Characterization of nanoscale conducting filament in high-k oxides by scanning tunneling microscopy and conductive atomic force microscopy

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**NANYANG
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UNIVERSITY**

SINGAPORE

**CHARACTERIZATION OF NANOSCALE CONDUCTING
FILAMENT IN HIGH-K OXIDES BY SCANNING
TUNNELING MICROSCOPY AND CONDUCTIVE
ATOMIC FORCE MICROSCOPY**

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SCHOOL OF ELECTRICAL & ELECTRONIC ENGINEERING

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ABSTRACT

By virtue of its simple structure, high operating speed and scalability, the resistive memory or RRAM is deemed a promising alternative to the charge-based memory, which is now facing severe scaling challenges. Of particular interest is the HfO₂ RRAM due to its immediate compatibility with mainstream integrated-circuit technology. A major problem is, however, the relatively high switching current. Currents on the order of 10⁻³ A are typically observed in large-area cells (~10⁻⁸ cm²). In a recent work, a substantial reduction of the switching current to ~10⁻⁵ A was achieved by scaling the cell area down to 100 nm².

Since one of the main strengths of RRAM is scalability, a further reduction of the switching current is deemed necessary in order to make ultra-high density memory application viable. At present, it is unclear to what extent could the switching current be reduced with cell area scaling. To address this question, resistance switching in HfO₂ is examined using a conductive atomic force microscope (C-AFM) and scanning tunneling microscope (STM) in this thesis. The excellent spatial resolution of C-AFM and STM enables the electrical properties of a thin dielectric to be probed over an extremely localized region. Through the C-AFM/STM technique, in this thesis, we examined resistance switching in a 4-nm thick HfO₂, within a region of ~2 nm in diameter and achieved an ultra-low current switching capability.

Furthermore, the unique abrupt reset behavior is observed in nanoscale RRAM with nanometer-level conducting filament (CF), on the contrary, the gradual current reduction trend is typically observed during the reset process in relatively large area RRAM device. We addressed the origin of the gradual resistance reset behavior by

studying, via STM/C-AFM, the reset characteristic of the nanoscale CFs and its relation with the macroscopic gradual electrical reset behavior in device level. The statistical result shows that the nanoscale CFs tend to exhibit abrupt resistance reset behavior with significant variations in the reset voltage and current. It is shown that this wide variation of reset voltage and current contributes to the gradual resistance reset behavior observed in large area RRAM device with multiple nanoscale CFs formed beneath the top electrode.

With the further scaling of the RRAM/MOSFET devices, electrical-stress-induced breakdown of the scaled thin gate oxide is a serious reliability issue that has received widespread attention for many years. Studies have shown that gate-oxide breakdown can be broadly classified as soft or hard. Ultra-thin gate oxides (< 5 nm) typically exhibit the former. As soft breakdown (SBD) typically does not lead to a total loss of transistor functionality, there has been much interest on the breakdown mechanism and its evolution towards eventual hard breakdown. With HfO_2 replacing SiO_2 as the gate oxide, recent attention was mostly centered on the reliability of the metal/ HfO_2 gate stack. It has been found that SBD of HfO_2 can be electrically reversed with a greater ease as compared to SiO_2 , prompting considerable interest on the recovery mechanism as well as the role of the metal electrode. In this thesis, we report that a nanoscale percolation path in SiO_2 and HfO_2 can be disrupted upon exposure to white light. The disruption is either complete or partial, depending on the resistance of the percolation path determined at the point of breakdown, i.e. the breakdown hardness. The electrical robustness of the light-restored oxide is tested and analyzed using statistical Weibull distributions. Unlike the classical photo-response behavior of narrow bandgap oxides and perovskites which is commonly manifested as an increase in electrical conduction due to the generation of excess charge carriers by the incident photons, the photo-

response here comes in the form of a disruption of electrical conduction through the nanoscale conducting filament or percolation path formed during breakdown. When that occurs the insulating properties of the breakdown oxide region can be restored. The disruption in electrical conduction caused by white-light illumination is proposed to occur through photon-stimulated migration of interstitial oxygen ions nearby the vacancy-filled filament, resulting in the migrating oxygen ions recombining with the vacancies in the filament. This unique photo-responsive behavior, which we termed as negative photoconductivity (NPC) of SBD HfO_2 , ZrO_2 and SiO_2 points towards the possibility of gate oxide reliability rejuvenation as well as the incorporation of optical functions into mainstream CMOS-based integrated circuits, e.g., imaging sensors and photodetectors with built-in non-volatile memory capability. As a photodetector, the relation between the CF disruption speed and the light intensity has been investigated, as well as the wavelength influence. The infrared light is proved to be effective for CF disruption on our device, indicating a possible room temperature infrared detector. The relationship between the photosensitivity/CF disruption speed and the stoichiometry of the oxide layer and sample temperature is presented as well. At last, an in-situ photosensitivity modulation approach through the adjustment of metal ions concentration in CF via electrical field is proposed.

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LIST OF ABBREVIATIONS

AFM	atomic force microscopy
ALD	atomic layer deposition
BD	breakdown
C-AFM	conductive atomic force microscopy
CCI	constant current imaging
CF	conducting filament
CHI	constant height imaging
CITS	constant current tunnelling spectroscopy
CMOS	complementary metal-oxide semiconductor
CVS	constant voltage stress
DIBL	drain-induced barrier lowering
ECM	electrochemical metallization
EELS	electron-energy loss spectroscopy
HRS	high resistance state
IC	integrated circuit
IL	interfacial layer
LED	light-emitting diode
LRS	low resistance state
MOS	metal-oxide-semiconductor
MOSFET	metal-oxide-semiconductor field-effect transistor
NPC	negative photoconductivity
NVM	non-volatile memory
PVD	physical vapor deposition
RRAM	resistive random access memory
RTA	rapid thermal annealing
RVS	ramp voltage stress

SBD	soft breakdown
SCE	short channel effect
SILC	stress-induced leakage current
SPM	scanning probe microscopy
STM	scanning tunnelling microscopy
STS	scanning tunnelling spectroscopy
TAT	trap-assisted tunneling
TCM	thermochemical memory
TDDB	time-dependent dielectric breakdown
TEM	transmission electron microscopy
UHV	ultra-high vacuum
VCM	valence change memory
XPS	x-ray photoelectron spectroscopy
XRD	x-ray diffraction

LIST OF SYMBOLS

μ	micro
κ or ε	dielectric constant
$\text{\AA}$	Angstrom
σ_{V_o}	ionic conductivity
D	diffusion coefficient
I - V	current-voltage characteristics
I - t	current-time characteristics
I_t	tunneling current
V_o	oxygen vacancy
O^{2-}	oxygen ions

Chapter 1 INTRODUCTION

1.1 Background

1.1.1 Scaling trend of semiconductor devices

The scaling of the semiconductor devices is the primary research activity of utmost importance to the microelectronics industry since the invention of the integrated circuits (IC). The shrinking of the dimensions of a single device enables more devices to be integrated into the area of the same size, thus significantly increasing the circuit density and functionality and reducing the manufacturing cost per single device [1-3]. In addition, the shrinking dimensions of the device also increase the operation speed and reduce the power consumption [4]. Therefore, scaling of semiconductor devices is one of the best approaches that achieves better performance, lower fabrication cost, and reduced power consumption simultaneously [5]. Fig. 1.1 shows the beneficial impact of scaling the dimensions of transistors as reported by Intel [6]. Apparently, the transistor density is increasing from generation to generation, while the cost per transistor is decreasing with new process nodes. In addition, from the performance profiles of Intel's mobile, laptop, and server products, we can see that the performances of all of them improved with scaling dimensions while the active power consumption is reduced. As a result, the power efficiency is enhanced tremendously via the scaling as can be seen in the performance per watt plot in Fig. 1.1.

Fig. 1.1: The beneficial impact of dimension scaling for semiconductor devices. The individual transistor area and the fabrication cost per transistor decrease. Regarding the product benefits, the performance increases while the active power consumption decreases, leading to significant enhancement in power efficiency [6].

The semiconductor industry has been following the scaling principle for the above-mentioned advantages since its foundation. In 1965, Gordon Moore, the co-founder of Intel, observed the scaling trend and predicted that the number of transistors integrated in a given space will be doubled every year. Later, the period was adjusted to 18 months due to the growing complexity of the fabrication techniques [7]. Fig. 1.2 shows the transistor count trends in various IC products including logic processing unit, volatile memory, and non-volatile memory (NVM) since 1970s [8]. Moore's law has been fulfilled for the past half century. An improvement in the performance and

reduction in the fabrication cost is the driving force for the semiconductor industry to follow Moore's law and continue scaling down the dimensions.

Fig. 1.2 The transistor count trends for various semiconductor components since 1970s. The exponential increase of the transistors per die confirms the prediction stated by Moore's law [8].

1.1.2 Scaling challenge of the conventional NAND flash memory

Non-volatile memory, whose data will not be lost without power supply, is a significant component for long term persistent data storage in an electronic system. As shown in Fig. 1.2, the NAND flash has been widely used and developed since 1970s by virtue of its immense advantages in fabrication compatibility with the mainstream Si-based CMOS manufacturing process and device scalability [9, 10]. Especially in the

past decade, the market for smart phones, tablets, and other personal mobile devices is rapidly growing. As the memory centers of all these devices, memory cells are facing a strong demand for further scaling down to achieve lower power consumption, higher speed, and lower fabrication cost to catch up with the moving pace of the market. However, when the feature size of the NAND flash memory cells comes to the sub-20 nm regime, it encounters a series of scaling challenges [11]. With the shrinking dimensions of the NAND flash, the interferences between surrounding cells are severe enough to cause program disturb errors [12-15]. In an individual cell, the short channel effect (SCE) becomes much more significant with a smaller channel length [16-19]. Consequently, the drain-induced barrier lowering (DIBL) effect will cause program disturb [20]. The SCE can be inhibited via a highly doped channel. However, the higher junction leakage is the trade-off to this SCE suppression approach [21]. Furthermore, the shrinking induced larger S-factor severely reduces the on/off ration of the NAND flash, which is a substantial parameter in the multi-level cell (MLC)/triple-level cell (TLC) bit technology [22].

1.1.3 RRAM – next generation NVM

On account of all the scaling challenges encountered by the NAND flash, the semiconductor industry has been seeking emerging NVMs to continue developing the roadmaps for memory cells and fulfill the growing performance–cost requirements and market demand.

To serve as the next generation NVM novel technology that replaces the conventional NAND flash, the candidates have to fulfill the following requirements listed:

1. Better scalability beyond sub-20 nm – This is the fundamental requirement for further scaling down.
2. Fabrication compatibility with mainstream Si-based CMOS manufacturing process – This allows easy transition from NAND flash to next generation NVM by avoiding enormous investment on the new fabrication techniques.
3. Better electrical performance, including faster operating speed and lower power consumption
4. Acceptable reliability such as good switching endurance and reliable retention time

Several novel NVMs technologies have been proposed as the potential candidates for the next-generation memory, among which the magnetoresistive random-access memory (MRAM), ferroelectric random-access memory (FeRAM), phase-change memory (PCRAM), and resistive random-access memory (RRAM) are attracting more researchers' attention. After the scientific investigation of these candidates, it is found that the materials constituting the MRAM and FeRAM are not compatible with the current Si-based CMOS fabrication technique [23, 24]. The challenge for the PCRAM is its high-power consumption [25]. Therefore, RRAM becomes the most promising candidate for the next-generation NVM, fulfilling the previously mentioned requirements [26-28].

1.2 Motivation

The resistive switching (RS) behavior has been broadly reported in many high-k dielectrics sandwiched between two metal electrodes [29-33]. This metal-insulator-metal (MIM) structure has become the most used configuration for the RRAM cell. The standard methodology to investigate the electrical properties of the RRAM cell at

the device level is carried out utilizing the semiconductor parameter analyzer (SPA) via metal electrodes probing at a probestation. The influence of the fabrication parameters for instance, the materials choice of active layer – the high-k dielectrics and metal electrodes, the thickness of the oxides, and the different doping impurities and concentrations to the RS performance – have been systematically studied at the device level [34-38].

However, the device performance measured by a probestation is the averaged macroscopic signal of the whole active area beneath the top electrode due to the inevitable area-averaged effect. Although they revealed the impact factors influencing the device performance, the lack of microscopic insights into the microstructural change during switching is a crucial obstacle in the thorough understanding of the switching mechanism. Furthermore, the dimension scaling is an eternal pursuit of the entire semiconductor industry, including the RRAM field. When the dimension of the RRAM device enters the nanometer regime, its electrical characteristics are not exactly the same as the macroscopic counterpart. Because the microscopic electrical characteristics are more sensitive to the atom arrangement, oxides stoichiometry, non-uniformity, and local defects, some unique behavior would appear in a nanoscale RRAM cell. Therefore, the atomic-level metrology equipment is vital to study the unique microscopic performance of the more advanced nanoscale RRAM. The motivation behind conducting this research is to utilize the superior spatial resolution of the ultra-high vacuum scanning tunneling microscopy/conductive atomic force microscopy (UHV-STM/C-AFM) to accurately measure the electrical characteristics and the physical topography of the nanoscale RRAM simultaneously, thus providing microscopic insights into the microstructural changes and defects distributions under various experimental conditions. This nanoscale characterization metrology would

enhance the understanding of the RRAM at a microstructure level and may reveal some unique behavior related to the more vulnerable nanoscale CF due to its ultra-small dimensions.

1.3 Objectives

The aim of this project is to study the unique microscopic performance of the RRAM device at a nanoscale level in various experimental conditions, further improving the fundamental understanding of the RRAM mechanism and exploring the new functionality of the RRAM high-k stack by providing microstructural insights with high spatial resolution UHV-STM/C-AFM. The detailed objectives are as follows:

- To study the prospect of the dimension scaling of the RRAM cell by creating a nanoscale CF of 2.5 nm in diameter; The switching capability and switching current will be examined.
- To reveal the role of an anode electrode on the reliability performance of the RRAM cell
- To study microstructural insights into the large RRAM cell by direct observation via the STM current map, revealing the origin of the macroscopic progressive reset behavior
- To explore the emerging NPC phenomenon on the large bandgap oxide materials conventionally used in RRAM cell
- To study the reliability rejuvenation capability of the NPC phenomenon on post-breakdown oxides
- To study the different photoresponses between RRAM and CBRAM, investigating the mechanism of the NPC phenomenon

- To study the impact factors on the photosensitivity of RRAM cell; The high temperature working capability and the broad spectrum detecting ability will be examined.
- To explore an in-situ photosensitivity modulation approach, making the photosensitivity electrically programmable according to actual needs

1.4 Organization of thesis

This thesis is divided into seven chapters organized in the following ways:

- *Chapter One* presents the background, motivation, objectives, and original contributions of the project.
- *Chapter Two* presents the literature review of the resistive switching behavior, including the historical overview of the RRAM researching activities and the technological overview of the recent development on the RRAM material issues, operating mechanism, and the electrical characteristics.
- *Chapter Three* presents the detailed experimental setup and the sample fabrication process. The STM/C-AFM characterization technique is briefly introduced.
- *Chapter Four* presents the study on the effects of scaling down on the switching current and the unique abrupt reset process on single nanoscale filament. The origin of the macroscopic progressive reset behavior at the device level is revealed by the direct observation of the multiple filaments via STM and the statistical analysis on the switching characteristics of those filaments. The impact of the anode electrode on the reliability performance of the RRAM device is investigated.
- *Chapter Five* reports the emerging negative photoconductivity (NPC) phenomenon on a metal oxides-based RRAM stack. The reliability rejuvenation capability is investigated on different materials and breakdown hardness. The electrical robustness of the NPC

induced reliability rejuvenation is statistically proved by the Weibull distribution compared with fresh oxides. The photoresponses in $\text{HfO}_2/\text{ZrO}_2$ -based RRAM and SiO_2 -based CBRAM are systematically studied and based on which the physical mechanism for the NPC phenomenon is proposed.

- *Chapter Six* provides a comprehensive study on the various impact factors on the photosensitivity of the soft-breakdown percolation path. A new TiN-mediated multi-level negative photoconductance property is revealed from the study and can be utilized as a convenient in-situ photosensitivity modulation approach.
- *Chapter Seven* presents the conclusion of this report and the recommendations for the future work.

1.5 Original contributions

The major contributions of this research lie in the utilization of high lateral resolution UHV-STM/C-AFM for the electrical characterization of RRAM oxides stacks at a nanoscale level, addressing the prospect of dimension scaling, advancing the fundamental understanding of the RRAM switching process by direct observation of the multiple filament distribution and electrical measurement at individual filament via nanoscale probing. The NPC phenomenon was first observed in the non-photo-responsive large bandgap oxide materials conventionally used in RRAM stacks. The prospect of the application of this NPC phenomenon on reliability rejuvenation and optical sensor was investigated systematically. The mechanism and impact factors of the NPC phenomenon were studied and the in-situ photosensitivity modulation approach was proposed. The detailed contributions of this research are listed as follows:

The ultra-low switching current was achieved by scaling down the cell area to $\sim 5 \text{ nm}^2$ with a minimized sidewall capacitance via STM/C-AFM nanoscale probing. The working capability and prospect of RRAM scaling down was confirmed and evaluated. The nanoscale CF is directly observed via STM scanning in ultra-high vacuum ($\sim 5 \times 10^{-10}$ Torr).

The unique abrupt reset behavior of the nanoscale CF was observed via STM/C-AFM probing, in contrast to the progressive and gradual reset behavior observed in large scale RRAM device. The current map via the STM localized measurement revealed the existence of multiple filaments beneath the top metal electrode in RRAM device after electroforming. The electrical characteristics information of each single filament was collected. After the statistical analysis, more than 70% of the CFs exhibit abrupt reset behavior with large variations in the reset voltages and currents. The summation of all the single filaments reproduced the I-V characteristics of the large-scale RRAM device. Therefore, it is found that the origin of the progressive reset behavior is the averaging effect among multiple filaments in large scale device, while the majority of the individual filaments exhibit abrupt reset.

The impact of the anode metal electrode was found by comparing the samples with and without the capped metal layer. The larger percentage of resistive switching at capped oxide sample proved the role of the capping layer as the oxygen ions reservoir during forming, which supplies the oxygen ions during bipolar reset. It advanced the fundamental understanding of the oxygen ions migration model for the resistive switching.

A new phenomenon, negative photoconductivity photo-response was discovered for the first time in large bandgap oxide materials conventionally used in RRAM stacks. The detailed photo-response characteristics were investigated for $\text{HfO}_2/\text{ZrO}_2$ -

based RRAM and SiO₂-based CBRAM stacks. By comparing the different NPC behavior of the RRAM and the CBRAM, the oxygen ions back migration model was proposed to explain the rapture of CF upon illumination.

The prospect of the application of the NPC phenomenon for oxides reliability rejuvenation was evaluated. The efficiency of the light-induce restoration of the SBD oxide was studied and proved to be better than electrical restoration with an opposite polarity to forming bias in SiO₂-based stacks. The influence of the breakdown hardness was also revealed. Only partial restoration can be achieved on severer breakdown of oxides upon the same illumination duration and intensity. The robustness of the light-induced oxide rejuvenation was investigated via time-dependent dielectric breakdown (TDDB) reliability check. Through statistical analysis, by comparing the Weibull distribution of the time taken to breakdown between the pristine and restored oxides, we found that the robustness of the fully restored oxide is similar to its pristine counterpart.

The impact factors on the NPC photo-response were investigated. It is found that the photosensitivity follows a lognormal distribution at a given light intensity. The mean value of the photo-response speed was 0.72 and 2.4 s/decade for 12.5 and 2.5 mW/cm² white light, respectively, implying a positive correlation. The photo-response speed showed a weak dependence on wavelength in the visible range. The broad-spectrum sensing capability was checked up to 850nm. The high temperature operating capability was also assessed. A slower response speed was observed at 390 K as compared to room temperature, attributed to the severer lateral propagation of the oxygen ions with higher thermal energy during forming process. The relationship between the photosensitivity and the oxygen stoichiometry was found to be positively

correlated by comparing the photo-response performance on an oxygen rich sample ($\text{Hf:O} = 1:3.3$) and an oxygen deficient sample ($\text{Hf:O} = 1:1.6$).

A new method, via the adjustment of the metal ions concentration in current percolation path by electrical stress, for modulating the photosensitivity in-situ according to actual needs is developed. The role of the metal ions is affirmed by comparing the photo-response between the samples with and without the bottom metal electrode. The suppression of the NPC is lost on non-metal sample. It is also observed that no NPC suppression occurred when applying positive bias to the C-AFM probe due to the lack of the metal ions diffusion into the oxide layer. The reverse polarity of electrical bias was found to be able to restore the photo-response of the oxides by driving the metal ions back to bottom electrode, facilitating the recombination between interstitial oxygen ions and the vacancies in CF.

Our research works have been published in established international conferences and peer reviewed journals, such as the Applied physics letters (APL), IEEE Journal of the Electron Devices Society (JEDS), Solid States Devices and Materials (SSDM) symposium, IEEE Electron Device Letters (EDL), and ECS Transactions (ECST).

Chapter 2 LITERATURE REVIEW

2.1 Introduction

This chapter is divided into three main sections to systemically review the RRAM and the oxide materials related issues by various research group. Section 2.2 reviews the historical development of the research activity on the topic of RRAM starting from the first observation in the 1960s to the first revival in 1990s and then the recent prosperity from 2004. The basic operation principle and cycle is reviewed as well. Section 2.3 reviews the categories of the RRAM and the research done on the investigation of corresponding mechanisms, namely the electrochemical metallization memory (ECM), valence change memory (VCM), and thermochemical memory (TCM). Section 2.4 reviews the present status and challenges of the RRAM and the oxide materials in terms of scalability issues, switching mechanism issues, reliability issues, and the optical-cum-electrical related research.

2.2 RRAM overview

2.2.1 The historical development of RRAM research activity

The first observation of resistive switching behavior of the oxide stacks was reported in 1960s [39-42]. The reported device had a simple three layers MIM

structure, namely metal-insulator-metal structure, with oxides sandwiched in between as shown in Fig. 2.1 [43]. The resistance of this device was reported to be able to switch between high resistance state (HRS) and low resistance state (LRS) under specific electrical bias. However, these early reports were not competitive enough compared to its rival – NAND Flash memory – in terms of electrical performance and reliability. The research activity did not attract much attention until the 1990s; the research activity on RRAM started to increase due to the discovery of the prevalent resistive switching behavior in complex perovskite oxides such as SrZrO_3 [44], SrTiO_3 [44] and the simple binary oxides such as ZrO_2 [45], HfO_2 [46], NiO [47], and TiO_2 [48]. At that time, many abbreviations, such as RRAM, RRAM, OxRAM, had been used for these devices. The prosperity of the research activities on RRAM was initiated by the paper presented by Samsung at the International Electron Devices Meeting (IEDM) 2004 [49]. A prototype was presented of the 1T1R structure making it possible for a commercialized crossbar memory array [49]. The switching stacks were integrated with conventional CMOS transistor acting as a selector in the memory array. The reliability performance was also demonstrated in terms of retention and endurance.

Fig. 2.1 (a) The schematics of a RRAM device consisting of the MIM structure. (b) The schematics of the unipolar resistive switching. (c) The schematics of the bipolar resistive switching [43].

2.2.2 The operation procedure and modes in RRAM

The typical operation procedure for RRAM devices normally consists of three processes: forming, set, and reset. The function and previous studies of each process are introduced as follows:

2.2.2.1 Forming and Set

The function of the forming process is to intentionally induce a soft breakdown in the oxides [50, 51]. The word soft indicates the breakdown hardness is under control and weak. The preset current compliance is the key factor to limit the breakdown hardness. During soft breakdown, the strong electrical field (> 10 MV/cm) breaks the metal-oxygen bonds. The released negatively charged oxygen ions will drift toward the anode accelerated by the electrical field, leaving numerous defects in the oxides. These defects are lack of oxygen ions, thus, being named oxygen vacancies, which causes the formation of the conductive filament (CF) [52, 53]. There are two types of RRAM oxides, amorphous and polycrystalline. It is reported that the CFs are more likely to be formed along the grain boundaries in polycrystalline oxides [54].

The set process is similar to the forming process. Its function is to generate the CF as well. The only difference is that forming process normally requires a larger bias. Because the fresh sample is more robust against soft breakdown due to the fewer intrinsic defects. While after the initial forming is done, the current percolation path has already formed. The subsequent reset process only repairs a small portion of the oxygen vacancies formed CF near the electrode. Therefore, the set process is carried out in a more oxygen deficient environment, leading to a smaller bias.

Apparently, the forming process increases the operation complexity of the RRAM device. So, the forming free RRAM are very desirable to simplify the RRAM operation. The relationship between the forming voltage and some parameters has

been reported. The oxide thickness is found to be effective for controlling the forming voltage – the thinner the oxide, the smaller the forming voltage [55-57]. It is reported that forming free characteristics can be achieved on the HfO_x dielectric layers thinner than 3 nm [55]. Certain papers also revealed the influence of the fabrication conditions on the forming free property [58, 59]. It is found that the annealing conditions are essential to the intrinsic defects in fresh sample, and the increasing number of intrinsic defects reduces the forming voltage to be comparable with the subsequent set process, thus being free from forming [60, 61].

2.2.2.2 Reset: Unipolar and Bipolar

There are two operation modes for the reset process depending on the bias polarity required for resistive switching as shown in Fig. 2.2 [26]. The unipolar reset is illustrated in Fig. 2.2 (a). The reset happens at the same polarity in set with a higher current than current compliance preset for set and a smaller voltage than set. In contrast, the bipolar reset must occur at the opposite polarity of the electrical bias to the set process as shown in Fig. 2.2 (b). Different models have been developed to explain the unipolar and bipolar reset behavior. Among them, the thermal dissolution process is able to explain most of the characteristics in unipolar switching [62], while the ionic migration process is more suitable for most of bipolar switching behavior [63]. However, the complete mechanism which can explain all the observations are still under investigation. Nowadays, the RRAM device is classified into three classes according to its operation mechanism – electrochemical metallization mechanism (ECM), valence change mechanism (VCM), and thermochemical mechanism (TCM), which will be discussed in detail in the subsequent section.

Fig. 2.2 The schematic diagram of (a) unipolar and (b) bipolar resistive switching [26].

2.3 Classification of RRAM and corresponding mechanisms

2.3.1 Electrochemical metallization (ECM)

Electrochemical metallization mechanism was developed to explain the resistive switching in conductive bridge random access memory (CBRAM) by metal ions diffused into or out of the solid electrolyte under opposite electrical bias [64]. The schematic diagram of its working principle is shown in Fig. 2.3 [65]. The key component is an electrochemically active metal electrode, which can inject metal ions into the electrolyte during the forming/set process as shown in Fig. 2.3A. Silver (Ag), copper (Cu), and nickel (Ni) are the most commonly used electrochemically active materials in CBRAM. In contrast to the anode materials, the cathode must be an electrochemically inert metal, such as gold (Au), tungsten (W), iridium (Ir), or platinum (Pt) to avoid the metal dissolution from it and its subsequent diffusion into the electrolyte during bipolar reset process. The insulating layer sandwiched between these two electrodes has to be ion-conductive. The study on the electrolyte materials

have shown that SiO_2 [66], Cu-doped Ge-Se [67, 68], and Ge-S [69] are suitable to serve as the insulating layer in CBRAM.

Fig. 2.3 The basic operation cycle of a CBRAM. A) The SET process: The growth of the Ag filament in electrolytes under positive bias applied to Ag electrode. B) The Ag filament connects both metal electrodes, leading to ON state (LRS). C) The RESET process: The dissolution of the metal filament under negative bias. D) The metal filament is ruptured, resulting in OFF state (HRS) [65].

The ECM type resistive switching was first reported in 1976 [70], in which silver was used as the electrochemically active electrode, and Ag-doped As_2S_3 was used as the insulating layer. Fig. 2.4 is the optical microscopy image of the metal filament growth from the cathode to the anode. Under positive bias, the Ag ions diffuse into the electrolyte and drift toward the cathode, from where the Ag ions discharge and accumulate [70].

Fig. 2.4 The growth of the silver filament from electrochemically inert electrode (Au) to electrochemically active electrode (Ag) under optical microscopy [70].

The typical switching cycle of the ECM RRAM is illustrated in Fig. 2.5 (a) [71]. A larger bias is required for the first electroforming process during the first I-V cycle. The reason is that the initial formation of the metal ions percolation path required strong energy to cause the microstructural change in the solid electrolyte. The subsequent SET process can easily form the metal filament by transporting the metal ions in the pre-formed channel created by forming process [71]. Furthermore, as seen in Fig. 2.5 (b), the forming voltage $V_{\text{SET, form}}$ is linearly proportional to the electrolyte thickness, while the SET voltage V_{SET} remains as a constant value for all the thicknesses ranging from 5 to 20 nm. This thickness independent SET voltage in ECM system can be explained by the theory that the pre-formed conducting channel can serve as a fast ion transportation path for the subsequent SET process, making the impact of the film thickness negligible [71].

Fig. 2.5 (a) The typical switching cycle of an ECM memory cell, Cu/ SiO_2 /Pt with electrolyte thickness of 15 nm. A larger forming voltage is clearly seen as compared to the subsequent SET process. (b) The relationship between the SiO_2 thickness and the forming voltage (blue), SET voltage (red) [71].

As discussed before, the growth of the metal filament starts from the electrochemically inert electrode [72, 73]. Considering the metal filament dissolution process during RESET, it is worthwhile to investigate where the dissolution starts. Therefore, an experiment has been carried out on an Ag/ H_2O /Pt sample with a coplanar structure [74], which allows the direct observation of the filament growth and dissolution during resistive switching by SEM. During the RESET process, it is found that the dissolution of the metal filament starts from the electrochemically active side, the negatively biased Ag [74]. An electrical field simulation was also shown to be consistent with the experiment observations (Fig. 2.6) [74]. The electrode shown in the simulation plot is at the Ag side, and the metal filament is Ag as well. It can be seen from Fig. 2.6 (c), at the early OFF state, the dissolution of the Ag filaments starts from negatively biased electrochemically active electrode.

Fig. 2.6: The numerical electrical field simulation for the RESET process in ECM system. (a) the overall view of the metal filament, indicating the simulated area. (b) The electrical field distribution at the ON state of the RRAM. (c) The microstructural change of the metal filament at the early OFF state [74].

2.3.2 Valence change memory (VCM)

The VCM resistive switching is commonly observed in many binary metal oxides without electrochemically active metal electrode injecting cations. Some multinary metal oxides with transition metal sublattices can exhibit VCM resistive switching as well. The first report about VCM type RRAM dates to 1960s on the Nb/NbO_x stacks [75]. During the first revival of the RRAM research activity in 1990s, the VCM effect was found to broadly exist in various manganites [76, 77], titanates [44], and zirconates [78].

There are many mechanisms proposed for VCM type RRAM. One big category is attributing the VCM switching to purely electronic effects. The charge trap model is one of those purely electronic models [79]. It is reported that the charges can be injected into the oxide thin film by Fowler-Nordheim (FN) tunneling and form the

metal nanoclusters with the defects or metal particles in the thin films such as polymeric [80, 81] and inorganic insulators [82]. The formed metal nanoclusters modify the resistance of the conduction path, thus resistive switching can be achieved by the formation and dissolution of the metal nanoclusters in the thin film. Another purely electronic model states that the charges injected would be trapped at interface states. The change in the interface states will modify the Schottky barrier between the metal electrode and the oxides, thus resulting in a resistive switching [83, 84]. Some research also showed that the injection of the charges into the perovskite-type oxides will cause the insulator-metal-transition (IMT), which causes the resistive switching in perovskite oxides, for instance, (Pr,Ca)MnO₃ [76, 85] and SrTiO₃:Cr [86]. A universal purely electronic model has been proposed by Rozenberg et al [87].

However, all purely electronic models cannot solve the voltage-time dilemma [88]. The importance of the anions transport has been gradually realized by most of the researchers in RRAM field and accepted as the present state of switching mechanism in VCM RRAM [89]. The aforementioned anions typically refer to oxygen ions, which are more mobile than metal ions in transition metal oxide. The motion of the oxygen ions leads to the accumulation of oxygen vacancies, which significantly changes the valence state, resulting in the conductivity of the percolation path. The broad existence of the valence state change caused by the transport of oxygen ions is the origin of the name “VCM” for this category of RRAM.

The numerical simulation of the oxygen vacancies profile along the percolation path in the oxides has been reported as shown in Fig. 2.7 under different applied bias [90, 91]. As can be seen from Fig. 2.7 (a), at low applied bias $V = 3$ mV, the oxygen concentration profile is linear, and the change amplitude is too small to be of

significant change in the conductivity of the oxides. The linear oxygen concentration is the result of balancing drift and diffusion currents based on this equation:

$$\frac{\partial V_o^{2-}}{\partial x} = \frac{\sigma_{V_o} E}{2eD_{V_o}}$$

where D denotes the diffusion coefficient and σ_{V_o} is the ionic conductivity. In contrast, in the oxygen vacancies profile under large applied bias $V = 1$ V, a significant increase of the oxygen vacancies concentration can be observed, which reaches the highest value near the cathode (Fig. 2.7 (b)) [91].

Fig. 2.7 The numerical simulation of the oxygen vacancies concentration profile in SrTiO_3 at (a) low applied bias [90] and (b) high applied bias [91].

This simulation result is validated by the optical images in the transmission mode of the Fe doped SrTiO_3 sample with applied bias as shown in Fig. 2.8 [91]. The darkness of the color indicates the Fe ions' concentration, and the color indicates the valence state, red for valence state of +4 and white for lower valence state due to the accumulation of the oxygen vacancies. During the forming process, the white region near the cathode will drift toward the anode due to the electrical field applied. Once the white region almost punches through the entire oxides, the resistance of the oxide stacks will drop dramatically, leading to a successful forming process.

Fig. 2.8 Optical images of transmission mode presenting the electroforming process in VCM system. Red color denotes a +4 valence state. White color denotes a lower valence state. The experiment was carried out at a temperature of 453 K and with an electrical field strength of 1 kV/cm [92].

Janousch et al. [53] complemented the VCM model by using X-ray fluorescence (XRF) and the infrared thermal image as shown in Fig. 2.9. The color scale in the XRF image of the Cr-doped SrTiO_3 denotes the oxygen vacancies concentration after electroforming. The oxygen vacancies formed conductive filament (CF) can be seen clearly, validating the proposed VCM model. In addition, the infrared thermal image presents the power dissipation across the conductive filament. The heat is more concentrated at the anode region. This observation validates the explanation that the oxygen vacancies start accumulation from cathode and propagates toward anode gradually, leading to the switching interface to be located near anode during resistive switching.

Fig. 2.9: (a) The XRF image of the Cr-SrTiO₃ sample after forming. The contrast is maximized by the strong energy used during XRF – 6004.3 eV. The color scale denotes the oxygen vacancies concentration. (b) The infrared thermal image of the same sample. The color scale denoted the heat dissipation. The total heat dissipation across the sample is ~150 mW [53].

The microstructural change due to the accumulation of the oxygen vacancies can be directly observed when the forming current enters the range of mA or higher and the active area is small, a high current density to be specific. Fig. 2.10 [93] presents the direct observations of the microstructural change, via scanning electron microscopy (SEM), in a 27 nm TiO₂ sandwiched between Pt electrodes. The current compliance preset for forming is 0.1 mA. Fig. 2.10 (c) is the top view of the sample surface, the microstructural change can be seen clearly. To check the microstructural change in the oxides, a focused ion beam (FIB) cut is made on the MIM stacks. As can be seen from Fig. 2.10 (d)-(f), the microstructural change in the oxides is proved as well [93].

Fig. 2.10 SEM images on the Pt/TiO₂/Pt sample after forming process. (a) Schematic diagram of the sample (b) Top overview (c) Top zoom-in view (d) side view after the FIB cut (e)(f) zoom-in side view showing the cross-sections of the microstructural change inside the oxides [93].

2.3.3 Thermochemical memory (TCM)

The TCM was first reported in the transition metal oxide NiO in 1960s [40]. The TCM cell normally presents a unipolar resistive switching behavior as shown in Fig. 2.11 [94]. The forming hardness is controlled by the preset current compliance of 1 mA. After forming, the current compliance is released to allow the unipolar RESET to happen at a necessary higher current and smaller voltage than forming. The subsequent SET process occurs at a relatively lower voltage compared to forming. The HRS resistance at the OFF state is reported to be proportional to the device area indicating a uniform current distribution across the oxides stack for the TCM system [95-97]. The thermal effects induced filamentary path model is introduced to the TCM system.

However, there is no conclusion about the number of filaments – whether it is the single filament system [95, 96, 98, 99] or multiple filament system [97, 100].

Fig. 2.11 Typical I-V characteristics of the unipolar TCM resistive switching on Pt/NiO/Pt sample. The thickness of the NiO layer is 50 nm. The current compliance preset is 1 mA for the forming process and 0.5 mA for the subsequent SET process [94].

The theory of the thermal breakdown induced filamentary path is proposed based on the study on the temperature dependence of the HRS and LRS resistance [101]. As shown in Fig. 2.12, the LRS resistance indicates a weak metallic behavior. The relative resistance ratio, namely the ratio between the resistance at 300 K and 5 K, is 1.6, which is below pure metallic conductive filament and above the stoichiometric semiconductor materials [102]. This relative resistance ratio implies that an impure metallic filamentary path has been formed during the forming process. After RESET, the HRS resistance presents typical semiconductor temperature dependence with thermal activation energy of $\sim 0.1 - 0.15$ eV [96, 102], like the virgin resistance before forming. Based on these observations, it is proposed that the impure metallic

filamentary path is formed by the thermal energy induced breakdown, whose hardness is controlled by the preset current compliance during forming, which serves as conducting path between the two electrodes. In the subsequent RESET process, the current compliance is released. The impure metallic filamentary path will be thermally ruptured again under the severer heating environment at a higher current level as shown in Fig. 2.11 [94].

Fig. 2.12 Temperature dependence of the LRS resistance after forming (blue), HRS resistance after RESET (green) and the virgin resistance before forming (red) [101].

2.4 Current research status and challenges for RRAM

One of the main motivations for the RRAM to be the next generation NVM replacing NAND Flash is the prospective scalability and induced low switching current, namely low operation power, which is extremely important for the mobile applications.

Numerous studies have been reported on various materials and structures to minimize the switching current, which has been summarized in the table below:

RRAM Structure	Switching Mode	SET Current	RESET Current	References
TiW/SiO _x /TiW	Unipolar	~ 100 μ A	~ 200 μ A	Yao et al. [103]
Pt/Gd ₂ O ₃ /Pt	Unipolar	10 mA	~ 30 mA	Cao et al. [59]
Pt/NiO/Pt	Unipolar	1 mA	> 1 mA	Kim et al. [104]
Ni(Co)/Cu ₂ O/Cu	Unipolar	~ 80 μ A	~ 100 μ A	Chen et al. [105]
Pt/Mn:ZnO/Pt	Unipolar	5 mA	~ 17 mA	Peng et al. [106]
Cu/ZnO/n ⁺	Unipolar	~ 500 μ A	~ 3 mA	Qinan et al. [107]
TiN/WO _x /W	Unipolar	-	-	Chien et al. [108]
Pt/NiO/W	Unipolar	~ 20 μ A	~ 500 μ A	Ielmini et al. [109]
Ti/ZnO/Ti	Nonpolar	20 mA	-	Andy et al. [110]
Pt/TiO ₂ /TiO _{2-x} /Pt	Bipolar	< 200 μ A	< 200 μ A	Yang et al. [111]
TiN/Al ₂ O ₃ /Pt	Bipolar	20 μ A	~ 20 μ A	Wu et al. [112]
Ti/ZrO ₂ /Pt	Bipolar	30 mA	~ 30 mA	Lin et al. [113]
Pt/Ti/TiO ₂ /W	& Bipolar	500 μ A	0.5&3 mA	Harmes et al. [114]
Pt/W/TiO ₂ /W				
Ir/TiO ₂ /TiN	Bipolar	1 mA	~ 2 mA	Park et al. [115]
Pt/ZnO/Pt	Bipolar	3 mA	~ 3 mA	Chiu et al. [116]
TiN/TiO _x /HfO _x /TiN	Bipolar	40-200 μ A	40-200 μ A	Lee et al. [117]
Ti/Mo:ZrO ₂ /Pt	Bipolar	<20 mA	< 30 mA	Wang et al. [45]
Ta/TaO _x /Pt	Bipolar	100 μ A	~ 100 μ A	Yang et al. [118]
IrO _x /TaO _x /WO _x /W	Bipolar	1 mA	627 μ A	Prakash et al. [119]
Pt/Ta ₂ O _{5-x} /TaO _{2-x} /Pt	Bipolar	200 μ A	~ 200 μ A	Lee et al. [120]
TiN/Ti/HfO ₂ /TiN	Bipolar	150 μ A	~ 100 μ A	Walczyk et al. [121]
Pt/TaO _x /Pt	Bipolar	< 170 μ A	< 170 μ A	Wei et al. [122]
Pt/Al/Pr _{0.7} Ca _{0.3} MnO ₃ /Pt	Bipolar	1 mA	~ 10 μ A	Seong et al. [123]
Ta/HfO ₂ /TiN	Bipolar	100 μ A	-	Chen et al. [124]
Ti/Al ₂ O ₃ /Pt	Bipolar	> 1 mA	~ 7 mA	Lin et al. [125]
TiN/TiON/HfO _x /Pt	Bipolar	50 μ A	30 – 50 μ A	Yu et al. [126]
Au(Pt)/SrTiO ₃ /Au(Pt)	Bipolar	2.8 $\pm$ 0.8A	2.5 $\pm$ 0.5mA	Szot et al. [127]
Au/SrTiO ₃ /Ti	Bipolar	10 mA	~ 2 mA	Sun et al. [128]
Cu/ZrO ₂ :Ti/Pt	Bipolar	1 mA	~ 10 mA	Liu et al. [129]
Ti/ZrO ₂ /Pt	Bipolar	5 mA	~ 4 mA	Wang et al. [113]
TiON/WO _x /W/TiN	Bipolar	100 nA	1 μ A	Ho et al. [130]
Pt/WO _x /W	Bipolar	10 mA	~ 10 mA	Kim et al. [131]
IrO _x /Al ₂ O ₃ /IrO _x ND/Al ₂ O ₃ /IrO _x	Bipolar	500 μ A	> 1 mA	Banerjee et al. [132]
Au/ZnO/Au	Bipolar	10 mA	~ 10 mA	Peng et al. [133]
n-Si/SiO _x /p-Si	Bipolar	2 μ A	~ 100 μ A	Mehonic et al. [134]
IrO _x /GdO _x /WO _x /W	Bipolar	1 mA	~ 1mA	Jana et al. [135]
IrO _x /Al ₂ O ₃ /GeNW _s /SiO ₂ /p	Bipolar	20 μ A	22 μ A	Prakash et al.

-Si				[136]
Pt/ZrO _x /HfO _x /TiN	Bipolar	< 200 μ A	$\sim$ 200 μ A	Lee et al. [137]

Table 2.1: The summary of the research on resistive switching, including various structures and materials. The corresponding switching mode and SET/RESET current are listed [26].

From the literature listed above, we may conclude that the switching current is normally in the range of mA for a large area memory cell $\sim 10^{-8} \text{ cm}^2$. The most significant reduction in the switching current was achieved on TiON/WO_x/W/TiN structure with a bipolar switching behavior [130]. The achieved SET current is 100 nA, while the RESET current is much higher – 1 μ A. The challenge for further scaling down still exists. Further investigation to evaluate the potential of the switching current scalability is required.

The filamentary-conduction model, based on the electric field-driven oxygen-vacancies (V_o 's) migration within an oxide, has been widely adopted to explain the resistance switching (RS) mechanism in a resistive random access memory (RRAM) cell [53, 89-93, 138-140]. However, the shortcoming of the conventional electrical characterization technique in resolving the microscopic details has limited further understanding of the conductive filaments' (CFs) evolution during an RS operation. Hence, some groups have resorted to various advanced microscopic characterization techniques, such as scanning probe microscopy (SPM) [141, 142] and scanning transmission electron microscopy & electron energy loss spectroscopy (STEM-EELS) [143-145] to reveal the micro-structural change that occurs in a metal-oxide after the RS operation. By using conductive atomic-force-microscope (C-AFM) probing, Celano et al. [141] observed a relatively large, a diameter of $\sim 50 \text{ nm}$, CF was created during electroforming and the diameter of the CF was reduced to $\sim 5 \text{ nm}$ after the reset

process. Deleruyelle et al. [142], on the other hand, reported the generation of multiple CFs during electroforming and the number of CFs was significantly reduced after reset process. Although the physical evidence on the formation and dissolution of CF(s) during the RS processes were reported, the role of CF(s) in electrical characteristics change, in particular, the gradual current reduction trend typically observed during the reset process in RRAM device remains ambiguous.

The existence of the VCM resistive switching in transition metal oxides is the fundamental part for RRAM cell. However, these transition metal oxides such as HfO_2 and ZrO_2 are the most commonly used high-k gate oxides in complementary metal oxide semiconductor (CMOS) industry. The forming process in RRAM in the meantime is equal to gate oxide breakdown in CMOS device, which is a well-known front-end reliability challenge [146]. In recent CMOS technology nodes, the traditional polysilicon/ SiO_2 gate stack has been replaced with a metal/high-k gate stack to fulfill the requirements of gate leakage-current and equivalent capacitance scaling. With this change, gate oxide breakdown is expected to become an even more pressing issue owing to the generally low breakdown electric field of high-k dielectrics [147] and the inevitable presence of a low-quality Si sub-oxide layer at the interface between the high-k dielectric and the channel [148]. Although the exact mechanism of gate oxide breakdown is yet to be confirmed, the process is broadly believed to involve the random generation of oxide defects under electric field and temperature stressing. The local increase in gate current and the associated thermal heating, as a result of the clustering of oxide defects, then sets off a positive feedback cycle that eventually leads to a short-circuit between the gate and channel [149]. Leveraging advanced atomic-scale characterization techniques, the location of the breakdown site, commonly termed as the percolation path, was shown to be oxygen deficient [150]. Thus,

electrical-cum-thermal induced generation of oxygen-vacancy defects have been commonly identified as the intrinsic cause of gate oxide breakdown.

Studies have found that breakdown involving relatively thin gate oxides (of ~5 nm or less in thickness) may not always lead to a total loss of transistor functionality, unlike in cases involving thick oxides [151]. The breakdown mode of thin gate oxides has been termed soft breakdown (SBD) to distinguish it from the catastrophic hard breakdown (HBD) associated with thick oxides. While the exact reasons for SBD are yet to be completely established, it is believed to be caused by the typically lower gate stress voltage used. As a consequence, the surge in current during breakdown transient is decreased or could be aborted in time to avoid the thermally induced structural changes that typically characterize HBD. The non-destructive nature of SBD has generated considerable interest in understanding the mechanisms that govern post-SBD evolution toward HBD, which would aid in assessing the additional reliability margin offered by SBD [152]. Apart from the retention of the transistor functionality, another notable difference between SBD and HBD lies in the ability of the former to exhibit a partial or complete recovery effect, which occurs either upon stress termination [153], during post-breakdown electrical measurement [154], or after thermal annealing [155, 156]. The extent of recovery is found to depend greatly on the types of dielectric and gate stack structure, as well as the level of current through the percolation path before the breakdown is interrupted (i.e. breakdown hardness). For instance, electrically induced breakdown recovery is found to occur more readily in the metal/high-k gate stack as compared to the polysilicon/SiO₂ gate stack [154, 157]. Breakdown recovery in the latter can generally be achieved only by thermal annealing [155, 156]. Studies which observed a dependence of breakdown recovery on metal gates with varying oxygen solubility [157] lend a strong support to the proposed

oxygen-vacancy defect model. The optically induced breakdown recovery is seldom reported. Only some studies on narrow bandgap oxides such as ZnO and perovskites [158-160] have reported that the multi-level resistance state can be achieved via illumination from the perspective of RRAM. The reliability research after illumination on the most commonly used gate oxides (e.g. HfO_2 , ZrO_2 and SiO_2) is still limited to the deep ultra-violet (UV) regime and beyond due to their large bandgaps (> 5 eV), and all of them were addressing the post-irradiation reliability issues [161, 162]. The reliability rejuvenation on longer wavelength illumination is seldom reported or worthwhile to investigate.

The optical related research in the perspective of RRAM is also limited. Visible-light-stimulated response of semiconductor devices [158, 160, 163-167] may potentially expand the functionalities of electronics, which are presently limited to electrical stimulations. It was shown [166] that the current flow through the multilayer Pd/ Al_2O_3 / SiO_2 /p-Si structure could be modulated in the Al_2O_3 by the trapping of electrons optically generated in the p-Si substrate. The finding provides a possible means for light-enabled information encoding in non-volatile memory applications. Light-stimulated resistive switching has been observed in structures such as the ZnO nanorod [165], BiFeO_3 thin film [160], $\text{TbMnO}_3/\text{Nb:SrTiO}_3$ [158], ZnO/SrTiO_3 [164], and $\text{TiO}_2/\alpha\text{-Fe}_2\text{O}_3$ [163] heterojunctions. Although the actual responses may vary in terms of material characteristics and fabrication conditions, and the underlying mechanisms still being subjects of further investigation, these studies demonstrate that light sources may serve as an additional parameter for enhancing semiconductor device functionalities.

With the exception of Ref. [166], where the photoconductivity effect arises from the electron-hole pair generation in the Si substrate, nearly all studies on light

stimulation reported to date have focused on photo-responsive oxides or perovskite materials having relatively small bandgaps (~ 3 eV or lesser) [158, 160, 163-165]. On the other hand, oxides such as SiO_2 and HfO_2 , which are widely deployed in mainstream integrated-circuit manufacturing, have been excluded due to their much larger bandgaps (~ 6 eV or larger), which render them non-photo-responsive. However, we reveal an intriguing observation that conduction through a nanoscale conducting filament in the HfO_2 , ZrO_2 , and SiO_2 – those large bandgap oxides – can be disrupted by white light, an effect which we termed as the negative photoconductivity (NPC) of the soft-breakdown large bandgap oxides.

Chapter 3 EXPERIMENTS

3.1 Introduction

This chapter presents the detailed experimental setup and sample preparation method for the research. It is divided into two main sections:

Section 3.2 presents the fabrication and preparation of the samples used in the research. *Section 3.3* illustrates the schematics of the UHV-SPM system working principle and its main components, including the ultra-high vacuum maintenance system, the control electronics, the scanning unit, and the data acquisition and processing system. The characterization techniques are briefly introduced, including constant current imaging (CCI), constant height imaging (CHI), scanning tunneling spectroscopy (STS), constant current tunneling spectroscopy (CITS), and the localized constant voltage stressing.

3.2 Sample fabrication and preparation

3.2.1 HfO₂/ZrO₂-based RRAM stacks

This section introduces the general fabrication process of the HfO₂/ZrO₂-based RRAM stacks used in the project. The specific samples used for different experiments may be adjusted based on actual needs (e.g. oxide thickness, with or without top metal

electrode, oxygen stoichiometry), but the standard fabrication procedures are the same as described in the following ways: Six-inch p-Si (100) wafers with resistivity less than $10 \Omega \cdot \text{cm}$ were sputter-deposited with 10-nm Ti at 375°C , 1.7×10^{-3} mbar, followed with 50-nm TiN (Ti/N ratio ~ 1.11) at 375°C , 8.2×10^{-4} mbar using a Unaxis Clusterline 200 Sputter system. Prior to the deposition of the two metal layers, the wafers were subjected to the standard RCA cleaning to remove the native oxide. After the TiN deposition, a 40-Å HfO_2 or ZrO_2 was grown via atomic layer deposition on a TiN/Ti/p-Si substrate at a temperature of 250°C , a pressure of 0.2 Torr, and a nitrogen flow rate of 20 sccm using a Cambridge Nanotech 200 Savannah. The high-k precursor used was tetrakis (dimethylamino) hafnium (for HfO_2) and tetrakis (dimethylamino) zirconium (for ZrO_2). The oxidizer applied was H_2O vapor. The deposition rate was $1.05 \text{ \AA/cycle}$. No post-deposition annealing was carried out. The wafers were diced into small test sample pieces, each of an area measurable in an AFM/STM system.

3.2.1 HfO_2 -based CBRAM stacks

As for the SiO_2 test samples, on a HF-cleaned p-type Si (100) substrate (of resistivity $5 \times 10^{-3} - 1 \times 10^{-2} \Omega \cdot \text{cm}$), a 30-nm Ti film followed by a 30-nm Cu film were deposited by the DC magnetron sputtering. Subsequently, a 10-nm SiO_2 layer was grown at 250°C via a parallel-plate plasma-enhanced chemical vapor deposition process using SiH_4 and N_2O gas sources to form the SiO_2/Cu stack. No top electrode deposition was carried out. For comparison, a $\text{SiO}_2(5\text{-nm})/\text{p-Si}$ stack was also fabricated; the SiO_2 here was deposited under exactly the same conditions. To facilitate consequent discussion, the SiO_2/Cu stack will be referred as the Cu sample and the SiO_2/Si stack as the control sample.

3.3 Ultra-high vacuum scanned probe microcopies

Virtually all scanned probe microscopies (SPMs) work on the same underlying principle. They take advantage of the special characteristic that piezoelectric materials possess. When a voltage is applied across one of these crystals, the unit cell expands or contracts (depending on the sign of the potential). Each small change in the unit cell size added up over billions or trillions of unit cells accumulates a measurable size difference. When this crystal is connected to something, that item (the sample or the probe) will move a small amount. The ability to control this motion on an atomic scale is one of the key requirements for an SPM. The second key requirement is the ability to produce a signal that depends on the topography of the surface:

In scanning tunneling microscopy (STM), as shown in Fig. 3.1, the detection signal is tunneling current from a very sharp tip to the surface. Since the current exponentially depends on the tip-sample separation, a small change in the distance produces a substantially measurable change in the current. When a feedback loop monitors this signal, it can change the voltage on the piezoelectric material to adjust the probe height and maintain a constant height. The voltage changes applied, as the tip is scanned, over the surface will map out the relative height variations of the surface.

Fig. 3.1: The schematics of an STM setup. A constant voltage bias is applied to the substrate of the sample to induce the tunneling current from the probe to the surface. The tunneling current is maintained at a constant value by the distance control and scanning unit by adjusting the height of the probe whose track reveals the topography of the sample surface. The tunneling current reduces exponentially based on the tip-sample separation. This property enables a highly sensitive height difference detection, thus a high-resolution topography detection [168].

The concept of conductive atomic force microscopy (C-AFM) is different, as shown in Fig. 3.2. In the most common operation mode, a probe is mounted on the end of a small cantilever that is scanned across the surface. When the probe is in contact with the sample, the deflection of the lever will change as it drags across the surface. With a suitable method of measuring the deflection, the feedback loop can change the

z-piezo element to maintain a constant deflection. The applied correction voltage, therefore, maps out the sample terrain on a very small scale. The most common detection scheme in use is to deflect a laser off the back of the cantilever and measure the deflection angle using a quadrant photodetector. This element outputs four voltages proportional to the intensity of light falling on each quadrant. As the spot moves, more light falls on some quadrants at the expense of the signal spot which is proportional to the cantilever deflection to be measured. Cantilever twisting can be determined by the lateral position of the spot and provides a measurement of the local frictional force.

Fig. 3.2: The schematics of a C-AFM setup. A constant force is maintained between the tip and the sample by monitoring the deflection of the laser beam reflected by the back of the cantilever. The moving track of the probe maps out the topography of the sample surface [169].

3.3.1 UHV SPM Instrumentation

The UHV SPM system used in our research supplied by RHK Tech consists of two operating modes as mentioned above: the STM mode and the C-AFM mode, while the instrumental components of the SPM system can be categorized into four parts: the UHV maintaining system, control electronics, scanning unit, and data acquisition and processing system, all of which will be discussed briefly in the subsequent subsections.

3.3.1.1 UHV maintaining system

Fig. 3.3 shows the schematics of the UHV maintaining system, which consists of a progressive chambers system and a complicated pumping system as shown in Fig. 3.4 with four types of pumps: mechanical roughing pump, turbo molecular pump, titanium sublimation pump, and sputter ion pump. The fast entry load-lock chamber is the first stage during the transfer of the sample into the SPM, which should be vented to a pressure higher than ambient pressure before opening the gate valve by using N_2 gas, assuring the N_2 flows out once the valve opens to avoid ambient air flushing into the fast entry load-lock chamber causing unexpected contamination. Subsequently, the sample is loaded onto the stage of the built-in transfer arm working on a magnetic attachment.

Fig. 3.3: Schematic view of the mechanical components of the RHK Tech UHV SPM system. Three chambers sequenced from low to high pressure: fast entry load-lock chamber, preparation chamber, and SPM chamber, with mechanical roughing pump and turbo molecular pump servicing fast entry load-lock chamber and titanium sublimation pump and sputter ion pump servicing the rest of the chambers for UHV. The whole system is mounted on three stabilizing air legs to isolate the vibration and mechanical noises from the surrounding.

The pressure will be pumped down by the two-level pumping system: the mechanical roughing pump is able to pump the pressure down to $\sim 10^{-4}$ Torr, and the turbo molecular pump can reduce the pressure by an additional 4 orders of magnitude on the basis of roughing pump pressure, achieving $\sim 10^{-8}$ Torr, which is the threshold pressure of the gate valves between fast entry load-lock chamber, preparation chamber and SPM chamber. The gate valve between the preparation chamber and the SPM chamber is always on, unless there is preparation work on-going in the preparation chamber such as UHV annealing, tip sharpening and sample degassing, in order to maintain the ultra-high vacuum condition in both chambers by the titanium sublimation pump and sputter ion pump. Hot cathode ion gauges are used to monitor the pressure in the fast entry load-lock chamber and the SPM chamber. The wobble stick provides the transferring function between the storage elevator, magnetic transfer

arm, and the measurement stage. The storage elevator can store up to eight sample holders or probe holders in the SPM chamber.

Fig. 3.4: The schematic of the pumping circuit indicates the details of the pumping system. The positions of each pump and valve and the air flow route are clearly indicated.

3.3.1.2 Control electronics

The basic concept of a scanned microscope is to take some signal (current, lever deflection, intensity) and transform it into a voltage that can then be applied to the feedback circuit that will adjust the z-piezo to maintain a constant value. The selected setpoint can be of any value from 0 (zero on the knob) to 1 V (10 on the knob) when operating in the STM mode, while the absolute limit of the signal is from 0 to 10 V. It is advantageous to have the extra margin between the maximum feedback condition and the absolute maximum signal for spectroscopy reasons. One can set a feedback condition and then perform spectroscopy measurements which are outside this setpoint so a larger sample space of conditions can be investigated. During spectroscopy, the feedback signal is not at a large value for a long period of time compared to imaging conditions, so this is usually not a problem for delicate samples. In the case of C-AFM,

the setpoint is the cantilever deflection which is expressed as a voltage produced by the position sensitive photodiode. The system transferring the detective signal into voltage and providing the probe movement control based on the closed-loop feedback circuit is the control electronics in the SPM system as shown in Fig. 3.5. It shows the control electronics in the STM mode, which is similar to C-AFM mode. The only difference is the detective signal, which is cantilever deflection in the C-AFM mode, but tunneling current in the STM mode. However, both signals are converted into voltage for the subsequent process, so these two modes share the same control electronics after signal conversion. Take the STM mode as an example. A current-voltage pre-amplifier (IVP) converts the tunneling current into voltage. The logarithmic amplifier connected after IVP converts the exponential relation between the tunneling current and probe-sample vacuum gap to a linear response, which enhances the dynamic range. Subsequently, the linear signal is fed into the first stage of the feedback electronics, the comparator. An error signal is generated based on the offset of the measured signal from the setpoint. The error signal is fed into the processing unit comprising an analog integrator and a proportional amplifier. The output signal from the processing unit is finally passed into a high-voltage amplifier to generate a driving signal that is applied on the piezoelectronic scanning tube, thus adjusting the tip-sample vacuum gap until the setpoint is achieved. The sensitivity of the high-voltage amplifier can reach $0.07 \text{ \AA/V}$ [170]. A sample-and-hold amplifier is built into the feedback circuit, which forces the error signal to be zero once set to the ON state. As a consequence, the feedback system will deem the current state as a balanced state, and the piezoelectronic scanning tube will be frozen, keeping the vacuum gap between tip and sample at a constant value. This function is extremely important for I-V characteristic measurement, which requires a stable tip remaining at

the same position during the whole measurement process and for constant voltage stressing for the time dependent dielectric breakdown (TDDB) test in a reliability study. There are two parameters influencing the feedback effect, the response time and gain. The feedback performance determines the reliability of the data acquisition. Therefore, the feedback parameters must be fine-tuned by experts with experiences and skills. A smaller response time or higher gain will cause a piezoelectronic scanning tube creep effect and a z-direction oscillation. However, a larger response time or a smaller gain may result in a longer reaction and feedback, and hence, cause the tip to crash onto the sample surface, damaging both tip and sample.

Fig. 3.5: The schematics of the SPM control electronics in the STM mode similar to C-AFM mode. By changing the current amplifier to deflection-voltage amplifier, the whole system is closed-loop negative feedback eliminating the discrepancy between the measured signal to the setpoint. The sample and hold amplifier can force the system to maintain the tip at a fixed position for I-V characteristics test and constant voltage stressing.

3.3.1.3 Scanning unit

The scanning unit of the SPM consists of the piezo drivers. Depending on the number of scanning drivers that are called scanning piezo tube, the scan head can be

classified into single tube scan head or multiple tube scan head. Single tube scan heads are one of the most common types of scan heads due to their good performance and ease of construction. There are several different ways that the metallization on a piezo tube can be sectored for utilization in a scan head. The metallization on the outside of the tube has been cut into four equal sections. The X and Y scan signals are applied to these four sections. The Z scan signal is applied to the inside of the tube. The X and Y offset signals are electrically summed into the Z scan signal. Stating the signals are summed means that the amplifier that drives a sector on the piezo tube provides the signals for both the scanning function for the tube as well as finding the offset positioning. This allows a small scan area to be imaged anywhere within the boundaries that can be reached by the scan tube without additional coarse offset capabilities.

Care must be taken so that all the input voltages to the amplifier do not saturate it. No damage will be done to the amplifier if it is driven to saturation, however, the image will be distorted. In this configuration, none of the offset amplifiers will be used. The summing of the scan and offset signals is done internally at the input of the high voltage amplifiers.

The total voltage range available to a piezo sector is ± 130 volts (± 215 volts with the high voltage option). This voltage is divided between the scan and offset functions. If the maximum scan area is selected, that is ± 130 volts (or 215 volts) are applied to the tube for the scan function, no offset range will be available for the offset function. The same is true for the Z sector. If the Z scan and offset are applied to the inside of the tube, the ± 130 volts (or 215 volts) available to that sector will serve both the scan and offset functions.

The single tube scan head has the advantage of having the largest possible range in the Z axis without the possibility of saturating the X and Y scan signals. However, the disadvantage of this design is that when the scan head is an STM, more care must be taken in physically locating the wire that carries the tunneling current as far away from the X, Y, and Z scan signals as possible so they do not couple into the input of the current preamplifier. If this wire is running through the center of the tube, extreme care must be taken to shield the wire. The Z signal is a relatively high frequency signal as compared to the X or Y scan signals, and it can be more easily coupled into the tip wire. This can cause false signals to appear in the current and lead to instability.

It must also be noted that shielding the tip wire will increase the input capacitance of the current preamplifier, and this will add to the overall system noise. The higher input capacitance can also make some high bandwidth preamplifiers unstable. The increase in noise due to the increased input capacitance is an inherent problem with current/voltage converters.

The difficulties in applying the Z feedback signal to the inner piezo tube only applies to the STM mode. There is no problem for other types of SPM, such as AFM, since there are no electrical signal wires routed through the center of the scan tube.

In order to overcome all the difficulties faced while using the single tube scan heads, a scan head that uses more than two tubes is used in our SPM system. In this case, the center scan tube is used for the X, Y, and Z scan signals in addition to the Z offset signal. The three outer tubes provide the X and Y offset motion as well as the inertial motion. This scan head design yields a fine electronic offset control as well as much larger coarse offsets that utilize an inertial offset system. The Z approach is accomplished by combining the X and Y offset signals to provide a rotary motion to a

specially constructed sample holder. A separate interface box, the Model PPC 100, is used to provide the signals necessary for the rotary motion.

This design has many advantages over the single tube one. For instance, a sample can be imaged over a very large range because the outer piezo tripod can be used to “walk” the tube scanner over macroscopically large areas of the surface to be imaged. Also, this setup has very good thermal and vibrational stability properties because of the concentric, matched scanner properties of the inner tube and outer tripod.

3.3.1.4 Data acquisition and processing system

The XPMPPro is the system installed on the workstation to do the computational automation work including data acquisition, processing, and analysis. The data acquisition system is of great importance, which decides the accuracy of the sample surface topography and its electrical characteristics. Therefore, the data acquisition parameters have to be tuned accordingly and carefully, including the voltage bias, setpoint current for the STM mode, setpoint force for the C-AFM mode, feedback constant time, feedback gain, scanning speed, and resolution. The data processing system can do some post-process work on the obtained data such as the Fourier transformation, image smoothing or sharpening, image shifting correction, and interpolation. The data analysis system serves to visualize the data as images, allowing the user to read the data more conveniently. It can help in generating topography images, current-voltage characteristics, and the current distribution maps from the raw data.

3.3.2 Characterization techniques

The commonly used characterization techniques of the SPM system are briefly discussed in this section.

3.3.2.1 Constant current imaging (CCI)

The constant current imaging mode is only applicable to the STM operation mode of the SPM system. The tunneling current is measured via the STM probe and then sent to the closed-loop feedback circuit to be compared with a preset setpoint current. The discrepancy signal is fed into a high-voltage amplifier, and the amplified signal will be sent to the piezo pod which will perform extensions or contractions according to the input signal, thus varying the gap between the STM probe and the sample to achieve a constant current during scanning. It is known that the tunneling current is a reverse exponential to the vacuum gap. So, the tunneling current is very sensitive to the probe-sample gap. Consequently, the CCI mode can provide an atomic scale level resolution in the Z axis to obtain a clear topography image. However, if the tested sample is thin ($\sim$ nm) and non-uniform in terms of conductance, the topography image may not be accurate and contain both the surface roughness data and the localized resistance data. As illustrated in Fig. 3.6, when the probe is scanning at a low resistant region, the tunneling current tends to increase. The feedback loop will retract the probe to increase the tunneling gap, thus maintaining the current at the constant setpoint.

Fig. 3.6: In the CCI mode, the tunneling current is kept at a constant value preset via the close-loop feedback system. The tip will be retracted at the surface bump and the leakage region (red) by the piezoelectric tube while scanning over the sample surface.

3.3.2.2 Constant height imaging (CHI)

In the constant height imaging mode, the feedback loop is disabled. As a result, the probe-sample vacuum gap cannot be adjusted, and the probe will move horizontally and remain at the same height, as illustrated in Fig. 3.7. With a constant voltage bias applied to the substrate, the tunneling current is sensed via the probe during scanning. Additionally, the recorded tunneling current data reveals the topography and electrical information of the test sample, which is similar to the CCI mode. Compared with the CCI mode, the CHI mode has a relatively faster scanning speed and a shorter acquisition time due to the lack of feedback system, which requires a reasonable response time. The only limit to the scan speed in the CHI mode is the response time of the current-voltage preamplifier, which is much shorter than that of the feedback system. The faster scan speed also reduces the chance of a thermal drift. However, the CHI mode can only be used for small area scanning, which can be considered as an atomically flat surface. There is no feedback system adjusting the height of the probe. This may cause the probe crashing into the sample surface when the surface roughness is more. Therefore, only the CCI mode is allowed for scanning large area.

Fig. 3.7: In the constant height imaging (CHI) mode, the tip height remains at a constant value while scanning across a sample surface. The current varies with the surface roughness and the resistance variations.

3.3.2.3 Scanning Tunneling Spectroscopy (STS)

STS is used to obtain the local current-voltage (I-V) characteristics of a specific point on the sample surface. However, the original RHK system cannot provide current compliance to limit the breakdown hardness. The voltage range applied to the sample is relatively small, -10 V to 10 V. To overcome these drawbacks of the RHK system, we externally connect the Keithley 4200 Semiconductor Characterization System to the RHK STM/C-AFM. The tip of the STM/C-AFM is connected to the SMU1 of Keithley 4200 for applying voltage, and the substrate is connected to the SMU2 for ground. By combining these two systems, the voltage ramping range is significantly extended from ± 10 V to a few hundred volts, and the breakdown hardness can be controlled precisely by the current compliance predefined. Keithley 4200 also improves the measurement resolution for low current measurement. The STM/C-AFM system provides the surface topography imaging capability for nanoscale device locating and measuring as well as the resistant current mapping capability discussed in the following section. During the electrical characterization, the feedback loop is disabled to maintain the tip-surface distance in the STM mode or to avoid the laser signal interference with the input illumination in the C-AFM mode.

3.3.2.4 Constant current tunneling spectroscopy (CITS)

The constant current tunneling spectroscopy (CITS) is a data acquisition technique to collect the I-V characteristics information of each pixel among the scanned area during the CCI scanning. Therefore, CITS can obtain both the CCI topography image and electrical characteristics of each pixel simultaneously. Fig. 3.8 shows the example of the spectra view of the CITS scanning. A sample-and-hold

amplifier is used to control the feedback on or off during the CITS scanning. The feedback is turned on during the CCI scanning. When the tip reaches the spectroscopy pixel, the feedback is turned off and a linear ramping bias is applied on the sample, thus the I-V characteristics of this specific pixel are recorded, as shown in Fig. 3.9. After the electrical data acquisition, the feedback loop is reactivated and the CCI scanning is resumed until the next spectroscopy pixel. This scanning and measurement process is repeated until all predefined pixels are tested. The moving track information of the tip generates the topography image illustrating the surface roughness and shape of the sample, while the electrical characteristics information of all the pixels generates a current image mapping the electrical property of the scanned area, as shown in Fig. 3.8.

Fig. 3.8: The current map extracted from the CITS at one selected bias. The blue dots denote the measurement pixels on which the I-V characteristics will be carried out during scanning.

Fig. 3.9: The schematic diagram of the I-V characterization at the desired location. The close-loop feedback system is disabled to maintain the tip position during the measurement. Then the localized I-V characteristics information at this location are extracted with a ramped voltage sweeping.

3.3.2.5 Localized constant voltage stressing

In reliability studies, a TDDB test is commonly used to evaluate the robustness of the thin film. In our STM/C-AFM system, this TDDB test can be conducted by the collaboration of the localized constant voltage stressing mode with the Keithley 4200. As shown in Fig. 3.10, the STM/C-AFM enables us to precisely position the tip on the specific nanoscale location of interest, and the position is maintained at the fixed position by switching off the feedback loop. The constant bias is applied to the sample via the tip connected to the SMU1 and the current is recorded until the localized breakdown occurs (auto exit condition preset on Keithley 4200 is triggered). The breakdown hardness can be controlled by the current compliance predefined in the Keithley 4200. The TDDB current-time (I-t) curve will be recorded for further reliability analysis.

Fig. 3.10: The schematics of the set-up for the localized constant bias stressing for the TDDB test. The tip position is maintained as constant by disabling the close-loop feedback system. The constant voltage is applied to the probe to trigger the breakdown at this specific location.

3.4 Summary

In summary, the experimental details are introduced in this chapter. The working principle of the SPM system is illustrated as well as the important sub-systems including the ultra-high pressure vacuum maintaining system, control electronics, scanning unit, and the data acquisition and processing system. Five most frequently used characterization techniques are briefly discussed, including the CCI image scanning, CHI image scanning, STS, CITS, and localized constant voltage stressing. The sample fabrication procedures are also illustrate.

Chapter 4 UNIQUE ELECTRICAL BEHAVIOR OF NANOSCALE CONDUCTING FILAMENT

4.1 Introduction

By virtue of its simple structure, high operating speed and scalability, the resistive memory or RRAM is deemed a promising alternative to the charge-based memory, which is now facing severe scaling challenges. Of particular interest is the HfO₂ RRAM due to its immediate compatibility with mainstream integrated-circuit technology. A major problem is, however, the relatively high switching current. Currents on the order of 10⁻³ A (e.g. [171]) are typically observed in large-area cells (~10⁻⁸ cm²). In a recent work, a substantial reduction of the switching current to ~10⁻⁵ A was achieved by scaling the cell area down to 100 nm² [172]. Since the current processing know-how generally limits any further reduction in cell area, alternative means, such as stack engineering, has been explored in an attempt to further reduce the switching current. It was shown that the insertion of a thin Al₂O₃ layer in between the TiN electrode and HfO₂ could help bring the current down to ~0.5 μ A [173].

Since one of the main strengths of RRAM is scalability, a further reduction of the switching current is deemed necessary in order to make ultra-high density memory

application viable. At present, it is unclear to what extent could the switching current be reduced with cell area scaling. To address this question, resistance switching in HfO_2 is examined using a conductive atomic force microscope (C-AFM) and scanning tunneling microscope (STM) in this chapter. The excellent spatial resolution of C-AFM and STM enables the electrical properties of a thin dielectric to be probed over an extremely localized region, as demonstrated in recent studies on the $\text{HfO}_2/\text{SiO}_x$ gate stacks (e.g. [174, 175]). Through the C-AFM/STM technique, in this chapter, we examined resistance switching in a 4-nm thick HfO_2 , within a region of ~ 2 nm in diameter and achieved an ultra-low current switching capability.

Furthermore, the unique abrupt reset behavior is observed in nanoscale CF, on the contrary, the gradual current reduction trend is typically observed during the reset process in relatively large area RRAM device. We addressed the origin of the gradual resistance reset behavior by studying, via STM/C-AFM, the reset characteristic of the microscopic nanoscale CFs and its relation with the macroscopic gradual electrical reset behavior in device level. The statistical result shows that the nanoscale CFs tend to exhibit abrupt resistance reset behavior with significant variations in the reset voltage and current. It is shown that this wide variation of reset voltage and current contributes to the gradual resistance reset behavior observed in large area RRAM device with multiple nanoscale CFs formed beneath the top electrode.

4.2 Ultra-low current switching with nanoscale CF

Resistance switching of a 4-nm thick HfO_2 dielectric is examined via conductive atomic force microscopy and scanning tunneling microscopy. The nanometer-size probe enables resistance switching in an extremely scaled region (~ 2 nm diameter) of the HfO_2 to be studied. Bipolar reset is observed to happen at an ultra-low current, on

the order of picoampere. The observation implies that a substantial reduction of the switching current from the present level ($\sim 10^{-5}$ A) is possible through further area scaling. The results also show that the resistance switching at such low current is determined by oxygen-ion migration between the metal electrode and the conductive filament.

4.2.1 Experiments

Test samples were 4-nm thick atomic-layer-deposited HfO_2 , formed on TiN/Ti/p-Si substrates (Fig. 4.1). Samples with a 0.8 nm Hf cap layer or a 50 nm TiN top electrode were also fabricated in the same run. Resistive switching measurement was performed in a RHK 3500 HT AFM/STM system in ultra-high vacuum or UHV ($\sim 5 \times 10^{-10}$ Torr) and at a temperature of 300 K. A diamond-coated Si probe with a radius of curvature of 100 nm was used for C-AFM measurement while a Pt/Ir probe (with ~ 80 at. percent Pt) was used for STM measurement. The C-AFM/STM probe was connected to a Keithley SCS4200 parameter analyzer to overcome the relatively low current measurement limit (10 nA) of the C-AFM/STM system. The voltage bias was applied to the probe with the substrate grounded. Forming was induced by a voltage ramp. Due to variation of HfOx morphology and the stochastic nature of the forming process, not all conductive filaments (CFs) formed were able to exhibit resistance switching. But the percentage of switchable CFs was observed to increase with reduction of the forming current compliance.

Fig. 4.1: The schematic diagram illustrating the test sample used and the C-AFM/STM measurement setup. For the latter, a vacuum gap of $\sim 5 \text{ \AA}$ exists between the probe tip and the HfO_2 surface. Direct connection of the probe to a parameter analyzer enables current larger than 10 nA (limit of the C-AFM/STM electronics) to be measured.

4.2.2 Biased-probe induced nanoscale CF

To ascertain the size of the resistance switching region induced by the probe, topography images before and after forming and after a bipolar reset were acquired (Fig. 4.2). The appearance (after forming) and disappearance (after reset) of the bright shade enclosed in the dashed box correspond to the formation and annihilation, respectively, of a CF in the HfO_2 . The diameter of the spot is 2.5 nm, in good agreement with the diameter of the probe contact area (2.8 nm) calculated according to [176].

Fig. 4.2 Topography images acquired (a) before and (b) after forming and (c) after a bipolar reset. The test sample is Hf/HfO₂/TiN.

The associated current-voltage (I - V) curves are depicted in Fig. 4.3(a). The increased current measured after forming (circle) confirms the formation of a CF at the probe contact area. The current rises steadily towards the compliance level, with no sign of any unipolar reset. Bipolar reset was achieved at ~ -0.3 V and at a low current of 25 pA. A positive-voltage sweep confirms the reset, with a subsequent set happening at ~ 2.5 V. The post-reset positive I - V curve (diamond) is comparable to the one measured prior to forming, indicating a nearly complete CF reset, as opposed to the usually partial reset seen in larger area cells. A similar observation of a very low reset current (< 1 pA) is obtained using STM measurement (Fig. 4.3(b)).

The ultra-low reset current of $\sim 10^{-12}$ A is significantly lower than those observed on large area devices ($\sim 10^{-5}$ - 10^{-3} A) [171, 172]. It is believed that resistance switching in large area devices is determined by not one but numerous CFs, with the diameter of individual filaments estimated to range from several tens to hundreds of nanometers [143, 144, 177]. Due to random distribution of dielectric defects and the dissipation of relatively large capacitive energy at the instant of forming, the size of the resultant filaments in a large area device could not be controlled and it varies widely over the

cell area. The switching of many CFs thus results in a large switching current. In our study, however, the size of the CF is directly determined by the size of the C-AFM/STM probe ($\sim 2\text{-}3\text{ nm}$; Fig. 4.2) and the compliance current. The small probe size limits lateral growth of the CF during forming. Coupled with a low current compliance ($\sim$ tens of nA), the CF formed has a relatively high resistance ($\sim 5 \times 10^9 \Omega$ at 0.3 V), resulting in a very low reset current.

Fig. 4.3 Current-voltage (I-V) curves recorded during forming, after forming and during reset under an opposite voltage polarity. (a) C-AFM; (b) STM. The forming current compliance is 50 nA for (a) and 10 nA for (b). Due to the vacuum gap, larger voltages were involved in STM measurement.

Another salient point of Fig. 4.3 is that the reset current is far lower than the current compliance of the forming step. This observation also differs from that for large area cells, whose reset current usually exceeds the forming current compliance. It is shown that current overshoot (due to parasitic sidewall capacitance) during forming leads to a CF having a smaller resistance than that intended by the current compliance [178]. In our measurement, the sidewall capacitance was minimal. It is believed that this has helped prevent current overshoot during forming and thus the resultant reset current is

lower than the forming current compliance. Without minimization of the sidewall capacitance, the reset current could still exceed the forming current compliance even when the active area is reduced [179].

Resistance switching in metal oxides were already studied in the past using the C-AFM method (e.g. [180, 181]). But the observed switching currents vary broadly ($\sim 10^{-10}$ - 10^{-7} A). It is believed that the main source of the variation lies in the different test samples used (e.g. different oxides (NiO, HfO) and electrodes (Au, Pt), oxide thicknesses and processing conditions, etc.). Thus, the results reported could not be simply compared. For instance, the type of electrode used is known to impact the nature of resistance switching, e.g. unipolar switching, which occurs at higher currents than bipolar switching, has been observed in samples employing the Ni or Ag electrode. Nonetheless, the picoampere reset currents depicted in Fig. 4.3 should be among the lowest reported thus far for the HfO₂ dielectric.

The results clearly show that there is room for substantial reduction of the switching current via cell-area scaling. Although an ultra-low switching current in the range of picoampere may be a promising projection, other considerations, in particular the leakage current of the select device, would become important at such a low switching-current level. It appears that the potential of RRAM functioning at picoampere level is realizable if a corresponding reduction of the select-device leakage to comparable or lower level is achieved. The latter, however, may be extremely challenging as evidenced through developments in transistor scaling.

4.2.3 Switching mechanism and electrode influence

Recent studies based on atomic-scale electron-energy loss spectroscopy [143, 144] have shown that oxide resistance decrease is linked to local depletion of the oxygen content, lending support to the hypothesis that bipolar resistance switching is driven by the migration of oxygen ions between the CF and adjacent metal electrode (e.g. [182]). STM measurement in UHV could provide further check on the hypothesis. The basic idea is illustrated in Fig. 4.4. The probe replaces the top electrode, allowing CF formation in an uncapped dielectric to be carried out. The vacuum gap between the probe and dielectric surface presents little barrier to the escape of oxygen ions, as compared to the bottom TiN electrode. This difference may affect the amount of oxygen ions accumulated near the anode during forming, which in turn impacts the ability of the CF to ‘switch’. For forming performed on an uncapped HfO_2 (Fig. 4.4(a)), one would expect the probability of obtaining a switchable CF to be much smaller under positive-voltage forming, as compared to negative-voltage forming. This is because in the former, oxygen ions driven towards the exposed HfO_2 surface during forming could readily escape. The lack of oxygen ions would then render the resultant CF non-switchable. On the other hand, the bottom TiN electrode limits the escape of oxygen ions under negative-voltage forming, thus increasing the likelihood of obtaining a switchable CF (Fig. 4.4(a)). For measurement performed on a sample with a top TiN cap layer, the likelihood of having switchable CFs after forming should be the same for both forming voltage polarities.

Fig. 4.4: Schematic diagrams illustrating a possible explanation for the large disparity in the likelihood of observing resistance switching following positive- and negative-voltage forming in the test sample without a TiN cap layer.

This expectation is indeed borne out by the results shown in Fig. 4.5. For a given forming polarity, the number of CFs exhibiting subsequent resistance switching is expressed as a percentage of the total number formed. For the sample without a TiN cap layer, 60 % of the CFs exhibit resistance switching after negative-voltage forming. The corresponding percentage for positive-voltage forming (20%) is significantly lower. On the other hand, while the percentage of CFs showing resistance switching after negative-voltage forming remains relatively unchanged (53%), that for positive-voltage forming has risen considerably to 50%, for the sample with a TiN cap. The influence of the TiN cap layer is clearly confirmed by the similar switching percentage on both polarities shown by the sample with symmetrical structure (cf. 4.4(b), 4.5(b)). These observations imply that oxygen-ion migration between the metal electrode interface and CF remains as the mechanism responsible for the ultra-low current resistance switching observed.

Fig. 4.5 Number of conductive filaments (CFs) exhibiting resistance switching (RS) following positive- and negative-voltage forming, expressed as a percentage of the total number formed. The test samples are (a) HfO₂/TiN(bottom electrode); (b) TiN(cap layer)/HfO₂/ TiN(bottom electrode). For each sample, more than 30 locations were tested.

4.3 Microscopic abrupt reset and macroscopic progressive reset

Filamentary-conduction model, based on electric field-driven oxygen-vacancies (Vo's) migration in an oxide, has been widely adopted in explaining the resistance switching (RS) mechanism in resistive random access memory (RRAM) cell [138-140]. However, the shortcoming of the conventional electrical characterization technique in resolving the microscopic details has limited further understanding of the conductive filaments (CFs) evolution during RS operation. Hence, some groups have resorted to various advanced microscopic characterization techniques, such as scanning probe microscopy (SPM) [141, 142] and scanning transmission electron microscopy & electron energy loss spectroscopy (STEM-EELS) [143-145] to reveal the micro-structural change occurred in a metal-oxide after RS operation. By using

conductive atomic-force-microscope (C-AFM) probing, Celano et al. [141] observed a relatively large, of diameter ~ 50 nm, CF was created during electroforming and the diameter of the CF was reduced to ~ 5 nm after reset process. Deleruyelle et al. [142], on the other hand, reported the generation of multiple CFs during electroforming and the number of CFs was significantly reduced after reset process. Although the physical evidence on the formation and dissolution of CF(s) during the RS processes were reported, the role of CF(s) in electrical change, in particular, the gradual current reduction trend typically observed during the reset process in RRAM device, remains ambiguous. In this session, we show, via scanning tunneling microscope (STM) and conductive atomic force microscope (C-AFM) probing, that the extremely scaled region (~ 20 nm²) of HfO₂ tends to exhibit abrupt current reduction behavior during reset process, which is in opposed to the gradual current reduction behavior typically observed in the large area HfO₂-based RRAM device. The wide statistical spread in the reset voltage and current, due to the stochastic nature of nanometer-size conducting filaments (CFs) formation, is shown to play a significant role in the gradual resistance reset behavior always observed at device level. This result offers an insight into the resistance reset mechanism in HfO₂ RRAM device.

4.3.1 Experiments

A 4-nm thick HfO₂ film was formed, via atomic layer deposition (ALD), on a TiN/Ti/p-Si substrate at a temperature of 250 °C and a pressure of 0.2 Torr. This was followed by sputter-deposition of ~ 50 -nm thick TiN to form the top electrode. The sample was then patterned to form $100\text{ }\mu\text{m} \times 100\text{ }\mu\text{m}$ metal-insulator-metal (MIM) capacitor (Fig. 4.6(a)). The precursor and the oxidizer used were Tetrakis (dimethylamino) hafnium and H₂O respectively. The electronic property of the HfO₂

film in a MIM capacitor was studied, via a high spatial-resolution STM, at nanometer scale in ultra-high vacuum ($\sim 5 \times 10^{-10}$ Torr) before and after *ex situ* electroforming via Cascade Microtech prober and Keithley SCS4200 parameter analyzer. In STM measurement, a Pt/Ir tip was used to induce (with the feedback circuit disabled) localized resistive change in the HfO_2 film. The current map of the HfO_2 film was acquired via current-imaging-tunneling spectroscopy (CITS) [175].

Fig. 4.6 Schematic diagrams illustrating the $100 \mu\text{m} \times 100 \mu\text{m}$ TiN/ HfO_2 /TiN test device and its cross-sectional view along A-A'.

4.3.2 Microstructural insights of RRAM device active region

A positive-voltage ramp was applied to the top electrode of TiN/ HfO_2 /TiN capacitor to induce electroforming. An abrupt (brown curve) current increase is observed at ~ 1.7 V and the forming process was interrupted by the pre-set current compliance limit (CCL) at 5×10^{-3} A (Fig. 4.7).

Fig. 4.7 current vs. voltage (I - V) curves recorded during electro-forming and reset process of the test device by using Cascade Microtech probe and Keithley SCS4200 parameter analyzer. Gradual current reduction (red curve) characteristic was clearly observed during negative-voltage ramp was applied to induce resistance reset.

Subsequently, the electronic property of the post-forming HfO_2 film was studied in ultra-high vacuum (UHV) STM/C-AFM chamber. Since tunneling electron is sensitive to the barrier height at the metal/oxide interface, a localized change can be sensed by the probe. The tunneling current (I_t) variations resulted from intrinsic microstructural change in HfO_2 may be distinguished from the current map (Fig. 4.8(a)-(d)) acquired via CITS technique; which involves the measurement of the local I_t spectra at all positions on the oxide surface, within the scanned area, with the feedback circuit turned off momentarily. The contrast in the current map denotes the local variations (at a given V_s) of I_t across the HfO_2 film, with the bright shades corresponding to the locations with a relatively higher I_t . Compared with the current map acquired during the pristine state (Fig. 4.8(a)), randomly scattered bright shades are clearly observed in

the current map of the post-forming HfO_2 film (Fig. 4.8(b)). A closer examination (green box in Fig. 4.8(b)) of the bright shades reveals the presence of nanometer-size CFs of diameter ranging from 1 - 25 nm (Fig. 4.8(c)). The resistance switching properties of the CFs were tested by applying a negative-voltage ramp to the STM probe, positioned over the bright shades (denoted by A to D) in the current map in Fig. 4.8(c). The drift correction function in the scan software was applied to minimize the probe drift issue. As shown in Fig. 4.8(e), it is interesting to note that, instead of the typical gradual current reduction behavior observed at device level (Fig. 4.7), red curve), an abrupt current reduction behavior is observed during the reset process of CFs A to D; note that the current decreases sharply at -0.6 V. The corresponding bright shades A to D in the current map (Fig. 4.8(d)), acquired in subsequent scan, clearly fade, implying a restoration from low- to high- resistance states. Fig. 4.8(f) shows the statistical breakdown of 30 tested locations exhibiting abrupt (42 %) and gradual (25 %) reset behavior. The rest (33 %) of the data points show unsuccessful reset. It is believed that these permanent CFs contribute to the relatively high current level, as compared to that of the pristine state, typically observed in the post-reset RRAM device [183].

Fig. 4.8: 500 nm $\times$ 500 nm current maps (color scale: 0-50 nA) of a TiN/HfO₂/TiN test device obtained at 2 V, via CITS: (a) pre-forming, (b) after *ex situ* forming by using prober and semiconductor parameter analyser; (c) zoom-in view (100 nm $\times$ 100 nm) of the area shown by the green box in (b), (d) after negative-voltage sweep was applied to the STM probe positioned over selected bright shades (labelled as A, B, C, and D) in the current map in (c) to induce localized resistance reset. (e) *I-V* curves recorded during a negative-voltage ramp was applied to the probe positioned over bright shades A-D. A successful resistance reset with an abrupt current reduction is observed at the reset voltage. (f) statistical breakdown of CFs showing gradual-, abrupt- and no-reset.

4.3.3 Origin of macroscopic progressive reset

In order to ensure that the abrupt resistance reset behavior observed in Fig. 4.8(e) is not due to the thermal drift effect of the STM probe or the vacuum spacing presents at the interface between the probe and test device, further examination by using C-AFM probe was performed. A heavily doped diamond-coated Si probe was connected directly to the Keithley SCS4200 parameter analyzer and positioned over the surface of $\text{HfO}_2/\text{TiN}/\text{Ti}/\text{p-Si}$ stack, which was reproduced under the exact process flow used in the MIM capacitor fabrication, for RS measurements. The estimated effective probe contact area on HfO_2 is $\sim 30 \text{ nm}^2$, calculated according to [176] and the nanoroughness at the probe apex may reduce the effective contact area on the sample surface. In Fig. 4.9(a), the statistical analysis reveals that, at a given CCL, more than 70% of the C-AFM measurements exhibit abrupt reset behavior and the same conclusion holds for other CCLs. The rest of the measurements show either gradual or unsuccessful reset. It is observed that the respective statistical spreads of the mixture of abrupt and gradual reset voltages (Fig. 4.9(b)) and currents (Fig. 4.9(c)) are significantly large due to the stochastic nature of CF formation. Since CFs were ruptured after reset [142, 144, 145] the C-AFM measured I-V curves of both abrupt and gradual resistance reset at various locations were added up to simulate the RS operation of RRAM device. As shown in Fig. 4.9(d), a gradual reset behavior typical to that observed in RRAM device (Fig. 4.7) is obtained, which is attributed to the wide variations of the reset voltages and currents of CFs. The measurements performed under different CCLs exhibit similar observation. This result reveals the resistance reset behavior of nanometer-size CFs, which is typically masked out at device level due to area-averaged effect, and provides insights into the gradual resistance reset behavior always observed in RRAM device.

Fig. 4.9 (a) Number of more than 30 C-AFM probe-measured locations, expressed as a percentage, exhibiting abrupt reset behavior; the rest of the data points exhibit either gradual or unsuccessful reset. Measurements were repeated for various CCLs. Statistical spread of the reset (a mixture of gradual and abrupt) voltage (b) and current (c) for each set of 30 locations formed at various CCLs. (d) Summation of the corresponding resistive switching I - V curves of the 30 locations (a mixture of gradual and abrupt reset) measured under CCL of 90 nA. Gradual reset behavior, similar to that typically observed in the large area RRAM device (Fig. 4.7), is obtained. The measurement data for other CCLs yield identical result.

4.4 Summary

C-AFM/STM study was made on the HfO_2 dielectric to assess the prospect of RRAM switching-current scaling with cell area. The results imply that in RRAM cells with an area of $\sim 5 \text{ nm}^2$ and minimal sidewall capacitance, a substantial reduction of the reset current down to the picoampere level may be achieved. The study also shows that in samples without a top TiN or Hf cap layer, the likelihood of observing resistance switching following positive-

voltage forming is greatly reduced as compared to negative-voltage forming. The outcome corroborates the notion that such ultra-low current bipolar resistance switching seen via C-AFM/STM is determined by oxygen-ion migration between metal-electrode and the CF.

The change in the electronic property of HfO_2 film, before and after electroforming, was studied at nanometer scale via STM/C-AFM. The result reveals that switchable CFs exhibit two types of reset behavior – abrupt and gradual current reduction. Although more than 70% of the CFs exhibit abrupt reset behavior, it is shown that the large variations in the reset voltages and currents of the CFs contribute to the gradual resistance reset behavior always observed in the large area TiN/HfO_x/TiN device.

Chapter 5 UNIQUE ELECTRO-OPTICAL BEHAVIOR OF CF: LIGHT-INDUCED ANNIHILATION OF NANOSCALE CONDUCTING FILAMENT IN METAL OXIDES

5.1 Introduction

Gate oxide breakdown, an outcome whereby the dielectric loses its insulating property, has been a well-known front-end reliability challenge for advanced complimentary metal-oxide-semiconductor (CMOS) technology that features SiO₂ with thickness less than ~5 nm [146]. In recent CMOS technology nodes, the traditional polysilicon/SiO₂ gate stack has been replaced with a metal/high-k gate stack in order to fulfill the gate leakage-current and equivalent capacitance scaling requirements. With this change, gate oxide breakdown is expected to become an even more pressing issue owing to the generally low breakdown electric field of high-k dielectrics [147] and the inevitable presence of a low quality Si sub-oxide layer at the interface between the high-k dielectric and the channel [148]. Although the exact mechanism of gate oxide breakdown is yet to be confirmed, the process is broadly believed to involve the random generation of oxide defects under electric field and

temperature stressing. The local increase in gate current and the associated thermal heating, as a result of the clustering of oxide defects, would then set off a positive feedback cycle that eventually leads to a short-circuit between the gate and channel [149]. Leveraging on advanced atomic-scale characterization techniques, the location of the breakdown site, commonly termed as the percolation path, was shown to be oxygen deficient [150]. Thus, electrical-cum-thermal induced generation of oxygen-vacancy defects has been commonly identified as the intrinsic cause of gate oxide breakdown.

Studies have found that breakdown involving relatively thin gate oxides (of ~5 nm or less in thickness) may not always lead to a total loss of transistor functionality, unlike in cases involving thick oxides [151]. The breakdown mode of thin gate oxides has been termed soft breakdown so as to distinguish it from the catastrophic hard breakdown (HBD) associated with thick oxides. While the exact reasons for SBD are yet to be completely established, it is believed to have been caused by the typically lower gate stress voltage used. As a consequence, the surge in current during breakdown transient is decreased or could be aborted in time to avoid the thermally induced structural changes that typically characterize HBD. The non-destructive nature of SBD has generated considerable interest in understanding the mechanisms that govern post-SBD evolution towards HBD, which would aid in assessing the additional reliability margin offered by SBD [152]. Apart from the retention of transistor functionality, another notable difference between SBD and HBD lies in the ability of the former to exhibit a partial or complete recovery effect, which occurs either upon stress termination [153], during post-breakdown electrical measurement [154], or after thermal annealing [155, 156]. The extent of recovery is found to depend greatly on the types of dielectric and gate stack structure, as well as the level of current through the

percolation path before the breakdown is interrupted (i.e. breakdown hardness). For instance, electrically induced breakdown recovery is found to occur more readily in the metal/high-k gate stack as compared to the polysilicon/SiO₂ gate stack [154, 157]. Breakdown recovery in the latter can generally be achieved only by thermal annealing [155, 156]. Studies which observed a dependence of breakdown recovery on metal gates with varying oxygen solubility [157] lend strong support to the proposed oxygen-vacancy defect model.

Although gate oxide breakdown presents a critical reliability issue threatening the useful lifespan of CMOS integrated circuits, recent years have seen it being exploited for next generation resistance-switching random access memory (RAM), most notably in valence-change type of resistive memory or RRAM devices involving transition metal oxides such as HfO₂, Ta₂O₅, etc. [184, 185]. Operation of this class of resistive memory devices first requires subjecting the oxide layer to a high voltage/oxide field to create a nanoscale conducting filament (akin to the ramped-voltage or constant voltage stressing that leads to the generation of an oxide percolation path), which places the device in a low resistance state. Subsequent repetitive switching between the low and a high resistance state is believed to occur via dissolution (partial or complete) and reformation, respectively, of the conducting filament through oxygen interchange with the metal electrodes, enabled by a sites of alternating voltage polarities applied to the electrode [186]. While the resistance-switching operation is typically accomplished by electrical stimulation, some studies have demonstrated light-enabled multi-level resistance switching in narrow bandgap oxides (e.g. ZnO) and perovskites [158-160].

In this chapter, we summarize our recent experimental evidence showing that electrical conduction through a nanoscale conducting filament in the SiO₂, HfO₂ and

ZrO₂ dielectrics can be disrupted upon exposure to white light [187, 188]. To-date, optical stimulation of these dielectrics for realizing device functionalities has seldom being explored, owing to the lack of photosensitivity in these materials. Because of their large bandgaps (> 5 eV), studies were only limited to the deep ultra-violet regime and beyond, addressing post-irradiation reliability issues [161, 162]. In our study, it was found out that after these oxides had suffered SBD, the breakdown site became photo-responsive, in that its electrical conductivity can be decreased upon illumination. The extent of decrease depends on the exposure time, enabling intermediate resistance values to be achieved through adjustments of this parameter. We termed the observed behavior "negative photoconductivity", as a contrast against the photoconductive response of narrow bandgap oxides and perovskites. The photosensitivity of SBD SiO₂, HfO₂ and ZrO₂ points towards the possible incorporation of optical functionality into mainstream CMOS integrated circuits. In detail, the light-induced annihilation of the nanoscale conducting filament can be utilized in two fields: restoring the post-breakdown gate oxides via illumination and detecting the light signal as an optical sensor. This new concept of optical sensor solves the main challenge faced by conventional optical sensor suffering from thermal generation [189-191], by virtue of its unique working principle not relying on light-stimulated carriers generation.

5.2 Light-assisted reliability rejuvenation: restoration of post-breakdown gate oxide

Electrical-stress-induced breakdown of the SiO₂ gate oxide is a serious reliability issue that has received widespread attention for many years [146]. Studies have shown that gate-oxide breakdown can be broadly classified as soft or hard [151]. Ultra-thin gate oxides (< 5 nm) typically exhibit the former. As soft breakdown (SBD) typically

does not lead to a total loss of transistor functionality, there has been much interest on the breakdown mechanism and its evolution towards eventual hard breakdown. With HfO₂ replacing SiO₂ as the gate oxide, recent attention was mostly centered on the reliability of the metal/HfO₂ gate stack [192]. It has been found that SBD of HfO₂ can be electrically reversed with a greater ease as compared to SiO₂ [154, 193], prompting considerable interest on the recovery mechanism as well as the role of the metal electrode [194].

In this section, we report that a nanoscale percolation path in SiO₂ and HfO₂ can be disrupted upon exposure to white light. The disruption is either complete or partial, depending on the resistance of the percolation path determined at the point of breakdown, i.e. the breakdown hardness. The electrical robustness of the light-restored oxide is tested and analyzed using statistical Weibull distributions.

5.2.1 Experiments

Localized breakdown of SiO₂ or HfO₂ film formed on a p-Si substrate was achieved using a diamond-coated Si probe in an RHK 3500 ultra-high vacuum ($\sim 5 \times 10^{-10}$ Torr) conductive atomic force microscope (C-AFM) as illustrated in Fig. 5.1(a). The contact area between the C-AFM probe and oxide is estimated to be 25.5 nm², based on an applied force of 28 nN and the properties of the diamond-coated Si probe [176].

The SiO₂ film is 5-nm thick, formed by a standard plasma-enhanced chemical vapor deposition process with SiH₄ and N₂O. The HfO₂ film was achieved by atomic layer deposition involving Tetrakis (dimethylamino) hafnium and water vapor and has a 4-nm thickness. The C-AFM probe was connected to a Keithley SCS4200 parameter analyzer and the substrate was grounded. Breakdown stressing, with a constant voltage

at the probe, was applied and interrupted when the current exceeded a preset compliance limit. A LED lamp, positioned at a quartz window of the C-AFM system, functioned as a white-light source. The light intensity at the sample surface was 1 mW/cm^2 , estimated based on the separation between the sample and light source, using a Daystar DS-05A solar meter. The entire experiment was carried out at 297 K. Negligible light-induced heating was confirmed by periodic measurement of the sample temperature using an infrared thermometer as shown in Fig. 5.1(b). As SBD exhibits initial relaxation after stress interruption, light exposure was carried out only after a 45-minute wait period. Probe stability was verified by monitoring the breakdown current for extended period (> 8 hours).

Fig. 5.1 (a) Schematic illustration of the experimental set-up. The inset is a magnified view of the probe-to-sample contact region, showing the probe contacting a nanoscale conducting filament (CF) formed in HfO_2 . (b) Sample temperature (measured by an infrared thermometer) as a function of time in the dark and under illumination. Dashed line depicts the average temperature for both cases.

5.2.2 Light-induced restoration on post-breakdown SiO_2 and HfO_2

Fig. 5.2 depicts a typical set of results for the SiO_2 film. The experimental sequence is shown in Fig. 5.2(a) and the time-dependent evolution of the current under constant-voltage stressing in Fig. 5.2(b). The current compliance limit in this case was

set at 0.5 nA. After an initial stress period where the current remained unchanged, a gradual increase of the current towards the compliance limit could be observed, signaling the onset of progressive SBD [195]. Clearly, the post-SBD I - V curve is significantly shifted towards the low-voltage regime (Fig. 5.2(c)). Interestingly, a shift towards the pre-stress curve is evident after a 10-minute light exposure. Upon a further 15-minute exposure, the I - V curve now almost coincides with the pre-stress curve (Fig. 5.2(c)), indicating that the insulating property of the breakdown spot has been restored.

Fig. 5.2(a) Sequence of experimental steps; (b) Evolution of current during constant negative-voltage stress, where the onset of progressive soft breakdown (SBD) is evident after ~ 800 s. Stressing was arrested when the current compliance (cc) limit of 0.5 nA was reached. (c) Current-voltage (I - V) characteristics, showing a near-complete restoration of post-SBD I - V curve to the pre-stress state after white-light illumination.

A similar restoration of SBD is obtained on the HfO_2 sample for negative- (Fig. 5.3(a)) and positive-stress-induced SBD (Fig. 5.3(b)). The similar response of post-SBD HfO_2 to light exposure implies a common restoration mechanism, which will be further discussed in section 5.4.

Fig. 5.3 White-light illumination can also restore the insulating property of the HfO_2 gate dielectric after it has suffered soft breakdown under (a) negative and (b) positive constant-voltage stressing.

5.2.3 Light-induced restoration vs. electrical-induced recovery

Since electrical induced recovery (via an opposite polarity voltage sweep) is commonly observed in the MIM RRAM structure. It is pertinent to also examine the effect of an opposite-voltage sweep on the post-SBD recovery of gate stacks. Fig. 5.4 shows the results. Unlike the RRAM structure, the gate stack structure is generally more resistant to electrical-induced recovery. As can be seen in Fig. 5.4, for the SiO_2/Si sample (SBD induced by negative CVS), the first positive-voltage sweep did not yield any apparent recovery of the I-V curve. Extending the voltage range during the second positive-voltage sweep resulted in a further breakdown, as is evident from the shift of the I-V curve to an even lower voltage regime. However, a nearly complete recovery was achieved by a 30-minute exposure to white-light after the second positive-voltage-sweep induced breakdown. The results show that white-light

illumination is much more efficient in inducing the recovery of breakdown gate stacks. Furthermore, as reported in some studies [196], a decrease of stress-induced leakage current (SILC) can occur under an opposite-voltage sweep due to emission of charges from oxide traps. While in our study, as shown in Fig. 5.4, no trapped-charge emission can be observed, which rules out the possible role of trapped-charge emission behind the observed light-induced breakdown recovery.

Fig. 5.4 Positive-voltage sweep (after soft breakdown (SBD) by negative constant-voltage stressing) yielded no substantial recovery (after pos-sweep 1) but a further SBD when the voltage-sweep range was extended (pos-sweep 2; after pos-sweep 2). Nearly full restoration was achieved by a 30-minute white light exposure after the second positive-sweep-induced SBD (post-illum).

5.2.4 Impact of breakdown hardness on light-induced restoration

The impact of breakdown hardness on white-light-induced restoration was also studied. Harder breakdown was induced by increasing the current compliance limit during stressing. As can be seen from Fig. 5.5(b), for breakdown induced at a higher current compliance limit, white-light illumination remains effective in restoring breakdown, but only partial restoration can be achieved for the same exposure period.

Fig. 5.5: (a) Complete restoration of SBD at a low breakdown-current compliance (cc); (b) partial restoration for higher cc.

5.2.5 Electrical robustness of light-restored oxide

A question of interest at this juncture would be the robustness of the white-light restored oxide against electrical re-stressing. To address this, the time-dependent dielectric breakdown (TDDB) reliability of the pristine and restored oxide are compared for the SiO_2/Si sample. The experimental sequence is summarized in Fig. 5.6(a). Prior to the first CVS, the I-V curve was measured (cf. Fig. 5.2(c)). A negative CVS was then applied. Fig. 5.6(b) shows the evolution of the current towards the first SBD (line) for two random locations on the SiO_2/Si sample. Prior to SBD, a gradual increase of current with time can be observed, indicating the onset of a progressive breakdown behavior typical of a thin gate oxide. When the increase in current reached a preset compliance level, the stress was automatically aborted by the parameter analyzer. I-V measurement was then taken continuously in the dark to monitor the post-stress relaxation effect until quasi-saturation was reached (after ~105 minutes). The final post-SBD I-V curve was recorded before the sample was subjected to white-light illumination. After 40-minute illumination the light source was removed and the I-V curve for the restored oxide was measured. Regardless of whether full reiteration

was achieved, the negative CVS was reapplied until the second SBD occurred. The same experimental procedure was repeated on 30 randomly selected locations on the SiO_2/Si sample.

Fig. 5.6(a) Experimental sequence used to assess the robustness of the light-restored oxide against electrical re-stressing under the same conditions as those used to induce the first soft breakdown. (b) A comparison of the current-time characteristics of the first and second SBD evolution, for two randomly selected locations on the SiO_2/Si sample.

For the two random locations depicted in Fig. 5.6(b), full restoration of the breakdown oxide was achieved as judged by overlapping pre-stress and restored I - V curves (cf. Fig. 5.2(c)). However, the time to second SBD can either be shorter or longer than the first. As the defect generation process leading to oxide breakdown is stochastic in nature, the Weibull distribution for the time to first and second SBD would have to be compared, as depicted in Fig. 5.7(a). In the distribution curve for the second SBD, the data points are classified according to whether full (solid) or partial (open) restoration was achieved during white-light illumination. Compared to the

distribution curve of the first SBD, the distribution curve of the second SBD features a prominent “tail”, but populated mainly by the early failures, upon restressing, of locations where the breakdown oxide was partially restored by the white-light illumination, i.e. the I-V curves for these locations fall at a lower voltage regime than their pre-stress counterparts. At these locations, the oxide was “weaker” in comparison to the original states and thus it failed at a much shorter times when subjected to the same negative CVS. On the other hand, for locations where the breakdown oxide was fully restored, the distribution curve of the second SBD can be seen to merge with that of the first SBD. This result shows that the fully restored oxide exhibits similar robustness against breakdown during electrical re-stressing. This can be verified by excluding locations where only partial restoration was achieved when plotting the Weibull distribution plot for the time to second SBD. The resultant distribution is nearly identical to that of the first SBD (Fig. 5.7(b)).

Fig. 5.7 Weibull distributions for the time to first and second soft breakdown (SBD) for the SiO_2/Si sample. The second SBD was induced by the same negative constant-voltage stressing of the location where the first SBD occurred and had been restored by light illumination. A total of 30 random locations were tested. (a) second SBD data for all locations (complete and partial restored); (b) second SBD data for only those locations where full restoration had been achieved.

5.3 New concept of optical sensor: negative photoconductivity phenomenon in RRAM oxides

Visible-light-stimulated response of semiconductor devices [158, 160, 163-167] may potentially expand the functionalities of electronics, which are presently limited to electrical stimulations. It was shown [166] that the current flow through the multilayer Pd/Al₂O₃/SiO₂/p-Si structure could be modulated by trapping, in the Al₂O₃, of electrons optically generated in the p-Si substrate. The finding provides a possible means for light-enabled information encoding in non-volatile memory applications. Light-stimulated resistive switching has been observed in structures such as the ZnO nanorod [165], BiFeO₃ thin film [160], TbMnO₃/Nb:SrTiO₃ [158], ZnO/SrTiO₃ [164] and TiO₂/α-Fe₂O₃ [163] heterojunctions. Although the actual response may vary with material characteristics and fabrication conditions, and the underlying mechanisms are still subjects of further investigation, these studies demonstrate that light sources may serve as an additional parameter for enhancing semiconductor device functionalities.

With the exception of ref. [166] where the photoconductivity effect arises from electron-hole pair generation in the Si substrate, nearly all studies on light stimulation reported to-date have focused on photo-responsive oxide or perovskite materials having relatively small bandgaps (~3 eV or lesser) [158, 160, 163-165]. On the other hand, oxides such as SiO₂, ZrO₂ and HfO₂, which are widely deployed in mainstream integrated-circuit manufacturing, have been excluded due to their much larger bandgaps (~6 eV or larger) which render them non-photo-responsive. In this chapter, we show that these wide-bandgap oxides can also be rendered photo-responsive following an electrical-stress induced breakdown. In particular, it is shown that white

light can either permanently or temporarily disrupt the nanoscale conducting filament in the oxides dielectric. In recent years, the HfO_2 dielectric has been intensively studied as the active layer of resistive random access memory (RRAM) devices [197-199], by virtue of its compatibility with the mainstream integrated-circuit manufacturing technology. In the HfO_2 RRAM device, the change between high and low resistance state is usually induced by applying an electric field, which modifies the oxide resistivity by repeatedly disrupting and reforming a nanoscale-width conducting filament through the oxide film separating two metal electrodes. Here, we reveal an intriguing observation that the conduction through a nanoscale conducting filament in the HfO_2 or ZrO_2 -based RRAM and SiO_2 -based conducting bridge random access memory (CBRAM) can be modulated by light. In addition, the filament resistance can be controllably changed to desired values by varying the duration of a light exposure. These findings point to the possibility of direct implementation of light-enabled functionalities as optical sensor using metal oxides-based devices.

The photogeneration process underpins the light detection capability of many semiconducting materials. Optical sensors based on the photogeneration mechanism, however, suffer from a severe interference due to thermal generation. For long wavelength detection, low temperature operation would be mandatory for suppressing the thermal generation effect. Thermal generation induced dark current noise is a major challenge in the development of advanced image sensors. The proof-of-concept for a nanoscale optical sensor based on the oxide breakdown path is presented in this section. The detection mechanism lies in the negative photoconductivity response of the breakdown path and is entirely different from the photogeneration process, thus avoiding the interference with thermal generation.

5.3.1 Experiments

Six-inch p-Si (100) wafers with resistivity less than $10 \Omega \cdot \text{cm}$ were sputter-deposited with 10-nm Ti at 375°C , 1.7×10^{-3} mbar, followed with 50-nm TiN (Ti/N ratio ~ 1.11) at 375°C , 8.2×10^{-4} mbar using a Unaxis Clusterline 200 Sputter system. Prior to the deposition of the two metal layers, the wafers were subjected to the standard RCA cleaning to remove the native oxide. After TiN deposition, a 40-Å HfO_2 or ZrO_2 was grown via atomic layer deposition on a TiN/Ti/p-Si substrate at a temperature of 250°C , a pressure of 0.2 Torr and a nitrogen flow rate of 20 sccm using a Cambridge Nanotech 200 Savannah. The high-k precursor used was tetrakis (dimethylamino) hafnium (for HfO_2) and tetrakis (dimethylamino) zirconium (for ZrO_2). The oxidizer was H_2O vapor. The deposition rate was $1.05 \text{ \AA}/\text{cycle}$. No post-deposition annealing was carried out. The wafers were diced into small test sample pieces, each of area for measurement in an AFM/STM system.

As for the SiO_2 test samples, On a HF-cleaned p-type Si(100) substrate (of resistivity $5 \times 10^{-3} - 1 \times 10^{-2} \Omega \cdot \text{cm}$), a 30-nm Ti film followed by a 30-nm Cu film were deposited by DC magnetron sputtering. Subsequently, a 10-nm SiO_2 layer was grown at 250°C via a parallel-plate plasma-enhanced chemical vapor deposition process using SiH_4 and N_2O gas sources to form the SiO_2/Cu stack. No top electrode deposition was carried out. For comparison, a $\text{SiO}_2(5\text{-nm})/\text{p-Si}$ stack was also fabricated; the SiO_2 here was deposited under exactly the same conditions. To facilitate later discussion, the SiO_2/Cu stack will be referred as the Cu sample and the SiO_2/Si stack as the control sample.

Resistive switching measurement was performed on $0.5 \times 0.5 \text{ cm}^2$ test sample, in a RHK 3500 HT AFM/STM system under ultra-high vacuum ($\sim 5 \times 10^{-10}$ Torr), at a temperature of 300 K. A diamond-coated silicon probe was used for the electrical measurement. For current compliance control during forming, the probe was directly connected to an external Keithley SCS4200 semiconductor parameter analyzer. The voltage was applied to the probe, which acted as top electrode for the test sample, simulating an extremely scaled metal-insulator-metal capacitor structure. The bottom TiN electrode was always grounded.

The white light source is a commercially available LED desk lamp. The illumination was directed through a quartz window of the C-AFM/STM system chamber, at 25 cm from the test sample. The irradiance intensity is measured by Daystar's DS-05A solar meter and the stated values are for a distance of 25 cm from the LED bulb.

Fig. 5.8: Schematic of the experimental setup used in this study. The probe of the ultra-high vacuum (UHV) conductive atomic force microscope is connected to a source/monitor unit of a semiconductor parameter analyzer. A voltage ramp applied to the probe is interrupted when an abrupt current increase is registered, indicating the formation of a conducting filament (cf) on the probe-contact site. A white LED lamp, placed at a quartz window of the UHV chamber, at a distance of ~ 25 cm from the test sample and at an angle of 45° , is used for the light exposure experiments.

5.3.2 Photoresponse in HfO₂/ZrO₂-based RRAM

Fig. 5.9(a) depicts the light-induced disruption of a nanoscale conducting filament in HfO₂, as evidenced from the comparison to the measurement on the same sample performed with no light exposure. Following the formation of a conducting filament using a positive voltage ramp (Fig. 5.9(b), the filament current was monitored at a probe voltage of 1 V as a function of time. The relatively large resistance ($\sim 10\text{M}\Omega$) of the filament is attributed to its very small diameter of several nanometers (as revealed later in Fig. 5.12). The estimated filament resistivity is on the order of $10^{-2} \Omega \cdot \text{m}$, corresponding to that of a semiconductor-like material. As can be seen in Fig. 5.9(a), the current decays slowly over the 2000-s time interval, in the absence of light exposure, as expected from post-electrical-stress relaxation. Re-measurement following the first 2000-s interval shows a constant current ($\sim 10^{-8} \text{ A}$), after the relaxation was completed.

Fig. 5.9 (a) The currents (at a constant bias of 0.5 V on the contacting probe) through a conducting filament without and with light exposure. After the first measurement in the dark was completed (circle), the measurement was restarted in the dark, with a brief exposure to white light (shaded) made midway through the observation period (square). The current decreased sharply to a very low level, indicating that the filament was disrupted during the light exposure. (b) Black Line: A steep current increase at $\sim 3 \text{ V}$ indicates the formation of a conductive filament at the point of the probe contact, as

confirmed by a high current measured in the reverse sweep. Red Square: The positive-voltage sweep after white light illumination reveals a very low current, similar to the preforming level (black line), indicating that the filament conduction was disabled by the light; the filament is subsequently reformed at ~ 2 V. Triangle: The filament is disrupted (reset @ ~ -1.7 V) during a negative-voltage sweep with no light exposure. Circle: After the negative-voltage reset, the current is around the pre-forming level, until the filament is reformed again at ~ 2 V. Arrows indicate directions of voltage sweep. The current compliance limit (CCL) during the first forming and subsequent set operations is 100 nA.

Interestingly, a significant decrease of the current, from $\sim 10^{-8}$ A to the measurement floor ($\sim 10^{-15}$ A) can be observed upon illumination with a white light, in contrast to the behavior shown in Fig. 5.10 for the control sample, which contains no oxides layer, compromising of metal electrode only. After the light source is removed, the current recovers slightly to $\sim 10^{-14}$ A and remains at this level for the remaining duration of the measurement. A subsequent positive voltage sweep yields a current similar to the pre-forming level (Fig. 5.9(b), square), thus confirming that the conducting filament was disrupted during the illumination. Apparently, the white light has “reset” the conducting filament to a high resistance state. A subsequent transition back to a low resistance state, however, occurs at a lower positive voltage as compared to the initial forming process, indicating that the oxide region concerned was not fully restored to its pre-forming state. Following a typical bipolar (electrical) reset using a negative voltage sweep (triangle), a post-electrical-reset current-voltage (I-V) curve (circle) comparable to the post-light-reset I-V curve (square) is attained, indicating that the effect of light is similar to that of the electrical reset on HfO₂. By alternating between the light and electrical reset modes, similar post-reset I-V curves are obtained regardless of the type of the prior reset mode.

Fig. 5.10 Current evolution of a TiN/Ti/p-Si sample (i.e. without an overlaying oxide layer), taken in ultra-high vacuum, in the absence and presence of white-light illumination. Upon illumination, an increase in the current can be clearly observed, as opposed to the decrease seen on oxide-capped samples.

The change in resistance in a specific time interval is determined by the amount of light energy that the filament received, indicating a possibility of achieving multiple resistance levels for a given filament. This is indeed observed in Fig. 3(b), where different levels of the conducting filament disruption can be controlled by changing the duration of light exposure. Upon illumination, the current is decreased from the low-resistance state (LRS) to a first high-resistance state (HRS1) in a 20-s interval. The current decrease is obviously arrested when the light illumination is removed, as is evident from the current plateau. When the illumination is resumed, the current is decreased to the next higher resistance state (HRS2). Clearly, by controlling the light exposure, one can generate multiple resistance values for the conducting filament. This result suggests the possibility of a light-enabled RRAM-resistance tuning approach, as an alternative to the electrical counterpart, for neuromorphic computing applications [200]. The electrical tuning method might be challenging because it requires the

control of a set current compliance limit (for DC switching) or set/reset pulse timing (for AC switching) [201]. In the meantime, the relation between the exposure dose and the resistance builds the fundamentals to function as an optical sensor, converting the light dose/intensity signal to electrical signal (resistance).

Fig. 5.11 An intermediate resistance level (HRS1) can be achieved by limiting the duration of exposure at a given light intensity; LRS – an initial low resistance state; HRS1 – an intermediate high resistance state after the exposure; HRS2 – a final high resistance state after the additional exposure. This result points to the possibility of realizing multiple resistance levels by modulating the duration of light exposure a conducting filament receives, as well as the nature functioning as an optical sensor.

To further illustrate that the disruption of current conduction observed in Figs. 5.9 and 5.11 is a consequence of light induced “dissolution” of the filament, current maps of a selected region of the HfO₂ before and after forming, and after various stages of light exposure are compared in Fig. 5.12. Compared to uniform current map before forming (Fig. 5.12(a)), the presence of a distinct bright shade, of ~4 nm in diameter, after forming (Fig. 5.12(b)) is due to the generation of a conducting filament.

Interestingly, after a 30-s exposure to white light, the level of brightness and size of the filament are drastically reduced (Fig. 5.12(c)), which correspond to a decrease in current. Upon further illumination, the filament became almost indistinguishable from the surrounding oxide region (Fig. 5.12(d)). The results confirm that white light can eradicate a conducting filament formed in the soft-breakdown HfO_2 .

Fig. 5.12 C-AFM current maps: (a) relatively uniform current distribution before forming; (b) a bright shade of ~ 4 nm in diameter denoting the conducting filament after forming (the peak current is >1 nA); (c) reduced filament size and brightness (i.e., current) after a 30-s white-light illumination; and (d) near-complete filament disruption upon a further 300-s illumination. Inset: Remnants of the filament are visible only at a much reduced current scale.

A similar behavior can be observed in ZrO_2 sample. A positive-voltage ramp was applied to the probe to induce electro-forming at a localized region of ZrO_2 under current compliance of 2×10^{-7} A (denoted by 1a in Fig. 5.13 (a)). An abrupt current increase was observed at 5.5 V. The increased current measured (in the reverse voltage sweep) after forming confirms the formation of CF. The low-resistance state (LRS)

current was monitored (at 0.5 V) in time-resolved measurement (Fig. 5.13 (b)). For the initial 52-s in dark ambient, the current (1b) level was constant at 1×10^{-9} A. However, as the white-light was turned on at 52-s, an instant current decay (by ~ 4 orders in magnitude) from 1×10^{-9} A to $\sim 10^{-14}$ A was observed. After illumination was turned off at 125-s, the current level remains constant at $\sim 10^{-14}$ A until 500-s. Clearly, the CF was disrupted in the reset transition, induced by the presence of white-light, and restoring to high-resistance state (HRS), even without applying electric-field across the region. The reset process was confirmed by the reduced current (2a) in the subsequent positive-voltage ramp in Fig. 5.13 (a); note that the current level ($\sim 10^{-12}$ A) at low (< 1 V) positive-voltage regime was similar to that of the initial resistance state before forming. The field-less LIR was consistently repeatable, with the sequence of the subsequent measurements were denoted by alphanumerical labels in Fig. 5.13 (a) and (b). To verify that the observed current decay was due to oxide microstructural change instead of piezo-legs expansion (thereby retracting probe away from sample surface and causing current reduction) upon illumination, time-resolved current measurement (at 0.5 V) was performed on TiN/Ti/p-Si sample (without oxide deposition on TiN layer). The result reveals no current decay under illumination (not shown). This is consistent with the constant current level of 5b measured in dark ambient (Fig. 5.13 (b)). These confirm that the current decay observed in Fig. 5.13 (b) is not related to external factors, but is attributed to light-induced microstructural change (i.e., disruption of CF) in ZrO_2 .

Fig. 5.13 Alphanumerical labels denote the sequence of measurements (a) Current-voltage (I - V) curves recorded during forming and set (after LIR in (b)) process under positive-voltage ramp, via probe, at a localized region of ZrO_2 . (b) Transient response of LRS current, after forming and set process in (a), at the corresponding region upon illumination at 52-s for a duration of 73-s. A significant current decay indicates reset process at the local region resulted from photo-response instead of electric-field-driven.

5.3.3 Photoresponse in SiO_2 -based CBRAM

Typical current-voltage (I - V) curves for the negative-voltage electroforming or SBD step (A) and subsequent dual-polarity voltage-sweep measurements are depicted in Fig. 5.14(a) and (b), respectively, for the SiO_2/Cu and SiO_2/Si stacks. Abrupt increase in the current to the compliance level marks the formation of a filamentary breakdown path in the SiO_2 . Despite the $2\times$ thicker SiO_2 , the electroforming voltage (at which the current-jump occurs) of the SiO_2/Cu stack is half that of the SiO_2/Si stack. The lower electroforming voltage of the former may be attributed to electric-field-induced migration of Cu ions into the SiO_2 during the negative-voltage sweep. Studies on Cu-based CBRAM [202-204] have found that under a large oxide field, Cu ions from the electrode may migrate into the oxide, leading eventually to the formation of a Cu filament. The presence of Cu ions increases the oxide field at the probe location, due to a decrease of the effective electrical SiO_2 thickness. This is believed to have facilitated the dissociation of Si-O bonds and the consequently breakdown of the SiO_2 at a lower voltage than in the SiO_2/Si stack. Atomic-scale spectroscopic studies

[205] have found an oxygen-deficient or vacancy-populated breakdown oxide region, implying that Si-O bond dissociation and field- and thermal-induced migration of the released oxygen ions away from the dissociated bonds results in SiO₂ breakdown.

Fig. 5.14: Current-voltage (I - V) curves of (a) SiO₂/p-Si and (b) SiO₂/Cu/Ti/p-Si stacks. A negative-voltage ramp (curve A, black) for electroforming was applied, followed by a positive-voltage ramp (curve B, red) and then a negative-voltage ramp (curve C, blue). Arrows indicate directions of voltage-sweep.

During the post-breakdown positive-voltage sweep (B) of the SiO₂/Si stack, no decrease in the current can be seen (Fig. 5.14(a)), indicating that breakdown recovery did not occur. This is apparent from the subsequent negative-voltage sweep (C), which yielded a similar I - V curve. Absence of breakdown recovery was obtained for 29 other breakdown locations on the SiO₂/Si stack. This observation draws similarity to the lack of breakdown recovery in the polysilicon/HfO₂/Si stack [194]. In contrast, breakdown recovery can be readily observed in the TiN/HfO₂/Si stack during a negative-voltage sweep applied to the TiN. The difference has been ascribed to the migration of O ions from the TiN interface region into the breakdown path. Resultant recombination between the O ions and vacancy (V_O) defects leads to the disruption of the path. Such a supply of O ions is, however, lacking in the case of the

polysilicon/HfO₂/Si stack due to the stronger Si-O bonds. The dissociation energy of Si-O bond is 8.29 eV, much larger than that of the Ti-O bond (6.91 eV) [206]. Thus, a possible reason for the absence of breakdown recovery in our SiO₂/Si stack is the lack of O supply from the Si interface region. O ions driven towards the Si substrate during the breakdown may also be “locked-in” by the formation of Si-O bonds, thus limiting their drift back to the breakdown path during the positive-voltage sweep. It should be mentioned that a further breakdown of the SiO₂ occurs when the range of the positive-voltage sweep is extended [187].

On the other hand, an obvious decrease in current can be seen for the SiO₂/Cu stack (Fig. 5.14(b)), indicating that breakdown recovery occurred during the positive-voltage sweep (B). The recovery is near-complete, as is evidenced by a consecutive negative-voltage sweep (B) which yielded an *I-V* curve like the pre-breakdown case. Unlike the SiO₂/Si stack, more than 80% of the 30 breakdown locations on the SiO₂/Cu stack exhibit near-complete recovery. The remaining percentage show partial recovery. This significantly enhanced breakdown recovery may be attributed to 1) the relative ease for Cu ions in the breakdown path to migrate back to the Cu electrode under a reverse electric field [202-204, 207, 208]; 2) the availability of O ions from the Cu interface region for reducing the vacancy defects in the breakdown path. The dissociation energy of the Cu-O bond is 2.98 eV [206], comparable to the Ti-O bond but substantially lower than that of the Si-O bond. Thus, O ions from the interface region of the Cu cathode may readily migrate back to the breakdown path, just like in the HfO₂/TiN [209].

Fig. 5.15(a) depicts the response of the breakdown path in the SiO₂/Cu and SiO₂/Si stacks to white-light illumination. The light intensity at the test sample surface

was $\sim 2 \text{ mW/cm}^2$, determined from a separate measurement involving a solar meter positioned roughly at the same distance from the light source as the test sample. In the 100-s period before the illumination, a constant current was recorded at the monitoring voltage-bias of -1 V , indicating that the breakdown path and the C-AFM probe were stable. Upon illumination at 100 s, a significant decrease of the breakdown current, from $\sim 10^{-12}$ to $\sim 10^{-14} \text{ A}$ (the measurement floor), can be observed in both cases, similar to the NPC response of the HfO_2/TiN stack [209]. A negative-voltage sweep applied after the illumination yielded I - V curves that are partially shifted back towards the respective pre-breakdown curves (Fig. 5.15(b)), indicating that some degree of photo-induced recovery of the breakdown path has occurred [210]. By alternating between electrical SBD and light exposure, the breakdown path in both stacks can be repeatedly switched between the electrical set (low resistance) and optical reset (high resistance) states, respectively. With our present set-up, the number of switching cycles is limited at ~ 70 , due to thermal drift of the C-AFM probe. It has been proposed [210] that optical reset proceeded with the photo-excitation of interstitial O ions surrounding the breakdown path, resulting in their migration and recombination with the vacancy defects in the path. Besides the electric-field directed migration of O ions (released from Si-O bond dissociation during the breakdown process) towards the anode, simulation has shown that these O ions may also propagate laterally outwards from the breakdown site due to Joule heating, and some of them remained in the proximity when the process is aborted [211]. The migration barrier for interstitial O ions within the oxide network is $\sim 0.11\text{-}0.27 \text{ eV}$ [212], which corresponds to $\sim 1.8\text{-}4.3 \times 10^{-20} \text{ J}$. Considering that the light intensity at the oxide surface is 2 mW/cm^2 or $2 \times 10^{-19} \text{ J/s} \cdot \text{\AA}^2$, it is plausible for photo-induced migration of the interstitial O ions to occur, resulting in the disruption of the breakdown path. In contrast, such reverse migration of

surrounding interstitial O ions to the breakdown site would not occur during voltage sweeping, as Joule heating would tend to favor the outward propagation of these ions instead. Thus, breakdown recovery could not occur in the SiO₂/Si stack during the voltage sweep (Fig. 5.14(a)).

Fig. 5.15. (a) Current-time (I - t) plots of the SiO₂/p-Si (Si) and SiO₂/Cu/Ti/p-Si (Cu) stacks showing the disruption of the breakdown path under white-light illumination. A low voltage of -1.5 V and -1 V, respectively, was applied to the C-AFM probe for sensing the breakdown current. The currents in both stacks show a steep decrease upon illumination at 100 s and remain low at $\sim 10^{-14}$ A after the light was turned off at 200 s. (b) Comparison of the forward and reverse-sweep current-voltage curves for the first electroforming and the re-forming step after illumination.

Electrical modulation of the optical reset in the SiO₂/Cu stack is demonstrated in Fig. 5.16. SBD of the SiO₂ was first induced by a negative-voltage sweep ($0 \rightarrow -8$ V at 1 nA compliance) applied to the C-AFM probe. The breakdown path was then checked for NPC response or further subjected to a varying number of the same negative-voltage sweeps before illumination was applied. The procedure was repeated on numerous randomly selected locations on the test sample. It should be noted that positive-voltage sweeping was not applied as this would disrupt the breakdown path and cause a reset electrically, like in Fig. 5.14(b).

Fig. 5.16: (a) Current-time (I - t) plots depicting the effect of white-light illumination on the breakdown path in the SiO₂/p-Si (Si) and SiO₂/Cu/Ti/p-Si (Cu) stacks, after subjecting each path to more than 15 negative-voltage sweeps. (b) Percentage of breakdown paths (out of a total of 30 each) which can still display the NPC behavior after a certain number of negative-voltage sweeps. (c) Averaged pre-illumination current-voltage (I - V) curve of 20 breakdown paths which show NPC behavior versus averaged I - V curves of 20 breakdown paths which lost their NPC behavior after more than 15 negative-voltage sweeps. (d) After numerous negative-voltage sweeps, a breakdown path can only be disrupted by a much higher light intensity.

For breakdown paths that were subjected to only a few (< 5) negative-voltage sweeps (inclusive of the electroforming step), a high percentage ($\sim 80\%$) of them display an NPC response during illumination, like in Fig. 5.15(a). In contrast, only a minority ($\sim 20\%$) of the breakdown paths can show the NPC response after being subjected to 15 negative-voltage sweeps prior to the illumination. The majority failed to register any NPC response, i.e. the breakdown current is unperturbed during illumination (Fig. 5.16(a)). The observations indicate that the NPC response of the breakdown path in the SiO₂/Cu stack can be manipulated by the number of times the

Cu electrode is positively biased with respect to the non-metal counter electrode (C-AFM probe).

However, the same procedure, when applied on the SiO₂/Si stack, did not impact the NPC response of the breakdown path. After more than 15 negative-voltage sweeps, the breakdown path can still be disrupted upon illumination (Fig. 5.16(a)), with no apparent difference from the case without any additional voltage sweeps applied (Fig. 5.15(a)). A study on 30 random breakdown locations show that all of them retain their NPC response after more than 15 sweeps. This shows that the NPC modulation effect seen in the SiO₂/Cu stack is linked to the Cu electrode.

Repeated voltage sweeps applied to the breakdown path may cause progression towards more severe hard breakdown, due to further dissociation of weak Si-O bonds within the breakdown region and propagation of the released oxygen ions further away from the breakdown site by Joule heating [211]. Consequently, the path may become less responsive to illumination because of reduced availability of interstitial oxygen in its proximity. To check this point, a comparison is made between the averaged pre-illumination *I-V* curve of 20 breakdown locations which were NPC responsive immediately after electroforming against 20 other locations which lost their NPC response after 15 repeated voltage sweeps (Fig. 5.16(c)). No significant difference between the two curves can be observed, implying that those locations which became non-responsive did not suffer more severe breakdown after the repeated voltage sweeps.

5.4 Mechanism of the light-induced disruption of the CF

The light induced resistance-reset phenomenon discussed above should be distinguished from the photo-related resistance switching effects reported in recent studies [158, 160, 163-167]. It was reported by Yu and Wang[167] that the resistance between two points along a thin Ti film could be continuously varied between two extreme values when a laser beam was scanned between these points. As shown in Ungureanu et al.[166] the current through the Pd/Al₂O₃/SiO₂/p-Si device biased in inversion was modulated by injecting optically generated minority carriers (electrons) in the p-Si substrate and trapping these electrons in the Al₂O₃ layer. Park et al.[165] found that the resistance of a ZnO nanorod RRAM device was switched to a lower value at a smaller voltage under light exposure. After the light exposure, however, the resistance would transit towards a higher value at a rate determined by the decaying persistent photoconductivity (PPC) effect [213]. A significant PPC effect in the ZnO/SrTiO₃ heterojunction obscured the electrically induced resistance switching of this device following light exposure [164]. In heterojunction structures, the PPC effect has been ascribed to the trapping of charges at interface defects, which modulate the junction barrier controlling current flow [158, 160, 163, 164]. A common feature in the abovementioned studies is that the test-sample resistance is modulated by a significant photoconductivity effect. In contrast, the HfO₂, ZrO₂, and SiO₂ are non-photo-responsive materials due to their relatively large bandgaps. In contrast to photo-responsive oxides, white light has no impact on the I-V curve measured during the forming/set steps performed on HfO₂. However, once the conducting filament is formed, a unique feature of the light-induced filament disruption (i.e., a “negative photoconductivity effect”) is observed in this study.

A possible explanation for the light-induced resistance reset phenomenon in HfO₂

is illustrated in Fig. 5.17, based on the oxygen migration model [138, 201, 214]. The proposed explanation is guided by two recent findings: (1) observation of an oxygen-depleted filament via atomic-scale electron-energy loss spectroscopy [143]; and (2) observation, by simulation, of oxygen ions released from the filament site during formation, in the vicinity of the filament [215]. Fig. 5.17(a) depicts the formation of an oxygen-deficient conducting filament through the HfO_2 layer when a voltage sweep is applied via the C-AFM probe. Electron transport through the hafnia film induces Hf-O bond breakage and out-diffusion (assisted by the temperature and electrical field distributions) of the released negatively charged oxygen ions, resulting in the formation of an oxygen-deficient (metal-rich) conducting filament. As the forming process is interrupted when the current reaches a compliance limit, some of the released oxygen ions remain in the interstitial positions in the vicinity of the filament [215] and may be subsequently driven back to the filament by the applied electrical field and temperature gradient during the electrically controlled reset [201]. The diffusion of interstitial oxygen ions entails the overcoming of an energy barrier of 0.3–0.6 eV [216]. At a low voltage (below the electrical reset voltage), the diffusion rate would thus be negligibly small. It is suggested that a white light illumination generates a photon-induced excitation of the oxygen ions over the diffusion energy barrier, hence accelerating their diffusion towards the vacancy-rich filament, as illustrated in Fig. 5.17(b).

The effect of the conducting filament dimension as determined by the current compliance limit (CCL) used during the DC forming process on light-induced reset is also studied and the results are shown in Fig. 5.18. When the conducting filament is formed at a low CCL (of 10nA), the light-induced reset state is relatively stable (i.e., after the light is turned off, the current remains constant at a low level throughout the

entire duration of the observation time). On the other hand, when the conducting filament is reformed at a higher CCL of 100 nA, the light induced reset is less complete and unstable (i.e., the current after illumination is much higher than the case of low CCL and can be seen to gradually increase back to the prereset level). Similar results are obtained on the $\text{ZrO}_2/\text{TiN}/\text{Ti}/\text{p-Si}$ sample. These observations are consistent with the model discussed in Fig. 5.17.

Fig. 5.17 Schematic illustration of the proposed mechanism for the light-induced resistance reset. (a) Formation of a conducting filament comprising oxygen vacancies, with the released oxygen ions populating interstitial sites in the filament vicinity. (b) Filament disruption by recombination between filament vacancies and photo-excited migrating oxygen ions (arrows) from the vicinity. (c) Filament formed at a higher current compliance has fewer interstitial oxygen in its vicinity due to increased lateral propagation of the released oxygen ions. (d) Partial filament disruption due to limited supply of photo-excited migrating oxygen ions, including weakly bonded lattice oxygen in the filament vicinity. Additional vacancies generated lead to oxygen back-diffusion (arrows) and filament reformation after light exposure.

When a lower CCL is used during DC forming, fewer oxygen ions are released due to a smaller required filament cross-section. Since the process involved is shorter (terminated once the low CCL is reached), a larger portion of the released oxygen ions populate interstitial sites in the immediate vicinity of the filament (Fig. 5.17(a)). These interstitial oxygen ions may then recombine with the filament vacancies during light-driven reset (Fig. 5.17(b)). On the other hand, a DC forming process using a larger CCL releases more oxygen ions (due to a larger filament cross-section) and also enables a larger share of the released ions to propagate further away from the filament as a result of the greater Joule heating and longer process involved (Fig. 5.17(c)).

Fig. 5.18: Influence of the CCL used to form the conducting filament on subsequent light induced reset to a high resistance state. Light of a given intensity and exposure duration (10 s) results in a complete reset or disruption of the filament formed with a lower CCL (a). On the other hand, partial reset is evident for the filament formed at a higher CCL, as can be seen from the much higher current at the end of illumination. Moreover, a post-exposure gradual recovery of the current towards the level prior to illumination can be observed.

Then, during a subsequent light exposure, a smaller share of the light-activated interstitial oxygen ions distributed throughout the dielectric volume may potentially

reach the filament, resulting in only partial filament disruption. As the recombination of filament vacancies may also involve light-stimulated migration of weakly bonded lattice oxygen ions in the filament vicinity towards the filament vacancies, the resultant vacancies formed would in turn trigger the back-diffusion and reformation of filament vacancies (Fig. 5.17(d)) after the light was turned off. This could explain the gradual recovery of the current towards the pre-illumination level.

A possible explanation for the loss of NPC response of the breakdown path in the SiO₂/Cu stack after repeated negative voltage sweeps is depicted in Fig. 5.19. It is reported that Cu ions precipitate and form a filament in a solid electrolyte [217] (which is SiO₂ here), with gaps in between the Cu filament and the SiO₂/probe interface. After electroforming, it is thus believed that the breakdown path is made up of both Cu-ion and V_O clusters (Fig. 5.19(a)). The existence of V_O's in the path makes it NPC responsive, as photon-stimulated migration of oxygen ions in the path's vicinity and their recombination with the V_O's in the path would disrupt it, leading to a partial restoration of the oxide resistance [188] (Fig. 5.15(b)). If a negative voltage sweep is repeatedly applied after electroforming, more Cu ions would be drawn into the path [207], occupying the V_O sites there to form a complete Cu filament (Fig. 5.19(b)). First-principle calculation [218] has shown that metal-ion migration in an oxide network is enhanced by the presence of V_O's. Disruption of the Cu filament requires not only the cleavage of Cu-Cu bonds but also the ionization of Cu to Cu⁺ or Cu²⁺. The Cu-Cu bonding energy is 2.08 eV [206] and the first ionization energy to form Cu⁺ is 7.73 eV [219], requiring a total energy of 1.57×10^{-18} J, $\sim 10 \times$ larger than the energy provided by the LED source used. Thus, the light used is unable to disrupt the breakdown path in the SiO₂/Cu stack after a complete Cu filament is formed.

To check the above hypothesis, a breakdown path was generated using a negative voltage sweep on a randomly selected position on the SiO_2/Cu stack. The path registered an NPC response when illuminated by white light of intensity 4.5 mW/cm^2 . After the illumination, the breakdown path was reformed using a negative-voltage sweep. This was followed by more than 15 negative-voltage sweeps before the path was subjected to white light of the same intensity. The path now failed to show any NPC response (Fig. 5.16(d)). The same breakdown path was then subjected to white light of successively higher intensity (11 and 27 mW/cm^2). Interestingly, an NPC response was recorded under the strongest illumination (having intensity $>10\times$ of that used in Fig. 5.16(a)), lending support to the proposed hypothesis.

Fig. 5.19: Schematic diagrams showing (a) the initial state of a breakdown path in the $\text{SiO}_2/\text{Cu}/\text{Ti}/\text{p-Si}$ stack after electroforming; (b) change in the path composition after numerous negative-voltage sweeps applied to the C-AFM probe. Cu ions drawn from the bottom Cu electrode into the breakdown region by the negative-voltage sweep (see dotted arrows) fill the oxygen vacancies present there, resulting in the formation of a complete Cu filament.

Experimental results have shown that the NPC response of the breakdown path in the SiO_2/Cu stack can be suppressed by multiple negative voltage sweeps applied to the non-metal counter electrode (or positive voltage sweeps applied to the Cu electrode) after electroforming. However, such an effect is not observed in the SiO_2/Si stack, where a non-metal Si electrode is used, pointing to a definite role by the Cu electrode in the observed NPC response modulation effect. A hypothesis involving Cu ions migration, due to the applied voltage sweeps, into the breakdown path and occupying the vacancy defects there to form a Cu filament is proposed. Consequently, the photo-induced oxygen-vacancy recombination (believed to have given rise to the NPC response) is suppressed and thus the NPC response is affected. Preliminary calculations have indicated that a stronger light intensity is needed to disrupt a Cu filament and have been supported experimentally.

5.5 Summary

Non-photo-responsive large bandgap oxide materials such as HfO_2 , ZrO_2 and SiO_2 are consistently found to become photo-responsive after suffering an electrical-stress induced SBD. Unlike the classical photo-response behavior of narrow bandgap oxides and perovskites which is commonly manifested as an increase in electrical conduction due to the generation of excess charge carriers by the incident photons, the photo-response here comes in the form of a disruption of electrical conduction through the nanoscale conducting filament or percolation path formed during breakdown. When that occurs the insulating properties of the breakdown oxide region can be restored to almost the pristine condition, as is confirmed by the similar robustness of the restored oxide against electrical-stress induced breakdown. The disruption in electrical conduction caused by white-light illumination is proposed to occur through photon-

stimulated migration of interstitial oxygen ions nearby the vacancy-filled filament, resulting in the migrating oxygen ions recombining with the vacancies in the filament. This unique photo-responsive behavior, which we termed as negative photoconductivity of SBD HfO_2 , ZrO_2 and SiO_2 points towards the possibility of gate oxide reliability rejuvenation as well as the incorporation of optical functions into mainstream CMOS-based integrated circuits, e.g., imaging sensors and photodetectors with built-in non-volatile memory capability.

Chapter 6 IMPACT FACTORS ON THE SENSITIVITY OF THE NEGATIVE PHOTOCONDUCTIVITY AND THE IN-SITU SENSITIVITY MODULATION APPROACH

6.1 Introduction

The discovery of the NPC phenomenon has been reported in the previous chapter, including its photo-response behavior and the reliability rejuvenation capability. A systematical study on the impact factors on the NPC sensitivity is carried out in this chapter, revealing the relationship between the photosensitivity and the illumination intensity, wavelength, oxygen stoichiometry and the working temperature. We present new evidence that the non-volatile negative photoconductivity (NPC) response of the ZrO_2 breakdown path can be suppressed or tuned to different levels by repeated application of a positive voltage-bias on the TiN electrode prior to light exposure. A negative voltage-bias does not produce such a tuning effect but can restore the NPC response suppressed by the positive voltage-bias before a re-breakdown step. In samples with a non-metal (Si) electrode, the NPC tuning effect is absent indicating that a positively biased TiN electrode is needed to produce the tuning effect. We

hypothesize that a positive voltage may induce the migration of Ti ions into the vacancy sites in the breakdown path. This then prevents the photo-assisted recombination of the interstitial-vacancy defect pairs, leading to a modulated NPC response. A negative voltage-bias expels the Ti ions back to the electrode and restores the NPC response.

6.2 Impact factors on the NPC sensitivity

6.2.1 Experiments

Fig. 6.1 is a schematic diagram of the measurement set-up. The test sample, comprising a 4-nm thick, atomic-layer deposited ZrOx or HfOx on a TiN/Ti/Si substrate, is situated in an ultra-high vacuum (UHV) conductive atomic force microscope (C-AFM). The diamond coated C-AFM probe serves two purposes: 1) to induce a nanoscale breakdown path via a voltage-ramp supplied by a parameter analyzer; 2) to function as the top electrode during subsequent testing. The light source is situated at a viewport of the UHV chamber, at ~25 cm away from the sample. To capture the real-time decrease of the breakdown path conductance, a standard pre-amp cum oscilloscope set-up was used. To achieve fast real-time measurement with high precision, the resistance change upon illumination is monitored by the oscilloscope with sampling rate 2.5 kHz, which responds much faster to the rapid change of signal, especially upon high-intensity illumination, than an SMU of Keithley 4200. The schematic of the setup details is shown in Fig. 6.2. (a). The monitoring bias is applied to the C-AFM tip through SMU, and the current signal is converted to a voltage signal by the current-voltage amplifier with the gain 20 pA/V. Fig. 6.2 (b) depicts a typical voltage-time plot captured by the oscilloscope, demonstrating the fast and precise

response to the signal change upon high-intensity illumination, 12.5 mW/cm^2 white light.

Fig. 6.1: Schematic diagram of the experimental set-up used in the work. The test sample is either a 4-nm thick ZrO_x or HfO_x , atomic-layer deposited over a TiN/Ti/Si or Si substrate. The sample is situated in the ultra-high vacuum (UHV) chamber of a conductive atomic force microscope (C-AFM). The UHV environment ($\sim 5 \times 10^{-10}$ Torr) prevents surface contamination during testing. In an actual sensor, the oxide layer will be protected by a top transparent electrode. The diamond-coated C-AFM probe acts as the top electrode, and is connected to either a parameter analyser for dc sweep measurement or a pre-amp cum oscilloscope set-up for real-time measurement. The light source is situated at the viewport of the UHV chamber, at $\sim 25 \text{ cm}$ from the sample. The light intensity at the sample surface is separately measured using a solar meter placed at same distance from the light source.

Fig. 6.2: (a) Schematic of fast real-time oscilloscope measurement setup. (b) Oscilloscope voltage-time plot with high precision, sampling rate 2.5 kHz. (c) Strong light intensity dependence of the photoresponse speed. The statistical distribution of the photoresponse speed under 2.5 mW/cm² (blue) and 12.5 mW/cm² (black) white light, with mean value of 2.40 s/order and 0.72 s/order, respectively.

6.2.2 Light intensity dependence

The ability of measuring the intensity of the incident light is the key requirement for an optical sensor. Therefore, as a new proof-of-concept for the optical sensor based on the negative photoconductivity of the nanoscale conducting filament, the validation of the light intensity dependence is required.

Fig. 6.3 depicts sub-1s current quenching response under white light illumination. A “linear” rate of current decrease is obtained on a log-linear scale as shown, giving a response time of 0.40 s per decade of current decrease. The sub-1s response is encouraging, given that the present set-up is not optimized. Further reduction of the response time may be expected on a complete sensor set-up including the microlens. The statistical variation in the response time of >25 different breakdown locations is found to fit the log-normal distribution (Fig. 6.4), showing a mean value of 0.72 s/decade for the intensity of 12.5 mW/cm². An expectedly slower response with the

mean value of 2.40 s/decade is obtained for a lower light intensity 2.5 mW/cm², showing the ability of the breakdown path to detect light of varying intensities.

Fig. 6.3: Real-time current evolution through the breakdown path, as captured by an oscilloscope during illumination. A logarithmic time dependence of the current decay is evident, with a rate of 0.4 s/decade. The gain of the pre-amp is 20 pA/V.

Fig. 6.4: Distribution of negative photoconductivity response time, defined as the time taken for the current to decrease by a factor of 10, as a function of different white light intensities. The data are found to best fit the lognormal distribution. A faster current decrease is obtained for a higher light intensity, indicating of the capability of the breakdown path to detect light of different intensities. The mean value of the

photoresponse speed is 0.72 and 2.40 s/decade for 12.5 and 2.5 mW/cm² white light, respectively.

Furthermore, the stronger light not only induces a faster response speed, but also influences the reset strength of the breakdown conducting filament. The reset strength is measured by the shift of I-V curve between low resistance state (LRS) before illumination and the high resistance state (HRS) after illumination. Fig. 6.5 depicts the distribution of the forming voltage (black), LRS voltage before illumination (red) and HRS voltage after illumination (blue). By comparing the mean values of those voltages, the light induced voltage shift is 3.10 V occupying 86.6% of the total voltage shift between forming and LRS upon strong light illumination 12.5 mW/cm². While the light induced voltage shift is only 1.72 V and the reset percentage is 44.3% upon weak light illumination 2.5 mW/cm².

Fig. 6.5: Distribution of the forming voltage, LRS voltage before illumination and HRS voltage after illumination. (a) For light intensity 12.5 mW/cm², the mean values of the voltages are 1.01 V, 4.11 V and 4.59 V for LRS, HRS and Forming voltages, respectively. Light induced voltage shift is 3.10 V, and reset percentage is 86.6%. (b) For light intensity 2.5 mW/cm², the mean values are 1.15 V, 2.87 V and 5.03 V, respectively. Light induced voltage shift is 1.72 V, and reset percentage is 44.3%.

6.2.3 Broad spectrum sensing capability and wavelength dependence

The broad spectral photodetective capability is of great importance to many fields including space research and military applications, where the measured objects, the rocket plume for instance, will emit various wavelengths from visible range to near infra-red [220]. Conventionally, multiple detectors are required to collect the light intensity information for different wavelengths. As a result, the complexity of the sensing system is inevitably increased. The demand for a broad spectrum photodetector which is able to detect a broad spectrum in the same pixel is increasing rapidly with the exuberant development of the space and military research nowadays. Therefore, in this section, the broad spectral photodetecting capability of the soft breakdown induced filamentary path is investigated. The testing wavelength ranges from visible to near infra-red. For visible range, the blue and red light are provided by the corresponding bandpass color filter using SugarCube LED white light illuminator as back light source. While for the infra-red light, a lamp consisting of infra-red LED arrays is used. The peak wavelength for the blue, red and infra-red is 450 nm, 650 nm and 850 nm, respectively.

The demonstration of the broad spectrum photodetective capability for the ZrOx sample is illustrated in Fig. 6.6. A typical testing cycle comprises two stages: 1) controlled electrical-induced soft breakdown; 2) light exposure. The parameter analyzer aborts the voltage-sweep (Fig. 6.6(a), circle) when a preset current compliance (50 nA) is breached, thus preventing the onset of a catastrophic thermal runaway. A re-sweep reveals significant current at low voltages, confirming oxide breakdown (square). Current through the breakdown path is stable in the dark (Fig. 6.6(b)), and is decreased sharply upon exposure to near-infrared irradiation (850 nm),

exhibiting a negative photoconductivity behavior. A subsequent voltage-sweep measurement reveals a shift of the current curve towards higher voltages (Fig. 6.6(a), triangle), indicating a partial restoration of the breakdown.

Fig. 6.6: (a) Current-voltage curves showing an abrupt increase in current at the instant of breakdown (circle). The voltage-sweep is aborted when the current increase exceeds a pre-set compliance level (50 nA). Post-breakdown measurement shows significant current conduction at low voltages (square). An evident decrease in the current level after near-infrared (NIR) (850 nm) illumination. (b) Current versus time curve showing a sharp decrease in current ($> 10^5$ orders) upon NIR illumination. Similar current “quenching” is observed upon exposure of the breakdown path to (c) blue (450 nm); (d) white and (e) red (750 nm) light. Colored or shaded regions denote the period of illumination.

A comparison of the current map measured before and after the near-IR illumination further confirms that the breakdown path is disrupted after illumination (Fig. 6.7). The measurement also reveals the size of the breakdown path (~ 7 nm in diameter). Similar negative photoconductivity response is obtained under white, red

and blue light illumination (Figs. 6.6(c)-(e)). These results clearly show the broad spectral light detection capability of the oxide breakdown path.

Fig. 6.7: C-AFM current maps. Before near-infrared (NIR) illumination (left), the breakdown path is denoted by the bright shade, of ~ 7 nm in diameter. After NIR illumination, no bright shade can be seen, indicating that the breakdown oxide had been restored by the illumination.

Measurement of the response time distribution under blue ($450 \text{ nm} \equiv 2.76 \text{ eV}$), white and red ($650 \text{ nm} \equiv 1.91 \text{ eV}$) light illumination of similar intensities yields a weak dependence (Fig. 6.8). The respective mean response time are 0.66, 0.72 and 0.81 s per decade. This result shows that the breakdown path has similar sensitivity to blue and red light. This is in contrast to the generally stronger wavelength dependence of semiconducting materials (e.g. Si) arising from the variation of the absorption coefficient [221].

Fig. 6.8: No apparent difference in the distribution of the negative photoconductivity response time or rate of current quenching under red and blue light illumination. The breakdown path appears to respond equally well to wavelengths across the entire visible light spectrum.

6.2.4 Oxide stoichiometry dependence

Dependence of the response time on oxide stoichiometry is illustrated in Fig. 6.10 for two HfO_x samples having Hf:O ratios of 1:1.6 (oxygen deficient) and 1:3.3 (oxygen rich), as determined from X-ray photoelectron spectroscopy analysis (Fig. 6.9).

Fig. 6.9: Hf 4f and O 1s core-level spectra measured by x-ray photoelectron spectroscopy. (a) Oxygen-deficient and (b) oxygen-rich HfO_x samples prepared by atomic-layer deposition (ALD). An oxygen-rich condition during the ALD process for HfO_x is achieved by lengthening the H_2O pulse so as to enhance the incorporation of O into the oxide being grown. An increase in the non-bonding O spectrum, relative to those for Hf-O is evident in sample (b). Symbol denotes experimental data; lines denote component spectra and best-fit curve to the measured data.

Fig. 6.10 shows the photoresponse speed statistical distributions for these two samples under white LED light with an intensity of 2.5 mW/cm^2 . Two differences are apparent. Under a given light intensity, the oxygen-rich sample has a faster response and a steeper distribution slope, as compared to the oxygen-deficient sample. In details, the oxygen-rich sample demonstrates a faster photoresponse with a mean value of 2.09 s/decade. While for the oxygen deficient sample, it is 48% slower, exhibiting the response speed of 3.10 s/decade on average. This result indicates that the oxygen content in the oxide plays an important role in the negative photoconductivity response of the breakdown path. In conjunction with recent reports that the breakdown path is made up of oxygen vacancy defects [222], the vacancy-interstitial recombination model proposed in last chapter is strongly supported.

Fig. 6.10: Distribution of negative photoconductivity response time or rate of current quenching (s/decade) for an oxygen-rich and oxygen-deficient HfO_x sample. Breakdown paths in the former clearly display a faster response and lesser variation in

the response speed. The differences clearly point to the role of oxygen in the negative photoconductivity response of the breakdown path.

6.2.5 High temperature working capability—temperature dependence

The conventional CMOS/CCD image sensor relying on positive photoconductivity suffers from dark current generation due to the thermal energy. This undesirable dark current interferes with the electrical signal, which could be overwhelmed at high temperature, because the dark current increases exponentially with the temperature. It doubles with every 7 K incensement in temperature [189]. On the contrary, the negative photoconductivity phenomenon is supposed to be immune from the dark current according to its unique working principle which does not rely on photoelectrons generation. Theoretically, our device relying on NPC should be able to work properly at high temperature.

To check the high temperature working capability, the sample is heated up to 390K in the UHV chamber to avoid possible surface oxidation. The distribution of the NPC response time at 295K and 390K is shown in Fig. 6.11. Apparently, this device works at high temperature, but at a relatively lower speed. The mean value of the NPC response speed is 3.68 s/decade at 390 K, while it is 2.22 s/decade at 295 K. The lower response speed may be attributed to the severer lateral propagation of the oxygen ions with higher energy due to the high temperature, which facilitate the oxygen ions diffusion during forming process [215]. As a result, the oxygen ions left at interstitial region is less than it is at 295K. Therefore, the lower interstitial oxygen ions concentration is supposed to trigger a lower recombination rate between interstitial oxygen ions and the oxygen vacancies. Experimentally, the oxygen concentrations

influence is checked in the previous section, which is consistent with this observation and explanation for temperature influence.

Fig. 6.11: Distribution of negative photoconductivity response time at different temperature. The mean value of the response time is 2.22 s/decade and 3.68 s/decade at 295 K and 390 K, respectively.

6.3 In-situ photosensitivity modulation

Wide bandgap oxides such as SiO₂, HfO₂, ZrO₂, etc. have played an integral role in the advancement of the CMOS technology. Besides serving as the gate oxide, they have also been intensively investigated for application in the resistive memory device [223-228]. Their relatively large bandgaps (> 5 eV), have made them thermally stable and resistant to electrical breakdown [229] but non-photo-responsive. Hence, they are not used as the active components for optical applications. Recent studies have shown that after electrical softbreakdown (SBD) of SiO₂, HfO₂ and ZrO₂, the breakdown site can be partially or fully restored by exposure to white light [187, 188, 230]. Because the breakdown current is decreased upon illumination, the effect has been termed “negative photoconductivity” (NPC) [188]. Through controlling the exposure dose, the breakdown current can be decreased to different levels [188]. Re-

testing of the restored breakdown sites revealed a time-dependent-dielectric-breakdown distribution like the first SBD [230], indicating that complete restoration was achieved at numerous locations. It has been proposed that photo-induced migration of surrounding oxygen interstitials leads to their recombination with vacancy sites in the breakdown path, which in turn restores the breakdown oxide partially or completely. While the exact mechanism is still elusive, the finding suggests the possibility of using these oxides as active components in optical applications.

In this section, we report a new effect related to the TiN electrode. Specifically, the NPC response of the ZrO_2 breakdown path, under a given illumination condition, can gradually be suppressed by applying positive-voltage sweeps to the TiN (relative to a non-metal counter-electrode) prior to light exposure. The suppressed NPC response can later be restored by negatively biasing the TiN and followed by a re-breakdown step. Such a behavior is, however, absent in the ZrO_2/Si stack (non-metal electrode). The results show that the breakdown path has a TiN-mediated multi-level programmable NPC property. Similar behaviors are also obtained for SiO_2 and other electrodes (Cu, Ni, and Ti). A possible mechanism is proposed.

6.5.1 Experiments

The test samples consist of the ZrO_2/TiN stack, fabricated on a p-Si substrate. After HF cleaning, a Ti adhesion layer was first deposited, followed by the reactive-sputter deposition of a 50-nm thick TiN bottom electrode. The ZrO_2 layer is 4 nm thick and was grown by atomic-layer deposition. Samples with the same thickness of ZrO_2 deposited directly onto the p-Si were also fabricated. The samples were loaded

into an ultra-high vacuum conductive atomic force microscope (C-AFM) system for measurement. A diamond-coated Si cantilever probe served as the top non-metal electrode. The ambient pressure was maintained at 3×10^{-10} Torr, which excludes the possibility of anodic oxidation.

The nanoscale spatial resolution of C-AFM has enabled current conduction through a very localized region to be studied [231-233]. The probe force was incrementally increased from a low value until topography and current maps were successfully obtained, to minimize mechanical damage to the thin ZrO_2 . Negligible low-voltage pre-breakdown leakage (Fig. 6.12) and the relatively high breakdown field (~ 12 MV/cm) [234] confirmed minimal oxide damage. After probe-oxide contact, the feedback circuit and laser were disabled to prevent interference to NPC response measurement, in accordance to other studies on photoactive materials [235, 236]. A similar approach of feedback disablement was adopted in our earlier study [175]. SBD was induced by a voltage ramp supplied by a parameter analyzer to the probe, with the TiN or Si electrode grounded. The breakdown current compliance was capped at 50 nA or below, necessary for minimizing hard breakdown due to the extremely localized probe contact area (~ 20 nm²) [188]. Exposure of the breakdown path to white light was achieved by a LED lamp position at a quartz window of the C-AFM chamber.

Fig. 6.12: (a) Evolution of leakage current through a breakdown path in the ZrO_2/TiN stack. After soft-breakdown (SBD) was induced using a positive-probe-voltage sweep,

measurement was first made in the dark for 400 s. In the second measurement, exposure to white light for 30 s was made, which saw the current decreasing abruptly upon illumination. (b) Current-voltage curves for the oxide region studied. The average breakdown field of the first SBD is ~ 12 MV/cm.

6.5.2 Gradual reduction of NPC sensitivity

The NPC behavior of a breakdown path in the ZrO_2/TiN stack is depicted in Fig. 6.12. The resistivity of the breakdown region is $\sim 10^3 \Omega \cdot \text{cm}$, which implies a semiconducting-like nature. The relatively low breakdown current (~ 0.1 nA) results primarily from the extremely small breakdown area. An abrupt decrease in the leakage current can be clearly observed upon exposure to white light, whereas the current remained nearly constant throughout when measurement was made in the dark (Fig. 6.12(a)). A post-illumination voltage-sweep yielded a partially “recovered” current-voltage curve (open circle; Fig. 6.12(b)), indicating that the breakdown path was disrupted by the white-light illumination. Direct evidence on the disruption of breakdown-path conduction was earlier provided by current maps of the breakdown region obtained before and after illumination [188]. For the breakdown and measurement conditions used, a current window (defined as the ratio of the pre- to pos-illumination current) of $>10^4$ is obtained.

Interestingly, the degree by which the current is quenched (or the current window) is gradually reduced if the breakdown path was subjected to multiple negative-voltage sweeps applied on the C-AFM probe (or positive-voltage sweeps applied on the bottom TiN electrode) prior to white-light illumination. This is illustrated in Fig. 6.13(a) for a breakdown location first induced using a negative-probe-voltage sweep. After SBD, the breakdown path was subjected to a negative-probe-voltage sweep again before it was exposed to white light. An NPC response was recorded but the

current did not decrease completely to the measurement floor (see Fig. 6.12(a)). SBD was then reinitiated at the same location and the procedure was repeated several times. In each repetition, the breakdown path was subjected to an increasing number of negative-probe-voltage sweeps before it was exposed to white light. Remarkably, the current window gradually narrows down as the number of pre-exposure negative-voltage sweeps is increased. The window for the case of 40 negativeprobe-voltage sweeps is only $\sim 3 \times$, a significant drop as compared to $\sim 10^4 \times$ in Fig. 6.12(a).

Photo-assisted recombination between oxygen dislodged from the breakdown location (and situated in surrounding interstitial positions) and vacancies in the breakdown path has been proposed to explain the NPC behavior [188]. The spatial distribution of interstitial oxygen is shown to depend on the Joule heating at the breakdown site [215]. A relevant question would be whether Joule heating caused by the multiple negative-voltage sweeps prior to light exposure have increased the lateral propagation of the interstitial oxygen, thereby limiting subsequent photo-assisted interstitial-vacancy recombination (hence recovery by light).

To check this, different numbers of positive-probe-voltage sweeps were also applied to a breakdown path before it was exposed to white light, following the procedure outlined above (Fig. 6.13(b)). In this case, the prior positive-probe-voltage sweeps did not have any effect on the current level after illumination. Regardless of the number of sweeps, the current is always decreased to the measurement floor upon exposure to white light. From this observation, one may rule out the possible Joule heating effect mentioned above. The results in Fig. 6.13(a) are thus unique to the case of negative-probe-voltage biasing. The different post-illumination current levels indicate that the NPC response can be tuned or programmed by a positive voltage-bias on the TiN electrode.

Fig. 6.13: (a) The level to which the current is decreased depends on the number of negative-voltage sweeps applied to the C-AFM probe before illumination. (b) Such dependence is not seen in the case where positive-voltage sweeps were applied before illumination. The negative- or positive-voltage sweep was made from 0 to -5.5 V or $+5.5$ V, subject to a current compliance of 50 nA.

6.5.3 Gradual recovery of NPC sensitivity

The loss of current window in the case of negative-probe-voltage biasing can be restored following several positive- probe-voltage sweeps, as illustrated in Fig. 6.14(a). A breakdown path was first created under negative-probe-voltage sweeping and exposed to white light, yielding the usual significant decrease in current (ref.). SBD was reinitiated and 70 consecutive negative-probe-voltage sweeps were applied. Subsequent light exposure did not result in any NPC response (triangle). A positive-probe-voltage sweep was then applied. During this voltage sweep, a decrease in current can be observed after ~ 3 V (Fig. 6.14(b)), similar to the bipolar reset behavior of the valence-change resistive memory [237]. SBD was then re-initiated at the same location under negative-probe- voltage sweeping and exposure to white light was immediately made. Remarkably, the breakdown path now re-exhibits some NPC response again, although the current did not decrease completely to the measurement floor. The above procedure was repeated but in each repetition, the number of positive-voltage sweeps was increased. Intriguingly, the current window is gradually

restored as the number of positive-probe-voltage sweeps is increased to 3.

Fig. 6.14: (a) Restoration of near-complete loss of NPC behavior of a breakdown path by positive-probe-voltage sweeping. The “ref.” curve is for the case without any applied negative-probe-voltage sweep before illumination. (b) Current-voltage measurements in the following order after the loss of NPC behavior in (a): 1) positive-voltage sweep; 2) negative-voltage sweep for re-initiation of SBD and 3) negative-voltage sweep after white-light exposure.

The tunable NPC response elucidated above is consistently observed on other randomly selected positions on the ZrO_2 after SBD. Although only the results for the ZrO_2/TiN stack are presented here, it should be mentioned that the same behaviors are also obtained on other oxide/metal stacks, e.g., HfO_2/TiN and SiO_2/Cu , SiO_2/Ti , SiO_2/Ni . However, the NPC tuning effect completely disappears in samples with the metal electrode replaced by Si, i.e., oxide/Si stacks. Fig. 6.15 shows an example for ZrO_2/Si stack where repeated negative-probe-voltage sweep made prior to light exposure is found to have no effect on the NPC response. A similarly large current window ($\sim 10^4 \times$) is obtained for the case of 0 or 50 negative-probe-voltage sweeps.

The experimental results presented so far have clearly indicated the followings: 1) the NPC response of a breakdown path in ZrO_2 can be suppressed by a positive voltage but not a negative voltage applied on the TiN electrode before whitelight illumination (Fig. 6.13); 2) the suppressed response can be restored by a negative

voltage applied on the TiN electrode (Fig. 6.14); 3) such an effect is completely absent in the ZrO_2/Si stack having the same oxide but a non-metal electrode (Fig. 6.15). These findings all point to a definite role of the TiN electrode in the observed NPC response suppression.

Fig. 6.15: The programmable NPC response revealed in the ZrO_2/TiN stack is not seen in the ZrO_2/Si stack. A similar number of negative-probe-voltage sweeps yields no apparent collapse of the current window.

6.5.4 Mechanism of the in-situ photosensitivity modulation

A possible explanation is proposed in Fig. 6.16 for the ZrO_2/TiN stack. Spectroscopy studies on SiO_2 have shown that the breakdown path is depleted of oxygen [150]. Thus, it is believed that the breakdown of ZrO_2 proceeds via the dissociation of Zr-O bonds. The released oxygen (O) ions migrate towards the anode (driven by oxide electric field) as well as laterally away from the breakdown site (driven by Joule heating) [215]. When the breakdown is aborted quickly, some O ions may remain in interstitial positions near the breakdown path (Fig. 6.16(a)). In the absence of illumination, reverse migration of the interstitial O ions to the vacancies in the breakdown path is prevented by an energy barrier, ~ 0.59 eV for ZrO_2 [238]. Under

illumination, photoexcitation of these interstitial O ions may enable them to overcome the energy barrier and migrate towards the breakdown path to recombine with the vacancies there (arrows), resulting in the disruption of the breakdown path [239, 240]. Photo-excitation and migration of O ions in MgO have been reported [240]. Having a migration barrier comparable to MgO, a similar mechanism may apply to the interstitial O ions surrounding the breakdown path in ZrO_2 .

A negative-probe-voltage draws Ti ions from the TiN electrode into the vacancy sites in the breakdown path (Fig. 6.16(b)). Electric-field-driven metal-ion migration has been proposed to explain the resistance switching of conducting- bridge resistive memory (e.g., SiO_2/Cu [241], Ag_2S [242], etc.). Field induced metal-ion-migration in the oxide network is shown to be enhanced in the presence of vacancy defects [218]. In the ZrO_2/Si stack, migration of Si ions into the breakdown path does not readily occur due to the relatively large Si-O bond dissociation energy [243]. With the Ti ions occupying some of the vacancy sites, subsequent recombination between vacancies and interstitial O ions would be inhibited. Repeated negative biasing of the probe draws more Ti ions into the breakdown path, resulting in a larger number of the vacancy sites being occupied by Ti ions and hence a greater inhibition of vacancy-interstitial recombination. A complete loss of NPC response occurs when most of the vacancy sites are occupied by the Ti ions (Fig. 6.16(c)).

A positive-probe-voltage sweep drives the Ti ions back to the TiN electrode, resulting in a reset (Fig. 6.14(b)). In addition, O ions from the ZrO_2/TiN interface region are drawn into the breakdown path, disrupting it via the reduction of the vacancies there, resulting in the bipolar reset behavior of the valence-change resistive memory [183]. Removal of Ti ions from the breakdown path restores its NPC response following the path's reformation under a negative-probe-voltage sweep (Fig. 6.16(a)).

The fewer number of positive-probe-voltage sweeps required for NPC restoration (Fig. 6.14(a)) as compared to the number of negative-probe-voltage sweeps needed to induce NPC loss (Fig. 6.13(a)) may be attributed to the smaller dissociation energy of Ti-Ti bonds (1.46 eV) as compared to those for Ti-O (6.86 eV) and Ti-N (4.81 eV) bonds [243].

Fig. 6.16: Schematic illustrations of the mechanisms underlying the negative photoconductivity (NPC) response of the breakdown path and photosensitivity modulation by the metal anode. (a) Breakdown path comprising mainly oxygen vacancy defects, with the released oxygen ions present in its vicinity. Photons excite the oxygen ions, causing them to migrate towards the breakdown path and recombine with the vacancies there (arrows). (b) A negative voltage applied to the probe draws metal ions from the anode into the vacancy sites in the breakdown path. As a result, oxygen-vacancy recombination is inhibited and the breakdown path loses partially its NPC response. (c) A larger number of negative-voltage sweeps results in metal ions completely filling the breakdown path and a total loss of NPC response. A positive-voltage sweep drives metal ions back to the cathode and draws oxygen from the cathode interfacial layer into the breakdown path, resulting in a rupture. A re-breakdown step regenerates the breakdown path and partially restores the NPC response. Complete restoration can be achieved with more positive-voltage voltage sweeps.

6.7 Summary

The relationship between the impact factors and the NPC photosensitivity is studied through statistical analysis. The photo-response speed is found to follow lognormal distribution, proportional to the light intensity and the oxygen stoichiometry while reverse proportional to the working temperature. The wavelength dependence is proved to be weak in visible range. These studies also validate the high temperature working capability (up to 390 K) and the broad spectrum sensing capability (up to near-infrared regime) of the NPC phenomenon in RRAM oxides stacks.

A new TiN-mediated multi-level negative photoconductance property of the breakdown path in ZrO_2 is revealed. The effect is only present when a positive voltage-bias is applied to the TiN electrode with respect to the non-metal C-AFM probe. A negative voltage-bias does not produce this effect but can restore the tuned response after a subsequent re-breakdown. The absence of this tuning effect in a sample with a non-metal (Si) electrode implies that it is due to the interaction between the breakdown path and the TiN electrode. Similar behaviors are obtained on other oxide/metal stacks, affirming the role of the metal electrode. It is proposed that under positive-voltage sweeping, Ti ions from the TiN electrode may migrate into the breakdown path and occupy vacancy sites there. As a consequence, the photo-assisted interstitial-vacancy recombination is inhibited, resulting in NPC response suppression. Besides the control of light-exposure dose [188], the results show that multi-level negative photoconductance can also be achieved through appropriate biasing of the TiN electrode, increasing the flexibility of the NPC phenomenon in possible light-mediated or sensing applications.

Chapter 7 CONCLUSION &

RECOMMENDATION

7.1 Conclusion

A systematic electrical-cum-optical characterization of RRAM oxides stacks at nanoscale level via the UHV-STM/C-AFM as well as a physical analysis via XPS assessed the prospect of the dimension scaling down to the nanometer regime and provided helpful insights into the unique performance of single nanoscale filament to advance the fundamental understanding of the switching mechanism. The vulnerable nanoscale filament formed by the STM/C-AFM probe also helped with the discovery of the NPC phenomenon. The key achievements are summarized as follows:

- The active area in the RRAM cell was scaled down to $\sim 5 \text{ nm}^2$ via the STM/C-AFM probing to assess the performance of the nanoscale CF. The ultra-low switching current in the pico-ampere regime was achieved. The microstructural change of the nanoscale CF was directly observed via the STM scanning.
- By correlating the STM/C-AFM nanoscale characterization with the conventional device level electrical characterization via the semiconductor parameter analyzer (SPA) at the probestation, the multiple filaments beneath the top metal electrode of the large-scale RRAM device were directly observed via localized STM

scanning. The electrical performance of the nanoscale single filament in the filament clusters was characterized via STM nanoprobng. More than 70% of the CFs exhibit abrupt reset behavior in contrast to the progressive reset on the large-scale device. Through statistical analysis on the variations in the reset voltage and current for all the single filaments, the origin of the progressive reset at the device level was contributed to the averaging effect among the multiple filaments. The summation of all the tested single filaments reproduced similar I-V characteristics to the device level RRAM.

- The role of the capping metal electrode as an oxygen ions reservoir was reported according to the observation that the percentage of the resistive switching is much higher compared to the uncapped sample. The sufficient supply of oxygen ions from the capping layer significantly increased the chance of resistive switching, which advanced the fundamental understanding of the oxygen ions migration model for RRAM.
- The negative photoconductivity (NPC) was discovered for the first time at the large bandgap oxide materials in the RRAM stacks which is conventionally considered as non-photo-responsive materials. However, after a soft-breakdown, the interstitial oxygen ions would be activated by the photon energy to overcome the diffusion barrier, leading back to a migration to the CF constituting the oxygen vacancies. The recombination between the oxygen ions and vacancies causes the rupture of the CF, thus a resistive reset behavior is displayed upon illumination. The mechanism was proposed based on the different observations between the $\text{HfO}_2/\text{ZrO}_2$ -based RRAM and SiO_2 -based CBRAM.
- The reliability rejuvenation capability of the newly discovered NPC phenomenon was assessed. The restoration efficiency of the NPC was proved to be better than

the electrical counterpart in SiO₂-based oxide stacks. The robustness of the light-induced restoration was also studied via the time-dependent dielectric breakdown (TDDB) reliability check. The Weibull distributions of the time to breakdown of the pristine sample and fully restored sample were found to be similar. It proved the robustness of the restored oxide against the subsequent electrical stressing.

- The impact factors of the NPC photosensitivity were studied. We observed that the photosensitivity was proportional to the illumination intensity and the oxygen stoichiometry, while inversely proportional to the working temperature. A weak wavelength dependence was also reported in the visible range. The high temperature working capability up to 390 K and broad-spectrum sensing capability up to 850 nm have been proved.
- The photosensitivity of the NPC was found to be gradually tunable and programmable via well-controlled electrical stressing. An in-situ photosensitivity modulation approach was proposed. Based on the loss of the NPC suppression behavior in the non-metal sample, the mechanism for the suppression effect was proposed to be the higher metal ions concentration in the CF prohibiting the recombination between oxygen ions and vacancies, remaining as the conduction path during and after illumination. The induced lower recombination rate resulted in lower photosensitivity and the remaining metal ions led to the higher HRS current observed.

7.2 Recommendations

The study on the brand-new NPC phenomenon in the conventional RRAM oxide stacks has shown very promising results for its future applications as an efficient

reliability rejuvenation approach and a possible optical sensor with a non-volatile memory property integrated. We believe that this project could be further extended in the following directions:

- The endurance data of the nanoscale filament with ultra-low switching current could not be obtained via C-AFM/STM measurement due to the thermal drift and instability of the probe in microscopic level for long-time testing on reliability issue. One possible solution is to fabricate a nanoscale crossbar device, via electron beam lithography (EBL), with an extended large electrode for being probed on by using probestation, which is a macroscopic contact not suffering from nanoscale thermal drift.
- The sensing spectrum is expected to be much broader than the 850 nm we have measured according to the low diffusion barrier of the interstitial oxygen ions in oxides. The threshold wavelength beyond which the NPC phenomenon would disappear is of great interest and importance for advancing the fundamental understanding of the NPC mechanism. The suitable infrared light source with tunable wavelength and intensity is being searched for this future study. The alignment method for the invisible light coupling onto the test position in a UHV chamber is being designed.
- The concept of combining the plasmonic effect with the NPC phenomenon is very attractive. The localized surface plasmon resonance (LSPR) effect in metal-insulator-metal (MIM), the conventional RRAM cell structure, allows the light to reach the oxides layer under the non-transparent top metal electrode. At the LSPR frequency, the light can be confined to the edge of the MIM cell and propagated into the oxides with decreasing intensity toward the center region. This concept abolishes the requirement of a transparent top electrode, making the optical

sensors based on the NPC phenomenon compatible with the main-stream CMOS technology. In addition, the specific resonance frequency due to the LSPR will make the optical sensor only sensitive to selective wavelength, which can be preset based on actual needs by adjusting the structure, dimension, and top metal materials. This work is currently ongoing. This concept has been preliminarily proved to be valid.

- Another long-term research direction is to utilize the NPC phenomenon to design an image sensor consisting of a crossbar array of sensing cells. The new type of image sensor would have a unique non-volatile property due to its essence of being a non-volatile memory cell, which allows the sensor to store the captured image without power consumption. Before finally achieving the crossbar array, the single crossbar device should be validated, which we are currently working on

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