Mechanisms, Conditions and Applications of Filament Formation and Rupture in Resistive Memories

Yuhong Kang

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Electrical Engineering

Marius K. Orlowski, Chair

Masoud Agah

Louis J. Guido

Jean J. Heremans

Majid Manteghi

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Abstract

Resistive random access memory (RRAM), based on a two-terminal resistive switching device with a switching element sandwiched between two electrodes, has been an attractive candidate to replace flash memory owing to its simple structure, excellent scaling potential, low power consumption, high switching speed, and good retention and endurance properties. However, due to the current limited understanding of the device mechanism, RRAMs research are still facing several issues and challenges including instability of operation parameters, the relatively high reset current, the limited retention and the unsatisfactory endurance.

In this study, we investigated the switching mechanisms, conditions and applications of oxygen vacancy (V_o) filament formation in resistive memories. By studying the behavior of conductive V_o nanofilaments in several metal/oxide/metal resistive devices of various thicknesses of oxides, a resulting model supported by the data postulates that there are two distinct modes of creating oxygen vacancies: i) a conventional bulk mode creation, and ii) surface mode of creating oxygen vacancies at the active metal-dielectric interface. A further investigation of conduction mechanism for the Vo CF only based memories is conducted through insertion of a thin layer of titanium into a Pt/ Ta₂O₅/Pt structure to form a Pt/Ti/ Ta₂O₅/Pt device. A space charge limited (SCL) conduction model is used to explain the experimental data

regarding SET process at low voltage ranges. The evidence for existence of composite copper/oxygen vacancy nanofilaments is presented. The innovative use of hybrid Vo/Cu nanofilament will potentially overcome high forming voltage and gas accumulation issues. A resistive floating electrode device (RFED) is designed to allow the generation of current/voltage pulses that can be controlled by three independent technology parameters. Our recent research has demonstrated that in a Cu/TaOx/Pt resistive device multiple Cu conductive nanofilaments can be formed and ruptured successively. Near the end of the study, quantized and partial quantized conductance is observed at room temperature in metal-insulator-metal structures with graphene submicron-sized nanoplatelets embedded in a 3-hexylthiophene (P3HT) polymer layer. As an organic memory, the device exhibits reliable memory operation with an ON/OFF ratio of more than 10.

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Abbreviation

ALD	atomic layer deposition
CBRAM	Conductive Bridge RAM
CC	compliance current
CF	conductive filament
CVD	chemical vapor deposition
EBPVD	electron-beam physical vapor deposition
FeRAM	ferroelectric RAM
GNP	graphene nanoplatelets
HRS	high resistance state
ISSCC	IEEE International Solid-State Circuits Conference
LRS	low resistance state
I-V	current-voltage
MIM	metal-insulator-metal
MRAM	magnetic RAM
NAND	negated AND
NVM	non-volatile memory
РЗНТ	poly(3-hexylthiophene)
РСМ	phase-change Memory

QPC	quantum point contact
RAM	random access memory
R _{OFF}	OFF-state resistance
R _{ON}	ON-state resistance
RFED	resistive floating electrode device
RRAM	resistive random access memory
SCL	space charge limited
SCLC	space charge limited current
SEM	scanning electron microscopy
SSD	solid state drive
ТМО	transitional metal oxide
Vo	oxygen vacancy

1 Introduction

This chapter reviews the current worldwide effort for nonvolatile memories, especially for resistive random access memory (RRAM), and provides a brief introduction to the motivation and challenges of this RRAM research. The basic device mechanism is presented and the major objectives in this area of research are addressed. The layout of the research dissertation is discussed.

1.1 Motivation and Challenges

Computer and internet technology is the fastest growing major market segment within the U.S. and worldwide, significantly ahead of the aerospace, defense and energy sectors in terms of sustained growth. Many new devices and applications requiring the handling and communication of large amounts of digital data are the fuel for this explosive growth. The next major requirement is substantially improved and enlarged memory devices, systems and architectures that make application-driven processing and communication possible.

Semiconductor memories are divided into two major categories, volatile memories or non-volatile memories (NVMs), based on the retention of the stored information. Volatile memories are fast in read/write but lose the stored information once the power is turned off. On the other hand, NVMs can store information after removal of power supply, which is very important for energy-efficient electronics and computing. Due to the advantages of high density, low power, fast access and small size, NVMs enable state-of-the-art portable personal devices such as smart phone and tablet computer [1]. As a result, NVM devices are being developed more rapidly than any other data storage technology. From data presented at IEEE International Solid-State Circuits Conference (ISSCC) 2013 [2], the major contributors to increased demand in terms of the number of devices in operation and the memory capacity of each device are smartphones, tablets, PC solid state drives (PC SSDs) and higher-performance Enterprise solid state drives (Enterprise SSDs). Table 1-1 shows the anticipated large increases in both the number of units and the memory capacity of each unit in these four market areas between 2010 and 2015 - individual increases of up to 6500%.

NVM by between 1500% and 6500% from 2010 to 2015 (presented at ISSCC 2013).									
	Market Driver		2010	2015	Combined				
			2010	2015	Transaga				

Table 1-1. Smartphones, Tablets, PC SSDs and Enterprise SSDs are Anticipated to Increase the Need for

Market Driver		2010	2015	Increase	
Smartphones	Millions of Units	300	1150	1500%	
	Capacity (GB)	6	24		
Tablets	Millions of Units	20	320	4500%	
	Capacity (GB)	27	71		
PC SSD	Millions of Units	5	130	6500%	
	Capacity (GB)	86	235		
Enterprise SSD	Millions of Units	1	14	4500%	
	Capacity (GB)	134	617		

1.1.1 Challenges in Flash Memory

Until now, NAND (Negated AND) type Flash memory dominates the market of nonvolatile memories, whose share of the market is above 90%. Individual cell sizes of NANDbased flash memories have decreased from 100nm for 4GB flash devices in 2004 to 20nm for 128GB flash devices available today. The great market success of flash memories has been based on the geometric scalability of floating-gate MOSFET cells and cell arrays; this manufacturing scalability is also responsible for the consistent decrease in the cell size of basic transistor switch elements and processing devices. Flash memory was invented by Toshiba in 1980s. The basic device structure and operating mechanism are shown in Fig. 1-1. The flash memory device is a MOSFET with an additional metal gate which is known as floating gate. When a high voltage (~20 V) is applied to the control gate (non-floating), the electrons can rearrange their migrating direction and arrive at the floating gate by Fowler-Nordheim tunneling. The electrons stay on the floating gate after the gate voltage is removed, since the floating gate is surrounded by insulator (SiO₂) and there is no way to leak out. Because of the charges stored on the floating gate, the threshold voltage of the device is significantly changed and the two states of the device (with and without charges on the floating gate) can be identified as "0" and "1" for data storage.



PROGRAMMING

ERASING

Fig. 1-1. Device structure and operating mechanism of a flash memory. In a flash memory device, a floating gate is inserted in the oxide of MOSFET. A high write/erase voltage is needed to charge or discharge the floating gate. Under the high electric field, electrons can tunnel through the gate oxide between the Si substrate and floating gate.

Memory devices are different from processing switches because they need to function by storing data for a very long time. For a 20nm-scale flash memory cell, about 100 electrons make up the stored charge. If the requirement on data storage is that charge storage should not decrease by more than 20%, no more than about 10 electrons can be lost by the cell. That means that over a period of 10 years, no more than 1 electron can be lost per year. This is a very challenging requirement as further decreases in cell size occur. Although flash memories are extremely successful, they are not the best solution for NVM applications. This is because 1) Flash memories are slow. The operating time is in the ms range, which does not satisfy the increasing high-speed requirement; 2) Flash memories are based on electronic charge and high writing voltage. The mechanism of flash memories requires a lot of energy to store and remove the charges, which is not energy-efficient enough for low power applications; 3) Flash memories

are basically MOSFET type devices. This means the scaling is quite difficult beyond 20 nm; 4) Endurance is limited. The flash memories can only switch on and off for thousands of times. This may be suitable for personal use like memory sticks, but not good enough for industrial and defense applications.

1.1.2 Emerging Memories

Several emerging memories have been investigated to potentially overcome the limitation of Flash memories. Examples are ferroelectric RAMs (FeRAMs) [3], resistive RAMs (RRAMs) [4,5,6], magnetic RAMs (MRAMs) [7], and phase-change Memory (PCMs) [8, 9]. Particularly, there has been an enormous interest in RRAMs for non-volatile memory applications because of their excellent scaling potential, low power consumption, high switching speed, and good retention and endurance properties [10]. RRAM implements memory function in terms of the change in resistance (rather than stored charge). The distinctive feature of most RRAM concepts consists of the formation and rupture of the localized, nanofilamentary nature of a conductive path in an insulating material between two electrodes (a metal-insulator-metal (MIM) structure). This two terminal attribute is directly associated with a high scalability potential, significantly beyond the scaling limits currently predicted for flash memory. Resistive switching phenomena have been observed in many oxides including transitional metal oxides such as TiO₂, HfO₂, Ta₂O₅, ZrO₂, perovskite-type complex transitional metal oxides (TMOs), and large bad gap high-K dielectrics [11,12,13,14,15].

Table 1-2 lists some of the emerging memories in comparison with flash memory in the basic operating parameters.

	Flash Memory	RRAM	PCM	MRAM	FeRAM
	NAND				
Storage	Charge trapped in floating	Filamentary	amorphous and	Magnetization of	Remnant polarization
mechanism	gate	formation and	crystalline phase	ferromagnetic	on a ferroelectric
		rupture	change	layer	capacitor
Cell elements	1T	1T1R or 1D1R	1T1R	1T1R	1T1C
Cell size	$\sim 4F^2$	$4F^2$	$4F^2$	8F ²	$12F^2$
Read time	0.1ms	<50ns	12ns	35ns	40ns
W/E time	1/0.1ms	300ps	100ns	35ns	65ns
Retention time	10 year	>10 Year	>10 Year	>10 Year	10 Year
Write cycles	1E4	1E12	1E10	1E12	1E14
Write	15	0.6	3	1.8	1.3-3.3
Voltage(V)					
Read	1.8	0.15	1.2	1.8	1.3-3.3
Voltage(V)					
Write Energy	2E-16	1E-13	6E-12	2E-12	3E-14
(J/bit)					

Table 1-2. Current emerging memories in comparison with NAND flash memory [1].

Compared to flash memories with a about 15V write voltage, a read time of 0.1ms and W/E time of 1ms/0.1ms, RRAMs operate at a much low voltage level with potentially less than 0.6 V and at a much faster timescale with a read time of 20ns and W/E time of 10ns/30ns. If compared to MRAM, RRAM has a simpler and smaller cell structure. PCM has similar two terminal structure, however, it requires an embedded heating element for the phase change

between crystalline and amorphous states, resulting in the device complexity increase and the switching speed reduction [4].

Fig. 1-2 shows the non-volatile memory trend in the past decade according to data presented in ISSCC 2013. RRAM would therefore avoid the scaling limit of NAND memory and be a strong candidate of the successor NAND Flash. Mass production of RRAM is anticipated around 2020.



Non-Volatile Memory Trend

Fig. 1-2. Non-Volatile Memory Trend, RRAM is a strong candidate of the successor NAND Flash (data presented at ISSCC 2013).

1.2 Background of RRAMs

Resistive random access memory (RRAM) is based on two-terminal resistive switching devices with a switching element sandwiched between two electrodes.

It was first reported in 1962 that hysteretic current-voltage (I-V) characteristics can be observed in metal-insulator-metal (MIM) structures of Al/Al₂O₃/Al, indicating resistive switching occurs as a result of applied electric field [16]. Resistive switching was later observed in semiconductor or metallic oxides such as BeO, TiO, NbO [5,17]. Complex transition metal oxides, such as perovskite-type magnates and titanates, have attracted attention since the report of switching from Pr0.7Ca0.3MnO3 (PCMO) [18]. In 2000, resistive switching was also found in another perovskite-type oxide, Cr-doped SrZrO3 (SZO), and the application of this material in NVMs was demonstrated [18].

Recent works on the switching elements of RRAM include a broad range of materials, including solid electrolytes (e.g. AgGeS, AgGeSe) [19] and other amorphous films such as amorphous silicon, amorphous carbon and even polymers, but mostly various oxides, such as perovskite-type oxides (e.g. Pr1-xCaxMnO3, SrTiO) [20], binary transition metal oxides (e.g. NiO, ZnO, TiO₂) [21] and wide bandgap high-k dielectric oxides (e.g. HfO₂) [22].

RRAMs are inherently more free from scaling problems than capacitance based memories. Crossbar RRAMs could achieve a minimum cell size of $4F^2$, where F is the minimum feature size. Furthermore, when the operation speed of RRAMs catches up, volatile memories could be potentially replaced, which would allow systems to power on and off without rebooting.

1.2.1 Resistive Switching Basics

The resistance measured between the two electrodes of MIM memory device determines

the memory state. When the resistance is high, the memory state is "0", also referred to high resistance state (HRS), or OFF state. When the resistance is low, the memory state is "1", also named as low resistance state (LRS), or ON state. Under the application of a programming voltage, the device transitions from high resistance state (HRS) to low resistance state (LRS). With an erasing bias, the device can switch back to the HRS. Once switched, the memory device retains the particular resistance level for a long time. The switching event from HRS to LRS is called "SET", and from LRS to HRS is called "RESET". Most RRAMs require the initial forming process of a fresh device.

The switching characteristics of RRAMs can be categorized into unipolar switching and binary switching. If the device can be written and erased with one polarity of bias, the device is called "unipolar switching" device. On the other hand, if the device has to be written and erased with different polarities of bias, the device is called "bipolar switching" device. Unipolar and bipolar switching behaviors are illustrated respectively in Fig. 1-3.



Fig. 1-3. Possible combinations of set and reset I–V characteristics: a) and b) bipolar switching; c) and d) unipolar switching.

Resistive memory devices generally show a LRS independent of device cell sizes once the memory is switched on. Therefore a filamentary switching is proposed for the SET process in such a device. As shown in Fig. 1-4, the active-metal/solid-electrolyte/inert-metal structure enables the sequences of the following Cu CF formation and reset processes: 1) the oxidation of an electrochemically active electrode metal such as Cu or Ag; 2) the drift and diffusion of the mobile Cu^+ (Ag⁺) cations under the high electrical field in the ion-conducting layer; 3) their reduction at the (inert) counter electrode leading to a growth of Cu dendrites, which form a highly conductive nanofilament resulting in the ON state of the cell. Fig. 1-4 also shows the reset of the device. Our recent studies indicate that the reset (dissolution) of metallic CFs might be mainly due to Joule heating, as both bias polarities can switch off the devices. The metallic nanofilament will not rupture until there is enough energy to remove metal atoms from it. During the formation process, a compliance current of less than 100uA is used to prevent device breakdown.



Fig. 1-4. The operational principle of the metal ion based migration resistive memories - schematic view of nanofilament formation.

On the other hand, oxygen vacancy (V₀) conductive filament can be also established in the same MIM device by applying a negative voltage bias on the top electrode [23,24]. As shown in Fig. 1-5, under negative bias voltages, the migration of Cu⁺ or other metal ions in the electrolyte is suppressed. Therefore the metal nanofilament cannot be formed between the electrodes. The O²⁻ ions or electrons migrate from the TaOx or metal/oxide interface, to the Pt electrode in the electric field pointing from Pt to Cu. The formation of oxygen vacancy must be accompanied by O₂ (gas) generation according to the electrochemical reaction $2O^{2-} \rightarrow$ $2V_O(TaO_x) + O_2(gas) + 4e^-$. The gas bubbles are observed in our fabricated devices as shown in Fig. 1-5c). Because the above reaction requires participation of electrons, the gas generation reaction is assumed to take place near the Pt-TaO_x interface. The vacancies V₀ left behind by migrating O²⁻ ions form a conductive filament and the resistive state changes. The ON resistance is also found to be independent of cell size. Through our study, the detailed mechanism for Vo CF formation associated with the shape and size of such CFs, the switching location and where oxygen ions or oxygen vacancies come from and how they migrate through the oxide is much more clear now. The gas accumulation and the higher forming voltages for Vo CF formation may cause the mechanical and electrical damage on the cells and then affect the overall device performance.



Fig. 1-5. The oxygen vacancy nanofilament formation. (a) oxygen vacancy generation; b) oxygen vacancy distribution, conductive path formation and gas accumulation; c) gas formation under microscope.

1.3 Design Issues of RRAM

RRAM has been an attactive candidate to replace flash memory owing to its simple structure, excellent scaling potential, low power consumption, high switching speed, and good retention and endurance properties. However, due to the current limited understanding of the device mechnism, RRAMs research are still facing several issues and challenges including instability of operation parameters [25], the relatively high reset current [26], the limitations in rentention [27] and the unstatisfactory endurance [28]. RRAM devices still show large stochastic

variations in switching characteristics. The relatively wide distributions in V_{set} , V_{reset} , R_{on} and R_{off} limit the device reliability and its smooth transition to commercialization. The trade off between the low power consumption and the retention is also severe [29, 30].

Various switching phenomena, such as unipolar and bipolar switching behaviors in RRAMs, have been explained by different physical mechanisms: a model based on electrochemical migration of oxygen vacancies [31], electrochemical migration of oxygen ions [32], Schottky emission [33], trap assisted electron tunneling [34], space charge limited conduction based trapping and detrapping of charge carriers [35,36], a electron hopping model [37, 38], a thermal dissolution model [39], a stochastic model [40], quantum point contact model [41,42] and others. Recent reports in coexistence of both metal cations and oxygen vacancy (Vo) anions in the same devices with similar properties indicate that these two behaviors may share the similar mechanism. Most resistive memory effects are related to the formation and rupture of a conductive filament. However, a comprehensive model for oxygen vacancy based resistive switching is still missing and hindering further development of this type of memory. Many models suggested that the oxygen ions/Vo inside the oxide layer mainly attribute to the formation and rupture of a Vo CF due to the redox reaction within the oxide layer [31,32]. It is, however, believed based on our recent work that O²⁻ or electron migrated from the metal/interface is critical not only for the form/set process, but also for the reset process [43,44].

There are also some contradictory reports in the types of carriers migrating inside the devices, charged Vo, neutral Vo or oxygen ions [31,32,43].

Our research is focused on the better understanding of device mechanism. A comprehensive surface and bulk mode model has been developed to describe the Vo or oxygen ion transport and filament formation in the oxides. The SET/RESET process at low voltage range can be explained based on space charge limited conduction. The resistive switching can be universally attributed to the changes of trap level distribution induced by trapping and detrapping of injected electrons or holes leading to the filament formation. The following work has been conducted:

- Fabricate and characterize various devices with various material properties of electrodes and electrolytes for investigation of possible mechanisms, as discussed in Chapter 2.
- Understand the nature of Vo filaments and how the properties of oxides and electrode/oxide interfaces affect Vo formation, migration and annihilation, and a space charge limited conduction model is presented, as discussed in Chapter 2, 3 and 4.
- Cu/SiO₂/Pt devices exhibit about 10 times reduction in reset current (~50uA) if compared to Cu/Ta₂O₅/Pt as discussed in Chapter 2.
- Investigate hybrid Vo/Cu CF to reduce the high forming voltages and gas accumulation for improved reliability, as demonstrated in Chapter 5.

 Investigate the possible reasons for the integer and partial quantuem conductance effects observed in the graphene/polymer devices and the future applications as presented in Chapter 8

1.4 Dissertation Objective and Organization

The objective of this work is to investigate the switching mechanism and conditions of formation and rupture of oxygen vacancy based filament in RRAMs, based on the electrical characterizations and data analysis. Such a study will lead to the optimization of device performance for nonvolatile memory applications.

This dissertation is organized in 8 chapters.

Chapter 1 introduces the motivation and objective of this research, the resistive memory basics and addresses the significance and challenges of RRAMs for non-volatile memory applications.

Chapter 2 presents fabrication and characterization of various types of metal oxide based resistive memories for better understanding of the switching mechanisms in RRAMs, especially for oxygen vacancy (Vo) conductive filament (CF) based switching. The quasi-static I-V sweeping is used to characterize the electrical performance of the devices.

Chapter 3 presents a comprehensive surface and bulk mode models for Vo based resistive switching in RRAMs, based on our device characterization data.

Chapter 4 presents the unique properties of Pt/Ti/Ta₂O₅/Pt devices by inserting a thin layer of Ti (10nm) into a Pt/Ta₂O₅/Pt between Pt electrode and Ta₂O₅. A carrier transport model based on SCL conduction is developed to explain the I-V characteristics of the SET and RESET processes at low voltage ranges in MIM based resistive memories. It suggests that the performance of RRAMs can be improved through the modification of the interface introduced trap distribution and bilayer device structures.

Chapter 5 presents the evidence for existence of composite copper/oxygen vacancy nanofilaments. Both composite CFs, Vo/Cu and Cu/Vo, display V_{form} at considerable lower voltages than monolithic CFs with analogous switching characteristics. The innovative use of hybrid Vo/Cu nanofilament will potentially overcome high forming voltage and gas accumulation issues.

Chapter 6 presents our recent research that in a Cu/TaOx/Pt resistive device multiple Cu conductive nanofilaments can be formed and ruptured successively between the active Cu and inert Pt electrodes. This chapter describes the key parameters to repeatable multi-filaments switching cycles with the appropriate choice of compliance current window for individual nanofilament formation and the choice of bipolar and unipolar reset. Controlled formation and rupture of multiple filaments may enable multilevel storage capability in a single RRAMs memory cell if the repeatability issue can be successfully addressed.
Chapter 7 presents a resistive floating electrode device (RFED) comprising two single memory switches antiserially merged at the common inert floating electrode. Such a device would allow the generation of current/voltage pulses that can be controlled by three independent technology parameters. It enables an inherent integrate-and-fire capability and is, for example, able to realize electronic version of transfer functions of a biological spiking synapse.

Chapter 8 presents our recent experimental data for integer and fractional quantum conductance occurring in graphene nanoplatelets doped organic polymer films at room-temperatures and in absence of any magnetic field, at the same time. At high GNP concentrations the MIM cell behaves as excellent conductor, at low GNP concentrations as stable insulator, and at medium concentrations displays a significant memory hysteresis effect. The control of concentration of graphene nanoplatelets allows tuning of the material from insulator via quantum conductor to a metallic conductor, opening thus new vistas in electronic applications.

Finally, Chapter 9 summarizes the recent work and provides possible future plan for further investigation.

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2 Fabrication and Characterization of Metal Oxide Based Resistive Memories

In this chapter, various types of metal oxide based resistive memories are fabricated for better understanding of the switching mechanisms in RRAMs, especially for oxygen vacancy (Vo) conductive filament (CF) based resistive switching. This work will lead to the optimization of device performance for low power consumption and high reliability. General device design and performance issues are discussed in the next chapter.

2.1 Introduction

Resistive switching of a Cu/TaOx/Pt device can be based on the formation of two types of conductive filaments (CF) in the same device: Cu or oxygen vacancy (Vo) CF depending on the polarity of switching voltage [1]. When the Cu or Vo CF forms, the resistance between two electrodes is switched from high resistance state (HRS) to low resistance state (LRS). A high current flowing through the nanofilament will generate significant local heating and high temperature to rupture the nanofilament. The device then transitions from LRS to HRS. With the two stable states, the device can be used as a nonvolatile memory cell to store data. The simple active-metal/solid-electrolyte/inert-metal structure allows a very compact integration compatible with the CMOS backend process. However, there are still several issues associated with RRAMs. One major obstacle is the relatively wide variations in programming parameters for SET/RESET switching voltages and for on/off state resistance values [2]. Such variations may be caused by the defect dominated charge transport involved into the possible multi-path formation and rupture.

Defects such as oxygen vacancies or metal cations, are well known to be essential for resistive memory devices [3].

Several selections or combinations of thin film metal oxides and electrode metals have been investigated during this study. The oxide materials are selected to Ta_2O_5 and SiO_2 due to its difference in bandgaps. Both materials are deposited with various thicknesses between 8nm and 32nm. The electrode metals include copper (Cu), platinum (Pt), titanium (Ti). Moreover, atomic layer deposition (ALD) and electron-beam physical vapor deposition (EBPVD) are utilized to deposit the thin layer of high quality oxide films. Material properties such as bandgaps, work functions and dielectric strength are considered.

2.2 Fabrication Processes

A typical RRAM device cross-section and a fabricated device array are respectively shown in Fig. 2-1(a) and (b). During this study, a variety of Cu/TaO_x/Pt, Cu/Ta₂O₅/Pt, Cu/SiO₂/Pt, Pt/TaO_x/Pt, Pt/Ta₂O₅/Pt, Pt/SiO₂/Pt and Pt/Ti/Ta₂O₅/Pt resistive devices have been fabricated in a crossbar array on a thermally oxidized Si wafer. A thin Ti layer is deposited on the thermally oxidized SiO₂ layer to improve the adhesion between the bottom Pt electrode and the thermally oxidized SiO₂ layer. All the metal electrodes including Pt, Ti and Cu, oxygen deficient TaO_x and SiO₂ thin films were deposited by e-beam physical vapor evaporation (EBPVD) and patterned by lift-off technology. For comparison, stoichoimetric Ta₂O₅ thin films were also deposited by Atomic layer deposition (ALD) technique. The top Cu and Pt electrodes run perpendicularly to the bottom Pt electrode.



Fig. 2-1. a) Schematic cross section of a Cu/TaO_x/Pt resistive memory device; b) fabricated device array.

The Si substrate is thermally oxidized to provide an insulating SiO₂ layer of about 1um as the foundation of resistive devices. The standard dry O₂/wet O₂/dry O₂ oxidation process is used. The electron beam physical vapor evaporation is selected as the deposition method for Cu, Pt, Ti, TaO_x, and SiO₂ layers. The melting points of those four materials are not very high so that ebeam deposition is an effective way for manufacturing prototypes in a university lab. To avoid sophisticated wet or dry etching steps, the lift-off technology is used for removing excessive materials and patterning the active region. Considering the requirement of lift-off, negative lithography is employed for defining the device active region. The MA-6 Karl Suss optical lithography in our lab can achieve the best resolution of 1 μ m. Therefore the dimensions of resistive device cells are in μ m range which is suitable for demonstrating the generic device characteristics.

2.2.1 E-beam Physical Vapor Deposition (EBPVD)

The oxygen-deficient TaO_x and SiO_2 thin films were respectively deposited by evaporating TaO_x pellets and SiO_2 pieces without O_2 injection to the evaporation chamber. Platinum is used as either the bottom inert electrode or top inert electrode.

The electron beam physical vapor evaporation system (PVD250) is illustrated in Fig. 2-2. A high energetic electron beam is emitted from an electron gun by applying a high voltage and focused on the materials located in the crucible at the bottom of the chamber. The target material is melted under the high energy electron beam, locally evaporated and deposited on the substrate above the crucible. The vacuum pump maintains the low pressure (\sim 1*10⁻⁶Torr) in the PVD chamber. The substrate chuck rotates constantly at 5 rounds/min during deposition to improve the thickness uniformity of the deposited thin film. The evaporation starts when the chamber pressure reaches \sim 10⁻⁶ Torr. The substrate temperature was monitored to be around 25 °C without heating the substrate chuck. The deposition rates and parameters of Pt, Cu, Ti, TaO_x and SiO₂ are listed in Table 2-1. The deposition rates can be monitored and measured by quartz crystal microbalance in PVD and the Filmetrics F20 optical system. The width of the metal lines varies between 1 µm and 35 µm. Each intersection of Cu and Pt lines is a single cell of a resistive switch.



Fig. 2-2. Schematic Illustration of the Electron Beam Physical Vapor Deposition System (EBPVD)

Material	Pt	Cu	Ti	TaO _x	SiO ₂
Layer Thickness (nm)	50	100	10	11, 16, 32	11, 16, 32
Deposition Rate (Å/s)	1	5	1	1	5
Melting Temperature (°C)	1768	1085	1660	1872	1610
E-Beam Current (mA)	180	120	80	150	25
Base Pressure (Torr)	2×10 ⁻⁶				
Density (g/cm^3)	21.45	8.93	4.5	8.2	2.65
Z-ratio	0.245	0.437	0.628	0.3	1
Tooling Factor	140	140	140	140	140

Table 2-1. Summary of material depositions using the EBPVD system

2.2.2 Atomic Layer Deposition (ALD).

Atomic layer deposition (ALD) is a chemical vapor deposition (CVD) technique. It has gained wide applications in the microelectronics industry, because high quality, conformal and accurately controlled thin films can be produced even in three-dimensional structures. ALD can be defined as a film deposition technique that is based on the sequential use of self-terminating gas–solid reactions. The growth of material layers by ALD consists of repeating the following characteristic four steps:

- 1. A self-terminating reaction of the first reactant with pretreated substrate material
- 2. A purge or evacuation to remove the nonreacted reactants and the gaseous reaction byproducts.
- 3. A self-terminating reaction of the second reactant or another treatment to activate the surface again for the reaction of the first reactant.
- 4. A purge or evacuation.

Steps 1–4 constitute a reaction cycle. The use of self-terminating reactions leads to the conclusion that ALD is a surface-controlled process, where process parameters other than the reactants, substrate, and temperature have little or no influence. Because of the surface control, ALD-grown films are extremely conformal and uniform in thickness.

As an example, one ALD reaction cycle of Ta_2O_5 deposition is illustrated schematically in Fig. 2-3. Tetrakis(dimethylamido)tantalum ($Ta(NMe_2)_5$) and H_2O are the two precursors used for the ALD deposition. Each reaction cycle adds a given amount of Ta_2O_5 to the surface. To grow a material layer, reaction cycles A to E are repeated until the desired amount of material has been deposited.

- A. Put a sample in the ALD reactor, which is hydroxylated from exposure to air, oxygen or ozone.
- B. Pulse in the Ta(NMe₂)₅ precursor; Ta(NMe₂)₅ will react with the OH groups on the sample surface and (CH₃)₂NH is formed as a gaseous byproduct. Ta(NMe₂)₅ does not react with itself and the formed monolayer passivates the surface.
- C. Remove unreacted Ta(NMe₂)₅ and (CH₃)₂NH molecules by evacuation and/or purging with nitrogen.
- D. Pulse water (H₂O) into the reactor. This will remove the N(CH₃)₂ groups, create Ta-O-Ta bridges, and passivate surface with Ta-OH. (CH₃)₂NH (Dimethylamine) is formed as a gaseous byproduct.
- E. Remove unreacted H₂O and CH₄ molecules by evacuation and/or purging with nitrogen.



Fig. 2-3. ALD Reaction Cycles for Ta_2O_5 Deposition. Tetrakis(dimethylamido)tantalum (Ta(NMe₂)₅) and H₂O are the two precursors used for the ALD deposition. Each reaction cycle adds a given amount of Ta_2O_5 to the surface.

During this study, Ta_2O_5 thin films were deposited by ALD using Cambridge NanoTech Savannah 100 ALD system. Nitrogen was used as carrier and purging gas. Tetrakis(dimethylamido)tantalum (Ta(NMe₂)₅) and water H₂O were used as precursors. During deposition, the precursor flow rate was set as 20sccm. The reactor temperature was 250C. Ta(NMe₂)₅ and H₂O pulse times were respectively 0.25s and 0.015s. The wait time between individual pulses is 5s and the deposition rate is about 0.47A/s. 340 cycles were conducted to form 16nm of tantalum oxide.

Figures 2-4 show the SEM image and the XPS data of Ta_2O_5 film deposited by ALD. The film is very uniform and dense. The XPS data at Ta4f indicates the high purity of Ta_2O_5 formed by ALD and the atomic ratio of O and Ta is about 2.1.



Fig. 2-4. SEM image (a) and XPS data (b) of TaOx deposited by ALD at 250C. The XPS data at Ta4f indicates the high purity of Ta₂O₅ formed by ALD

2.2.3 Samples Fabricated during this Work

During this study, several metal oxides such as oxygen deficient TaO_x, stoichoimetric Ta₂O₅, and SiO₂ were investigated for further understanding of the resistive switching (RS) mechanism and for optimization of device performance [4]. The first two are amorphous tantalum oxides deposited by different deposition methods associated with different defect concentrations and thin film densities. SiO₂ has a much higher bandgap (~9ev) than that of tantalum oxide (~4.4ev). It is of lower defectivity than Ta₂O₅. In addition, devices with metal electrode combinations including Cu/oxides/Pt, Pt/oxides/Pt, Pt/Ti/oxides/Pt have been investigated to study the electrode dependence of resistive switching. Cu and Ti are typical active metals, while Pt is inert metals. The metallic and oxygen vacancy based CFs are observed in the same Cu/TaOx/Pt memory, while only oxygen vacancy CF can be formed in Pt/TaOx/Pt devices. It is reported that the devices using Ti and Ta top electrode device display improved Vo CF switching [5, 6, 7]. Chapter 4 explains the role of Ti in device functionality and the switching mechanism involved.

Table 2.2 lists the main properties of the materials and devices fabricated during this work. The main focus is to design several combinations of metal oxides and metals to figure out the possible forming/set/reset mechanism. The oxide materials are TaO_x , Ta_2O_5 and SiO_2 with various thicknesses between 8nm and 32nm. The electrode metals include Cu, Pt, and Ti. Material properties such as bandgaps and work functions are also listed in Table 2.2. General characterizations of oxide based resistive switching memories are given in this chapter. More detailed studies are presented in Chapter 3, 4, 5, 6 and 7.

Table 2-2. Summary of Samples Fabricated in This Work.

wafer #	Device Stack	Layer Thickness (nm)	Insulator	Material
			Deposition	Properties
A1	Cu/TaO _x /Pt	100nm/32nm/50nm	EBPVD	Work function:
A2	Cu/TaO _x /Pt	100nm/16nm/50nm	EBPVD	Cu: 4.3ev
A3	Pt/TaO _x /Pt	50nm/16nm/50nm	EBPVD	Pt: 5.3ev
B1	Cu/Ta ₂ O ₅ /Pt	100nm/16nm/50nm	ALD	Ti: 4.33ev
B2	Pt/Ta ₂ O ₅ /Pt	50nm/8nm/50nm	ALD	Au: 5.1ev
B3	Pt/Ti/Ta ₂ O ₅ /Pt	50nm/3nm/11nm/50nm	ALD	Bandgap:
B4	Pt/Ti/Ta ₂ O ₅ /Pt	50nm/10nm/11nm/50nm	ALD	Ta ₂ O ₅ :~4.4
C1	Cu/SiO ₂ /Pt	100nm/32nm/50nm	EBPVD	SiO ₂ : 9
C2	Cu/SiO ₂ /Pt	100nm/16nm/50nm	EBPVD	TiO ₂ : 3.5
C3	Cu/SiO ₂ /Pt	100nm/11nm/50nm	EBPVD	GNPs: 0ev
C3	Pt/SiO ₂ /Pt	50nm/16nm/50nm	EBPVD	
D1	Cu/P3HTGNPs/Au	100nm/700nm/50nm	Drop	
			Deposition	

2.3 Resistive Switching in Cu/TaO_x/Pt Devices

The switching properties of both Cu and V_o CF in Cu/TaOx/Pt devices are characterized by quasi-static DC measurement. The I-V characteristics are measured with Keithley 4200-SCS at room temperature. A compliance current is applied to the device for forming and set operations in order to avoid destructive breakdown, while a much higher compliance current is used for reset process. Transient switching behavior is also evaluated using an oscilloscope and a waveform generator. During the characterization, the bottom Pt electrode is grounded and a voltage bias is applied to the top electrode.

2.3.1 Bipolar and Unipolar Switching in Cu/TaOx/Pt Devices

I-V characteristics of bipolar and unipolar switching in the Cu/TaO_x/Pt device are shown in Fig. 2-5. At about -2 V, a V₀ CF is formed under the compliance current of 0.1 mA, and the device transitions from HRS to LRS. Under negative bias voltages, the migration of Cu⁺ ions in electrolyte is suppressed [8]. In Fig. 2-5(a), the reset current for V₀ CF in the bipolar switching mode is 2 to 3 mA, and the reset voltage is 1.2 V. The R_{on} and R_{off} are 187 Ω and 663 M Ω , respectively. The Vo CF can also be reset by a negative voltage at -1.2 V as shown in Fig. 2-5(b). This is the case for the unipolar switching. The reset voltage has the similar magnitude as one for the bipolar switching. This polarity independence validated the assumption that the rupture of the CF is triggered by Joule heating. Under positive bias voltages, Cu conductive filament is formed by Cu⁺ ion migration in the high electric field, being reduced and accumulated on the Pt electrode. Figs. 2-6(c) and (d) respectively show the bipolar and unipolar switching of Cu CF. In both cases, the Cu CF forms above 2 V and the compliance current is 0.1 mA. The R_{on} and R_{off} are 288 Ω and 566 M Ω , respectively. The reset current and voltage of Cu CF is about 2 mA and 1 V for bipolar switching, and about 6 mA and -1.5 V for unipolar switching.



Fig. 2-5. I-V characteristics of bipolar and unipolar switching in Cu/TaO_x/Pt devices. (a) Bipolar switching of V₀ CF. (b) Unipolar switching of V₀ CF. (c) Bipolar switching of Cu CF. (d) Unipolar switching of Cu CF.

Fig. 2-6 shows the statistical V_{set} and V_{reset} distributions for the V_O CF conduction. The V_{reset} distributions show narrow and symmetrical shape, indicating the reset mechanism is voltage polarity independent requiring the similar magnitude of reset current. Cu CF conduction has the similar V_{reset} distribution as the Vo CF. This confirms that the rupturing of the V_O and Cu filament is mainly thermally driven by the local Joule heating.



Fig. 2-6. V_{set} and V_{reset} distributions of Cu/TaO_x/Pt devices with V_o CFs. Both positive and negative reset voltages can be used to rupture the conductive filaments.

The ON-state resistance R_{on} does not depend on the device area as shown in Fig. 2-7, confirming the set process is based on formation of a local conductive filament. The OFF-state resistance R_{off} decreases with the device area, suggesting within statistical variations the leakage current is homogeneous across the cell.



Fig. 2-7. R_{on} at different device area. R_{on} does not depend on device area, which indicates the filamentary type switching in the devices.

2.3.2 Compliance Current effect

Once the metallic or oxygen vacancy nanofilament is formed between the two electrodes, it will grow laterally with the electrical field and thus the CF diameter is increased and the CF resistance is further reduced until the current reaches the compliance. This subsequent growth process is generally controlled by the bias compliance current (I_{CC}). The dependence of R_{on} on the compliance current for Cu or Vo CF is respectively shown in Fig. 2-8(a) and (b), which can be described as

$$R_{ON} = \frac{A}{I_{cc}^{n}} \tag{2-1}$$

Since R_{on} depends on I_{cc} , multi-bit storage in a single device can be implemented by controlling the cell LRS by different programming current. The multi-level switching based on R_{on} change has been demonstrated on various types of resistive memory devices [9]. R_{on} for Cu and Vo CF have similar trend. In contrast to metallic (Cu, Ag) CFs, where the exponent n for various devices is found universally to be $n \approx 1$, we find n=1.36 for Vo CFs. This data will be discussed in the next chapter. It is noted that $V_{set(min)}$, required to switch the memory from HRS to LRS, can be extracted using small voltage sweeping rates [10].



Fig. 2-8. Dependence of R_{on} as a function of the compliance current applied to the device during the set operation. (a) Cu CFs (b) Vo CFs .

2.3.3 Transient Switching Behavior

Fig. 2-9 (a) presents the switching transient behavior of such devices. The top curve is the input 6V voltage pulse sent from a waveform generator with a width of 500ns and a rise time of 5ns to write the device from OFF state to ON state. The bottom curve is the monitored voltage across a resistor in series with the memory device. The responding current through the memory is then measured. It is noted that the rise time difference between the input signal (top curve) and the output signal (bottom curve) is about 80ns, which indicates a switching speed is less than 100ns for the device. It is also observed that the higher the pulse voltage, the shorter the switching time can be achieved. The switching time is reported to reach 300ps level [11]. The cycling endurance for Cu CF based devices are also conducted and shown in Fig. 2-9 (b). The write (4.5V) and erase pulses (-3V) of about 100us in pulse width are used for the endurance test. The device can switch on and off for 10^4 times.



Fig. 2-9. a) the switching speed is less than 80ns; b) endurance cycle of 10^4 is achieved, the ON/OFF ratio is 10^4 .

2.3.4 Thermal Effect

The temperature coefficients of R_{on} (TCR) are measured from 6 °C to 20 °C, as shown in Fig. 2-10 (a) and (b). The temperature coefficient α is 0.003 K⁻¹ for Cu CF, and 0.001 K⁻¹ for V₀ CF. The measured TCR for Cu CFs are quite close to the reported data from NiO-based ReRAM

devices and Cu CF based CBRAM [12,13]. As the Cu atoms in Cu CFs are not as dense as the bulk copper, the measured TCR for the Cu nanofilament is less than but close to the bulk value of Cu, 0.0039 K⁻¹. It can serve as an identifier of Cu as the basic building block of the nanofilament. The difference between the two coefficients underscores that two different conduction mechanisms are at work. Fig. 2-10(c) shows very constant low resistance state (LRS) and high resistance state (HRS) distributions of a Vo CF based Cu/TaO_x/Pt device with the retention time up to 20 hours. The LRS is about 490 Ω and HRS is about 530 K Ω with an ON/OFF ratio about 10³. The retention property of this type of device has been characterized at 85°C. The read voltage of 0.05V is used to measure R_{on} and R_{off}.



Fig. 2-10. a) TCR of a Cu CF; b)TCR of a Vo CF; c) Retention tests at 85C for up to 20 hours. The LRS and HRS stays nearly constant.

2.4 Comparison of $Cu/TaO_x/Pt$ devices with TaO_x deposited by ALD and EBPVD

In this work, we compared two types of Cu/TaOx/Pt devices with tantalum oxide deposited by two different deposition methods: atomic layer deposition (ALD) and electron beam physical vapor deposition (EBPVD). ALD at low temperature generally produces "pinhole free", stoichoimetric Ta₂O₅, conformal and dense amorphous thin films, as compared to EBPVD, which deposits oxygen deficient, amorphous and low density thin films with less conformal sidewall coverage. This material study gives insight into the mechanisms leading to forming, set and reset of Cu and Vo nanofilaments and how the properties of dielectrics affect the overall device performance. Since, both, the tantalum oxide material and the two deposition techniques, are widely used in CMOS manufacturing process, their impact on RRAM performance is of considerable interest.

Typical I-V characteristics of Cu CF and Vo CF formations for both ALD and EBPVD deposited tantalum oxides are shown in Fig.2-11(a). At a certain V_{form} , an initial forming operation on a fresh memory cell is observed when the cell changes from high resistive state (HRS) to a low resistive state (LRS). Under positive bias voltages, Cu conductive filament is formed by Cu⁺ ion migration in the high electric field and electrodeposition on the Pt electrode. For the Vo CF forming, the bias voltage sweeps along the negative axis. Under negative bias voltages, the migration of Cu⁺ ions in electrolyte is suppressed. Therefore the Cu nanofilament cannot form a conductive path between electrodes. The electrochemical reaction may occur in the TaO_x layer and metal/TaOx interface. The O²⁻ ions migrate from the Cu electrode or inside TaO_x layer to the Pt electrode and get oxidized there in the electric field pointing from Pt to Cu. The vacancies V₀ left behind by migrating O²⁻ ions form a conductive filament and the resistive state changes. An evidence for V₀ formation is the observation of gas (O₂) bubble formation

under the negative bias. Gas bubble formation is never observed under positive bias. The LRS is attributed to the formation of a Vo CF in agreement with [5]. As show in Fig.2-11, an ALD Ta₂O₅ based device has typically Vo and Cu CF forming voltages of about -6.5V and 3.5V, respectively, much higher than those of EBPVD devices, which are around -3V and 2V, respectively. To have a broader statistics such forming operations have been repeated on many ALD and EBPVD fresh cells and the resulting $V_{form}(V_0 \text{ ALD})$, $V_{form}(V_0 \text{ PVD})$, $V_{form}(Cu \text{ ALD})$, and $V_{form}(Cu \text{ PVD})$ distributions are shown in Fig. 2-12(b). Clear separations of the two distributions of $V_{form}(V_0)$ of about 2V and two distributions of $V_{form}(Cu)$ of 1.5V are observed. Due to a larger amount of free volume in EBPVD TaO_x than in ALD Ta₂O₅, a faster formation of Cu and V_0 CFs can be achieved in EBPVD TaO_x than in ALD Ta₂O₅, resulting in lower forming voltages required for the initial formation of Cu and Vo CFs in EBPVD devices.



Fig. 2-11. a) Typical I-V characteristics of forming voltages for Cu and VO CFs in ALD and EBPVD devices; b) V_{form}(Cu ALD), V_{form} (Cu PVD), V_{form} (V_O ALD), V_{form} (V_O PVD) distributions of Cu/Ta_xO_y/Pt devices.

The dielectric constants of both tantalum oxide films are measured by Keithley C-V test and extracted by ac capacitance values. ALD deposited Ta_2O_5 based devices have a higher dielectric constant, about 38, much higher than EBPVD deposited TaO_x , of around 16. This difference for the same film thickness of 16 ±1 nm is rather high. How the differences in dielectric films are related to the device parameters is not clear. However, the different dielectric constant affects significantly the capacitance of the device in the on-state and has to be taken into account in high speed pulse applications. The XPS data indicates that stoichiometric Ta_2O_5 is formed by ALD, while non-stoichiometric (oxygen-defficient) TaOx is deposited by EBPVD. The much lower dielectric constant for EBPVD TaO_x may indicate lower density of the TaO_x film and higher concentration of defective traps. The reduced level of defects may be related to the much higher device yield (90%) for ALD than for EBPVD (70%) devices.

After the initial forming and reset operation, the set voltage is then swept from 0 to 4V and the reset voltage is from 0 to -2V for bipolar switching of Cu CFs. The devices are also characterized for unipolar switching of V₀ CFs. The set voltages for both ALD and EBPVD devices are found to be in the same range around -2.5V for Vo CFs and 1.5V for Cu CFs. This may indicate that O^{2-} has a higher potential barrier than Cu⁺ for the redox reaction at the electrode/oxide interface. It leads to the difference in mobilities of Cu⁺ and O²⁻, requiring higher fields for O²⁻ migration. Therefore, the set voltage for Cu CF is lower than that of V₀ CF. This is also in agreement with the observed independence of Vset in EBPVD samples with different TaO_x thicknesses of 16nm, and 32nm. In the case of EBPVD devices, V_{form} for both Cu and Vo CFs increased considerably with the TaO_x thickness while V_{set} and V_{reset} voltages were independent of the TaO_x thickness. This finding confirms the hypothesis that in the reset operation, the filament is ruptured at a single small gap assumed to be close to the electrode interfaces. This gap is so small (1-4 nm) that it is ruled by electron tunneling mechanism and is no longer affected by the dielectric thickness.

The consecutive bipolar and unipolar switching characteristics of the Cu and V_0 nanofilament are performed on single Cu/ALD-Ta₂O₅/Pt and Cu/EBPVD-TaO_x/Pt devices.

Typical I-V characteristics for Vo and Cu CFs in a Cu/ALD-Ta₂O₅/Pt is shown in Fig. 2-12. In Fig. 2-12(a), the set and reset voltages for Cu CF change respectively from 0.98V to 2.27V and from -0.68 to -0.98V, respectively. In Fig. 2-12(b), the voltage ramps first along the negative axis and then the negative axis. The set voltages for V₀ CF vary from -2.05V to -2.89V and the reset voltages vary from -0.97 to -1.44V. It is noted from the slope of reset I-V curve that the ON resistance of the Vo CF does not change as much as that of the Cu CF. We observed similar R_{on} properties for EBPVD devices. The R_{on} distributions of Cu and Vo CFs for ALD are much tighter than for EBPVD. This might be due to the much higher level of defects in EBCVD TaO_x that in ALD Ta₂O₅ films.



Fig. 2-12. a) Repeated bipolar switching characteristics for Cu CF in a Cu/ALD-Ta₂O₅/Pt device. b) Repeated unipolar switching characteristics for V₀ CF in a Cu/ALD-Ta₂O₅/Pt device.

The bipolar and unipolar switching cycles have been repeated on different Cu/Ta_xO_y/Pt devices. Fig. 2-13 shows the statistical V_{set}, V_{reset} and ON resistance (R_{on}) distributions for the Cu and V₀ CF conduction. It can be seen in Fig. 2-13 (a) and (b) that set and reset voltages for Vo CF in ALD and EBPVD devices are similar, but the absolute values are more scattered for EBPVD devices, resulting in the overlap of the set and reset voltage windows for Vo switching. In Figure 2-13 (c), R_{on} distributions for Vo CF in ALDed devices are much tighter than the distributions of EBPVD TaO_x. The narrow distribution of R_{on} in ALD devices is attributed to

significantly lower defect levels in Ta₂O₅ than in EBPVD TaO_x. The variability of R_{on} in EBPVD devices is likely related to greater variability of defect densities in the TaO_x films or oxide/electrodes interfaces. It is also observed that in ALD devices Vo CFs switch more reliably than Cu CFs. For ALD devices R_{on} of Vo CFs generally vary from a hundred ohms to less than 1K Ω , while the R_{on} of Cu CFs range from a few hundred ohms to 50K Ω . This wide variation of R_{on} (Cu-CF) entails wide V_{reset} distribution which may interfere with V_{reset} and V_{set} for Cu CFs. It has been observed that Cu CFs with larger R_{on} display considerable instability leading in some cases to self-dissolution and volatile switching behavior [14].



Fig. 2-13. (a) $V_{set}(Cu ALD)$, $V_{set}(Cu PVD)$, $V_{reset}(Cu ALD)$, $V_{reset}(Cu PVD)$ distributions of $Cu/Ta_xO_y/Pt$ devices; (b) $V_{set}(Vo ALD)$, $R_{reset}(Vo PVD)$, $V_{reset}(V_O ALD)$, $V_{reset}(V_O PVD)$ distributions of $Cu/Ta_xO_y/Pt$ devices; (c) $R_{on}(Cu ALD)$, $R_{on}(Cu PVD)$, $R_{on}(V_O ALD)$, and $R_{on}(V_O PVD)$ distributions of $Cu/Ta_xO_y/Pt$ devices. (d) Reset-set instability of $Cu/TaO_x/Pt$ resistive memory devices. The I-V characteristics are divided into three sections: (1) Cu CF formation (b) Cu CF rupture (c) V_O CF formation.

Fig. 2-13 (d) shows a switching cycle of a Cu/TaO_x/Pt device with reset voltage sweep from 0 V to -4 V. Section (1) shows the formation of Cu CF and the device resistance transitions from HRS to LRS. With -0.6 V reset voltage the Cu CF ruptures and HRS restores in section (2). The reset voltage sweep extends to -4 V and at -2.5 V the device resistance state changes for the second time. The desired HRS switches to the undesired LRS. This phenomenon is named reset-set instability of bipolar resistive switching memory.

When a negative voltage bias is applied to the resistive device, Cu ion migration is suppressed. According to aforementioned switching mechanism, the second resistance state transition is caused by the V_0 CF when the set voltage of V_0 CF is very close to the reset voltage of Cu CF. Due to the fluctuation of set and reset voltages, the operating window between sections (2) and (3) is difficult to accurately predict. However, for memory applications, this instability must be overcome to protect the data stored in each cell.

In general, the large variations of V_{set} , V_{reset} , R_{on} and R_{off} poses a serious challenge for this type of memory device. Based on our study, the wide distributions of V_{set} V_{reset} , and R_{on} can be narrowed down by employing a bilayer structure. A low forming voltage can be also obtained. The atomic layer deposition method can be used to deposit dielectrics with a relatively low defectivity for the thin SET/RESET switching region, while sputtering or EBPVD can be used to deposit the second layer dielectrics of a higher defectivity.

2.5 Characterization of Cu/SiO₂/Pt Devices

Silicon oxide materials have long been used as gate dielectrics for metal-oxidesemiconductor field effect transistors due to its unique properties such as wide bandgap, low defectivity, and superior interface quality to Si substrate. Meanwhile, the diffusion and drift of Cu ions into Si and SiO₂ material is a well known issue hindering the use of Cu as the interconnection metal for in CMOS based devices. In this work, it is discovered that pure SiO₂ would not be a good solid electrolyte for Vo based resistive switching, but a good material candidate for Cu CF based memory. Stable Cu CF switching and low programming current were observed in W/Cu-SiO2/Cu [15]. Vo CF formation in such devices is yet reported. Cu/SiO₂/Pt devices are therefore investigated here to find out the conditions for Vo CF formation in SiO₂.

The reliable bipolar and unipolar switching on Cu CF formation and rupture are achieved in Cu/SiO₂/Pt (11nm, 16nm and 32nm SiO₂) devices, similar as those in Cu/TaO_x/Pt and Cu/Ta₂O₅/Pt devices. Cu CFs are respectively formed at 3V and 5.4V for 16nm and 32nm SiO₂ memories and reset at -0.7V as shown in Fig. 2-14 (a). A low RESET current of about 70uA can be obtained when the Icc is set as 10uA, shown in Fig. 2-14 (b). R₀ is about 25Kohm. The filament conductance is then about $0.5G_{0.0}$ ($G_{0}=2e^{2}/h=7.75e^{-5}S$, the corresponding quantum resistance is about 12.8Kohm), It brings some interesting questions about the quantum point contact formed in such a Cu filament. The quantum point contact formed in a thin metal wire has a quantum conductance of G_0 . Based on the quantum point contact theory, the resistive memory would have a limitation on the minimum ON resistance, thus the RESET current cannot be reduced to some extremely low number. Further investigation will be conducted in Chapter 4. The experimental results reveal that reliable nonvolatile switching for Vo CF cannot be achieved in Cu/SiO_x/Pt devices with SiO_x of 16nm and 32nm. During the initial voltage sweeping, such devices experience the similar near dielectric breakdown behavior as shown in Fig. 2-14 (c). The subsequent voltage sweepings may render the Vo CF formation in some devices, volatile or nonvolatile. However, the Vo CF switches unstably and usually last for one or two cycles. When d_{SiO2} is reduced to 11nm, the Vo CF could be readily formed, set and reset as noted in Fig. 2-



14(d). These results indicate that the dielectric thickness is also critical to the operation of Vo CF-based filamentary switching. We will discuss this consideration in the next chapter.

Fig. 2-14. a) Typical I-V characteristic of bipolar switching of Cu CF in Cu/SiO_x/Pt memories; b) A Cu CF can be set with a Icc of 10uA, and reset with a peak current of about 70uA. A low power device is achieved; c) The initial negative voltage sweeping applied to a Cu/SiO₂/Pt device, indicating a near dielectric breakdown behavior. Vo CF cannot be formed in Cu/SiO_x/Pt devices with SiO_x thicknesses of 16nm and 32nm; d) Typical I-V characteristic of unipolar switching of Vo CF in a Cu/SiO_x-11nm/Pt memory;

2.6 Characterization of Pt/Oxide/Pt Memories

Noble metals such as Pt have a very low negative heat of metal oxide formation that no metal oxide interface layer can be formed between Pt and a dielectric material. There would be no Pt ion and Pt atom penetration under an external electric field. Therefore, Pt can serve as a reference against other metals for the study of metal ion penetration in dielectrics.

Based on the properties of Pt discussed above, Pt is used as both top and bottom electrodes to study exclusively oxygen vacancy based nanofilaments in RRAMs. The oxides selected for this study include TaO_x (16nm), Ta_2O_5 (8nm) and SiO₂ (16nm). As known, sub-oxide TaO_x has higher concentration of defects than stoichiometic Ta_2O_5 , but both of them are leaky oxides if compared to SiO₂. The bandgap of tantalum oxide is about 4.4eV, while SiO₂ has a bandgap of 9eV. Our characterization results indicate that there is no observation of Vo CF formation in all the Pt/SiO₂/Pt (16nm) devices, and most of Pt/Ta₂O₅/Pt (8nm) and Pt/TaO_x/Pt (16nm) as shown in Figure. 2-15, 2-16 and 2-17. Meanwhile, Vo CF can be formed in a few Pt/TaO_x/Pt and Pt/Ta₂O₅/Pt devices with both voltage polarities. However, the devices can switch on and off only a few times with relatively high reset current (~10mA) before the CF can no longer be ruptured or formed. Fig. 2-15, 2.16 and 2.17 respectively presents the typical I-V characteristic of these three types of devices. As the voltage increases, the I-V curves for Pt/SiO₂/Pt, Pt/TaO_x/Pt and Pt/Ta₂O₅/Pt devices in Fig. 2-15 (a) and (b), Fig. 2-16 (a) and (b), and Fig. 2-17 (a) and (b) indicate the devices being approaching to dielectric breakdown, and no Vo CFs are formed.



Fig. 2-15. I-V Characterizations: a) no Vo CF is formed in Pt/SiO₂/Pt devices with positive bias voltages; b) no Vo CF is formed in Pt/SiO₂/Pt devices with a negative bias voltage.

Fig. 2-16 a) and b) shows Vo CF cannot be formed in most of Pt/Ta₂O₅/Pt devices by both positive and negative voltage bias. Fig. 2-16 C) indicates that Vo CFs cannot be formed at the compliance of 0.1mA in a few devices and behave as diodes, while in Fig.2-16 d), the formation and rupture of a Vo CF is achieved in a Pt/Ta₂O₅/Pt device with an increased compliance current of 1mA and a high reset current of about 8mA. Such devices can only switch On and OFF for very limited cycles. Overall, no reliable switching is achieved in these devices.



Fig. 2-16. a) and b) No Vo CF can be formed in most of Pt/Ta₂O₅/Pt devices with positive and negative voltage polarities; c) No Vo CF is formed in Pt/Ta₂O₅/Pt devices with a compliance current of 0.1mA;
d)Vo CF is formed in a few Pt/ Ta₂O₅/Pt devices with a compliance current of 1mA and reset with a high reset current(~8mA); such devices can only switch On and OFF for very limited cycles.

Fig. 2-17 a) and b) demonstrates Vo CF also cannot be formed in most of pt/TaO_x/Pt devices by both positive and negative voltage bias. Fig.2-17 c) shows a much larger forming and reset voltages for Vo CF in some Pt/TaO_x/Pt, (Vform: ~ -9V; Vreset:~ -4.5V) than in Cu/TaO_x/Pt (Vform: ~-4V; Vreset: ~-2.5V). It is also noted in Fig. 2-17 d) that the forming and set voltages have similar values in a few devices. Such devices can only switch On and OFF for very limited cycles. In conclusion, all the Pt/oxide/Pt devices cannot switch reliably. The oxygen vacancies might be too limited to support the reliable memory functionalities, probably due to the lack of Vo source either from the Pt/oxide interface or the bulk oxides.



Fig. 2-17. a) and b) No Vo CF can be formed in most of Pt/TaO_x/Pt devices with positive and negative voltage polarities; c) Vo CF is formed in a few Pt/TaO_x/Pt with a negative voltage at -8.3V and Vreset at-4.1V; d) Vo CF is also formed and subsequently set in a few Pt/TaO_x/Pt device with a positive voltage bias at +9V and +9.2V. Such devices can only switch ON and OFF for very limited cycles.

2.7 Conclusions

This study gives us a clear insight into the mechanisms of Vo formation. All the experimental data brings up the following important hypotheses:

1) Oxygen vacancy defects or mobile ions are mostly located near the active metal/oxide interfaces than inside the bulk oxides. Active metal/oxide interfaces not only serve as a reservoir for mobile metal ions, but also for oxygen ions or oxygen vacancies;

2) Oxides mainly function as the ion migration electrolyte. The proper concentration of defects in oxides and the proper oxide thickness are also required for reliable resistive switching.

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3 Multilevel Resistive Switching with Oxygen Vacancy Filaments in Pt/TaO_x/Cu and Pt/TaO_x/Pt Devices

During this study, it is demonstrated that multilevel switching of oxygen vacancy (Vo) conductive filaments (CF) is characterized by the relation Ron=A/Iccⁿ between ON-state resistance (Ron) and compliance current (Icc). In contrast to metallic (Cu, Ag) CFs, where the exponent n for various devices is found universally to be $n \approx 1$, we find n=1.36 for Vo CFs. An exponent n>1 may imply two distinct mechanisms responsible for the formation of Vo CFs. 1st mechanism is similar to the formation mechanism for metallic CFs and accounts for the unity part of the exponent, while the 2nd mechanism is responsible for the remainder (n-1). This hypothesis is corroborated by data of Vo CFs in resistive switching cells with and without active electrodes such as Pt/TaOx/Cu and Pt/TaOx/Pt and also on Pt/SiO2/Cu and Pt/SiO2/Pt devices.

3.1 Introduction

The resistive switching devices have recently been of interest to both industry and academia [1,2,3,4,5,6,7,8,9]. The two-terminal devices exhibit figure eight-like pinched current–voltage (I–V) hysteresis switching between high resistance OFF state (R_{OFF}) and low resistance ON-state (R_{ON}) of the memristive characteristics [2,3]. Conductive bridge random access memory (CBRAM) is being extensively explored as a promising candidate for a resistive memory device [10]. The CBRAM device consists of an active anode, an insulating layer, and an inert cathode. The anode consists of Cu, Ag or Ni, which can dissolve, in the insulating layer [11,12,13]. The insulating layer is a solid-state electrolyte, such as GeSe, GeS₂, TiO_x, HfO_x, or TaO_x. When a positive voltage is applied to the active electrode, Cu or Ag cations migrate through the solid electrolyte to the inert cathode (Pt or W). The Cu or Ag cations are

electrochemically deposited on the cathode and form a nanoscale conductive filament (CF) in socalled FORM and SET processes. The ON/OFF ratio of CBRAM is usually higher than 10^3 , allowing multilevel switching in a single memory cell to store more than one bit of data. When different levels of compliance current (Icc) are applied to a CBRAM device, a characteristic dependence of LRS resistance (R_{ON}) on Icc is observed:

$$R_{ON} = \frac{A}{I_{cc}{}^n} \tag{3-1}$$

where n is a fitting parameter close to 1 for metallic CFs and A is a constant in units of volt. The Ron–Icc relation valid for in eq.[3-1] has been reported to be numerous anode/electrolyte/cathode material systems [14,15,16,17,18,19,20,21]. In [21] it has been shown that the constant A in eq.[3-1] is universally correlated to the minimum SET voltage (Vset(min)) for all metallic conductive filaments reported so far. Vset(min), required to switch the memory from OFF- to On-state, can be extracted from Vset measurements at small voltage sweep rates. Since such an analysis is largely lacking for oxygen vacancy CFs, this study is to close this gap. Our results show that for Vo CFs the exponent n is significantly larger than 1 possibly indicating that there are two mechanisms responsible for formation of Vo CFs. Experimental data on resistive switching Pt/I/Cu and Pt/I/Pt cells with dielectric I=ALDTa₂O₅, EBPVDTaO_x, EBPVDSiO₂ are evaluated to elucidate the formation mechanisms of oxygen vacancy nanofilament.

3.2 Experimental Results

In Fig. 3-1, a typical set and reset bipolar and unipolar operation for Vo CF in Pt/TaO_x(16 nm)/Pt is shown. The Vset=-2.1 V at Icc =0.1 mA and Vreset=-0.9 V. Similar data has been obtained for Pt/Ta₂O₅(16 nm)/Cu devices. While the ranges of set and reset voltages are the same

for both PVD and ALD devices, the forming voltages for ALD devices are significantly higher($\Delta V \approx 2V$) than for PVD cells. In Fig. 3-2, the Ron of Vo CFs is shown as a function of the



Fig. 3-1. Set and (a) bipolar and (b) unipolar reset of Vo conductive filament.

compliance current Icc. On a double logarithmic scale, one can see that Ron decreases linearly with Icc, according to eq.[3-1]. The parameters extracted parameters are A=0.022 and n=1.36. This constitutes a significant departure from n=1 found for all metallic CFs. As a consequence of n>1, the constant A can no longer be interpreted as the universal minimum switching voltage [21]. However, locally, i.e. for a small Icc interval, we can still fit the data to eq.(3-1) with n=1



Fig. 3-2. Ron versus Icc for Vo CF in Pt/Ta2O5/Cu device with 16 nm Ta_2O_5 .

and extract following values for the constant A in units of volt: for Icc \approx 10nA A=1.7V, for Fig.3-2 Ron versus Icc for Vo CF in Pt/Ta2O5/Cu device with 16 nm Ta₂O₅. Icc \approx 0.1mA A=0.52 V, and for Icc =10mA A=0.06V. One is then led to the conclusion that at low Icc currents the minimum set voltage is high and at high Icc currents very low. As in [17] we have measured the set voltage of Vo CF as a function of voltage sweep rate v. We find that as in the case of metallic CFs the SET voltage decreases linearly with the logarithm of v. However, in contrast to metallic CFs, the Vset for Vo CF does not saturate at a minimum set voltage, even at such slow ramp rates as v=1x10⁻⁵ V/s. Since this latter value is the lowest ramp rate achievable with our Keithley 4200-SCS equipment, it remains uncertain whether a minimum set voltage could have been established at even lower voltage ramp rates.

3.3 Vo Formation

There is a wide consensus [10] that at the interface between the active electrode (Cu) and the metal oxide dielectric a redox reaction is taking place:

$$Cu \leftarrow \rightarrow Cu^+ + e^-$$
 (Reduction-Oxidation) (3-2)

When positive bias is applied to the active electrode Cu^+ ions migrate toward the inert electrode (Pt) and are stopped at the Pt interface, extending thus the inert electrode into the oxide. This aggregation of Cu atoms grows then at an ever-accelerated rate toward the active Cu electrode until a complete bridge is formed. In other words, the mechanism is that of piling Cu atoms upon Cu atoms supported by ever increasing electric field between the inert electrode extended into the dielectric and the active Cu electrode. In case of negative bias, the oxidation reaction [22] provides an efficient injection mechanism of electrons into the oxide while Cu^+ ions are returned to the Cu electrode. It is crucial to consider the action of electrons under a negative bias. The electrons are injected and may charge and dislodge the negative oxygen ion from the metal oxide matrix leaving behind a neutral oxygen vacancy Vo according to the reaction:

$$\mathrm{SiO}_{x}+2\mathrm{e}^{-} \rightarrow \mathrm{SiO}_{x-1}+\mathrm{O}^{2-}=\mathrm{SiO}_{x}\mathrm{Vo}+\mathrm{O}^{2-} \tag{3-3}$$

It should be noted that a similar reaction would be possible for singly charged oxygen ion. However, a singly negative oxygen ion has been ruled out as highly unstable in a metal oxide matrix. At this point it is important to consider the spatial location where such reaction [23] is taking place. Since the redox reaction [22] takes place at the Cu/TaOx interface and produces a large number of electrons, the creation of Vo will take place at the interface as well. Since the oxygen vacancy is known to provide a local Fermi level close to the conduction band, the vacancy will extend the active electrode into the oxide and act as a conduit of more electrons. Thus it is likely that another Vo will be formed below the first one extending thus the partial Vo filament deeper into the oxide. This, in turn, leads to an increased electric field between the end of the partial Vo CF and the inert electrode Pt. This growth mechanism is illustrated in Fig.3-3. Clearly, this self-accelerating mechanism is similar to the formation of Cu CF at positive bias, described above. The competing mechanism for creation of oxygen vacancies is that electrons migrate into the oxide and at some point undergo reaction (3) but now randomly in the bulk rather than at the surface as illustrated in Fig. 3-3(a). Over the stress time, more and more of vacancies will be generated in the same way leading to an intermediate state depicted in Fig. 3-4(b). This process of creating increased density of vacancies will reach a critical concentration of vacancies allowing for a conductive percolation path between the two electrodes as shown in Fig. 3-4(c). Note that this mechanism will be present irrespective of the nature of the top electrode. Obviously, the second mechanism of Vo formation represents a very stochastic

process and lacks the self-accelerating feedback of the first mechanism. Hence, it is less efficient in creating a Vo conductive nanofilament. In general case, both mechanisms will be at work at the same time, cooperating and enhancing each other. However, it is possible to separate them by considering two cells with and without the active electrode: Pt/TaOx/Cu and Pt/TaOx/Pt. In Pt/TaOx/Cu the first mechanism will be present with a copious injection of electrons at the



Fig. 3-3. Surface-initiated V_o filament growth triggered by reactions (2) and (3). This mode of filament growth is self-accelerating as the growing extension of the partial filament causes ever-increasing electric fields. For (a), (b), and (c) see explanation in the text.



Fig. 3-4. Random bulk growth of the Vo filament triggered by reaction [3] only. For (a), (b), and (c) see explanation in the text.

Cu/TaOx interface while this mechanism will be missing in the Pt/TaOx/Pt cell. We observe no formation of Vo CFs in all the Pt/SiO2 (16nm)/Pt, most of Pt/Ta2O5(8nm)/Pt and

Pt/TaOx(16nm)/Pt devices. Formation of Vo CF could be observed in a few Pt/TaOx/Pt and Pt/Ta2O5/Pt devices at both voltage polarities. However, in those cases, the devices can switch on and off only limited number of times with relatively higher reset current (~10mA) before the CF can no longer be ruptured or formed. Fig. 3-5 shows forming and set characteristics for a Pt/TaOx/Pt device . The form and set voltages are significantly higher than for the Pt/TaOx/Cu cell. Thus it is much easier to create a Vo CF in Pt/TaOx/Cu than in Pt/TaOx/Pt devices for the same TaOx thickness, requiring larger electrical fields or longer times for the case when the set operation is performed at a constant voltage stress. In Fig.3-6 the set operation for the Pt/Ta₂O₅/Pt (8nm Ta₂O₅) cell is shown at two different set currents. It was found that for all set currents below 0.1 mA no nonvolatile Vo CF could be formed. Only for compliance currents



Fig. 3-5. Switching characteristics of V_o CF in Pt/TaO_x(16 nm)/Pt resistive devices. (a) Forming and reset operations. (b) Forming and set operations under positive bias.



Fig. 3-6. a) No Vo CF is formed in Pt/Ta₂O₅/Pt devices with a compliance current of 0.1mA; b)Vo CF is formed in a few Pt/Ta₂O₅/Pt devices with a compliance current of 1mA and reset with a high reset current(~8mA); such devices can only switch On and OFF for very limited cycles.



Fig. 3-7. Failed attempts to form V_o CF in Pt/SiO₂/Pt devices with $d_{SiO2}=16$ nm. (a) at positive voltage bias. (b) at negative voltage bias.

above 1 mA stable non-volatile Vo CFs could be formed. At higher set currents the cell could be set and reset but less than 10-20 times before it was permanently damaged. Due to lower level of electron injection caused by absence of the active Cu electrode, Pt/TaOx/Pt shows a much larger forming and reset voltages for Vo CF in Pt/TaOx/Pt, (Vform ~ -9V; Vreset~ -4.5V) than in Cu/TaOx/Pt (Vform ~-4V; Vreset ~ -2.5V). To investigate the role of a dielectric further, we have fabricated Pt/SiO₂/Cu and Pt/SiO₂/Pt devices. The SiO₂ thickness for Pt/SiO₂/Pt devices is

16nm. The thicknesses of SiO2 layer of $Pt/SiO_2/Cu$ devices are $dSiO_2=32$, 16, and 11 nm. SiO_2 is known to be very stable and not susceptible to oxide damage via Vo formation. For both kind of devices with $dSiO_2 = 32$ nm we were unable to form Vo CF even at voltages as high as 15V. Corresponding, typical I-V characteristics are shown in Figure 3-7. The results of Vform, Vset, and Vreset for the devices considered in this study are summarized in Table 3-1. It is clearly seen, that it is much more difficult to form a Vo filament for Pt/I/Pt devices than for Cu/I/Pt devices; for the same oxide thickness it is more difficult to form a Vo filament in Ta₂O₅ than in TaOx, and finally, for the same materials Vform increases with the thickness of the dielectric. At the same time, it is seen from Table 3-1 that Vset for Vo filaments is the same for all devices when the Vo filament can be formed and reset reliably. This finding indicates that during the reset only a small portion of the Vo CF has been ruptured while a major portion of the partial Vo CF remains intact. During the subsequent set operation, the bridging of the gap in the ruptured Vo CF appears to be largely independent of the matrix material. However, for the forming operation, due to a larger amount of free volume in EBPVD TaOx than in ALD Ta₂O₅, a faster formation of Cu atoms and Vo CFs can be achieved in EBPVD TaOx than in ALD Ta2O5, resulting in lower forming voltages required for the initial formation of Cu and Vo CFs in EBPVD devices. The comparison between the two different dielectrics further confirms the hypothesis that in the reset operation the filament is ruptured resulting in a single small gap assumed to be close to the Pt electrode interface. This gap is small, of the order of 1-4 nm, and in terms of conductivity is ruled by electron tunneling mechanism and is no longer affected by the dielectric thickness or by the material properties close to the TaOx/Pt interface. The experiments demonstrate the crucial role of the active electrode and the oxidation reaction [2] induced by it in the formation of the Vo CFs. Also the circumstance that $Pt/Ta_2O_5/Pt$ cells were switchable only a

wafer #	Device Stack	Layer Thickness (nm)	V _{For}	$_{m}(V)$	V	set	Notes	
			Cu CF	Vo CF	Cu CF	Vo CF		
A1	Cu/TaO _x /Pt	100nm/32nm/50nm	~ 4.5	~ -7	2	~-2.5	Stable Vo CFs	
A2	Cu/TaO _x /Pt	100nm/16nm/50nm	~ 2	~ -4	1.5	~-2	Stable Vo CFs	
A3	Pt/TaO _x /Pt	50nm/16nm/50nm	No	~ -8	No	~-2.5	Not stable	
B1	Cu/Ta ₂ O ₅ /Pt	100nm/16nm/50nm	~ 3.5	~ -6	~2	~-2.5	Stable Vo CFs	
B2	Pt/Ta ₂ O ₅ /Pt	50nm/8nm/50nm	No	~ -6	No	~-5	Not stable	
C1	Cu/SiO ₂ /Pt	100nm/32nm/50nm	~ 5.5	No	~3	No	No Vo CFs	
C2	Cu/SiO ₂ /Pt	100nm/16nm/50nm	~ 3	No	~ 2	No	No Vo CFs	
C2	Cu/SiO ₂ /Pt	100nm/11nm/50nm	~ 3	-4	~ 2	-2	Stable Vo CFs	
C3	Pt/SiO ₂ /Pt	50nm/16nm/50nm	No	No	No	No	No CFs	
	d >> ξ	d ~	ž			d < ξ		

Table 3-1. Vform, Vset, and Vreset for the devices considered in this study.

Fig. 3-8. A percolation model for Vo CF formation as a function of a dielectric thickness. a) the thickness $d \gg \xi$ -no Vo CF can be formed; b) $d \sim \xi$ -Vo CF can be formed but switch unreliably; c) $d < \xi$ -Vo CF can be formed and switch reliably.

few times before suffering permanent damage points to a large component of the stochastic formation of a critical concentration of Vo conducive to irreversible conductive path(s) between the two electrodes. For Cu/SiO₂/Pt devices with a dSiO₂ =16 nm or 32nm no Vo CF could be formed. For dSiO₂ = 11 nm the Vo CF could be readily formed, set and reset. These results

indicate that the dielectric thickness may also be critical to the operation of Vo CF-based filamentary switching. We explain this behavior by the percolative Vo cluster size model illustrated in Figure 3-8. This model supplements the surface and bulk model explained in Fig. 3-3 and Fig. 3-4. In SiO₂ devices the activation energy to form O²⁻-Vo pairs is much larger than TaOx and Ta₂O₅. Hence, both the surface-initiated and bulk mode Vo CF growth mechanisms are ineffective in generating sufficient levels of oxygen vacancies to create a conductive percolation path. A sufficiently high concentration of Vo can be translated into a maximum Vo cluster size ξ . Our data on SiO₂ devices indicates that both dSiO₂=32 nm and 16 nm are larger than maximum length of oxygen vacancy cluster, but dSiO₂=11 nm length comes in the range of characteristic lengths of oxygen vacancy clusters as shown in Figure 3-8.

3.4 Conclusions

A comprehensive study of oxygen vacancy formation has been conducted for several dielectrics and different combination of Cu and Pt electrodes. The formation mechanism of oxygen vacancy nanofilament is different from the formation of nanofilaments formed by metal ions. While Cu and Ag formation is dominated by one mechanism of piling metal ions upon each other and extending the inert electrode into the dielectric, the formation of Vo CF is a synergy of two different mechanisms: (i) a surface-initiated and (ii) a bulk mechanism. We believe that the presence of the two mechanisms manifests itself in the exponent n of the relation (1) being, in case of Vo CFs, substantially larger than unity. The surface-initiated mechanism accounts for n=1 for both metal and oxygen vacancy nanofilaments, while n-1>0 is indicative of the bulk mechanism for vacancy formation. The experimental data of the various memory cells has shown clearly the importance of the oxidizable (active) electrode in the formation of stable and resettable Vo CFs. The bulk model of Vo CF formation applies also to the generation of Vo-O²⁻

pairs at the surface but is fed by the large supply of electrons at the oxidizable (Cu) electrode. The supply of electrons at the surface comes directly from the active electrode under the negative voltage bias. The oxygen vacancy cluster formation mode provides a larger cross-section to capture an electron in the dielectric layer and is more efficient in transporting the electron to the next site to extend the partial filament toward the counter electrode. This model allows consistently explanation of the various phenomena observed in the resistive switching devices discussed here. Among the Pt/I/Pt devices only Pt/TaOx/Pt devices were amenable to formation of Vo CFs if the dielectric thickness is sufficiently small. The results presented here shed also light on the possible mechanisms of generation of a permanent damage (dielectric breakdown). For example, when the maximum size of Vo clusters formed in dielectrics with high activation energy is in the range of the dielectric film thickness, the ON state may result in several parallel conductive paths. Such a configuration is difficult to rupture since the current in a given branch may be not high enough to initiate a rupture along several conductive paths.

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4 Resistive Switching of Pt/Ti/Ta₂O₅/Pt Memories

In this Chapter, we further investigate conduction mechanism for the Vo CF only based memories and how to modify electrode, oxide and the interface properties to improve the device performance in terms of power consumption and reliability. To achieve these goals, a thin layer of titanium is inserted into a Pt/Ta₂O₅/Pt structure to form a Pt/Ti/Ta₂O₅/Pt device for this study. A space charge limited (SCL) conduction model is used to explain the experimental data regarding SET process at low voltage ranges. Such SCL conduction effect is reported in some resistive memories [1,2,3]. However, a detailed study has not been conducted to clarify the underlying charge transport mechanism. In this chapter, a model based on SCL conduction is proposed and investigated. The model is matched very well with the SET experimental data at the low voltage ranges. The major traps are considered to be the oxygen vacancies introduced by TiO_x .

4.1 Introduction

The previously studied Pt/oxide/Pt devices have demonstrated limited or no switching cycles, which might be due to the lack of a reservoir of ions at the Pt/oxide interfaces and inside the oxides to support repeated switching, indicating that the metal/dielectrics interface may play a critical role in resistive memory effect. The Vo CF based switching behavior observed in Cu/oxide/Pt devices also leads to this hypothesis. The oxidation reaction at the Cu/oxide interface provides an efficient injection mechanism of electrons into the oxide, which may charge and dislodge the negative oxygen ion from the metal oxide matrix leaving behind a neutral oxygen vacancy V_o, and thus to enable a reliable memory effect. The Cu/oxide interface planting on the voltage polarity,

resulting in the possible coexistence of both Cu and Vo CFs. Oxygen vacancies are reported to be the most predominant type of defects in oxygen deficient metal oxide dielectrics such as TiO_x , HfO_x, TaO_x, and ZrO_x[4,5]. It is found that an ordered oxygen vacancy filament induces several defect states within the band gap of the TiO_x , such as shallow and deep defects or traps, and can lead to the defect-assisted electron transport[4]. The +2 oxygen vacancies are found to be most stable oxygen vacancies during migration and neutral Vo is most stable if no electrical field is applied. Oxygen vacancies in Ta₂O₅ display deep unoccupied states and shallow occupied defect states. The neutral and +2 positive vacancies are found to be most stable [5].

4.2 Experiments and Results Discussion

During this study, a Ti layer (3nm or 10nm) is inserted into a Pt/Ta₂O₅/Pt structure to form a Pt/Ti/Ta₂O₅/Pt device and deposited by EBPVD on the Ta₂O₅ (11nm, ALD) thin film. A number of the devices are annealed at 350C for 5 minutes in N₂ in ALD chamber to study the effect of annealing on interface oxide formation. Like aluminum metal surfaces, titanium metal oxidizes immediately upon exposure to air or in contact with some oxides, and a passive titanium oxide coating is formed to protect the bulk Ti metal from further oxidation and Ti ion from further diffusion [6,7,8,9]. The reason we chose Ti is due to this strong oxygen gettering property. The Ti cation injection is thus suppressed as the oxidized TiO_x film is not easily reduced back to the Ti. Al and Nb also have the similar properties. Therefore it can partially or totally reduce the Ta₂O₅ layer to a defect rich tantalum sub-oxide, at the same time, naturally forming a thin layer of titanium oxide TiO_x at the Ti/Ta₂O₅ interface where Ti and Ta₂O₅ are in contact. Such a design would possibly enable the formation of a Pt/Ti/TiO_x/TaO_x/Ta₂O₅/Pt structure, and an oxygen vacancy rich region in Ti/TiO_x/TaO_x area and thus lead to the formation and rupture of only Vo CF in the memory device. The devices with a 3nm Ti thin layer exhibit the similar characteristics as the Pt/Ta₂O₅/Pt devices. No Vo CFs can be formed reliably in such devices. However, the devices with a 10nm Ti layer function reliably as resistive memories, and display some distinctive switching properties if compared to the Cu/Ta₂O₅/Pt devices. 3nm Ti layer may not be able to create enough Vo to enable CF formation. Note TiO_x is likely to be much more conductive than TaO_x, and could function as an extension of the top electrode. The results are discussed as followed.

As opposed to the Cu/ Ta_2O_5/Pt devices, the reliable bipolar switching are only achieved in Pt/Ti/Ta₂O₅/Pt (10nm Ti and 11nm Ta₂O₅) devices with a positive bias on the top Pt/Ti electrode for FORM and SET, and a negative bias for RESET operation. The devices fail to reset if a positive bias is applied on the top electrode (Cu/Ta₂O₅/Pt device can be reset with both bias polarities) and cannot reliably be set if a negative bias is applied. Typical switching characteristics are presented in Fig. 4-1a), b) and c) for $Pt/Ti/Ta_2O_5/Pt$ devices with different bias combinations, and without post annealing. Fig. 4-1a) shows the reliable bipolar switching for such a device. The fresh device is initially formed at about 4.63V during a voltage sweeping from 0 to 5V, and reset sharply around -1V (not shown in Fig. 4-1a) during a voltage sweeping from 0 to -2V. The subsequent SET occurs at 1.62V, much smaller than the forming voltage (4.63V), and is followed with a gradual RESET at a negative voltage bias. Fig. 4-1 b) presents the unipolar switching with a positive bias for forming, SET and RESET, it is found that the device cannot be switch off and Ron is even further decreased. This indicates that the RESET with a positive voltage would further strengthen the conductive filament and leads to the thickening of the filament. This is different from what we observed from Cu/Ta₂O₅/Pt and Pt/ Ta₂O₅/Pt devices, which can be turned off with both positive and negative polarities, mainly due



to joule heating. The RESET for this new device may occur through the joule heating and the recombination of oxygen vacancies and oxygen ions, and promoted by the asymmetric

Fig. 4-1. Typical I-V characteristic: a) Bipolar switching of Vo CF in Pt/Ti/Ta2O5/Pt memories; b) Unipolar switching with a positive bias to form, set and reset. The device cannot be reset; c) Devices cannot be formed and set with a negative bias; d) Bipolar switching of Vo CF in an annealed Pt/Ti/Ta2O5/Pt memories;

 $Pt/Ti/TiO_x/TaO_x/Ta_2O_5/Pt$ device structure. The TiOx/TaOx region is an oxygen vacancy rich area or a defect rich area, if compared to Ta_2O_5 layer. Fig. 4-1 C) shows that Vo based CF cannot be formed in such a device even with a higher compliance current (Icc=5mA) if using a negative voltage bias. It is also noticed that the negative voltage sweepings may render the CF formation in some devices, volatile or nonvolatile. However, the CF switches unstably and usually last for one or two cycles. This phenomenon is also observed in Pt/Oxide/Pt device, due to the limited oxygen ion or Vo concentration at Pt/Oxide interface and inside oxides, not high enough to support repeated switching.

Based on the previous study on Cu/Ta₂O₅/Pt devices, it is not expected to observe the reliable Vo based resistive switching in such a Pt/Ti/TiO_{2-x}/TaO_x/Ta₂O₅/Pt structure if a positive bias is applied on the top electrode, since Ta₂O₅/Pt interface, TaO_x and Ta₂O₅ bulk layer cannot continuously provide enough oxygen ions or electrons for repeatable switching. However, the device turns out to form and set only with a positive bias. In this case, TiO_x could dominantly function as a reservoir of oxygen vacancies with a positive charge of 2 [3,4], which migrate towards the bottom electrode if a positive bias is applied. The TaO_x and Ta_2O_5 layers (the thicknesses of both layers are not known, Ta_2O_5 may have a thickness of a little less than 8nm) might provide some oxygen ions or Vo for filament formation. Fig. 4-1 d) shows a typical reliable bipolar switching for such a device annealed at 350C. Compared to the non-annealed device, the forming voltage of the annealed ones is reduced from about 5V to 2.5V, suggesting the further oxidization of Ti and reduction of Ta_2O_5 into oxygen deficient TiO_x and TaO_x occur at an elevated temperature, resulting in the decrease of stoichiometric Ta₂O₅ thickness. The set and reset characteristics are similar as the non-annealed devices, indicating that the rupture and reformation of the filament occurs at a very small area, most likely inside Ta_2O_5 .

Based on above electrical data and analysis, the underlying switching mechanism of the $Pt/Ti/Ta_2O_5/Pt$ device can be attributed to the formation/rupture of oxygen vacancy filament due to redox reaction under the appropriate bias on the top electrode (TE), as illustrated in Fig. 4-2. When a positive bias is applied on the top P/Ti electrode, the oxygen ions mainly from TiO_x, and partially from TaO_x and Ta₂O₅ would migrate towards Pt/Ti side and leave oxygen vacancies

behind. As TiO_x and TaO_x are more oxygen deficient, the Vo concentration would be higher in TiO_x/TaO_x than in the remaining Ta_2O_5 layer. The Vo profile during forming is shown in the Fig. 4-2a). As the voltage further increases, Vo^{2+} formed in TiO_x would migrate towards TaOx and Ta₂O₅, based on the following electrochemical reaction: $TiO_{x-1}Vo^{2+}+TaO_{x-1}Vo+TaO_{x-1}Vo+TaO_{x-1}Vo$ $_{1}Vo^{2+}$. It is reported that +2 charged oxygen vacancies in TiOx are most stable during drifting under electrical field. Neutral or +2 oxygen vacancies in TaOx are most stable [4, 5]. Those oxygen vacancies display deep occupied states and shallow unoccupied states in the bandgap. The Vo concentrations in TiO_x/TaOx/Ta₂O₅ increase with the voltage, until a filament or percolation path is formed. The conical shape of the Vo filament is achieved with a small tip located at the Ta₂O₅ side due to stoichiometric nature and low defectivity of Ta₂O₅, if the compliance current is relatively low, as shown in Fig. 4-2b). The TiOx/TaOx section would have a much lower resistance than Ta₂O₅ area. If a very high compliance current is used during SET, the filament would grow and approach cylindrical shape, and its resistance will decrease. It would then require a high current to rupture the filament. Owing to unique design of asymmetric Vo profile in $TiO_x/TaO_x/Ta_2O_5$, there is most Vo in TiO_x and less Vo in Ta_2O_5 . The flowing of Vo^{2+} into Ta_2O_5 layer would dominate over the flowing of oxygen ions from Ta_2O_5 if a positive bias is applied. The rupture of Vo CF is unlikely under such a bias. Therefore, the positive RESET bias cannot be used to reset a device as it would instead strength the filament tip and make it hard to be reset (Fig. 4-2c). RESET only occurs with a negative bias and at $TaOx/Ta_2O_5/Pt$ interface or inside the Ta_2O_5 layer, where the transport of oxygen vacancies from TiO_x/TaOx is suppressed, and the oxygen ions coming from TaOx and Ta₂O₅ can migrate to Ta_2O_5 layer and recombine with the Vo tip (Fig. 4-2d) and e)). As a result, the filament breaks and the device is back into HRS state. The experimental results prove this hypothesis. The

quantum conductance G_0 is observed right before the final conductance drop during reset process, as shown in Fig. 4-5 b) and c). Further RESET would lead to the total rupture of the filament. Such a Vo profile engineering is critical for improving the device performance. The subsequent SET/RESET operations are all confined in the thin Ta₂O₅ layer.



Fig. 4-2. Schematic illustration of charge transport in a Pt/Ti/Ta2O5/Pt device.

4.2.1 Space Charge Limited Conduction Model

To investigate charge transport mechanism during SET and RESET, I-V data were analyzed by fitting it to common charge transport expressions of dielectrics, listed in Table 4-1.

Conduction	Expressions	Interface or bulk effect	Voltage dependences				
Schottky emission	$J = A^* T^2 e^{\frac{-q(\phi_B - \sqrt{qE/4\pi\varepsilon_0\varepsilon})}{kT}}$	Interface	$lnJ \propto \sqrt{V}$				
Poole- Frenkel emission	$J \propto E e^{\frac{-q(\phi_B - \sqrt{qE/\pi\varepsilon_0\varepsilon})}{kT}}$	Bulk	$\ln\left(\frac{J}{V}\right) \propto \sqrt{V}$				
Fowler- Nordhiem emission	$J \propto E^2 e^{\frac{-4\sqrt{2m^*}(q\phi)^{3/2}\sigma\left(\frac{\Delta\phi}{\phi}\right)}{3hqE}}$	Interface	$\ln\left(\frac{J}{V^2}\right) \propto 1/V$				
Space charge limited	$J = \frac{9\varepsilon_0\varepsilon_r\mu_n V^2}{8d^3}$	Bulk	$J \propto V^2$				
Ohmic	$J = qn\mu_n E + qp\mu_p E$	Interface, bulk	$J \propto V$				
Parameters:							
A^* =effective Richardson constant; T=temperature; q=electron charge; Φ_B =barrier height;							
<i>E</i> =electrical field; ε_0 =vacuum permittivity; ε =dynamic permittivity; ε_r =static permittivity;							
<i>m</i> =effective mass; <i>d</i> =thickness; μ_n =electron mobility; μ_p =hole mobility							

 Table 4-1 Possible Conduction Mechanisms in MIM devices: [10]

The carrier transport mechanisms in MIM structures generally include ohmic conduction, space charge limited conduction (SCL), Schottky emission, Poole-Frenkel (P-F) emission and Fowier-Nordheim (F-N) tunneling, in which SCL conduction and Poole-Frenkel emission are bulk dominated mechanisms while Schottky emission, F-N tunneling are electrode/bulk interface dominated mechanisms. These different types can be distinguished via its I-V correlation as listed in Table 4-1.

Through the curve fitting, the well known four different I-V characteristics including SCL based conduction are clearly observed in the I-V SET curve of an annealed Pt/Ti/Ta₂O₅/Pt device, as shown in Fig. 4-3 a). Other conduction mechanisms such as Poole-Frenkel, Schottky emission and Fowler-Nordheim do not fit the I-V characteristics. Similar SCL based conduction effect is also reported in some resistive memories [1,2] and observed in the Pt/Ta₂O₅/Cu devices

we fabricated [11,12]. However, a detailed study has been not reported. A model based on SCL conduction is proposed and investigated in this chapter. The charge transport behavior in this device at low voltage region can be explained by the one carrier injection (we will focus on electron injection) trap-controlled SCL conduction mechanism based on Lampert's theory [13], and is described as followed.

Based on the Lampert's theory of space charge limited current, some valuable information can be obtained through carrier injection into the low mobility materials and from the current-voltage dependence of the material. This method has been used to evaluate the defect or trap properties of low-conductivity materials. If the mobility is low, which is the normal situation with many oxides, then the injected electrons (in this case, we only consider electrons) are likely to accumulate in the bulk or fill the electron traps, the accumulated charge influences the conduction current. The SCL based conduction is generally observed when the electrode contacts are highly carrier injecting. It is thus very suitable for the study of the SET/RESET operation because the conductive filament is formed or ruptured at a very small area during the SET/RESET process, and the remaining filament sections can be assumed to be connected to the top and bottom electrodes "ohmically" after the initial forming. When the density of injected electrons exceeds the density of traps in the insulator, the current rise sharply until it reaches the trap free space charge limited current. Fig.4-3a) summarizes the fitting results of A to D regions, depending upon the mechanism that is operative.



Fig. 4-3. a) I-V characteristics for an annealed device in a log-log plot; b) Left: prototype curves for a single set of traps, I corresponds to F0(Fermi level) lying above Et(trap energy level), II corresponds to F_0 lying below Et; Right: prototype curves for two sets of traps; the solid line corresponds to F_0 lying above one set of traps and below the other set, the dashed curve to F0 lying below both sets of traps [12].

A region: at low voltage range, I-V characteristics follow ohmic conduction, because the thermally generated free carriers inside the oxides are dominating over the injected carriers. The carrier transit time is equal to the Ohmic relaxation time [14]. The current density J is given by Ohmic current

$$J = N_e e\mu E = N_e e\mu \frac{V}{d} \tag{4-1}$$

where n is electron density (only electron carrier is discussed), μ is the electron mobility, E is the electrical field, V is the voltage applied to the MIM device, d is the insulator thickness. The slope of the double logarithmic line is 1.

B region: As voltage increases and reach V_T , the I-V curve transitions from Ohmic conduction (A region) to SCL conduction (B region). When V> V_T , the injected charge carriers dominate the thermally generated carriers. The transit time for injected carriers is too short for their charges to be relaxed by the thermally generated carriers. The conduction behavior shown in Fig. 4-3a) suggested that the space charge limited current (SCLC) is controlled by a single set

of shallow traps (the trap energy level lays above Fermi energy level F_0)[13], corresponding to the II curve shown in the left plot of Fig. 4-3b). The current density due to SCL is given by

$$J = \theta \frac{9}{8} \varepsilon_0 \varepsilon \mu V^2 / d^3 \tag{4-2}$$

where θ is the trapping parameter, which is given by

$$\theta = \frac{n_c}{n_t + n_c} \tag{4-3}$$

$$n_c = \frac{N_c}{1 + \exp\left(\frac{E_c - E_f}{kT}\right)} \tag{4-4}$$

$$n_t = \frac{N_t}{1 + gexp(E_t - E_f)/kT} \tag{4-5}$$

where n_c and n_t are the numbers of electrons and traps, N_c and N_t respectively refer to the density of free electrons in the conduction band and the density of electron traps, g is the degeneracy factor for the traps, k is Boltzman's constant, T is material temperature and E_f is the electron quasi-Fermi level. The current is controlled by the trapping parameter θ , the ratio of free electrons to trapped carriers. The slope of the double logarithmic line is 2.

C Region: Trap filled limited (TFL) current. As voltage continues to increase, the density of injected electrons is approximately equal to the density of traps. At a sufficient high voltage, the last trap is filled and the current increase sharply. The current should directly switch to the trap free SCL conduction if there is only single or very few sets of traps in oxide. This threshold voltage is referred as trap filled voltage limited, V_{TFL} . V_{TFL} is

$$V_{TFL} = \frac{eN_t}{2\varepsilon_0\varepsilon} d^2 \tag{4-6}$$

The slope of the double logarithmic line in Fig. 4-3a) is calculated about 20. If traps are distributed within a relative wide range of trap level energies, the trap filled limited current will rise more gradually. One simple possible representation of the distribution of traps is exponential distribution.

$$N_t(E) = N_0 \exp\left(\frac{E - E_c}{kT_t}\right) = N_n \exp\left(\frac{E - F_0}{kT_t}\right)$$
(4-7)

where T_t is a temperature parameter characterizing the trap distribution. An I-V characteristic for the SCL conduction based on such an exponential trap distribution has been derived [13]

$$J = e\mu N_c \left(\frac{2l+1}{l+1}\right)^{l+1} \left[\frac{l\varepsilon\varepsilon_0}{(l+1)N_t}\right]^l \frac{v^{l+1}}{d^{2l+1}}$$
(4-8)

where $l=T_t/T$, T_t is larger than T. The power law relation is revealed in Eq. (4-8) and evident in some of our experimental data during SET and RESET processes.

D region: Trap-free space charge limited current. As all the traps are filled, SCL conduction current switches to the trap free trap filled SCL current described by

$$J = \frac{9}{8}\varepsilon_0 \varepsilon \mu V^2 / d^3 \tag{4-9}$$

The slope of double logarithmic line is 2.

Even though C and D regions in Fig. 4-3a) fit well with the SCLC model, the SCLC may not be able to be used to describe the memory transition behavior from HRS to LRS (the filament formation with the sharp TFL transition C region and the subsequent D region) because the SCL model is based on the bulk effect and the assumption that the charges are uniformly distributed within the insulator. Further investigation is needed. This study will be limited to the low voltage range of SET process before the transition from HRS to LRS occurs.

The space charge limited current is also clearly observed in a $Pt/Ti/Ta_2O_5/Pt$ device without annealing and a Cu/TaO_x/Pt device during SET operation for Vo CF formation, as shown in Fig. 4-4 a) and b).



Fig. 4-4. The SCL conduction model is used to explain I-V characteristics at low voltage ranges during SET operation. a) a Pt/Ti/Ta2O5/Pt device; b) a Cu/TaOx/Pt device.

Fig. 4-5 a) shows a typical RESET curve after the initial forming operation, while b) and C) display typical I-V RESET characteristics after the subsequent SET. It is clearly found that I-V RESET curve after the initial forming and before the sharp RESET occurs is very much linear (Icc=1mA and Ron is usually less than 500 Ω) as shown in Fig. 4-4a). However, it is generally not linear after subsequent SETs with a Icc of 1mA or less. Ron values is normally above 600ohm, as noted in Fig. 4-5 b) (Ron=708 Ω , Icc=1mA) and Fig.4-5 c) (Ron=3.6k Ω , Icc=50uA). When the Ron is about $3.6k\Omega$ shown in Fig. 4-4c), the current increases linearly with voltage from -0.3 to -0.3V and displays a function of $I \propto V^4$ at relatively high voltage from -0.3V to -0.5V and 0.3 to 0.5V. The lower Icc, the higher Ron and the higher I-V nonlinearity achieved, and the device resets more gradually. The increase of nonlinearity with Ron indicates that the electron conduction mechanisms might be different for different levels of Ron. In addition, the RESET operations usually display final sharp current drops as shown in Fig. 4-5 b) and 4-4 c), respectively at around -1.85V and -1.96V, and both the electrical conductance changes from conductance quantum G_0 to $0.5G_0$ ($G_0 = 2e^2/h$). In most of devices, before this final sharp RESET, the device behaves as a conductive filament with a conductance larger than G₀. It is also noted

that before this sharp drop, the I-V curves exhibit the power law relations. After the drop, the current/voltage has an exponential dependence on voltage.



Fig. 4-5. I-V characteristics of RESET operation. a) RESET after initial forming, Icc=1mA, Ron=189Ω;
b) RESET after a SET with a Icc of 1mA, Ron=708Ω; c) RESET after a SET with a Icc of 50uA,
Ron=3.6KΩ; The I-V curves are not linear when Ron is larger than 700Ω; d) Curve fitting of Fig. 2-19C from -0.5V to 0.5V window. I is roughly a function of V⁴.

The curve fitting of Fig. 4-5 b) obeys I $\propto V$ at low voltage region, and I $\propto V^{1.3}$ at higher voltage region. The curve fitting of the Fig.4-5 c) from -0.5V to 0.5V is given in Fig. 4-5d). The current has a linear relation with V from -0.3 to 0.3V and has about a function of V⁴ from 0.3V to 0.5V and from -0.5V to -0.3V. The power relation fits with the SCL conduction if assuming

that the trap in the oxide has a exponential distribution in the oxide, however, due to the bulk effect nature of SCLC, we are concerned if such a model can be used to describe the filament state of LRS. Further investigation is needed.

To further study the RESET process, transitions from the LRS to HRS is controlled by applying successive voltage sweepings with increasing stop voltage as shown in Fig. 4-6. The first, second and third RESET occur respectively by a voltage sweeping from 0 to -0.8V and from -0.8V back to 0, from 0 to -1.2V and from -1.2V back to 0, from 0 to -1.6V and from -1.6V back to 0. The Ron is increased from initial $1.65 \text{K}\Omega$ (7.8G_0 , measured at -0.1 V) to $6.83 \text{K}\Omega$ (1.89 G_0 measured at -0.1V) after the first RESET, and then to 12.9 K Ω (G₀ measured at -1.2V) and 24.4K Ω (0.52 G₀, measured at 0.1V) after the second RESET, indicating the quantum conductance can be achieved during the gradual rupture of the Vo filament. It is noted that once the I-V curve reaches G₀ in the conductance during the second RESET sweeping, no hysteresis can be observed in the subsequent reset. Through the curve fitting, all the three RESET curves have linear relationships with V at low voltage range. The curve fitting for the first RESET from 0.12 to 0.5V is $I=V^{1.3}$, for the second RESET from 0.15V to 0.8V is $I=V^{2.5}$. The third RESET curve is very nonlinear and displays exponential relation with V from 0.3 to 1.0V. The final reset totally ruptures the filament. Such a memory can be gradually turned off by consecutive voltage sweepings and would enable multiple level switching.



Fig. 4-6. Transition from LRS to HRS by applying successive voltage sweeping with increasing. The first RESET is conducted with a voltage sweeping from 0 to -0.8V and from -0.8V back to 0, the second RESET is conducted with a voltage sweeping from 0 to -1.2V and from -1.2V back to 0, the third RESET is conducted with a voltage sweeping from 0 to -1.6V and from -1.6V back to 0. The device can be gradually turned off by consecutive voltage sweepings.

4.2.2 Temperature Coefficients of Resistance

The temperature coefficients of R_{on} (TCR) are measured to verify the conductive filament in Pt/Ti/Ta₂O₅/Pt is Vo based CF instead of metallic filament. The TCRs are measured from 25 °C to 55 °C with different compliance currents applied during the SET operation, as shown in Fig. 4-7 a) and b). The typical temperature coefficient of resistance α is positive for a R_{on} (usually less than 700 Ω) if being set with a compliance current of 5mA (0.0006 K⁻¹), 10mA (0.00093 K⁻¹) or higher. However, a large negative value α is obtained when a compliance current of 1mA (-0.004 K⁻¹) or less is used, and Ron is usually larger than 700 Ω . The measured positive α is quite close to the reported data from Vo CF based Cu/Ta₂O₅/Pt ReRAM devices, 0.001 K⁻¹, but much less than that of metal Cu filament, 0.003 K⁻¹. It can serve as an identifier of Vo as the basic building block of the nanofilament. The positive α associated with small Ron implies the electron transport is based on metallic conduction, and hindered by electron collision within the conducting channels as temperature increases. It suggests that the oxygen vacancies in such a case are located very close to each other and forming multiple conducting channels with a high concentration of Vo in the filament. On the other hand, a negative α is often observed in semiconductors or insulators, where there are limited number of free carriers and the increase of temperature will result in the increase of free electrons and holes and then the conductivity. For a larger Ron associated with negative α situation, oxygen vacancies are located with a certain distance to each other and therefore of a relatively lower concentration in the formed conductive filament. The conduction is believed to be dominated by electron hopping through oxygen vacancies and between localized states (oxygen vacancies can be treated as defects and introduces localized states or defect levels within the bandgap of the oxide).



Fig. 4-7. a) temperature coefficients of R_{on} for Vo CFs formed at different Icc (1mA, 5mA and 10mA), Vo CF formed at 1mA has a negative temperature coefficient (-0.004 K⁻¹); b) Vo CFs formed at 5mA and 10mA display a positive temperature coefficients (about 0.001 K⁻¹).

4.2.3 Minimum Set Voltage

Fig. 4-8 a) shows the I–V characteristics of a $Pt/Ti/Ta_2O_5/Pt$ device cell in quasi-static switching at three different voltage sweep rates v, spanning almost two orders of magnitude. It can be seen

that the SET voltage decrease with decreasing ramp rate. Fig. 4-8 b) shows the SET voltage dependence on the voltage sweep rate v. As v varies from 1V/s to 16V/s, the SET voltage is almost proportional to the logarithmic of v. As v is less than 1V/s, the SET voltage stays more or less constant. A minimum SET voltage around 1.15V is reached when the sweep rate is small enough. This constitutes a significant departure from minimum SET voltage of 0.17V found for the Cu CFs, implying the formation of oxygen vacancy based CF in Pt/Ti/Ta₂O₅/Pt may require more energy than that of metal based CF in Cu/TaO_x/Pt devices.



Fig. 4-8. a) I-V characteristics of a 20um \times 20 m Pt/Ti/Ta₂O5/Pt resistive switching device. The voltage sweep rates v are 0.022V/s, 0.22 V/s and 2.2 V/s. The compliance current is 0.5mA; b) Dependence of SET voltage on voltage sweep rate. The horizontal dash line is the saturated SET voltage which is 1.15V. The inclined dash line is the fitting curve for the SET voltage at high sweep rates.

Fig.4-9 a) shows the SET operation of a Pt/Ti/Ta₂O₅/Pt device. It is noted that the subsequent Vset voltages is determined by the conductance at HRS level, which might be influenced by the ruptured filament gap formed by the previous RESET process. The higher OFF resistance or the lower OFF conductance, the high SET voltages required to set the device. It is also noted that OFF resistance in the Pt/Ti/Ta₂O₅/Pt device has much narrow distribution than in Cu/TaOx/Pt and Cu/Ta₂O₅/Pt devices. It would be due to the design of Vo concentration profiles in Pt/Ti/Ta₂O₅/Pt through the triple layer structure TiO_x/TaO_x/Ta₂O₅. The switching area is

confined in the Ta_2O_5 layer of lowest Vo concentration, resulting in reducing variations in V_{SET} , V_{RESET} , I_{RESET} , R_{OFF} and R_{ON} , and the overall power consumption and increasing the device reliability. To achieve further reduction in set and reset current, the conductivity of Vo reservoir layer such as TiO_x/TaO_x can be modified through the change of Ti thickness or replacing Ti with other active metals.



Fig. 4-9. a) I-V characteristics for SET operation of a Pt/Ti/Ta2O5/Pt device; b) the conductances at HRS level determines the gap distance, and thus the potential barrier height and the SET voltages.

4.3 Conclusions

A thin layer of Titanium is inserted into a Pt/ Ta₂O₅/Pt structure to form a Pt/Ti/Ta₂O₅/Pt device and a Vo CF based resistive memory is achieved with improved performance in terms of low power consumption and reliability. A carrier transport model based on SCL conduction is developed to explain the I-V characteristics of the SET process at low voltage range in MIM based resistive memories, suggesting that the trap properties at HRS can be studied through the SCL model. The performance of RRAMs can be improved through the modification of the interface introduced trap distribution and switching materials. It is also critical to design an asymmetry structure to achieve the reliable RESET behaviors.

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5 Composite Vo/Cu and Cu/Vo Nanofilaments in Cu/Ta₂O₅/Pt Devices

This chapter presents the evidence for existence of composite copper/oxygen vacancy nanofilaments. The composite conductive nanofilment (CF) is a serial resistive connection of Cu and Vo CFs forming a composite Vo/Cu CF where the Cu filament segment is formed first and Vo filament completes the composite CF. A composite CF has been also formed in reverse order as Cu/Vo. Both composite CFs, Vo/Cu and Cu/Vo, display V_{form} at considerable lower voltages than monolithic CFs with analogous switching characteristics.

5.1 Introduction

The current worldwide RRAM based research is mostly focused on the formation and rupture of monolithic metallic or oxygen vacancy conductive filaments (CF). However, both types face issues associated with device reliability [1,2]. The metallic nanofilament based RRAMs have relatively wide distributions in set/reset voltages and the ON/OFF resistances, thus leading to a difficulty in reliable programming of the memories. Oxygen vacancy CF based RRAMs require a much higher forming voltage (about -7Volts, compared to 3.5V for Cu CF based Cu/Ta₂O₅/Pt devices). The gas accumulation due to the electrochemical reaction may deform or even damage the cell, resulting in the overall device degradation [3].

Part of the study is to develop and demonstrate hybrid copper/oxygen vacancy-based RRAM for NVM applications. The innovative use of such hybrid Vo/Cu nanofilament will potentially overcome the problems for highly reliable operations: 1) the initial formation and rupture of Cu CF is used to reduce the forming voltages of devices. The rupture is anticipated to occur at the active metal/oxide interface with the formation of a small gap in the Cu CF. The device is then off; 2) the subsequent formation and rupture of oxygen vacancy CF by a negative bias is used for

set and reset operations to achieve narrower distributions in device parameters; 3) oxygen gas accumulation is largely decreased as the set and reset of Vo CF only occurs at the small gap area.

Switching of a resistive Cu/TaOx/Pt device can be based on the formation of two types of CFs in the same device: Cu or oxygen vacancy (Vo) filaments depending on the polarity of switching voltage [3]. The two types of conduction can be distinguished by different values of the temperature coefficient (α) of resistance defined as:

$$R(T) = RT_0[1 + \alpha(T - T_0)]$$
(5-1)

where T_0 is room temperature, and $R(T_0)$ is the resistance at T_0 . In this chapter, we present evidence for composite Cu and Vo single CF observed in Cu/Ta₂O₅/Pt devices with a Ta₂O₅ deposited by atomic layer deposition (ALD). The characterization of the temperature dependence of the filament resistance is an effective way of exploring the properties of the elusive nanofilaments [4,5,6,7,8,9]. We have characterized the Cu/TaOx/Pt cell structures with PVD oxygen deficient TaOx of 32, 16, and 8 nm thickness [10,11,12]. The comparison of electrical behavior between the PVD and ALD tantalum oxide cells is described elsewhere [13].The ALD tantalum oxides have been selected for this study as they give larger forming voltages for both Cu and Vo CFs with much tighter distribution than for the PVD tantalum oxide samples.

5.2 Observation of Composite Vo/Cu and Cu/Vo Nanofilaments

We define the forming voltage, V_{form} as the voltage at which a Cu or Vo bridge is being formed for the first time in a fresh device. First, we characterize V_{form} of Vo CF in two different circumstances. In each case, a fresh (unstressed) cell is being used. In our measurements the Pt electrode is grounded and the bias is applied to the Cu electrode.



Fig. 5-1. I–V characteristics of forming and resetting Vo-1 CF, Cu-1 CF, Vo-2 CF, and Cu-2 CF. (a) form and reset Vo-1 CF with unipolar switching; (b) form and reset Cu-1 CF with bipolar switching; (c) form and reset Vo-2 CF with bipolar and unipolar switching; (d) form and reset Cu-2 CF with unipolar and bipolar switching. In all four cases, voltages of negative polarities reset the devices.

In the first case of characterization (see Fig. 5-1a), a negative voltage sweep begins at 0. At $V_{form}(V_0-1) = -6.70$ V a forming operation is observed when the cell changes from high resistive state (HRS) to a low resistive state (LRS). Since under negative voltage the migration of Cu+ ions is suppressed, the LRS is attributed to the formation of a Vo CF in agreement with findings in Ref. 1. Fig. 5-1a shows also the subsequent unipolar rupturing of the Vo CF at $V_{reset}(V_0) = -1.27$ V. The temperature coefficient of the monolithic Vo CF in ALD Ta₂O₅ is $\alpha(Vo) = 0.0008-0.0018$ K⁻¹, i.e. a very similar value measured for Vo CF in PVD TaOx. [3] The rather wide range of $\alpha(Vo)$ coefficients indicates variation of Vo CFs perhaps due to different percolation path architecture of the Vo nanofilaments, see Ref. 7. In the second case of Vo

formation, a fresh cell is subjected first to a positive voltage sweep as shown in Fig. 5-1b: at $V_{form}(Cu-1) = 3.49$ V the cell enters the LRS state when a monolithic Cu CF is formed. The Cu bridge is subsequently reset in a bipolar mode at $V_{reset}(Cu) = -1.19$ V. The temperature coefficient of the monolithic Cu CF is α (Cu-Ta₂O₅(ALD)) = 0.0020 K⁻¹, which is slightly lower than α (Cu-TaO_x(PVD)) = 0.003 K⁻¹ measured in PVD TaO_x. [1] This may be attributed to much denser ALD Ta₂O₅ film compared with PVD TaO_x of the same thickness. Due to a larger amount of free volume in PVD TaO_x than in ALD Ta₂O₅, higher ionic concentration of Cu atoms can be achieved in PVD TaOx than in ALD Ta2O5. After the Cu CF has been ruptured, a negative voltage sweep is applied to the cell and a forming event in Fig. 5-1c is observed at $V_{\text{form}}(Vo-2) =$ -2.64 V. Since transition from HRS to LRS state occurs on the negative voltage axis we identify it with the formation of the Vo CF. In principle, at negative voltage a Cu⁺ ion could be extracted from the tip of the ruptured and would migrate toward the Cu electrode. Once Cu⁺ reaches the Cu electrode the neutralized Cu⁺ ion would dissolve in the Cu electrode and render a complete Cu bridge formation impossible. Thus the forming of a fully conductive CF must be attributed to other mechanism than Cu filament. The only known available mechanism is the assumption that the CF is completed by a formation of a partial Vo filament. One observes, however, a significant voltage difference for Vo CF formation for the two scenarios: $V_{form}(Vo) = V_{form}(Vo)$ 2)– $V_{form}(Vo-1) = 4.06 V$. Statistics of resulting $V_{form}(Vo-1)$ and $V_{form}(Vo-2)$ distributions are shown in Fig. 5-2. A clear separation of the two distributions of V_{form}(Vo) of more than 2.5 V is observed.



Fig. 5-2. Forming voltage distributions of monolithic and composite nanofilaments $V_{form}(Cu-1)$, $V_{form}(Cu-2)$, $V_{form}(V_O-1)$, and $V_{form}(V_O-2)$ in Cu/Ta₂O₅/Pt devices.

5.3 Hybrid Cu/Vo and Vo/Cu Nanofilament Model

The discrepancy between the two forming voltages shown in Fig. 5-2 can be explained with the model of a composite nanofilament shown in Fig. 5-3.



Fig. 5-3. Hybrid nanofilament model, four CFs are shown: a monolithic Vo CF associated in Fig. 5-1 and 5-2 with Vo-1 CF, a monolithic Cu CF associated in Fig. 5-1 and 5-2 with Cu-1 CF, a hybrid Vo/Cu CF associated in Fig. 5-1 and 5-2 with Vo-2, and a Cu/Vo CF associated in Fig. 5-1 and 5-2 with Cu-2 CF.

In the first case, a pure Vo CF is being formed across the entire thickness of Ta_2O_5 dielectric at a rather high electric field of 4.2 10^6 V/cm. In the 2nd case Vo CF is formed on the top of the remnant of the Cu bridge (3rd CF in Fig. 5-3). The Cu bridge pedestal is the result of

the rupturing of the monolithic conductive copper bridge (2nd CF in Fig. 5-3). According to Refs. [14,15,16] the rupturing of Cu CF leaves a major portion of the bridge intact. The rupturing creates a small gap in the CF near the Cu electrode interface. The Cu pedestal extends thus the voltage of the Pt electrode deep into the Ta_2O_5 dielectric, thus increasing the local electric field at the same applied voltage when compared with a device free of any Cu CF formation.

Assuming that the V_0 bridge formation occurs in both cases at about the same critical field, we can calculate the height of the partial Cu bridge to be 12 nm or larger as indicated in Fig. 5-3 from the difference of forming voltages. The width of the ruptured gap of Cu CF can be estimated to be smaller than 4 nm, since the localization of Cu CF formation is predetermined by advantageous material properties for the Cu CF formation but not necessarily advantageous for Vo CF formation. Although there is some controversy [17,18,19] about the dissolution of the metal CF at inert (here Pt) electrode instead of the active (here Cu) electrode, the above estimate is in agreement with currently discussed dissolution mechanisms, [13,14,20] independent of whether the rupture of the CF happens at the Cu or Pt electrode. From the preceding analysis we identify the Vo-1 CF with monolithic oxygen vacancy CF (1st CF in Fig. 5-3) and Vo-2 with composite Vo/Cu CF (3rd CF in Fig. 5-3). Similarly, the Cu-1 CF is identified with monolithic Cu CF (2nd CF in Fig. 5-3) while Cu-2 CF with a composite Cu/Vo CF (4th CF in Fig. 5-3).

In principle, the reduction of the forming voltage for Vo CF could be caused by the degradation of the dielectric material under high voltage stress due to the creation of high levels of defects. To quantify this effect, fresh samples have been used and subjected first to a high positive voltage stress up to a predetermined voltage 3.5 V. This voltage has been selected to be slightly higher than average forming voltage $V_{form}(Cu-1)$ see Fig. 5-2. Only those cells which didn't set (i.e. cells that remained in a high resistance state) have been used for a subsequent

forming process of Vo CF at negative bias and the respective V_{form}(Vo-stress) values have been monitored. The range of V_{form} (Vo-stress) is found to be between -5.6 V and -7.5 V and thus overlaps with the distribution of $V_{form}(Vo-1)$ and is well-spaced by 3V from the distribution of V_{form}(Vo-2). In one case, a fresh sample was stressed up to 4 V without forming Cu CF. The subsequent negative bias stress yielded formation of Vo CF at -6.43 V, clearly out of range for the $V_{form}(Vo-2)$ distribution and well within the $V_{form}(Vo-1)$ distribution. Hence, it can be concluded that even a stress at high positive voltage (leading in most cases to Cu CF formation) does not create sufficiently high levels of defects in Ta₂O₅ to reduce the forming voltage for Vo CF. Only when a Cu CF is formed and reset, a drastic reduction in formation voltage of Vo CF can be observed. One could expect that some larger shift of the V_{form}(Vo-stress) distribution should be observed, since during a high positive voltage stress up to 3.5 V some partial Cu bridges may come into being. The partial bridges extend the Pt electrode into the dielectric and thus should reduce the subsequent forming voltage V_{form}(Vo-stress) of vacancy oxygen bridge. The absence of such shift in our data can be explained by the formation dynamics of the Cu bridge which occurs very quickly when the voltage reaches the critical V_{form} . Since in this experiment the V_{form}(Cu) has been not reached, the partial Cu bridge remains very small and thus does not affect the formation of Vo CF.

As already mentioned, monolithic Vo and Cu CF nanofilaments can be distinguished by their respective temperature coefficient of resistance. For the composite Vo/Cu bridge described above, we measure α (Vo/Cu) $\approx 0.001 \text{ K}^{-1}$ which is close to the coefficient of Vo-CF values. The temperature coefficient α is measured in the temperature range 278 K–323 K. The lower temperature bound is dictated by moisture condensation on the sample on the probe station and the upper abound is dictated by the risk of altering/damaging a switching cell permanently. In Fig. 5-4 it can be seen that the temperature dependence of the pair Cu and Cu/Vo and the pair Vo and Vo/Cu are similar. This similarity between monolithic Cu and Vo and composite Cu/Vo or Vo/Cu CFs can be explained in terms of individual resistance of the two constituent bridges as shown in Fig. 5-3. The pedestal Cu bridge has a low resistance compared with the tip making contact with the active electrode. This follows from a geometrical approximation of the Cu bridge assumed here to have a truncated cone shape [22]. A simple calculation of the resistance of a cone is given:

$$R_{cone} = \rho h / (\pi ab) \tag{5-2}$$

where ρ is the resistivity, h denotes the height, a and b the radii at the top and the bottom of the cone, respectively shows that the major portion of the total Cu CF resistance can be attributed to the tiny tip of the cone as illustrated in the following example. Referring to Fig. 5-3, we assume for a monolithic Cu cone a bottom radius of $r_b = 8$ nm and top radius of $r_t = 0.5$ nm. This cone can be decomposed into two cones in series separated at the dashed line at 12 nm as shown in Fig. 5-3. The geometrical parameters for the bottom cone are h = 12 nm $r_b = 8$ nm, and $r_t = 2.375$ nm while for the top cone h = 4 nm $r_b = 2.375$ nm, and $r_t = 0.5$ nm. It can be calculated from the above cone resistance formula that 84.2% of the total resistance of the cone shaped CF resides in the small top cone of 4 nm height. Thus the dominant part of the resistance of the Vo/Cu composite CF resides in the VO partial CF. The effective α coefficient for two resistors of different materials (Cu and Vo) in series is given by:

$$\alpha_{eff} = \frac{R_{Cu}(T_0)\alpha_{Cu} + R_{Vo}(T_0)\alpha_{Vo}}{R_{Cu}(T_0) + R_{Vo}(T_0)}$$
(5-3)

where R_{Cu} and R_{Vo} are the on-resistances of Cu and Vo CF conical segments, α_{Cu} and α_{Vo} are the temperature coefficients of resistance of the partial Cu and V_O CFs respectively. From the above equation, it can be seen that the relative resistance of the partial bridges formed last largely

determines the effective coefficient α eff. For $R_{Cu}(To) << R_{Vo}(To)$ we obtain $\alpha_{eff}(Vo/Cu) \approx \alpha_{Vo}$. The measured value of $\alpha(Vo/Cu) \approx 0.001 \text{ K}^{-1}$ indicates indeed that the Vo partial bridge accounts for the bulk of the resistance of the composite V₀/Cu CF. Above considerations provide strong evidence that such a CF is a hybrid CF comprising a serial combination of Cu CF and Vo CF as depicted in Fig. 5-3.



Fig. 5-4. Temperature dependence of normalized on-state resistance of monolithic (Cu and Vo) and composite (Cu/Vo and Vo/Cu) nanofilaments.

An analogous experiment has been performed for the formation of Cu CF under two different scenarios analogous to the formation of Vo CF described above. In the first case a fresh sample was subjected to positive voltage sweep as shown in Fig. 5-1b with $V_{form}(Cu-1) = 3.49 \text{ V}$ for Cu CF. In the second case, a fresh sample has been subjected to a negative voltage sweep leading to Vo formation at $V_{form}(Vo) = -6.4 \text{ V}$ (Fig. 5-1a). The Vo CF was then ruptured in unipolar mode at $V_{reset}(Vo)=-1.27 \text{ V}$. Only then the cell was subjected for the first time to a subsequent positive voltage stress leading to formation of the Cu bridge at $V_{form}(Cu-2) = 0.79 \text{ V}$, as shown in Fig. 5-1d. A large difference of $V_{form}(Cu-1) = 3.49 \text{ V} - V_{form}(Cu-2) = 2.70 \text{ V}$ between the two forming voltages is observed. Statistical distribution of the two forming voltages for Cu CF is shown in Fig. 5-2. The centroids of the two distributions are separated by

more than 3 V. The composite Cu/Vo CF consists mostly of Vo with a low resistance value and of a small part of Cu CF with a high resistance value (4th CF in Fig. 5-3).

The temperature coefficient of resistance of this composite CF is $\alpha = 0.0025 \text{ K}^{-1}$ confirming the above assumption of a Vo/Cu composite CF. From critical field calculations the length of the Cu bridge appears to be 4 nm long, corresponding to the ruptured gap of the V₀ CF initially formed. In case of Cu/Vo CF where we start with monolithic Vo CF, the location of the rupturing of Vo CF is less evident than in the case of Cu CF but is assumed to take place at near the Pt electrode. Nanofilaments are difficult to observe directly, and the few reports [21,22] appear to confirm the cone shape of monolithic metallic nanofilaments. In principle, with the same methods one should to be able to observe the composite nature of the nanofilaments postulated here.

5.4 Characterization of Composite CF

In Fig. 5-5a repeated unipolar characteristics of Vo/Cu CF are shown. Since both reset and set operations occur at negative voltages the composite Vo/Cu CF is ruptured and formed by rupturing and reforming of the Vo segment. One can see that the set voltages vary between -2.49 and -3.3 V, whereas the reset voltages are tighter distributed and vary between -0.97 V and -1.3 V. Fig. 5-5b shows the switching characteristics for the Cu/Vo composite CF, whose rupturing and setting is achieved by the rupturing and setting of the Cu segment of the CF. The set voltages varies between 0.99 V to 2.33 V, whereas the reset voltages range from -0.63 to -0.94 V. It is noted that the LRS resistance of the Vo/Cu CF does not change as much as that of the Cu/Vo CF. The reason for the difference in Ron spread may be due to the fact that in case of Cu/Vo the Vo "pedestal" may consist of several incomplete percolation paths and the partial Cu CF connects from set to set operation with a different percolation branch resulting in a larger spread of R_{on}.

For comparison, the I-V characteristics of monolithic Vo and Cu CFs are measured. The set and reset voltages for monolithic Vo CFs are from -2.12 V to -4.87 V and from -0.99 V to -1.30 V, respectively. The set and reset voltages for monolithic Cu CFs are from 0.32 V to 0.82 V and from -0.16 V to -0.86 V, respectively. The set and reset voltages for Cu CF and Cu/Vo CF are much smaller than for Vo and Vo/Cu CFs.



Fig. 5-5. (a) Repeated unipolar switching characteristics for Vo/Cu CFs in a Cu/Ta₂O₅/Pt device; (b) Repeated bipolar switching characteristics for Cu/Vo CFs in a Cu/Ta₂O₅/Pt device.

5.5 Conclusions

Evidence for formation of a composite conductive nanofilament has been presented. The sequence and physics of rupturing and setting events with greatly reduced setting voltages argue for the existence of composite nanofilaments. The temperature analysis of the resistance of Cu, Vo/Cu, Vo, and Cu/Vo nanofilaments supports also the hypothesis of a hybrid nanofilament. The composite CF can occur in two manifestations Cu/Vo and Vo/Cu depending on which part of the composite bridge has been formed first and subsequently ruptured. The first formed CF when ruptured serves as a pedestal for the formation of the complementary part of the bridge. The resistance of the composite nanofilament is largely determined by the partial nanofilament

formed last which constitutes the weakest (high resistance) segment of the hybrid nanofilament. The composite CFs display greatly reduced forming voltages and have analogous switching characteristics to monolithic CFs. The use of hybrid Vo/Cu nanofilament will potentially enable low forming voltages with decreased in device deformation for reliable switching operations.

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6 Formation and Rupture of Multiple Conductive Filaments in a Cu/TaOx/Pt Device

Our recent research confirms that in a Cu/TaOx/Pt resistive device multiple Cu conductive nanofilaments can be formed and ruptured successively between the active Cu and inert Pt electrodes. This chapter describes the key parameters to repeatable multi-filaments switching cycles with the appropriate choice of compliance current window for individual nanofilament formation and the choice of bipolar and unipolar reset. Controlled formation and rupture of multiple filaments may enable multilevel storage capability in a single RRAMs memory cell if the repeatability issue can be successfully addressed.

6.1 Introduction

The Cu/TaOx/Pt resistive devices are typically set and reset by respectively applying positive and negative voltages to the Cu electrode while the Pt inert electrode is grounded. A single Cu conductive filament (CF) or nanobridge forms and ruptures during the set and reset operations. Most of the studies of resistive switches report on a single conductive CF formation. However, successive formation of multiple CFs is, in principle, possible, and would be advantageous for a multi-bit NVM storage cell. In the past, there were a few reports on multiple CF formation [1,2]. However, its mechanism and how to reliably control the formation and rupture of multiple CFs has been not thoroughly explored. Wu et al. reported on uncorrelated multiple conductive CF formation and rupture in NiSi/HfO₂-SiO₂/p⁺Si MIS structure [1]. The composite electrolyte HfO₂/SiO₂ is extremely thin with $25\text{\AA}/15\text{\AA}$. Despite the thinness of the electrolyte, the set voltages are rather high resulting in very high electrical fields of a 10^6 V/cm: the 1st set voltage is measured at 4.2V and the 2nd at 4.8V. The ratio of the current level jumps is over 4000 whereas for practical applications a ratio of ~1 is desirable. The reset voltages are

-1.3V and -1.7 V with current ratio larger than 100. Liu et al. report also a multiple CF formation in a different type device: Cu/ZrO₂:Cu/Pt [2]. The ZrO₂ electrolyte is 40 nm thick. ZrO₂ is deposited together with a thin Cu layer and a 600°C RTP anneal step is inserted causing Cu diffusion into the dielectric. The high doping of Cu in the CF electrolyte explains why 1st set voltage is observed at a very low value of 0.32 V followed by a series of small, discrete steps of current increase, which would be very difficult to sense. The 1st and 2nd reset voltages occur almost at the same value of -0.3V, precluding thus a targeted reset operation of an individual CF. Moreover, the I-V characteristics of these devices suffer from reproducibility problems which are a common challenge to all resistive switching devices. In this chapter, we present multiple CF formation and rupture in a single Cu/TaO_x/Pt device where current jumps for set and reset are of the same magnitude. This device is of interest since it uses materials already in use in CMOS manufacturing processes and offers potentially more reproducible I-V characteristics [3].

6.2 Observation of Multiple Cu Filament

The I-V characteristics are measured with Keithley 4200-SCS at room temperature. Fig. 6-1 shows the typical I-V characteristic of this device for the initial forming and reset operation. The device switches from the off state to on-state at about 4.07 V with the current jumping to the compliance current of 10µA, and then is reset at ~ -3.26V. Via these operations, the single conductive CF with relatively high Ron = 950Ω is repeatedly formed and ruptured.



Fig. 6-1. I-V characteristics of the device for the forming operation. The compliance current of 10µA is used for the set operation.

We have measured the temperature coefficient of resistivity α of Cu CF resistance given by $R_{on}(T) = R_{on}(0) [1 + \alpha(T-T_0)]$, where T_0 is room temperature, and $R_{on}(0)$ the resistance at T_0 . The measured temperature coefficient α is 0.0033 K⁻¹ from 0 to 20°C. This value for the CF is slightly lower than a coefficient of bulk Cu (0.0039 K⁻¹) and serves as an identifier of the Cu CF. An I-V characteristics of two-CF formation and rupture is shown in Figure 6-2b. After the initial forming and reset operation, the device is switched off. The voltage is then swept from 1 to 5V for the set and from -3V to -6V for the reset operation. Small 1 mV/step is used to resolve the multiple CF formation and rupture. The compliance current is set as 15 mA. It can be seen that the first current jump occurs at $V_{set-1} = 2.80V$ and is followed by ohmic current behavior characterized by a $R_{on-1}=760\Omega$. The ohmic resistive behavior indicates the 1st Cu CF is formed. Then at Vset-2 = 4.14V another sharp increase in current is observed followed by an ohmic behavior with a different slope of 447 Ω . The second jump in current is associated with the formation of the 2nd Cu CF with $R_{on-2} = 1085\Omega$. For the reset operation the voltage is swept then from -3V to -6V. The 1st CF is ruptured at -5.32V while the 2nd CF is still intact. From the remaining resistance measured at 780 Ω , the ruptured bridge can be clearly identified. The resistance of the ruptured bridge is $R_{on-1} = 780 \times 447/(780-447) = 1035\Omega$. Clearly, this is the resistance of the 2nd CF, R_{on-2} . The remaining unruptured CF must be therefore the 1st bridge to be formed in set operation; indeed the measured 780 Ω is very close to 760 Ω measured in the set operation. Thus the CF formed, as the 2nd CF, is the CF, which ruptures first during the reset operation. The remaining CF is ruptured at -5.61V. In Fig. 6-2b a set operation is shown at a reduced compliance current of $I_{cc} = 5mA$. Here, the 1st CF formation is observed at $V_{set-1} = 3.6 V$ and the 2nd CF formation at 4.0 V. Due to I_{cc} limitation, the second slope observed in Fig. 6-2b and characterized by a resistance of two bridges in parallel can be observed only during the back sweep to 0V.



Fig. 6-2. (a) The I-V characteristic indicates the two conductive CF formation and rupture. The voltage sweeping is first from 1V to 6 V and then from -3V to -6V with a sweeping step of 1mV/step. (b) The formation of the 2nd CF at a lower compliance current, 5 mA. The voltage sweeping is first from 0V to 5 V and back from 5V to 0V with a sweeping step of 10 mV/step.

In general, in order to form a 2nd CF, a large voltage drop over the 1st CF must be kept to maintain high electric field between the electrodes. This requires two conditions: 1) the Ron of the 1st CF has to be high enough (\geq 700 Ω) and this requires low compliance current during the set operation of the 1st CF, and 2) the compliance current used for formation of the 2nd CF has to be high. These two conditions combined provide high electrical field across the dielectric, to

ensure formation of the second bridge, while limiting the current to avoid damaging the device. The second condition requires the compliance current to be high (~5mA) for Ron-1 of about 1000 Ω . If the Ron_1 can be further increased, the compliance current level can be reduced. Under these circumstances the voltage drop, ΔV , even in presence of a 1st CF can be maximized (ΔV >3V).

6.3 Controlled Formation and Rupture of Multiple Cu Nanobridges

A promising approach for a controlled formation of two CFs consists in formation of 1st CF with high Ron-1 under a low compliance current of 10–100 μ A in a first voltage sweep, followed by a formation of the 2nd CF in a second independent voltage sweep. Such a sequential multi-CF formation is shown in Fig. 6-3a. The 1st CF with R_{on-1} = 1K Ω has been formed at V_{set-1} = 4.3V (not shown, similar to Fig. 6-2). During the second sweep 2nd CF is created at V_{set-2} = 3.3V with R_{on-2} = 625 Ω . During a back sweep a resistance of the two CFs in parallel can be extracted to be R_{par} = 375 Ω (Figure 6-3a).



Fig. 6-3. (a) Creation of the 2nd Cu CF at Vset-2 = 3.3V after the 1st CF has been already formed in a preceding voltage sweep. (b) The formation of two metal CFs and the rupture of the 2nd CF in unipolar mode.

A controlled rupturing of the two CFs can be accomplished by rupturing one of the two CFs in the unipolar mode and the other in a bipolar mode as shown in Fig. 6-3b. The sweep is

partitioned in following segments: a) voltage is first swept from 0 to 5V; b) the current jumps at 3.64V to 2.91mA to form the 1st CF; c) the current jumps at 3.92V to Icc = 5mA to form the 2nd CF; d) voltage continues to sweep to 5V; e) and f) voltage sweeps back from 5V to 0; g) voltage sweeps from 0V to 3V to reset the device with a higher compliance current; h) the 2nd CF is ruptured at 2.43V in unipolar mode and the current drops to nearly 2 mA, i) voltage continues to sweep to 3V; j) voltage sweeps back from 3V to 0V. Subsequently, a negative voltage sweep leads to the rupture of the 1st CF (not shown). Thus, the reset of both CFs has been decoupled at different voltages of 2.43 V (unipolar) and -4.80V (bipolar). The rupture of the 2nd CF in segment h) could be explained from the Joules heating argument. One obtains $R_{on-1} = 1037\Omega > 1000$ $R_{on-2} = 711\Omega$. The power in parallel CFs is obtained as P1~ $R_{on-2}^2 \times R_{on-1}/(R_{on-1}+R_{on-2})^2 \approx 172\Omega$ and $P_2 \sim R_{on-1}^2 \times R_{on-2}/(R_{on-1} + R_{on-2})2 \approx 250\Omega$. Thus, more joules heat is absorbed in the 2nd CF leading to its rupture first. However, this explanation does not hold for the rupturing of the CFs shown in Fig. 6-2a where the 2nd CF has a higher resistance than the 1st CF, $R_{on-1} = 760\Omega < R_{on-1}$ $_2 = 1085\Omega$. The reason that the CF formed second is always ruptured first, either in unipolar or bipolar operation, appears to be related to the detailed structure of the CF rather than the relative value of Ron. The critical element of a CF is the tip of the cone touching the Cu electrode. The tip of the CF formed second is less exposed to current and remains more fragile (higher local Ron-loc) than the tip of the Cu CF formed first at a lower voltage. Hence the CF formed second ruptures first. The device with I-V characteristics shown in Fig. 6-3b could be switched in some samples stably and repeatedly without sustaining any damage with very similar set and reset voltages. Other samples showed that there is a window for the creation of the 2nd bridge. The compliance current during the formation of the 2nd bridge must be high enough to produce sufficient voltage drop across the electrolyte, but it has to be kept to a minimum in order to keep

the 1st bridge weak enough to allow it to rupture during a reset operation. The retention of the two conductive states has been characterized at room temperature. After 1st CF and 2nd CF have been established a read voltage of 0.01 V is used to measure R_{on-1} and $Rpar = R_{on-2} \times R_{on-1} / (R_{on-1} + R_{on-2})$, the resistance of the two bridges in parallel. Fig. 6-4 shows very uniform R_{on-1} , R_{par} and R_{off} distributions with retention time up to 105 s. Here $R_{on-1} = 780\Omega$, while $R_{par} = 403\Omega$, resulting in $R_{on-2} = 845\Omega$.



Fig. 6-4. Retention property of 1st CF and both CFs along with the no CF state.

The unipolar and bipolar transitions in the conductance state have been reported in several papers, both for Cu resistive as well as for binary oxide resistive memory [4,5,6]. Unipolar switching of Cu CF has been demonstrated on our device [7] and shows similar behavior as the published data. Both positive and negative sweeps can reset the devices from low to high resistance state. The consensus is that the reset process is attributed mainly to Joule heating and hence it's largely independent of the voltage polarity.

Our resistive switches, when stressed at high negative voltage V_{ap} , displayed in some cases switching behavior that cannot be attributed to Cu⁺ ion migration, since under this bias Cu+ ion migration is suppressed, but to oxygen vacancies V₀ left behind by migrating O²⁻ ions [7,8]. The resistive switching under negative bias voltage, attributed to the migration of oxygen

ions, can be explained by percolation models [8,9]. R_{on} of this type switching is the same for 10µm and 25 µm devices, which means the switching is localized and CF-based. The measured Ron temperature coefficients are $\alpha = 0.0013$ K⁻¹, i.e almost three times lower than the temperature resistivity coefficient for Cu nano-filament, clearly indicating a different conduction mechanism. Ron of the both Cu CF shown in Fig. 6-2 and found that both CFs are characterized by $\alpha = 0.0033$ K⁻¹, excluding the possibility that one or both of the nanofilaments could be Vo CFs, and underscoring that the two CFs formed sequentially must be Cu CFs. The present device offers a potential for reproducibility of the formation of two CFs. The solid electrolyte could be replaced by a bilayer of two different electrolytes, e.g. TaSiO/TaO with different Cu diffusivities offering improved stability and performance [10]. The distribution of the set voltages could be tightened by providing a local Cu pile up in the dielectric provided by a local targeted Cu implantation [11]. Once the V_{set} for the 1st CF is stabilized, our data indicate that V_{set} for the 2nd CF.

6.4 Conclusions

In conclusion, the Cu/TaOx/Pt resistive devices display multiple conductive CF formation and rupture at discrete well-separated voltage levels. Analysis of the forming and rupturing operation clearly indicates that the CF that has been formed second (at a higher V_{set}) is first to rupture (lower $V_{reset-1}$) during the reset operation. The CFs can be formed and ruptured in a single sweep or sequentially. The rupture of the 1st and 2nd CF can be decoupled at opposite polarity voltage intervals, ensuring integrity of the multibit reset operation. Both CFs have been identified as Cu CFs by their temperature resistivity coefficients that is close to the respective coefficient for bulk Cu. Control of individual set and reset operations may pave the way for a deployment of a multi-filament cell for multibit NVM RAM.

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7 Operation of a Floating-Electrode Memristive Device

During this study, we have investigated and demonstrated a structure comprising two single memory switches formed back-to-back such that the single inert electrode can be allowed to electrically float - referred to as a resistive floating electrode device (RFED). Specifically, a resistive device with a floating electrode is manufactured as a stack of layers Cu/TaO_x/Pt/TaO_x/Cu in a crossbar array comprising two single resistive switches antiserially merged at the common inert floating electrode. The device exhibits four states, namely, HRS/HRS, HRS/LRS, LRS/HRS, and LRS/LRS, where HRS and LRS are the high- and low-resistance states of a single switch. During transitions between the states, the lifetime of the LRS/LRS state can be rendered very short. This property lends itself to generation of current/voltage pulses that can be controlled by three independent technology parameters.

7.1 Introduction

Solid electrolyte materials using ionic transport between an oxidizable anode and inert cathode are among the most promising candidates to replace the conventional floating-gate device based non-volatile memory beyond the 11 nm technology node [1]. A single Cu/TaO_x/Pt switch relies on electrochemical deposition and rupture of a conductive filament (CF) of the active Cu electrode [2]. There exists a minimum V_{set} voltage applied across the switch at which a CF is being formed. When the voltage applied to the Cu electrode is swept to a positive voltage, the current will remain substantially zero until a critical voltage V_{set} is reached; at which a conductive Cu nanofilament is formed connecting the Cu and Pt electrodes. When the CF is established, the cell switches abruptly from a high resistive state (HRS) characterized by R_{off} (1-900 MΩ) to a low resistive state (LRS) characterized by R_{on} (70-6000Ω), yielding R_{off}/R_{on}≈10³-10⁷. As the voltage becomes negative, at some voltage bias, V_{reset}, the nanofilament will rupture,

and the cell reverts from LRS state to non-conductive HRS state. The rupture of the CF triggered by a critical current I_{reset}=V_{reset}/R_{on} is believed to be caused by the Joules heating effect [3,4]. In principle, under high negative bias conductive oxygen vacancy (V₀) CF may also be observed [5]. However, the corresponding set voltages are of opposite polarity and the set voltages for the V₀ CF are much larger than for the Cu CF $|V_{set}(V_0)>2\times|V_{set}(Cu)|$ [5]. The range of forming voltages at which oxygen vacancy CFs are formed is between -6 V and -8 V[5]. This voltage regime is never entered in this work. The absence of V₀ CFs is further corroborated by our findings that Cu and V₀ CFs have different thermal coefficients of resistance [6]. The temperature resistance coefficient (α) of the Cu CF is 0.0033 K⁻¹, which is close to $\alpha_{Cu(bulk)}=0.0039$ K⁻¹of bulk Cu. The coefficient for V₀ CF is $\alpha_{V_0}=0.0013$ K⁻¹. Moreover, it has been observed [7] that V₀ CF formation is accompanied by a bubble formation in large area cells, which is never observed under voltage conditions used in this work.

7.2 **RFED** Structures

A structure comprising two single switches formed back to back such that the single inert electrode that can be allowed to electrically float is referred to as a resistive floating-electrode device, or RFED. An RFED comprises two single individual Pt/TaOx/Cu switches merged at the common inert Pt electrode, as shown in Fig. 7-1(a). The process and electrical characterization of Cu/TaOx/Pt devices have been reported in the previous chapter and detail elsewhere [6, 8]. Fig. 1(a) shows the compact integration of the RFED, whereas Fig. 7-1(b) shows an electrically equivalent RFED as an antiserial circuit of two single independent resistive switches manufactured in independent crossbar arrays and connected by flying probes on the probe station.



Fig. 7-1. Illustration of an RFED constructed from two single resistive switches A and B (a) as an integrated device and (b) as an antiserial connection of two independent switches. (c) Programming of a conductive state in an RFED.

7.3 **RFED** Switching and Characteristics

The concept of the operation of the RFED device is explained in Fig. 7-1(c) showing a graphical plot of voltage applied to RFED and the resulting current there through. Before any bias voltage is applied to the RFED, no CF is formed and the HRS/HRS state of the RFED is as depicted by circle 1. As a positive bias is applied, at a threshold $V_{th-on(A)}$, a 1st bridge will be formed in the resistive switch A of the RFED. However, since the CF is formed in only one of the switches (circle 2), the RFED remains in a non-conductive state and the current is substantially zero even at positive bias voltages considerably greater than the threshold voltage

 $V_{\text{th-on}(A)}$. When the bias voltage is then swept to a negative voltage and a threshold $V_{\text{th-on}(B)}$ is reached, a bridge is formed in the other switch B (circle 3) and the RFED becomes conductive. The 1st CF formed at threshold V_{th-on(A)} remains in place as long as its reset current value is not exceeded. If the bias voltage is swept further, V_{th-off(A)}, is reached and the 1st CF is ruptured (circle 4) and RFED becomes non-conductive. Once RFED is in ON state, either bridge can be selectively ruptured. Inspection of Fig. 7-1(c) reveals that when V_{th-on(B)} and V_{th-off(A)} converge to a similar value, the ON state of the RFED can be maintained only in a very narrow voltage interval, i.e. the ON state will be destroyed as soon as it has been created. In order to enable a voltage window for the ON state, the $V_{\text{th-on}(B)}$ has to be smaller than the voltage $V_{\text{th-off}(A)}$. The measured characteristics of the RFED device are shown in Fig. 7-2(a). Here, voltage has been swept first on the negative voltage axis and the 1st CF in switch A has been established (not shown). During the subsequent positive voltage sweep, the 2^{nd} CF in TaO_x electrolyte is established at V_{th-on(A)}=0.9V but is followed by the rupture of the 1st CF because of excessive I_{reset} through switch A. Thus, there is a small time lag between the formation of the 2nd CF in switch B and rupture of the 1st CF in switch A, by the mere fact that the formation of the 2nd CF is an ineluctable precondition for the rupture of the 1st CF. From the foregoing it is evident that RFED is in ON state only when the two individual switches have different and non-symmetric I-V hysteresis characteristics. The lack of operating window could be remedied by an appropriate choice of suitable electrolyte material for switch A and switch B, resulting in sufficiently asymmetric behavior of the individual switches. However, the costly and cumbersome material solution can be circumvented by a simpler and flexible solution of application of compliance current. The problem of a vanishing voltage window for the ON state of RFED is solved by the use of a compliance current constraint as demonstrated in Fig. 7-2(b). Here, under I_{cc} constraint of 15 mA both bridges can be connected and maintained for considerable time over a voltage interval of $\Delta V=2.8-2.1=0.7V$. For smaller compliance currents the conductive state window widens and becomes infinite at about I_{cc}=4mA. Clearly, an I_{cc} constraint can effectively decouple the V_{set} for the 2nd CF from the V_{reset} of the 1st CF. Thus dialing of a specific value of the I_{cc} can effectively decouple between V_{th-on(B)} and V_{th-off(A)}. By virtue of this decoupling effect, a new programming and erase operation of a memory cell based on the RFED device can be designed based on an appropriate choice of I_{cc}.



Fig. 7-2. Measured I-V characteristics of RFED device. a) CF in switch B is formed first at a negative bias. Next, 2^{nd} CF is formed in switch A at a positive voltage 0.9V. Rupture of the 1^{st} bridge follows the formation of the 2^{nd} CF. No I_{cc} is imposed. b) I_{cc} of 15 mA has been imposed. After the bridge has been formed in the switch A at positive voltage the 2^{nd} bridge in switch B is formed at V_{th-on(B)}=-2.1 V. The formation of the 2^{nd} bridge is followed by the rupture of the 1^{st} bridge at V_{th-of(A)}=-2.8 V.

7.4 Pulse Generation Control

As shown in Fig. 7-3(a), the ON-state may be destroyed as soon as it has been created. The instability of the LRS/LRS state is a desired condition for generation of a pulse. A circuit of two independent switches shown in Fig. 7-1(b) is now exclusively used to investigate the generation of a pulse. The dependence of the *R*on of a single resistive switch on the compliance current during the set operation is crucial here. *R*on strongly decreases with increasing compliance current [9,10].

Using the RFED circuit [see Fig. 7-1(b)], one of the resistive switches (B) can now be preprogrammed to a conductive state with a specific Ron value while switch A is off. Then, the two individual devices are antiserially connected. Fig. 7-3(a) shows the I-V characteristics of the antiserial arrangement of both switches subjected to a negative voltage sweep without a compliance current limitation. Here, $R_{on(B)}$ is 202 Ω under $Icc = 100 \ \mu$ A. A sharp pulse at -2.92 V can be observed. The pulse height is 3.7 mA, and the time width is 40 ms. After the two switches have been disconnected, it was found that switch B is off and switch A is on. At -2.92V, the bridge in switch A is formed, rendering the RFED conductive. In an independent experiment, switch A has been preprogrammed with $R_{on(A)} = 630 \ \Omega$ under $I_{cc} = 20 \ \mu$ A. In the resulting RFED characteristics [see Fig. 7-3(b)], a short pulse at 1.72 V is observed. The pulse height is 1.7 mA, and the time width of the pulse is 10 ms. Thus, the pulsewidth could be quadrupled with a three-fold reduction in Ron. With the widening of the pulse, the pulse height is increased by, roughly, a factor of 2. The Icc may be imposed also on the RFED configuration, limiting the surge of current through the fully conductive RFED circuit. Therefore, the rupture of the connected CF in switch B will be delayed. It will take more time at a reduced current level to generate enough Joule heat to rupture the CF.

Three technology parameters have been identified for the control of the pulse height and pulse width. The first parameter is the *R*on of the switch that has been preprogrammed into a conductive state, as already demonstrated in Fig. 7-3(a) and (b). The lower is the *R*on of the first CF, the lower is the overall series resistance of the RFED, and the higher is the *I*reset for both single switches, and hence, the higher is the current pulse observed in Fig. 7-3(a) and (b). The second parameter controlling the pulse is the voltage sweep rate applied to an RFED



Fig. 7-3. Measured RFED pulses (insets show the pulses on an expanded voltage scale). a) and b) no I_{cc} limitation, voltage sweep 1V/s with 0.01V/step. a) R_{on} (B)=202Ω; pulse height p_H=3.7 mA, the pulse width p_W=40ms, the onset of the pulse V_{on}=-2.9V; b) R_{on} (A)=630 Ω; p_H=1.7mA, p_W=10ms,V_{on}=1.7V. c) and d) Pulses for two different sweep rates v_R: c) v_R=1V/s: p_H=9mA, p_W=20ms,V_{on}=3.4V; d) v_R=0.25V/s, p_H=4.4mA, p_W=3.5s, V_{on}=1.6V. e) and f) Pulses for two different compliance currents: e) I_{cc}=15 mA: p_H=6.6mA, p_W=40ms, V_{on}=4.9V; f) Icc=2mA: pH=2.0mA p_W=50ms, V_{on}=2.6V.

configuration. With increasing voltage ramp rate, the pulse height should increase and the pulse width should decrease. When the voltage ramp rate increases, the thermal stress caused by Joule heating [3, 4] integrated over time is smaller at the same current level. Hence, the reset will be retarded, and a higher current is needed to rupture the CF. These qualitative predictions are confirmed by pulses shown in Fig. 7-3(c) and (d). For a sweep rate of 1 V/s, we obtain a pulse height of 5.9 mA and a pulse width of 20 ms. With a sweep rate of 0.25 V/s, one obtains a pulse height of 4.4 mA and a pulse width of 3.5 s. Thus, a four-fold decrease in sweep rate results in a 175-fold increase in pulse width. The third parameter is the compliance current *I*cc applied to the RFED. A lower I_{cc} will lower the pulse height and increase the pulsewidth to reach the critical thermal stress required for reset. At a sufficiently low *I*cc, the width of the pulse will become

infinite when the current drops below the I_{reset} . In Fig. 7-3(e) and (f), a comparison between two cases of pulse generation is shown for no *I*cc constraint and $I_{cc} = 2$ mA, respectively. In case of no I_{cc} limitation, the pulse height is 6.6 mA, the pulse width is 40 ms, and the onset of the pulse $V_{on} = 4.9$ V; for $I_{cc} = 2$ mA, the pulse height is 2.0 mA (= I_{cc} by default), the pulse width is 50 ms, and $V_{on} = 2.6$ V. Thus, with decreasing I_{cc} constraint, the height of the pulse decreases, whereas the pulse width increases. At I_{cc} of about 0.5 mA, the pulse width becomes infinite, as the CF can no longer be ruptured.

7.5 Conclusions

Highly nonlinear dynamics arises from novel serially and antiserially connected resistive switches with a common inert electrode. The RFED can generate well-controlled pulses as a result of the dynamic input of the voltage waveform. The I–V characteristic of a pulse is stable and repeatable. It lends itself as a device with an inherent integrate-and-fire capability [11] and is, for example, able to realize electronic version of transfer functions of a biological spiking synapse [12]. Although realizations based on complex CMOS circuits have been conceived [12], the RFED offers an extremely compact realization requiring a single crossbar array intersection resulting in a single, via occupying $4F^2$, area (F being the minimum feature size). The height and the width of the pulse can be fashioned by virtue of three technology parameters, namely, the Ron of the preprogrammed single switch, the voltage sweep rate, and the compliance current applied to the RFED configuration. An imposition of an appropriate compliance current constraint allows engineering the voltage window sustaining the ON-state, as well as to decouple the negative voltage I–V hysteresis from the positive I–V hysteresis, which is of interest for a memory cell operation based on an RFED. Other interesting RFED properties are being explored by replacing one or both of the individual switches by a volatile switching device [10].

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8 Observation of Quantum and Partial Quantized Conductance in Polymer-suspended Graphene Nanoplatelets

Near the end of the study, quantized conductance is observed at room temperature in metal-insulator-metal structures with graphene submicron-sized nanoplatelets embedded in a 3-hexylthiophene (P3HT) polymer layer. In devices with medium concentration of graphene platelets, integer multiples of conductance $G_0=2e^2/h(=12.9 \text{ k}\Omega)^{-1}$ are observed. In some devices partial quantized conductance steps are observed, including a series with (n/7)×G₀ steps. As an organic memory, the device exhibits reliable memory operation with an ON/OFF ratio of more than 10. In absence of magnetic Landau levels, we attribute the quantized conduction to the existence of a 1D electron waveguide along the conductive path. The partial quantum conductance results likely from non-unity transmission coefficients of the first waveguide modes.

8.1 Introduction

Graphene [1] has attracted much attention owing to its extraordinary properties such as quantum electronic transport [2,3], a tunable band gap [4], extremely high mobility [5], and high elasticity modulus [6]. One of the most promising characteristics of graphene is the ability of charge carriers to travel through it ballistically over hundreds of nanometers. Recent developments in the preparation of high-mobility graphene [7,8] made it possible to study the effects of quantum confinement in graphene nanostructures. Tombros et al [9] observed quantized conductance at integer multiples of $G_o = 2e^2/h$ (here e is the elementary charge and h Planck's constant; $G_o = 77.5\mu$ S) at zero magnetic field in a suspended graphene nanoconstriction at a temperature of 4.2 K. The observed quantized conductance was attributed to the graphene zigzag or armchair edges that provide effective boundary conditions for the quantum mechanical wave functions. In 1998, Frank et al [10,11] observed conductance of multiwalled carbon nanotubes (sheets of graphene rolled up into cylinders) to be quantized at room temperature. The experiments were performed using multiwalled carbon nanotubes attached to the tip of a scanning probe microscope which is gradually lowered into a liquid mercury contact. The conductances measured in the experiment are consistent with G_o conductance per nanotube. Calculations by Sanvito et al [12] have shown that interwall interactions between adjacent nanotubes not only block some of the quantum conductance channels, but also redistribute the current nonuniformly over an individual tube and modify the density of states near the Fermi level, giving rise to integer and non-integer conductance values. Observations of integer and fractional quantum Hall effects in graphene systems reported [13,14] are not further discussed in the context, as they presuppose existence of Landau levels that can be ruled out in our case of absent magnetic field. Nevertheless, irrespective of its origin, an extension of quantized conductance to ambient temperature conditions in the absence of a magnetic field is highly desirable and would provide added freedom, on the one hand to investigate finer features of quantized conductance, and on the other to develop graphene-based applications of superior novel quantum devices and memory cells.

Here, we present the experimental observation of integer and partial quantized conductances at room temperature and in zero magnetic field in metal-insulator-metal (MIM) structures with graphene nanoplatelet (GNP) ribbons suspended in a 3-hexylthiophene polymer (P3HT) layer interposed between metal (Cu and Au) electrodes. By integer or partial quantized conductance we mean that the 2-contact conductance of the device shows transitions in integer units of G_0 or repeatable fractions of G_0 , respectively, as function of applied voltage.
8.2 Device Fabrication

Our graphene-based MIM devices have been fabricated on a thermally-oxidized silicon wafer using standard semiconductor processes. The thermally oxidized silicon wafer was first cleaned using acetone and subsequently rinsed in isopropanol and deionized water. The wafer was then patterned photolithographically and deposited with a bottom gold (Au) electrode using electron-beam physical vapor deposition (EBPVD). The graphene nanoplatelet (GNP) powder provided by PPG Industries [15] was first dispersed into the toluene and further exfoliated for one hour by ultrasonication. Poly(3-hexylthiophene) (P3HT) was subsequently dissolved into the GNP solution and ultrasonicated for another hour. According to the manufacturer of GNP [16,17], GNPs comprise one or more layers of one-atom-thick planar sheets of sp²-bonded carbon atoms densely packed in a honeycomb crystal lattice. The number of stacked layers is typically between 5-30. The lateral dimension of the flakes ranges between 100 nm and a few mm. The graphene platelet ribbons are substantially flat, but when made thin by exfoliation they can be curved, curled or buckled indicating a single flake or a stack of a few carbon sheets [16, 17]. Ultrasonication has been found to be a very effective method in overcoming the van der Waals forces between the individual carbon sheets leading to uniform dispersions of single flakes or very thin stacks of flakes. The resulting P3HT(GNP) dispersion was then dropdeposited onto the bottom metal Au electrode and covered by islands of copper (Cu) electrodes also using EBPVD deposition to form Au/P3HT(GNP)/Cu devices. The thickness uniformity of the P3HT(GNP) film is +/- 50 nm. Spin coating of the dispersion has been tried but resulted in poor adhesion to the subjacent Au electrode. The graphene concentrations in the P3HT(GNP) solutions vary from 0.05mg/ml to 0.2mg/ml. The devices have an area of (2/3) mm x (2/3) mm. The thicknesses of the layers are 60 nm, 700 nm, 150 nm, for gold, P3HT(GNP), and copper,

respectively. The P3HT(GNP) layer is thick enough to accommodate non-horizontally positioned GNP ribbons.



Fig. 8-1. a) Schematic of the graphene based organic memory device; b) SEM image of the graphene nanoplatelets suspended in an organic solvent and deposited on a silicon wafer.

The schematic of the graphene-based MIM structure is shown in Fig. 8-1(a). Fig. 8-1(b) shows a scanning electron microscopy (SEM) image of GNPs dispersed in an organic solvent and deposited on a silicon wafer after ultrasonication. Dispersion of graphitic nanoparticles in polymers is an active field of research aiming at the development of promising new materials [18,19,20]. Our SEM images confirm that after ultrasonication GNPs appear thinner and flake-like. It is however, difficult to ascertain analytically whether the exfoliated GNPs consist of one or a few graphene layers. Nevertheless, the frequently observed warping points to very thin ribbon stacks consisting of very few and possibly one graphene layer. SEM cross-sections did not provide any further evidence as single layers and thin stacks of graphene could not be distinguished. For each concentration, ten devices with the same structure and the same active area were fabricated. For comparison and assessment of the role of graphene nanoplatelets, six Au/P3HT/Cu structures have been fabricated with no graphene nanoplatelets.

8.3 Device Characterization and Results Discussion

Four types of samples have been fabricated with regard to GNP content in the polymer: i) no GNP, ii) 0.05 mg/ml, iii) 0.1 mg/ml, and iv) 0.2 mg/ml of GNP concentration. All of the devices without GNP display no integer, nor partial quantum conductance effects as shown in Fig. 8-2. From these four types of devices, only devices with 0.1 mg/ml show integer and partial quantized conductance as shown in Figs. 8-3. In general, roughly 25% of the 0.1 mg/ml devices



Fig. 8-2. I-V characteristic of Au/P3HT/Cu cell with no GNP doping.

exhibit integer quantized conductance, 25% partial quantized conductance, and remaining 50% no quantized conductance. Figure 8-3 (a) shows typical current-voltage (I-V) characteristics. Starting at zero voltage, the voltage is first swept at a fixed ramp rate $\upsilon=0.225$ V/s (V(t)= $\upsilon\times$ t) from 0 V to +2 V (polarity according to Fig. 8-1 (a)). The current is observed to increase gradually and ohmically in the low-voltage region, and then abruptly increase at three voltages, specifically at 0.72 V to 10 μ A, at 1.22 V to 162 μ A and at 1.87 V to 409 μ A. The initially high-resistance state (HRS) of R_{off} \approx 100 k Ω is reduced during the voltage sweep to a final low-

resistance state (LRS), of $R_{on} \approx 5 \text{ k}\Omega$. When the voltage is swept back from +2 V to 0 V, a clear hysteresis in the I-V characteristics is observed. This hysteresis effect lends itself to memory applications [21].



Fig. 8-3. a) I-V characteristics of an Au/GNP/P3HT/Cu device (GNP concentration: 0.1mg/ml); b) Conductance as functions of the voltage.

Fig.8-3 (b) shows the conductance as a function of voltage for the same device. It can be clearly seen that the conductance is stepwise quantized approximately in multiples of G_0 . Rather than displaying flat plateaus quantized at specific conductance values as function of voltage, the samples display a slope in conductance *vs* voltage. To characterize the slope between conductance transitions in terms of energy, we have calculated the energy dissipated between the discrete conductance transitions. For the first sloped step (between $V_1 = 0.72$ V and $V_2 = 1.22$ V) we obtain it using the linear voltage ramp v:

$$E_{step}(1) = \int_{t_1}^{t_2} I(t) \cdot V(t) dt \approx \int_{V_1}^{V_2} (G_0 / \nu) \cdot V^2 dV = \frac{G_0}{3\nu} (V_2^3 - V_1^3)$$
(8-1)

Using the data from Fig. 8-3(b) we obtain $E_{step}(1) = 1.03 \times 10^{15}$ eV. This dissipated energy corresponds to approximately 900 meV per electron, much higher than $k_BT \approx 26$ meV, and thus

thermal effects can be ruled out for being responsible for the sloped conduction. Explanations for the slope are offered later in the chapter, in the context of quantized conductance. In Fig. 8-4 subsequent data is shown for the same device after it has been returned to the HRS state at 0 V. The voltage is ramped again from 0 V to +2 V and then back to 0 V. The new set of I-V characteristics also display quantized conduction steps but in this case the conductance step height is $\frac{1}{2}$ G₀ instead of approximately G₀ as in Fig. 8-3(b). Fig. 8-3 and 8-4 show typical behavior of the devices, where the I-V characteristics will not reproduce exactly, but always display a similar pattern of discrete steps in conductance. In Fig. 8-5 another instance of quantized conductance is presented, where integer q and partial quantized conductance transitions coexist, obtained on a different device yet fabricated at the same GNP concentration of 0.1 mg/ml. Upon a voltage sweep from 0 V to +2 V and then back from +2 V to 0 V, this device shows a similar hysteresis as present in the I-V characteristic in Fig. 8-3 (a).



Fig. 8-4. a) I-V characteristics for the same device as in Fig. 8-2 for a subsequent data set; b) Conductance as a function of the voltage.

Fig. 8-5 (b) shows the details of the conductance transitions, as extracted from the I-V characteristic in Fig. 8-5 (a) near V=1.3 V...1.45 V. It can be seen that the conductance changes

in a quantized step of G_o from low conductance to 1 G_o , from 1 G_o to 2 G_o and from 2 G_o to 3 G_o . A sequence of smaller conductance steps below 1 G_o is also observed indicating that the partial quantized conductance coexists with integer quantized conductance. The best fit to the partial quantized conductance transitions below 1 G_o can be obtained by assuming fractions of 1/7, 2/7, 3/7, 4/7, 5/7, and 6/7 G_o , although 3/7 is slightly off the experimental value. Between 1 G_o and 2 G_o , partial conductance transitions are also apparent, albeit less pronounced. These partial



Fig. 8-5. a) I-V characteristics of an Au/GNP/P3HT/Cu device (GNP concentration: 0.1mg/ml); b) Conductance as functions of the voltage; c) reset operation of the same device.

conductance transitions closely follow the same multiples of 1/7, as transitions with 8/7, 9/7, 11/7, and 13/7 G_o can be clearly identified. In the integer conductance transition, from 2 G_o to 3 G_o , only a rudimentary partial quantized conductance can be discerned. The behavior shown in Fig. 8-5 (b) has been observed for several devices and can be repeated on the same device with a slightly changed pattern and length of the steps. Fig. 8-5 (c) shows a typical RESET operation. The current follow roughly Ohm's law with an on-state resistance of 8.9K Ω , and rupture abruptly at the reset voltage, -0.7V.

As we consider Au/P3HT/Cu cells for potential memory applications, we have performed the "set" operation (from the HRS to the LRS state) under imposition of a compliance current (I_{cc}), which is commonly used in ReRAM memory cells less the device be damaged. I_{cc} is the maximum current that is allowed to flow through the device. In resistive RAM devices the I_{cc} limitation has no impact on the threshold voltage V_{set} at which the device transitions abruptly from the HRS to the LRS state, but it determines the resistance R_{on} of LRS state of metallic filaments according to R_{on} = *const*/I_{cc} [22]. In Fig. 8-6 a wide hysteresis curve of the I-V characteristic for I_{cc} = 0.1 mA is shown, where it can be seen that V_{set} = 1.5 V. Discrete quantized conductance transitions can be observed at 1.32 V, 1.46 V, and 1.48 V. The step heights are 0.22Go, 0.37Go, and 0.19Go, respectively.



Fig. 8-6. I-V characteristics of the Au/P3HT(GNP)/Cu cell with 0.1 mg/ml GNP: a) set operation with compliance current Icc-0.1mA imposed; b) observation of fractal quantum conductivity at 1.4V extracted from Fig. 8-6(a).

Quantized conductance is also observed when a fresh device is formed with a negative bias. In Fig. 8-7 (a) the I-V characteristics for a "set" operation at a negative bias is shown. Fig. 8-7(b) shows the extracted conductance as a function of voltage. Again partial conductance transitions can be observed. Interestingly, quantized conductance was never observed during the "reset" operation.



Fig. 8-7. I-V characteristics of the Au/P3HT(GNP)/Cu cell with 0.1 mg/ml GNP at a negative bias. a) current vs voltage; b) conductance of the set transition at a negative bias extracted from Fig. 8-7(a).

There are several reports on integer and partial quantized conductance observed in resistive switching devices [22,23,24]. Integer quantized conductance has been observed in resistive switching devices at 300 K and attributed to the formation of Cu nano-filament in TaO_x between the metal electrodes [22]. Li [25] and Csonka [26] have reported partial quantized conductance measured on Cu and Au nanowires respectively, and attributed it to the presence of adsorbed organic molecules and hydrogen, respectively.

Following the explanation adopted for nano-filaments and quantum point-contacts in mesoscopic physics [27,28], we explain the observed quantized conduction in terms of a 1D electron waveguide, the explanation adopted for nano-filaments and quantum point-contacts [27,28]. The waveguide may be realized by a conducting bridge consisting of a few Cu atoms between two adjacent graphene platelets or between a graphene platelet and one of the metal electrodes, dominating the resistance of the device. The bridge forms a constriction of width of the order of the Fermi wavelength of the electron. For a width approximately half of the Fermi wavelength one transverse mode will contribute to conductance $(1G_0)$, for wider constrictions second and higher modes are transmitted. Each mode contributes a unit G₀ to the conductance if the transmission coefficient of the mode through the constriction is unity (perfect transmission without backscattering) [27, 28]. Yet the transmission coefficients of the modes depend on the environment the constriction connects to (the equivalent of an electromagnetic impedance mismatch), here the graphene platelets and the two metal electrodes. A non-unity transmission coefficient results in a correspondingly reduced and partial quantized conductance. The addition of partially transmitted modes then results in the observed partial quantized conductance. The observed slope of conductance vs voltage follows from the observation that the transmission coefficients of the modes through the electron waveguide are a function of the applied voltage.

This is a reasonable assumption given the observed imperfect transmission and the fact that the applied voltage will change the electrostatic environment of the constriction, thereby changing the transmission coefficients as well. In that context, we surmise that the role of graphene platelets, apart from providing a conductive path, is to provide a 2D electron gas with a Fermi wavelength that is readily tunable by a change in the electrostatic environment and hence by the applied voltage. This would furthermore explain why we see the quantum effects only at medium concentration of graphene platelets. At medium concentration high chance exists to form a single 1D electron waveguide somewhere in the device, dominating the resistance and with a constriction size of the order of the Fermi wavelength that can be modulated by the applied voltage. At high concentration of graphene platelets, many individual graphene platelets or stacks of graphene platelets form a multitude of parallel conductive paths and the quantum effects are washed out. At low concentrations the probability of forming even one bridging constriction is low. It should be noted that the area cross section of our devices is large (<0.09 cm²). At a GNP concentration of 0.1 mg/ml we find a 50 % chance that one graphene nanoribbon will span the entire dielectric distance. At a GNP concentration of 0.05 mg/ml not a single case of bridging has been observed. On the other hand, at concentration of 0.2 mg/ml, the very high measured conductance value points to multiple graphene nanoribbons parallel bridging the two metal electrodes. While the highly conductive devices with GNP concentration of 0.2 mg/ml do not display quantized conductance effects, they are a good material candidate for stretchable transparent electrodes [26]. The broad range of electric tunability of organic films points to the universal potential of graphene nanoplatelets, depending on their concentration in an organic dispersion, for a wide spectrum of applications.

We note that the non-unity transmission coefficients can be caused by the memristive properties of the device. In contrast to conventional resistors and capacitors, the resistor and capacitor in memristors [25] are voltage or current dependent, or more generally they depend on the total voltage flux (defined as the time integral of the applied voltage) or on the total charge (defined as the time integral of the applied current). Accordingly we would have an experimental demonstration of a quantum memristor, achieved by the sensitivity to the electrostatic environment, of the transmission coefficients through an electron waveguide.

8.4 Conclusions

We have observed integer and partial quantized conductance occurring at room temperature in organic polymer films doped with graphene nanoplatelets. The quantized conductance is likely a result of a 1D electron waveguide physics, with voltage-tunable transmission coefficients. The control of concentration of graphene nanoplatelets allows tuning of the material from insulator via quantum conductor to a metallic conductor, opening thus new vistas in electronic applications.

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9 Summary and Future Works

9.1 Summary

This research report presents our recent work in the investigation of mechanisms, conditions and applications of filament formation and rupture in resistive memories. The following is a summary of the findings:

(1) Various oxide based RRAMs such as Cu/TaO_x/Pt, Cu/Ta₂O₅/Pt, Cu/SiO₂/Pt, Pt/TaO_x/Pt, Pt/Ta₂O₅/Pt, Pt/SiO₂/Pt and Pt/Ti/ Ta₂O₅/Pt have been fabricated and characterized. The study in property engineering of electrode and oxide materials improves the understanding of the device mechanism and lead to possible optimization of device performance.

(2) The resulting model supported by the data postulates that there are two distinct modes of creating oxygen vacancies: i) a conventional bulk mode creation, and ii) surface mode of creating oxygen vacancies at the active metal-dielectric interface.

(3) A charge transport model based on space charge limited (SCL) conduction is developed to explain the I-V characteristics of the SET process at low voltage range in MIM based resistive memories. It is realized that the SCL conduction model can be used to study the useful information regarding the traps or defects in the switching material.

(4) Hybrid Cu/Vo and Vo/Cu CF formation are observed in Cu/Ta₂O₅/Pt devices. The innovative use of Vo/Cu CF has been proposed for the improvement in device performance.

(5) A resistive floating electrode device (RFED) comprising two single memory switches connected anti-serially are investigated and demonstrated. This property lends itself to generation of current/voltage pulses that can be controlled by independent technology parameters. Such a

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device would enable an inherent integrate-and-fire capability and is, for example, able to realize electronic version of transfer functions of a biological spiking synapse.

(6) Multiple Cu conductive nanofilaments can be formed and ruptured successively between the active Cu and inert Pt electrodes in a Cu/TaOx/Pt resistive device. The key parameters to repeatable multi-filaments switching cycles are evaluated. Controlled formation and rupture of multiple filaments may enable multilevel storage capability in a single RRAMs memory cell if the repeatability issue can be successfully addressed.

(7) Quantized conductance is observed at room temperature in metal-insulator-metal structures with graphene submicron-sized nanoplatelets embedded in a 3-hexylthiophene (P3HT) polymer layer. In devices with medium concentration of graphene platelets, integer multiples of conductance $G_0=2e^2/h(=12.9 \text{ k}\Omega)^{-1}$ are observed. In some devices partial quantized conductance steps are observed, including a series with (n/7)×G₀ steps. As an organic memory, the device exhibits reliable memory operation with an ON/OFF ratio of more than 10. In absence of magnetic Landau levels, we attribute the quantized conduction to the existence of a 1D electron waveguide along the conductive path. The partial quantum conductance results likely from non-unity transmission coefficients of the first waveguide modes.

9.2 Future Works

Based on the research presented in this dissertation, there is still more work can be done in the design of device materials and structures for optimized performance.

(1) based on our current conduction mechanism models, further investigate bilayer or triple layer structure and high K dielectric materials for better control of Vo concentration profiles to achieve low power consumption (sub µA reset current).

(2) Further investigate the SCLC model for SET operation.

(3) Further investigate the precise control of concentration of graphene nanoplatelets allows tuning of the material from insulator via quantum conductor to a metallic conductor, opening thus new vistas in electronic applications.

10 Publications

Journal Papers:

[1] Y.Kang, T. Liu, T. Potnis and M. Orlowski, "Composite Cu/VO and VO/Cu Nanofilaments in Cu/Ta2O5/Pt Devices", ECS Solid State Lett. **2** (7) Q54-Q57, 2013

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Conference Proceeding Papers:

[1] Y. Kang, G. Ghosh, M. Orlowski, "Multilevel Resistive Switching with Oxygen Vacancy Filaments in Pt/TaOx/Cu and Pt/TaOx/Pt Devices," ECS Fall Meeting, 2015

[2] Y. Kang, H. Ruan, M. Orlowski, "Nonvolatile Memory Based on Polymer-Suspended Graphene Nanoplatelets with Fractional and Integer Quantum Conductance at 300K and Zero Magnetic Field," ECS Fall Meeting, 2015

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Intellectual Property:

[1] M. Orlowski, *et al.*, "Volatile switching device," VTIP No.:12-088.