into short-term memory (STM) and long-term memory (LTM) based on the retention time, corresponds to the plasticity in neuroscience [207]. Thus, the synaptic transistor can also mimic the human memory by taking the UV light stimulus and channel conductance as the external stimulus and memory level, respectively. As shown in Fig. 6.2(c), the post-synaptic current increases after each UV light pulse; and the current decays during the interval period between two pulses. The former and latter are analogous to the enhancement of the memorization through stimulation/impression and the forgetting behavior in human brain, respectively. In the synaptic transistor, the transition from STM to LTM can be realized by repeating the UV pulse stimulus, which is analogous to the rehearsal in human daily life. To study the transition from STM to LTM in the synaptic transistor, a series of UV light pulses with fixed intensity, width and interval (which are 3 mW/cm², 100 ms, and 100 ms, respectively) were applied to the IGZO channel, and the conductance was recorded with V_D of 0.5 V immediately after the last pulse of a pulse series. Fig. 6.4(a) shows the decays of the normalized channel conductance change recorded after the last pulse of the UV pulse series of 10, 50, and 90 pulses, respectively. The synaptic weight (i.e. the channel conductance) of

the synaptic transistor decays very fast at the beginning and then slowly, which is indeed analogous to the human memory [206]. The decay of the channel conductance can be described by [220]

$$\Delta G(t) / \Delta G_0 = \exp[-(t / \tau)^\beta] \quad (6.3)$$

where $\Delta G(t)=G(t)-G_{init}$ and $\Delta G_0=G_0-G_{init}$; $G(t)$ is the channel conductance at time t ; G_0 is the channel conductance recorded immediately after the last pulse of a pulse series; G_{init} is the channel conductance before any UV light stimulus; τ is the characteristic relaxation time; and β is an index between 0 to 1. The decay behavior described by Eq. 6.3 is analogous to the well-known Ebbinghaus forgetting curve, which describes how information is forgotten over time by the human brain [220]. The characteristic relaxation time (τ) can be obtained from the fitting to the experimental data with Eq. 6.3. As shown in Fig. 6.4(a), the conductance decay behavior of the synaptic transistor can be well described with Eq. 6.3. Both the channel conductance change and characteristic relaxation time yielded from the fitting increase with the UV light pulse number, as shown in Fig. 6.4(b), which is analogous to the memory behavior of the human brain that repeating stimulus can strengthen the impression and decrease the forgetting rate. The increase of both the channel conductance and characteristic relaxation time is the strong evidence for the transition from STM to LTM [204]. Besides the pulse number, the pulse width also has an effect on the memory strength and forgetting rate, which is demonstrated by the result shown in Fig. 6.4(c). In the experiment of Fig. 6.4(c), 20 successive UV light pulses with fixed intensity (3 mW/cm²) and pulse interval (100 ms) but varied pulse widths were applied to the IGZO channel. Both the channel conductance and characteristic relaxation time increase with the pulse width, indicating that the transition from STM to LTM can also be realized by increasing the UV light pulse width. Based on the above discussion, the channel conductance is regarded as the memory level in the human memory. The increase and decay of the channel conductance are quite similar to the impression

strengthen and forgetting behavior in the human brain. However, compared with the human brain, the response time of our device is slow due to the relatively wide UV light pulse width. To solve this, a narrow UV light pulse is needed as the stimulus in the future research.

Fig. 6.4. (a) Decay of the normalized channel conductance change recorded after the last pulse of an UV pulse series for various pulse numbers (N). The pulse intensity, pulse width and pulse interval are 3 mW/cm², 100 ms, and 100 ms, respectively. The lines are the best fittings to the experimental data with Eq. 6.3. (b) ΔG_0 and τ yielded from the fittings in (a) as a function of the UV light pulse number. (c) ΔG_0 and τ as a function of the UV light pulse width. In the experiment of (c), 20 successive UV light pulses with the intensity of 3 mW/cm² and pulse interval of 100 ms were applied to the synaptic transistor.

6.6 Summary

In conclusion, an UV pulse-stimulated synaptic transistor based on IGZO - Al₂O₃ thin film structure has been demonstrated. The synaptic transistor exhibits the behaviors of

synaptic plasticity like the paired-pulse facilitation. In addition, the brain's memory behaviors including the transition from short-term memory to long-term memory and the Ebbinghaus forgetting curve can be also mimicked with the synaptic transistor. The synapse-like behaviors and memory behaviors of the synaptic transistor are due to the trapping and detrapping of the photo-generated holes at the IGZO/ Al_2O_3 interface and/or in the Al_2O_3 layer.

Chapter 7 CONCLUSION AND RECOMMENDATIONS

7.1 Conclusion

This thesis examines the electrical and optoelectronic properties of the transition metal oxides including the HfO_x , NiO , and IGZO thin films with the focus on the fabrication, characterization, and device applications of these metal oxide thin films. The potential applications of these transition metal oxide thin films in non-volatile memory, p - n junction diode, UV photodetector, and artificial synapse have been studied. The results in this thesis have enhanced the understanding of the electrical and optoelectronic properties of the transition metal oxide thin films. This section briefly summarizes the overall research presented in this thesis.

7.1.1 Resistive switching in HfO_x -based RRAM device

The HfO_x -based RRAM device with MIM structure has been fabricated. Stable bipolar resistive switching behavior has been observed at both the room and elevated temperatures. The current conduction mechanisms of both LRS and HRS are examined with temperature dependent I - V characteristics. For LRS, ohmic conduction with little temperature dependence has been observed, which could be attributed to the very small activation energies of the carrier conduction in the oxygen vacancy based conductive filament. For HRS, when the applied electric field is low, the current conduction follows the ohmic conduction; when the applied electric field is high, the current conduction follows the Poole-Frenkel emission model. Multibit storage is realized in one RRAM cell by controlling the switching operation

conditions. Impedance spectroscopy has been used to study the multilevel high resistance states in the HfO_x -based RRAM device. The high resistance states can be described with an equivalent circuit consisting of three components R_s , R , and C corresponding to the series resistance of the TiON interfacial layer, the equivalent parallel resistance and capacitance of the leakage gap between the TiON layer and the residual conductive filament, respectively. These components show a strong dependence on the reset stop voltage, which can be explained in the framework of oxygen vacancy model and conductive filament concept. Both the CVS and RVS methods have been used to study the speed-disturb time dilemma. Compared with CVS, RVS is proved to be an effective method with faster speed and low cost. The HfO_x -based RRAM device was also successfully fabricated with the 180 nm Cu BEOL process platform. The RRAM device in this Cu interconnection technology shows the similar bipolar resistive switching performance as in the conventional Al interconnection technology.

7.1.2 Resistive switching in $p\text{-NiO}/n\text{-IGZO}$ thin film heterojunction structure

The as-fabricated $p\text{-NiO}/n\text{-IGZO}$ heterojunction structure shows the typical rectifying property with the rectification ratio of 10^3 at the bias voltage of ± 1.5 V. After applying a large enough negative forming voltage, stable bipolar resistive switching can be achieved with tight distributions for both the resistance states and transition voltages. The transition between the HRS and LRS can be attributed to the connection and rupture of the oxygen vacancy based conductive filament. The current conduction mechanisms of both LRS and HRS are examined with temperature dependent I - V characteristics. For LRS, ohmic conduction with little temperature dependence has been observed, which could be attributed to the very small activation energies of the carrier conduction in the oxygen vacancy based

conductive filament. For HRS, Schottky emission model with the Schottky barrier height of ~ 0.31 eV can be used to describe the current conduction. Multibit storage can be realized by controlling either the compliance current in the set process or the reset stop voltage in the reset process.

7.1.3 The diode and ultraviolet photodetector applications of p -NiO/ n -IGZO thin film heterojunction structure

The p -NiO/ n -IGZO thin film heterojunction structure has been fabricated for both diode and UV light photodetector applications. The p -NiO thin films with different conductivity can be achieved by introducing different amount of O₂ gas during the sputtering deposition. The n -IGZO thin films with different conductivity can be achieved by O₂ plasma treatment with different durations. For diode application, both the conductivity of the NiO and IGZO thin films has a strong influence on the rectifying property of the heterojunction diode. The best rectifying performance can be achieved for the diode that consists of both high conductive NiO and IGZO thin films. For the UV photodetector application, a high spectrum selectivity can be achieved due to the filter function of the top p -NiO layer. The overall performance of the p -NiO/ n -IGZO photodetector is highly dependent of the conductivity of the NiO layer. The best performance can be achieved with NiO thin film with the highest conductivity. The photodetector in our work shows good repeatability and fast response.

7.1.4 A light-stimulated synaptic transistor with synaptic plasticity and memory functions based on IGZO_x-Al₂O₃ thin film structure

The IGZO-based thin film transistor with Al₂O₃ as the gate oxide has been fabricated for the synapse application. The UV light is used as the stimulus for the first time. The synaptic

plasticity like the paired-pulse facilitation has been emulated in this synaptic transistor. The memory behaviors including the transition from the STM to LTM and the Ebbinghaus forgetting curve have also been mimicked with the UV light stimulus. The synapse-like behaviors and memory behaviors of the synaptic transistor are due to the trapping and detrapping of the photo-generated holes at the IGZO/Al₂O₃ interface and/or in the Al₂O₃ layer.

7.2 Recommendations

The thesis presents the studies of the electrical and optoelectronic properties of the transition metal oxide thin films and their applications in non-volatile memory, *p-n* junction diode, UV photodetector, and artificial synapse. In order to make the studies more comprehensive, the following recommendations have been proposed.

7.2.1 Fully transparent non-volatile memory based on ITO/*p*-NiO/*n*-IGZO/ITO structure

The transparent electronics is an emerging class of devices in an intriguing technological paradigm. It provides a variety of applications that cannot be realized by the conventional Si-based technology. As for the transparent RRAM device, it can be integrated with the transparent display to produce a class of system-on-glass. The demonstration of the transparent RRAM device is the first step to the realization of transparent electronic system. The transition metal oxide thin films like the ITO, NiO, and IGZO thin films are wide bandgap materials with high transmittance for visible light. Thus, it is possible to fabricate transparent RRAM device based on *p*-NiO/*n*-IGZO thin film heterojunction structure with ITO as the electrodes.

7.2.2 The integration of RRAM device with the TSV interposer

The 2.5D TSV (through Si via) interposer has been considered as a cost-effective and high performance integration approach for logic and memory. However, this approach employs the chips attachment on the interposer side by side, between which the communication is achieved by Cu interconnect and micro-bumps on top of the interposer chip. Although the bandwidth between memory and logic is improved a lot as compared to the wire bonding approach due to the wide I/O provided by micro-bumping in TSV interposer, the bandwidth is still largely limited by Cu wire length, i.e., typically >1 mm, between logic and memory. In the future work, we propose to integrate the RRAM devices directly on the TSV interposer. By doing this, the communication between logic and ReRAM can be achieved vertically through Cu layers and micro-bumps, which avoids the limitation of the Cu wire length. In addition, the number of the bonded logic chips can be increased as there is no more memory chip bonded on TSV interposer.

7.2.3 The implementation of neuromorphic system with bipolar RRAM device

The memristor, which is frequently used as an artificial synapse in the implementation of neuromorphic system, is essentially a bipolar RRAM device. In this thesis, we have already successfully fabricated two types of RRAM devices, including the HfO_x -based RRAM device and $p\text{-NiO}/n\text{-IGZO}$ heterojunction structure, both of which show good bipolar resistive switching performance. Thus, we propose to use these RRAM devices to emulate the synaptic plasticity and memory functions of biological synapse.

LIST OF PUBLICATIONS

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