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電子工程學系電子研究所碩士班

碩士論文

氮氧化鉭薄膜於電阻式記憶體的製作與轉態特性之研究

Study of Resistance Switching Characteristics and Fabrication in TaON Thin Film for Resistive Random Access Memory

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摘要

由於近幾年來，非揮發性記憶體的研究與發展備受關注，又因為傳統浮閘快閃記憶體無論在垂直或水平微縮上受到挑戰，所以發展新穎式的非揮發性記憶體是重要的趨勢。其中又以電阻式非揮發性記憶體元件具有低耗損能量、低操作電壓、高記憶密度、且具快的操作速度快以及高耐久度等優點，最重要的是結構簡單(金屬/介電質/金屬），使其成為最具有取代快閃記憶體的新穎式非揮發性記憶體元件。

在本篇論文中，主要是研究探討氮化鈦/氮氧化鉭/白金結構與氮化鈦/氮氧化鉭/銅結構的電阻式記憶體的轉態特性探討和電流傳導物理機制。其實驗內容主要可以分為四大部分，第一部份為白金上電極結構元件的二極性基本電性與轉態機制研究，且強調正負形成電壓的機制差異。第二部份為銅上電極結構元件的二極性基本電性與轉態機制研究。第三部份為利用變溫、定電流等量測方式來證明兩元件的轉態機制與差異，探討在薄膜內轉態的情形以及上電極對轉態有甚麼影響。第四部份為兩元件的單極性基本電性與轉態機制研究，並與雙極性轉態機制做比較。

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Abstract

Recently, there are intensive researches and development of various non-volatile memories gradually. Because the traditional floating gate flash memory in terms of vertical or horizontal scaling is being challenged. One of the most important advanced memories is the resistance random access memory (RRAM). The device has the advantages of low power consumption, low operating voltage, high density, fast speed and high endurance and retention. The most important attribute of the device is that it has a simple structure (metal / dielectric / metal).Thus, we may eventually replace Flash memory with RRAM for non-volatile memory application.

This thesis is the studying the resistive switching properties and the physical mechanism of current conduction of structure of titanium nitride / tantalum oxynitride / platinum and the structure of titanium nitride / tantalum oxynitride / copper . The content can be divided into four parts. In part one, we study the bipolar resistive switching characteristic of structure TiN/TaON/Pt, and propose a model which oxygen ions migration makes the device's resistance switched and focus on positive and negative Forming explanation. In part two, we change top electrode to copper and study the bipolar resistive switching characteristic of structure TiN/TaON/Cu. We also propose a model which copper ions redox and electron-migration makes the device's resistance switched. In part three, we use many experiments like temperature measurement, constant current stress measurement to prove two devices' mechanisms. With different methods we study the resistive switching phenomena in film and what effect will happen in different top electrode. In final part, there is unipolar characteristic in two devices and we explain resistive switching mechanism of two devices as well.

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完成整個碩士的畢業論文，是我人生中非常寶貴的經驗與歷程，使我深深的體會到要呈現優秀的實驗數據是一件不容易的事，需要擁有精良的實驗製程機台和精密的量測儀器，至此更學會許多製程及量測的技術。首先，我要感謝的是我的指導教授施敏和張鼎張博士，在他深入淺出的教導之下，使我受益良多，獲益匪淺，很快就接受那些新觀念，他也指引我實驗的方向，使我能完成此畢業論文，接著，要感謝薄膜電晶體平面顯示及半導體積體電路實驗室的各位學長姐們，其中，我要特別感陳仕承學長的指導，不管是儀器的操作與使用、理論概念的釐清抑或是數據的討論，都給了我莫大的幫助，感謝黃正杰學長幫我切FIB與看TEM。感謝富彥、美娜、書瑋、原瑞、柏鈞、敏甄、佳盛、志豪、宛芳、德智、詠恩、冠張、禹鈞、侑廷、聖堯、學志、文宏、侑廷、耿維、君寶、天宇、慶恩等學長姐於研究過程中給予建議及指正，感謝一起走過這段日子的同學們：柔妙、菀琳、儀憲、凱弘、雅琪、承瑋、國孝、偉立、岳恆、祐松、冠任、志誠等，感謝你們的陪伴與鼓勵

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邱奕介 謹識

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Chapter 1

Introduction

In the advanced rapidly age, more and more technology products are invented to improve people's lives. The people's demands for consumer electronics are surged. No matter what types of consumer electronics are. Such as, mobile phone, smart phone, camera, GPS, and so on, any product is created to let human convenient. Those consumer electronics all must have memory which can save data permanently and can't let data lose. However, in present, in order to carry conveniently, the products are designed smaller and smaller. Thus, the memories also become smaller and smaller and doesn't affect their capacity. Even the capacity of memory is increased. Due to the memory Flash encountering above problems, making new evaluation of memory device are significant subjects in the near future. The ideal memory devices own advantages, such as simple structure , low energy consumption ,higher storage density , higher operation speed, better endurance and retention.

Recently, the development of traditional memory devices have encountered some problems .Therefore, we will have to further research new structure or new material. The recent studies indicate that RRAM devices have the benefits of non-volatile, low energy consumption, high retention and endurance, fast programming. Most important thing of all is that the RRAM has a simple structure (metal-insulator-metal) which lets device fabrication easy. In spite of the wonderful characteristics of RRAM, there is not a complete and clear system to explain the resistive switching mechanism of RRAM.

This study purposed to develop new material and research resistive switching mechanism for different top electrode. We also use some equipment to certify resistive switching mechanism. In the device fabrication, we choose the material Pt, the insulator of TaON , TiN to make our device .Because those materials have been used in the traditional CMOS process. For example, TaN is used to resist copper diffusion, TiN is used to be anti-reflection layers or adhere layers, Pt is inertia metal. In addition, we substitute our device top electrode Cu for Pt.

Chapter 2

Literature

2-1 Introduction of Memory

We know that the memory can be distinguished simply into two types: volatile and non-volatile. The volatile memory needs power to maintain their memory state. When the power is turned off, the charges will lose and cause data to disappear. However, the memory has advantages of fast access speed. The volatile memories include two types: SRAM (Static Random Access Memory) and DRAM (Dynamic Random Access Memory).

Comparing with the volatile memories the non-volatile memory can't lose their data when the power is turn off. In the other way, we can conserve our data for a long time without giving any energy. When supplying the power, the information can be programmed, erased, or read. The Flash memory the typical non-volatile memory is the most widely used now. However, we encounter critical problems recently. Due to increasing density of storage, we have to scale down our devices. When the devices are scaled down continuously, the tunnel oxide layer will go thinner. The consequence which the charges can leak and lead to loss all stored information will happen. The other problem is that the programming and erasing are slow.

Recently many non-volatile memories are developed. The memory can be divided into four types: (1) FeRAM (Ferroelectric Random Access Memory) (2) MRAM (Magnetic Random Access Memory) (3) PCRAM (Phase Change Random Access Memory) (4) RRAM (Resistance Random Access Memory). The comparisons of memory characteristic of non-volatile memory are listed in **Table2-1. [1]**

2-2 Advanced Non-volatile Memories

2-2.1 FeRAM (Ferroelectric Random Access Memory)

The ferroelectric feature is the some substance having P-E hysteresis effect. When giving the external voltage to them, the interior ions movement cause polarization phenomenon **Figure 2-1. [2][3]**Besides, the produced electric dipole doesn't completely disappear as removing the voltage. This phenomenon is called remnant polarization. The direction of remnant polarization is different as applied different direction of electric field. From the direction of remnant polarization **[4]** we can distinguish the signals of "1" and "0". The FeRAM has many advantages, such as low power operation, high density, and low voltage operation, but the FeRAM also face the limits of size.

2-2.2 MRAM (Magnetic Random Access Memory)

The access mechanism of MRAM is that using top and bottom two conductive metal layers, and the middle layer is tunneling magnetic resistive (TMR) or giant Magnetoresistance (GMR) cell. The top is the bit line and the bottom is the word line like **Figure 2-2. [5]** .When giving a pulse to bit line, the magnetic field is induced by the current. In that time, the current will affect the direction of polarization to shift in free layer. If giving a pulse current to word line, as well, the polarization direction of free layer will be changed completely by induced magnetic. Therefore, two polarization of ferroelectric layer will be arranged forward (In the moment low magnetic resistive is ordered "0") or be arranged reverse (In the moment high magnetic resistive is ordered "1"). The data which are stored will not lose for a long time just like hard disk. It has characteristic of low power consumption, fast response time, and high density of storage. The MRAM is a complex and spin-electric device. Thus, if we want to achieve ultra high density of storage and a good performance, we need to solve some critical problems, such as vortex, the leakage current effect of access, power consumption and thermal stability. Therefore, we need to improve further those disadvantages.

2-2.3 PCRAM (Phase Change Random Access Memory)

The major material of the PCRAM is Chalcogenide. After adsorbing thermal energy, Chalcogenide will become two reversible type: amorphous and poly-crystal. As the current pass through the small area for a long time to maintain high temperature, the atoms can arrange into poly-crystal .This poly-crystal has low resistance. **[2]** Therefore, we define the different resistance of amorphous and poly-crystal states. The amorphous state is "0"and the poly-crystal state is "1" like **Figure 2-3[2]**. In the contrast, when the current only pass for a short time, the atoms can't arrange into uniform structures. So it becomes amorphous and the resistance of amorphous is high. There are some advantages in PCRAM. For example, the fast programming speed, less power consumption, high reliability, and process compatibility. But the heat produced will affect the around devices. Maybe solve this problem first.

2-2.4 RRAM (Resistance Random Access Memory)

The RRAM is made of a transistor and a resistor like **Figure 2-4 [6]**. The resistor has a structure MIM (metal-insulator-metal).The top and bottom metals are the electrodes. And then, middle thin insulator film is a switching layer. The basic mechanism of access is that when giving the appropriate voltage to top or bottom electrode, the resistor’s resistance will change. We can decide that higher resistance state is “0” and lower resistance state is “1”.The main switching characteristic could be divided into two types: unipolar and bipolar. Unipolar **Figure 2-5(a) [7]** is that switching between high resistance state and low resistance state is controlled by the applied voltage magnitude rather than polarity. On the contrary, bipolar **Figure 2-5(b) [7]** is that switching was dependent with voltage polarity and magnitude. The main materials of insulator film can be divided into three types: (1) Perovskite (2) organic materials (3) transition metal oxide. There are many advantages in RRAM .Such as, low cost, simple structure, low operating voltage, fast access speed, high retention and endurance, high density of storage. Therefore, thanks to so many advantages, the greatest potential method is that we substitute RRAM for the Flash memory.

2-3 The Materials of RRAM

There are various materials which can be observed the resistive switching, such as perovskite, transition metal oxides, and organic materials.

2.3.1 Perovskite

One extensively studied material group is perovskite. The perovskite structure is ABO_3.The “A” is the cation with the longer radius and is localized at the eight corner of the crystal structure. The “B” is the cation with the shorter radius and occupies the body-centered of crystal. The “O” is the oxygen ion and is situated at the face-centered of crystal like **Figure 2-6 [8]**. In the electric and magnetic characteristic Perovskite is special. By doping characteristics of Perovskite are affected.Thus, recently many materials derived from perovskite are Cr-doped $SrZrO_3$ **[9]**, BSZT**[10]**, and PrCaMnO3 **[11]** and so on.

In 2000, A. Beck et al. **[9]** said that the SrZrO3 film doping with Cr can enhance the device. The bottom electrode is SrRuO3 or Pt. The top electrode is Pt or Au. Applying positive voltage is SET, and applying negative voltage is RESET.SET is that making the state of device from high resistive state to low resistive state. And then, RESET is that making the state of device from low resistive state to high resistive state. The resistance switching depends on polarity of applied voltage.

BSZT is(Ba,Sr)(Zr,Ti)$O_{3.}$The material has already been studied as high-k dielectric for a long time **[10]**.Someone uses BSZT as RRAM with doping V, Cr and so on. Due to the more compositions and the more complex chemical environment, the control of the composition proportion is not easy as binary oxides.

PCMO (PrCaMnO3) has the famous Perovskite structure and has electric and magnetic characteristics, like magnetoresistance **[11]** and colossal electroresistance . **[12]**

In 2000, Sawa et al.**[13]** discovered electric hysteresis curve in

Ti/PCMO/SRO device and think the resistance switching at the interface between Ti and PCMO. Liu et al. **[14]** fortunately changed the resistance of Ag/PCMO/Pt structure by electric pulse without magnetic field under the room temperature. In the **Figure 2-7**, the resistance depends on electric field polar direction and the on/off ratio is about three orders. They also thought that ferromagnetic clusters would be arranged directionally to form filament path for carrier passing through the conductive clusters. On the other hand, reverse bias could also rearrange ferromagnetic clusters to higher resistive state. However, this oxide contains more than three elements, so the crystal structure, process technology and stoichiometry are difficult under the control. For the current semiconductor process technologies the material is difficult to connect with. In addition, the board needs to have a good crystalline substrate before producing high quality film, and efficient etching process has not yet been made.Thus, the type of material has its limitation in volatile resistive RAM development in the future.

2.3.2 Transition metal oxides

Currently using a variety of transition metal oxide thin films in resistive memory.In the ternary transition metal oxides $BaTiO_3$, and $SrTiO_3$ and their doping elements have received attention. And then, in binary transition metal oxides TiO_2, Ta_2O_5, ZnO, ZrO_2, HfO_2, Nb_2O_5, NiO, MoO_3,, CuxO with WO_3 and so on have received attention in the current. These oxides in the physical and chemical have their unique characteristics, and their characteristics perhaps are related with metal electrode with a barrier and work function.

In 2008, B. Gao **[15]** had also observed resistance switching of the ZnO thin films deposited on Pt/Ti/SiO_2/Si. The resistance switching of the device is bipolar **Figure 2-8** and cathode is Pt **(a)** or TiN **(b)**. They proposed a oxide-Based RRAM Switching Mechanism in Reset process about ion-transport-recombination.

In 2004, S. Seo et al. **[16]** had discovered resistance switching of the NiO thin films also deposited on Pt/Ti/SiO_2/Si. The resistance switching of the device is bi-stable symmetric **Figure 2-9**. They thought that the reason of the resistive switching is the contribution of nickel vacancies.

2.3.3 Organic materials

In 2002,L. P. Ma et al. **[17]** had observed an organic bi-stable device and the structure is made of organic/metal/organic as **Figure 2-10**. When giving a voltage over a critical value, the resistance switching from high resistance state to low resistance state is SET. The high resistance state restored by giving a reverse voltage is RESET, and the high resistance state was maintained without voltage. The structure of organic/metal/organic has a non-volatile feature.

2.4 The Resistive Switching Mechanism of RRAM

In the near future, the phenomenon of the resistance switching has been found out continuously in a variety of materials. Besides, many people have proposed some models in order to explain the mechanism of resistive switching. The switching mechanism can be distinguished into two types: bulk control and interface control. Bulk control is that the switching region is occurred in the insulator layer. The resistive switching model like filament, charge-trap in small domains and conduction paths are classified in Bulk control. Interface control's switching region is occurred in the layer which is between the metal layer and insulator layer.

We will discuss these mechanisms respectively.

2.4.1 Filament

The fundamental theory is that the formation and rupture of the conductive filaments in the insulator, like **Figure 2-11 [18]**. The Figure shows the mechanism of filamentary type RRAM. Applying the voltage to make the filament formed in insulator layer is Forming process, and the device maintain in on state. After that, rupturing the filaments to make the device changed to off state is Reset process. Then, the filaments formed again to on state is Set process. The Joule heating effect **Figure 2-12 [19]**, redox processes induced by cation migration, redox processes induced by anion migration or anodization near the interface between the metal electrode and the insulator layer are considered to form and rupture the filaments.

2.4.1.1 Joule heating effect

Joule heating is the main phenomena in the unipolar resistive switching. In 2007,

Y. Sato et al. **[20]** had found out the temperature of filaments with NiO2 thin film. The temperature in each Reset process was the same from thermal conductive equation .We can calculate the temperature of conductive path. They defined that the reset process is a thermal chemical reaction with electrical current heating.

2.4.1.2 Redox processes by cation migration

The principle is that when giving the positive voltage on top electrode, metal atoms will be oxidized to metal ions. The metal ions are driven by the positive electricity. Due to positive voltage on the top electrode, the metal ions will be moved to bottom electrode by the downwards electric field. As soon as the metal ions arrive at the bottom electrode, it will be reduced to the metal atoms. When the above process happens continuously, the metal atoms will be deposited gradually until the filament formed makes the top electrode connected with the bottom electrode. This phenomenon is on state. On the contrary, applying the positive voltage on bottom electrode is the process of rupturing the filaments. The above process will make the metal atoms in the filament oxidized to metal ions and moved to top electrode by the upwards electric field. And then the phenomenon is off state. The device is just like **Figure 2-13**. **[21]**

2.4.1.3 Redox processes by anion migration

In 2006, M. Fujimoto et al. **[22]** had observed resistance switching behavior of the Pt/TiO2/TiN/Pt device like **Figure 2-14**. The device Pt/TiO2/TiN/Pt **[23]** has the bipolar resistive switching characteristic. When giving a negative pulse, donor concentration could be increased. The upwards electric field was produced and made oxygen ions depart from bonding and flow to bottom electrode. In that time, the oxygen vacancies were left. The above process makes device switched to on state. On the other hand, when giving a positive pulse to the top electrode, the oxygen ions were filled up the oxygen vacancies. When the oxygen vacancies disappeared in the film, the device were switched to off state .These processes was shown in **Figure 2-15[22]**. They thought that giving a pulse to the electrode was enough for the donor concentration abrupt increasing or decreasing in the layer.

2.4.2 Charge-trap in small domain

In 2004, M. J. Rozenberg et al.**[24]** create a model to explain multilevel resistive switching phenomenon. In this mechanism the insulator is at medium and top and bottom is two electrodes .Besides, contained metallic domains which is the same as charge traps in the real system like dopants , vacancies, metallic clusters, nano-domains, and so on. The three kinds of domains is in the **Figure 2-16 [24]**.The top and bottom domains are smaller than medium. When giving a negative pulse to fill up the bottom domains and then to let the top domains in vain. Due to low probability of carriers transferred into the filled bottom domains, carriers were transferred out of the emptied top domains to the electrode. Thus, the system was at high resistance state. On the contrary, they gave a positive pulse. Due to carriers transferred from the bottom electrode to the empty bottom easily, carriers were transferred from the fully filled top domains to the top electrode. Therefore, the system came back to low resistance state.

2.4.3 Modified Schottky barrier model

In the metal/insulator/metal structure the work function is not the same in these materials that constructs the different contact situation between them. The contact condition can be distinguished two kinds: Ohmic contact and Schottky contact. The mechanism of Schottky barrier model is introduced by A. Sawa et al. **[18]**. The structure of device is Ti/PCMO/SRO. Ti and PCMO become the Schottky contact. Due to the catching oxygen ability, Ti will catch many oxygen ions at the interface and leave many oxygen vacancies in the interface. Oxygen vacancies are positive charge and make the energy band bended. If the vacancies are too much, the Fermi level will never changed by given bias. The barrier height will not be changed. When giving the reverse bias, the electrons will be accumulated at the interface. On the contrary, the electron will be depleted like **Figure 2-17[18]**. They considered the more or less of charges can alter the height and width of barrier and make the resistance switched high or low.

2.5 The Mechanism of Current Conduction

Even though the current flowing though the ideal insulator has to be zero, the current can pass through the insulator at higher temperature or higher electric field actually. Thus, the device has leakage current. In the RRAM, when we operate the device, there are much current conduction. Such as Ohmic conduction, Schottky emission, Poole-Frenkel emission, space charge limit current, and so on. Fitting current in current-voltage curve can let us understand what current conduct in operation process in insulator. There are four current conductions in our equipments, so we introduce the current conduction mechanism in advance.

2.5.1 Ohmic conduction

Generally, applying to the condition of low electric field region in which thermally-generated carriers are dominant in conduction. When giving the external electric field, the free electron flowing can generate the current.

$$J = qN_c \mu E \exp\left(\frac{-\Delta E_{ac}}{kT}\right)$$

which, N_c = effective density of state

$\Delta E_{ac} (= E_C - E_F)$ = electron activation energy

2.5.2 Schottky emission

When the electrons jump over interface barrier between the metal and insulator or metal and semiconductor by the heat, the phenomenon is called Schottky emission. And then, in electric field the electron flowing can generate the current. The Schottky emission is related strongly with temperature. Lowing the barrier height will happen when the image charges caused by electrons. Thus, due to lowing barrier, making the electrons can hop through the barrier easily. The barrier height is affected by the materials' work-function .The interface trap, defect, carrier density, and process condition can also make the barrier change. If the barrier height is higher, the less electrons can jump over the barrier with the heat.The formula of Schottky emission is

$$J = A^{**} T^2 \exp\left[\frac{-q\left(\phi_B - \sqrt{qE_i / 4\pi\varepsilon_i}\right)}{kT}\right] \text{ or } J \propto T^2 \exp\left[\frac{q}{kT}\left(a\sqrt{V} - \phi_B\right)\right]$$

which, A^{**} = effective Richardson constant

$\varepsilon_i = \varepsilon_r \varepsilon_0$, ε_r = dynamic dielectric constant

ϕ_B = barrier height

2.5.3 Poole-Frenkel emission

Poole-Frenkel emission is similar to Schottky emission mechanism. Poole-Frenkel emission is that the electrons overcome the barrier caused by the defects in the insulator by the heat. And then, under the electric field the electron flowing generates the current. The Poole-Frenkel emission is also related strongly with temperature, while electric field plays a more important role in Poole-Frenkel emission than in Schottky emission, which implies that field effect has greater impact on defect-related behavior. The barrier height is determined by the deep of defect. And then, the barrier lowering in the Poole-Frenkel emission is twice as large as that in Schottky emission, because of the captured charges being fixed not like image charges in the metal. The deeper defects make less electrons hop through the barrier. The formula of Poole-Frenkel emission is

$$J \propto E_i \exp\left[\frac{-q\left(\phi_B - \sqrt{qE_i/\pi\varepsilon_i}\right)}{kT}\right] \quad \text{or} \quad J \propto V \exp\left[\frac{q}{kT}\left(2a\sqrt{V} - \phi_B\right)\right]$$

which, $\varepsilon_i = \varepsilon_r \varepsilon_0$, ε_r = dynamic dielectric constant

ϕ_B = barrier height

2.5.4 Space charge limited current

The electrons restricted to inject the insulator by the electrons existing in insulator that is Space charge limited current. The block phenomenon happens. The formula of space charge limited current is

$$J = \frac{9\varepsilon_i \mu V^2}{8d^3} \quad \text{or} \quad J \propto V^2$$

which, μ = mobility

The **Table 2-2 [25]** is the every current conduction .That shows the relationship between the current and electric field, the current and voltage, or other factors.

	Flash	CBRAM	FeRAM	MRAM	ORAM	PCRAM
Maturity	High Volume Product	Single Cells	Niche Products	Product Samples	Single Cells	Product Demonstrators
Density	4Gb	-	32Mb	16Mb	-	64Mb
Cell Size [um^2]	0.025	-	0.6	1.4	-	0.5
Embeddability	Yes	Yes	Yes	Yes	Yes	Yes
Nonvolatile	Yes	Yes	Yes	Yes	Yes	Yes
Random Read Access	80ns/10μs	<200ns	50ns	30ns	<200ns	50ns
Random Write Access	~10μs (erase 100ms)	<200ns	75ns	30ns	<100ns	50ns
Destructive READ	No	No	Yes	No	No	No
Write Endurance	10^6	$>10^5$	$>10^{12}$	10^{15}	10^5	$>10^{12}$
Write Voltage	Vdd+~10V	Vdd	Vdd	Vdd	Vdd+~2V	Vdd
Companies (Criteria: IEDM, ISSCC, VLSI publication during last 3 years)	Actrans Systems, eMemory Tech., Fujitsu, HaloLSI, Infineon, Intel, Macronix, Motorola, Powerchip, Renesas / Hitachi, Samsung, Sandisk, Sony, SST, ST, Toshiba		Agilent, Fujitsu, Hynix, Infineon Matsushita, Oki Ramtron Samsung Sanyo Toshiba TI	IBM Infineon Motorola NEC Renesas Samsung Sony	Infineon	Hitachi Intel Macronix Ovonyx Samsung ST

Table 2-1Comparison different memory technology **[1]**

過程	表示式	電壓和溫度關係性
Tunneling	$J \propto \mathscr{E}_i^2 \exp\left[-\frac{4\sqrt{2m^*}(q\phi_B)^{3/2}}{3q\hbar\mathscr{E}_i}\right]$	$\propto V^2 \exp\left(\frac{-b}{V}\right)$
Thermionic emission	$J = A^{**}T^2 \exp\left[\frac{-q(\phi_B - \sqrt{q\mathscr{E}_i/4\pi\varepsilon_i})}{kT}\right]$	$\propto T^2 \exp\left[\frac{q}{kT}(a\sqrt{V} - \phi_B)\right]$
Frenkel-Poole emission	$J \propto \mathscr{E}_i \exp\left[\frac{-q(\phi_B - \sqrt{q\mathscr{E}_i/\pi\varepsilon_i})}{kT}\right]$	$\propto V \exp\left[\frac{q}{kT}(2a\sqrt{V} - \phi_B)\right]$
Ohmic	$J \propto \mathscr{E}_i \exp\left(\frac{-\Delta E_{ac}}{kT}\right)$	$\propto V \exp\left(\frac{-c}{T}\right)$
Space-charge-limited	$J = \frac{9\varepsilon_i \mu V^2}{8d^3}$	$\propto V^2$

Table 2-2 Basic current conduction **[25]**

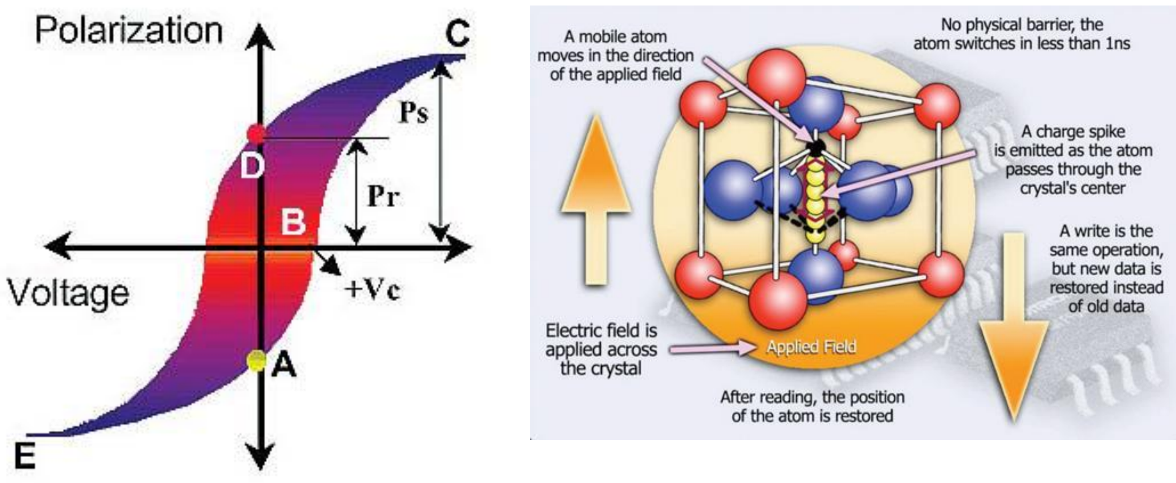


Figure 2-1 The P-E hysteresis of ferroelectric material **[2][3]**

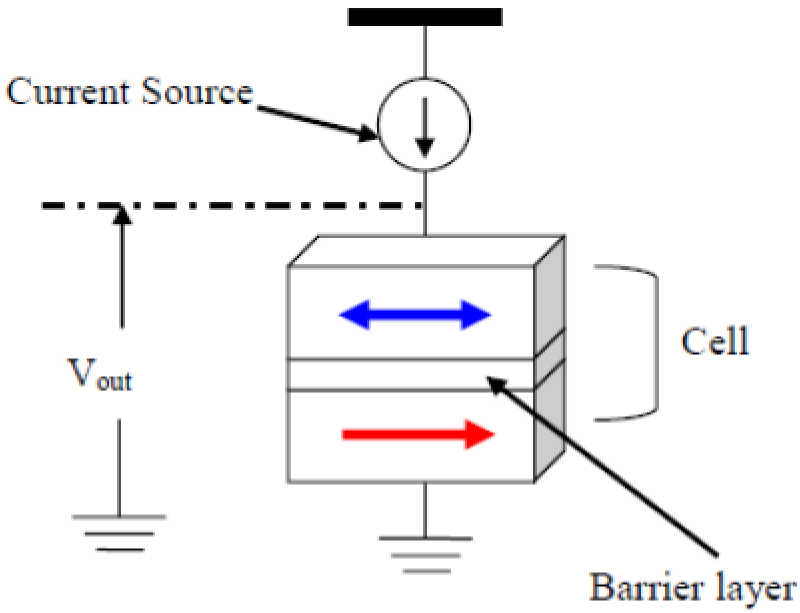


Figure 2-2 The MRAM structure operating schematic diagram **[5]**

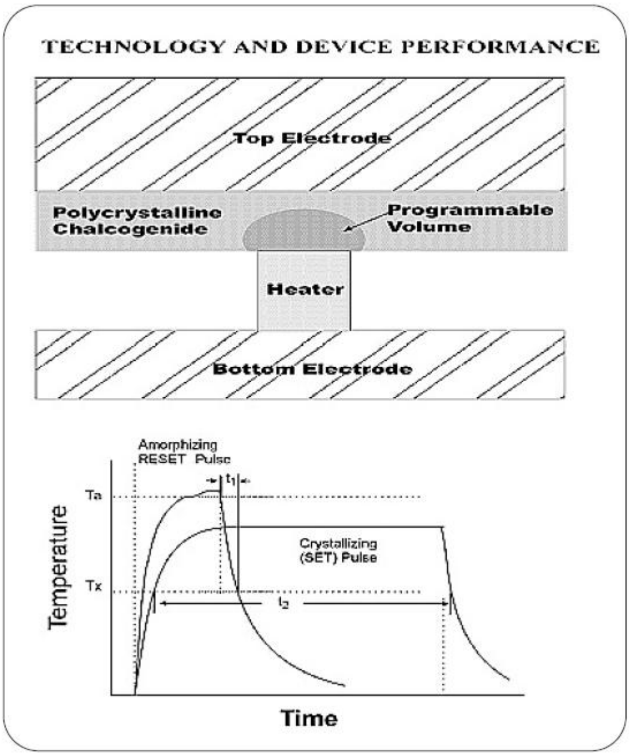


Figure 2-3 The PCRAM structure diagram and operating schematic diagram **[2]**

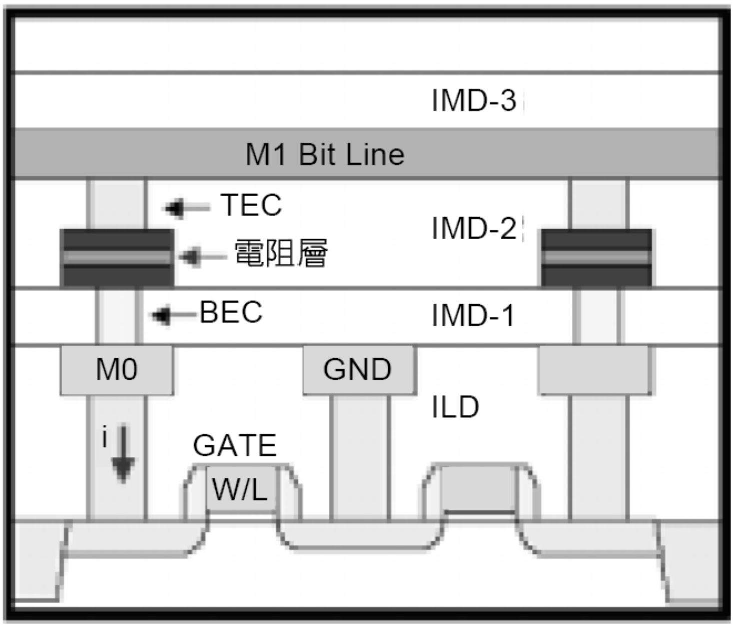


Figure 2-4 The RRAM structure diagram **[6]**

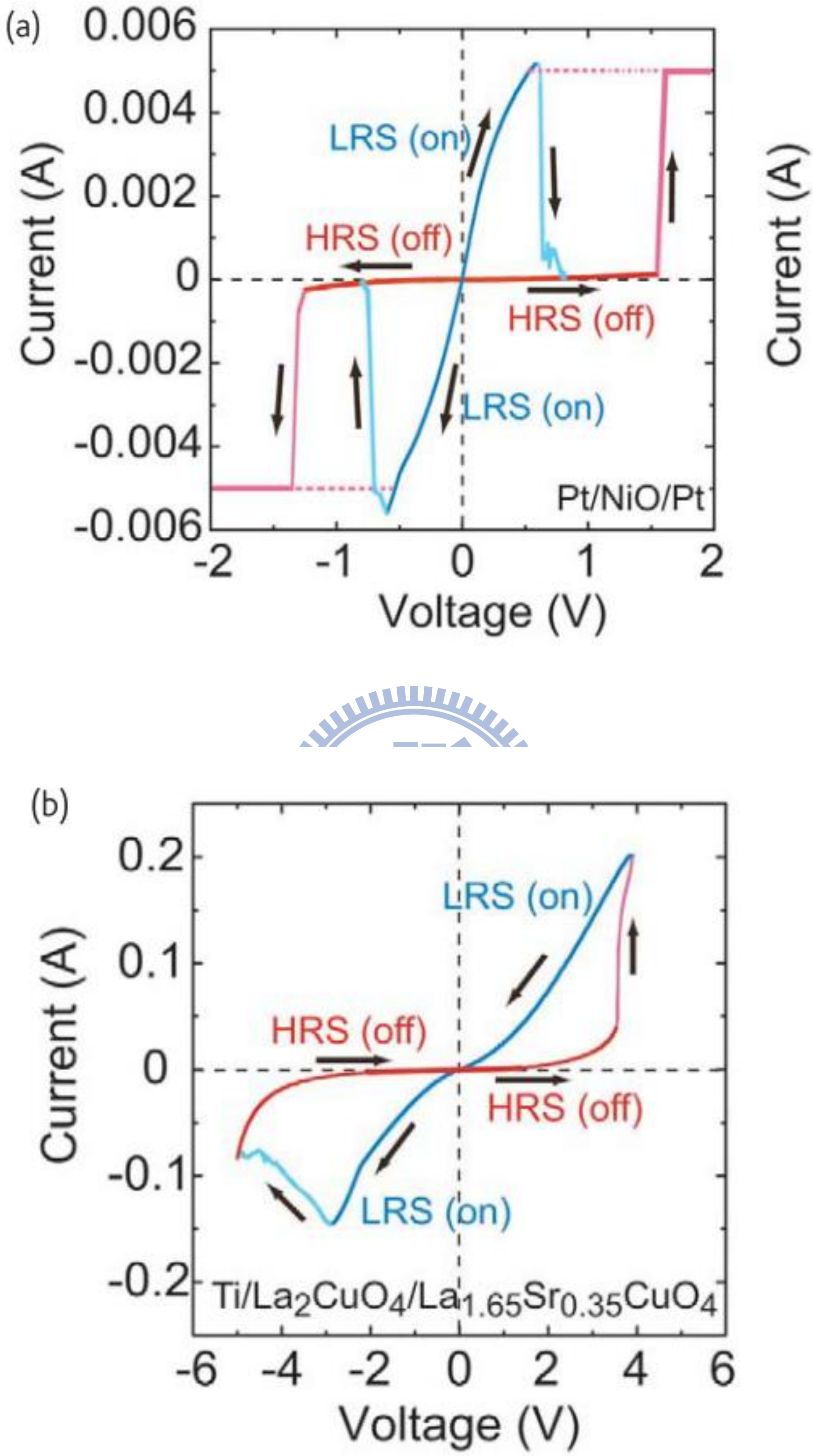


Figure 2-5 (a) Nonpolar (unipolar) switching (b) Bipolar switching **[7]**

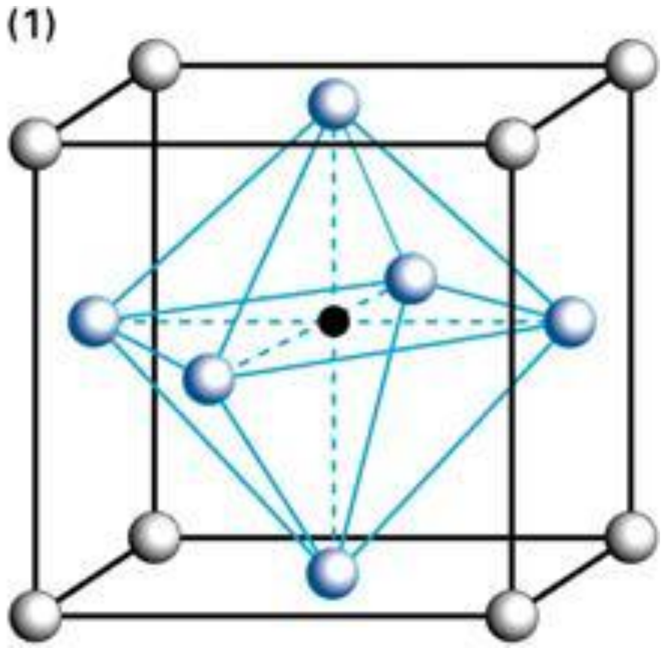


Figure 2-6 Perovskite structure **[8]**

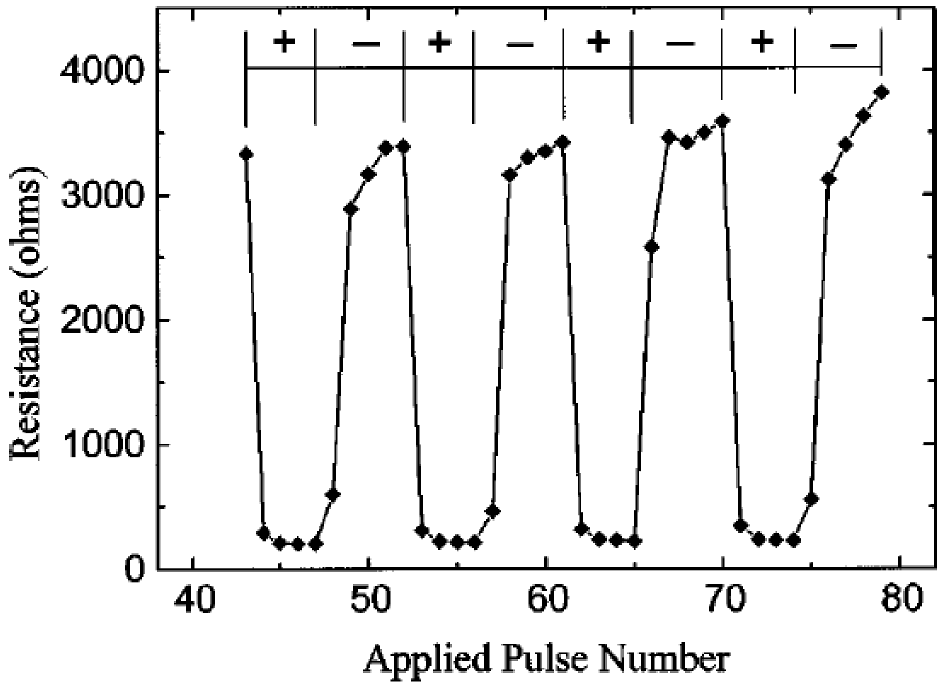


Figure 2-7 Nonvolatile resistance v.s. electrical pulse number for a PCMO thin film sample **[14]**

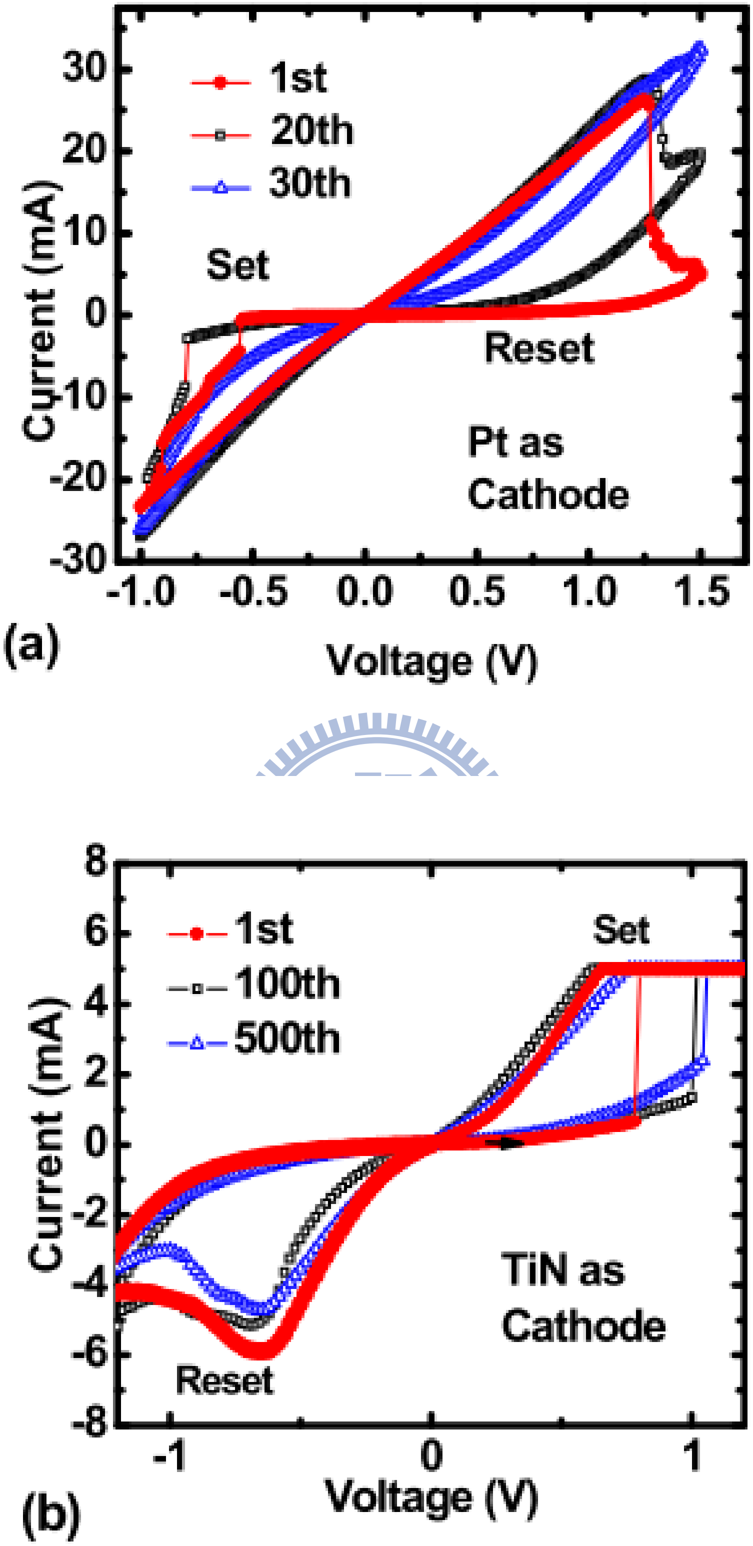


Figure 2-8 Switching curves of ZnO device: (a) with Pt as cathode, and (b) with TiN as cathode.**[15]**

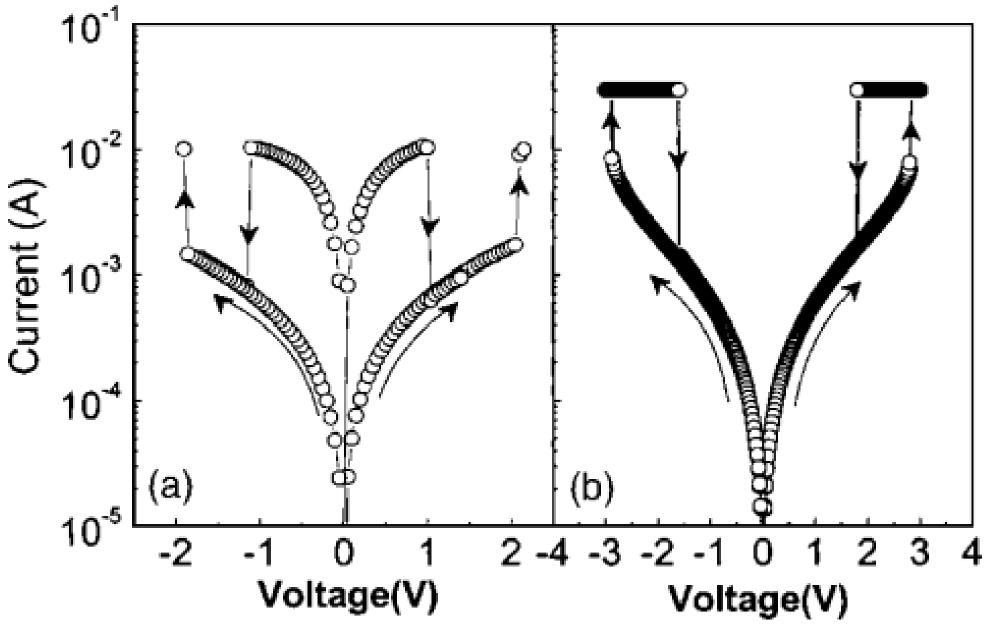


Figure 2-9 The device of the resistance switching is bi-stable symmetric **[16]**

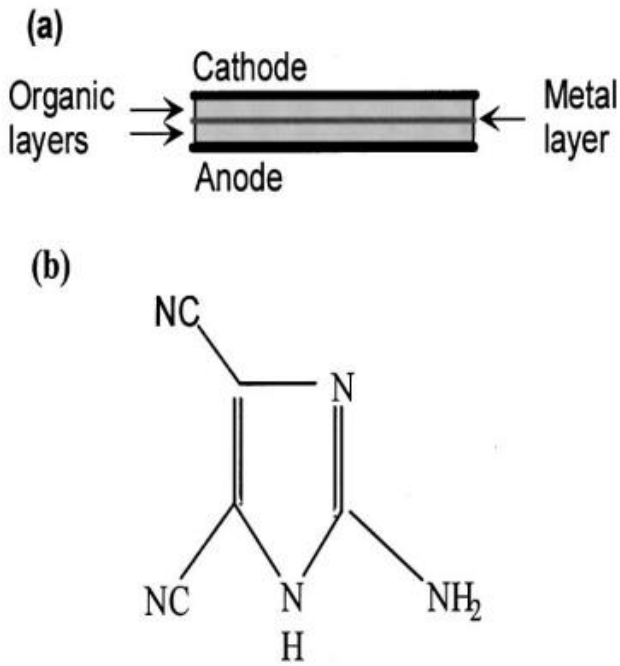


Figure 2-10 The structure of the device and the chemical structure of the organic material **[17]**

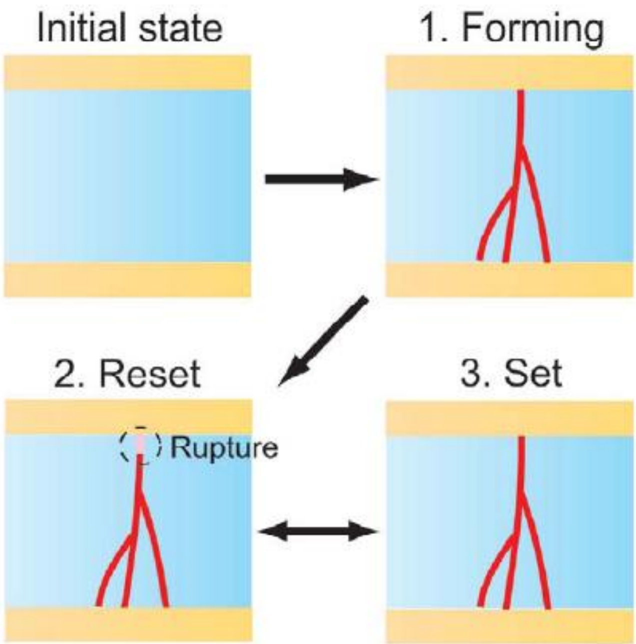


Figure 2-11 the formation and rupture of conductive filaments, (1) forming, (2) reset and (3) set process **[18]**

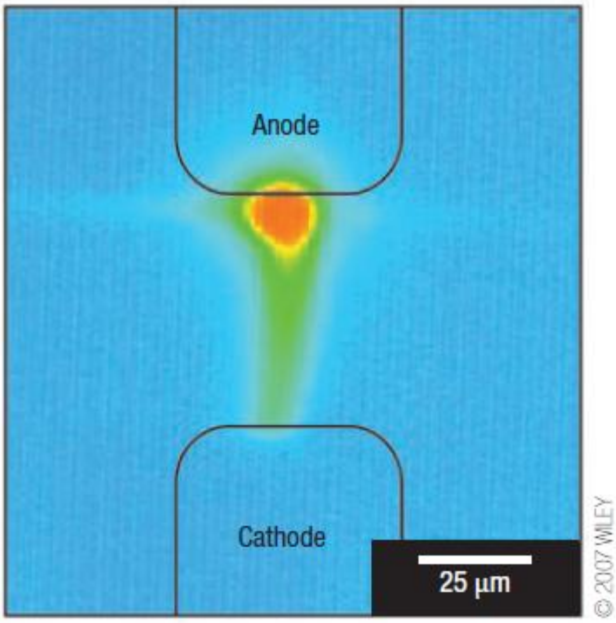


Figure 2-12 The temperature distribution of Joel heating effect **[19]**

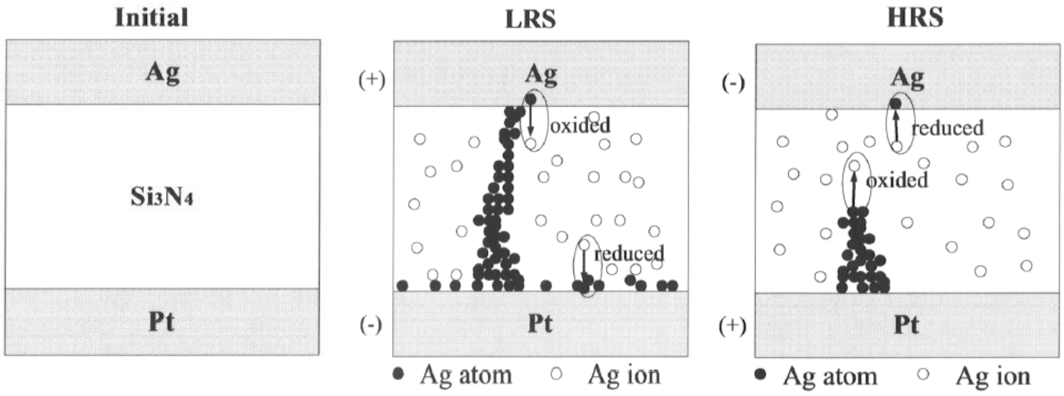


Figure 2-13 The sketch map of Redox processes by cation migration **[21]**

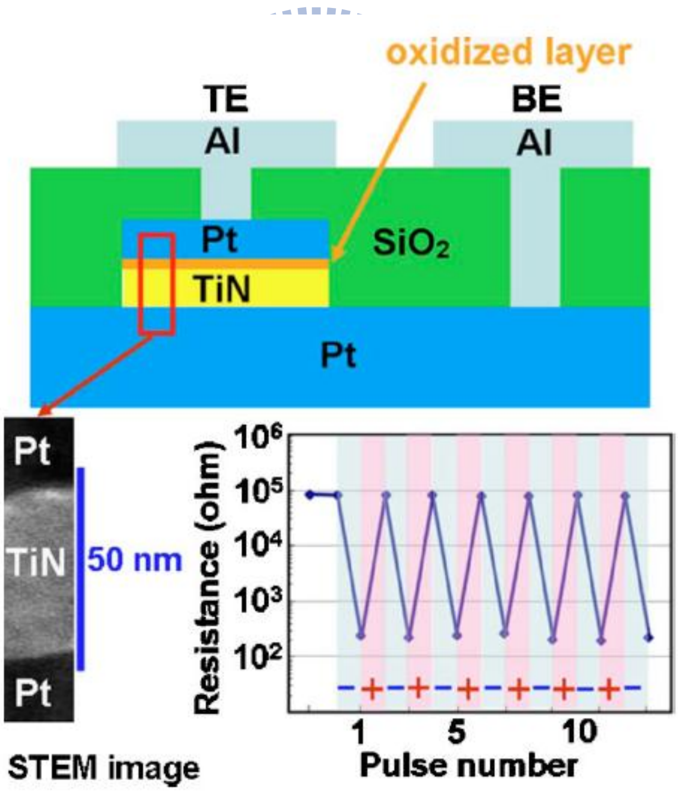


Figure 2-14 The sketch map of Redox processes by cation migration **[22]**

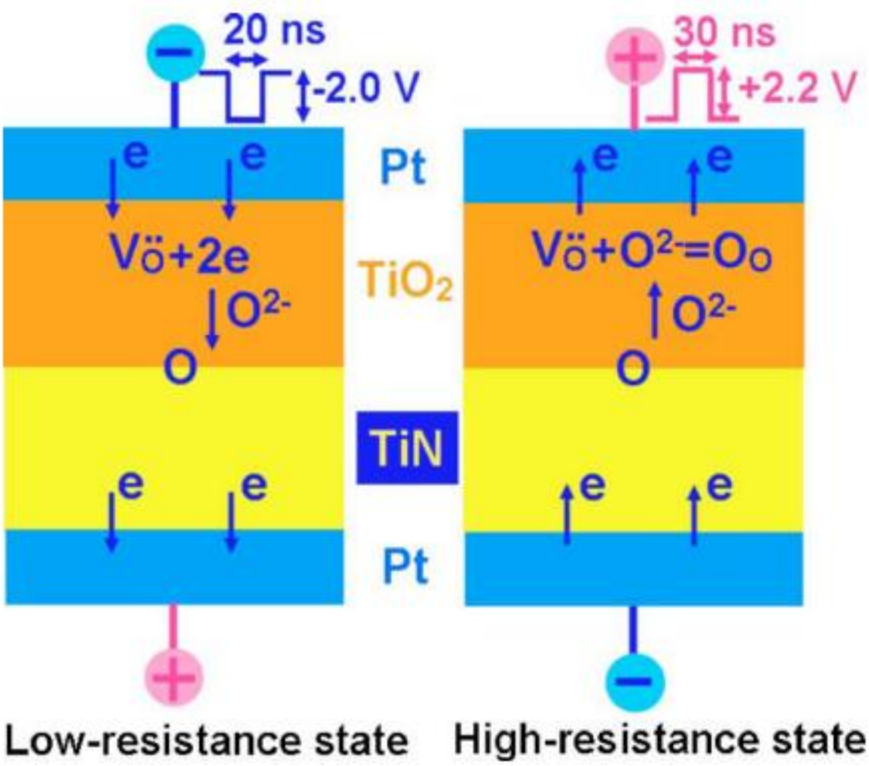


Figure 2-15 The mechanism of redox processes by anion migration **[22]**

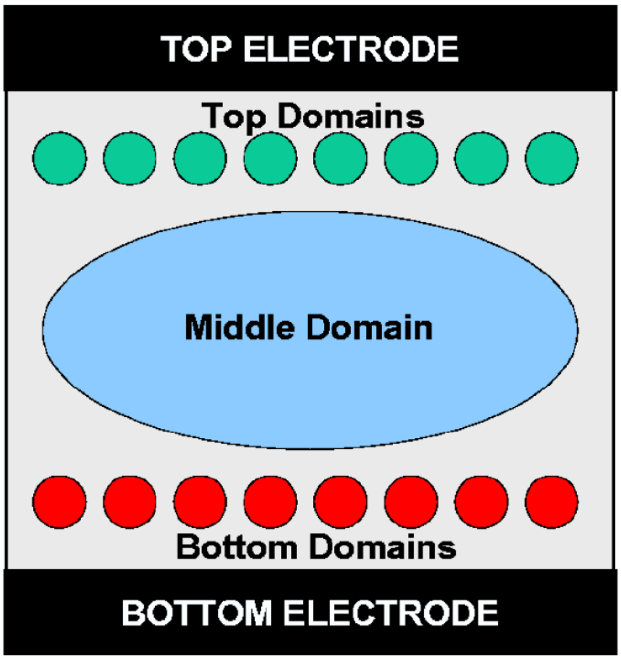


Figure 2-16 Schematic view of the model with three kinds of domains **[24]**

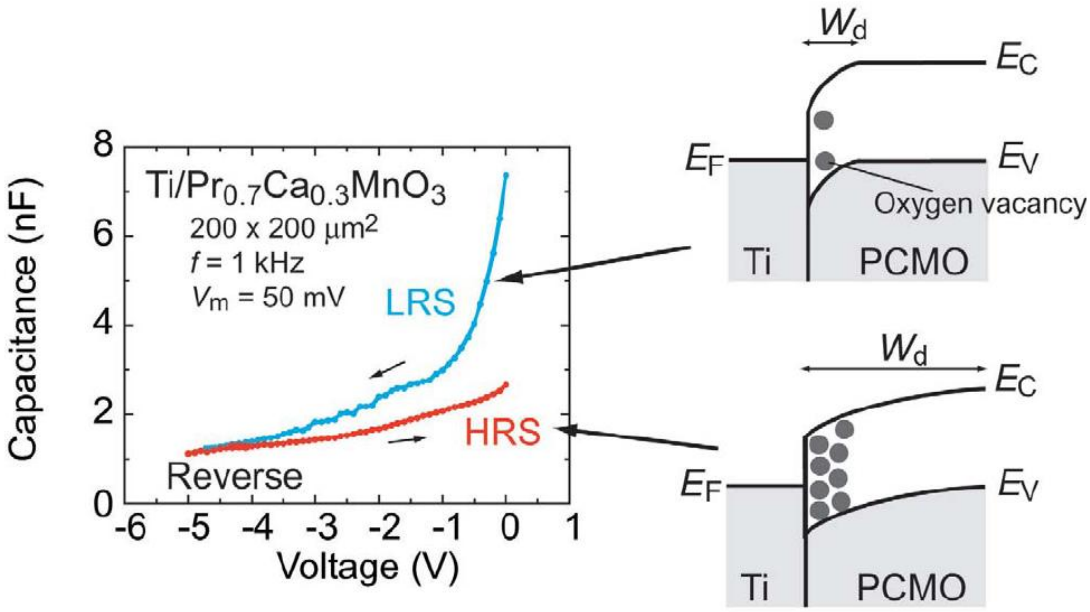


Figure 2-17 Schottky barrier model and Schematic view of the model **[18]**

Chapter 3

Experiment

We specify the process flow, material analysis ,and electrical measurement of every structure in this chapter.

3-1 Process Flow

There are two devices in the experiment. The one has insulator TaON and the top electrode Pt , and the other has insulator TaON and the top electrode Cu. The same thickness of insulator TaON in two devices is 20nm and the bottom electrode is the same material TiN. The insulator TaON is deposited by radio-frequency magnetron sputtering and the top electrodes Pt and Cu are deposited by DC magnetron sputtering. Finally, the produced structures of two devices are Pt/TaON/TiN and Pt/Cu/TaON/TiN.

3-1.1 Pt/TaON/TiN

First, getting the defined via size devices are that the TiN bottom electrode has defined within photo-resist protecting the exposed bottom electrode and without photo-resist on via hole. The insulator TaON is deposited by radio-frequency magnetron sputtering on bottom electrode TiN and the recipe is **Table 3-1**. After depositing TaON, the Pt top electrode is deposited by DC magnetron sputtering on insulator like **Table 3-2**. Lifting off the photo-resist on bottom electrode is final step. **Figure 3-1(a)** is the schematic diagraph of device Pt/TaON/TiN .

3-1.2 Pt/Cu/TaON/TiN

First , getting the defined via size devices are that the TiN bottom electrode has defined within photo-resist protecting the exposed bottom electrode and without photo-resist on via hole. The insulator TaON is deposited with the insulator of device Pt/TaON/TiN simultaneously by radio-frequency magnetron sputtering on bottom electrode TiN at the same time with and the recipe is **Table 3-1**. After depositing TaON, the Cu top electrode is deposited by DC magnetron sputtering on insulator like **Table 3-3**. And then, the Pt which protects Cu from oxidized is deposited by DC magnetron sputtering on insulator like **Table 3-2**, but deposition time/thickness is 80 sec/ 10nm. Lifting off the photo-resist on bottom electrode is final step. The **Figure 3-2(a)** is the schematic diagraph of device Pt/Cu/TaON/TiN .

3-2 Material Analysis of Pt or Cu/ TaON / TiN Structure

In order to understand the structure of Pt / TaON / TiN, there are some methods of the material analysis to be used to analysis the device.

3-2.1 Material analysis of N&K

The **Figure 3-4** shows thickness of film TaON. The analysis is that energy gap is 2.5eV **[26]** and thickness is about 20nm.

3-2.2 Material analysis of Mid-IR

The **Figure 3-5** shows bonding of film TaON. The N -Ta-O, Ta -O, and Ta-N is the main bonding **[27][28]**.

3-2.3 Material analysis of XPS

X-ray photoelectron spectroscopy (XPS) is a quantitative spectroscopic technique and a power tool. Using the method can measure the elemental composition, chemical state and electronic state of the elements existing within a material. XPS spectra are obtained by using X-rays to shoot the thin films and simultaneously detecting the kinetic energy and number of electrons escaping from the material.

The X-ray photoelectron spectroscopy (XPS) pictures **Figure3-6(a)** and **Figure3-6(b)** show the composition of the insulator of TaON. According to XPS, we can observe that the peaks existing in the Ta 4f7/2 spectra **Figure3-6(a)** are Ta metal Ta 4f7/2 (21.8eV) , Ta metal Ta 4f5/2 (23.7eV), TaON Ta 4f7/2 (25.8eV), and TaON Ta 4f5/2 (27.7eV). On the other hand, the peak exists in the O 1s spectra **Figure3-6(b)** is TaON (530.8eV)**[26]**.

3-2.3 Material analysis of TEM

The **Figure 3-1(b)** shows the image of cross section for Pt /TaON/ TiN structure. The thickness of TaON which matches with N&K is about 20nm. The **Figure 3-2(b)** shows the image of cross section for Pt /Cu/TaON/ TiN structure. Its TaON thickness 20nm also matches with N&K.

3-3 Electrical Measurement

In the experiment, using the Agilent-4156 and Agilent B1500 to do the electrical measurement is the main method. Applying bias on the bottom electrode TiN and top electrode Cu or Pt grounded like **Figure 3-3**.

The recipe of film TaON	
Target	4” TaN
Substrate temperature	room
Working pressure	8m torr
Gas flow	Ar 30 sccm O_2 30 sccm
power	RF 100 W
Deposition time/thickness	2000 sec/20nm

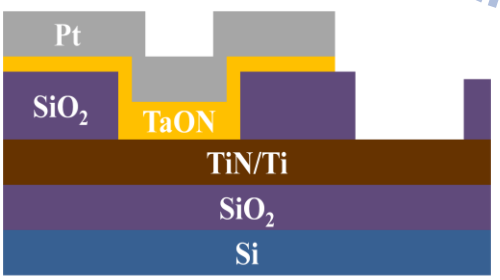
Table 3-1

The recipe of film Pt	
Target	4” Pt
Substrate temperature	room
Working pressure	8m torr
Gas flow	Ar 30 sccm
power	DC 100 W
Deposition time/thickness	500 sec/80nm

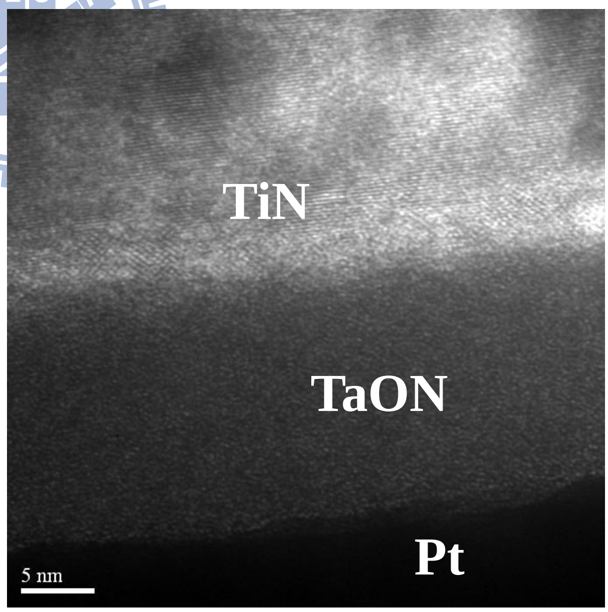
Table 3-2

The recipe of film Cu	
Target	4” Cu
Substrate temperature	room
Working pressure	4m torr
Gas flow	Ar 30 sccm
power	DC 200 W
Deposition time/thickness	200 sec/100nm

Table 3-3

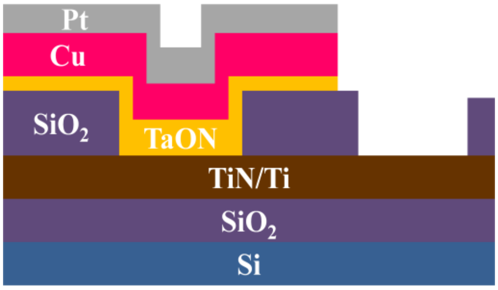


(a)

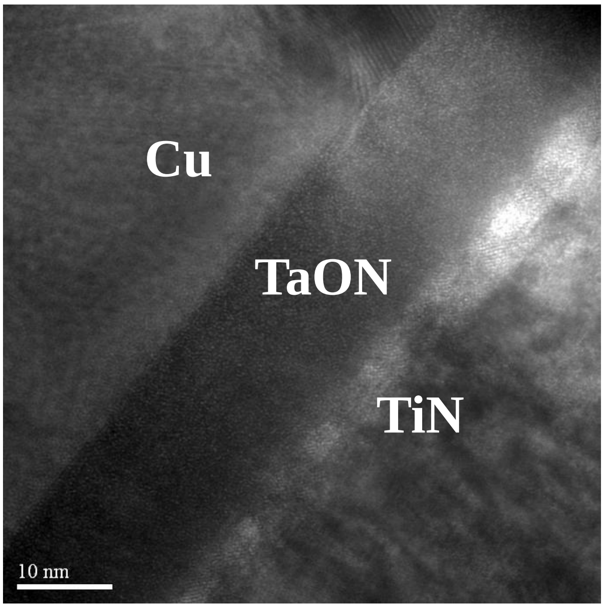


(b)

Figure 3-1 (a)Pt/ TaON/TiN device’s schematic diagraph
(b) The image of cross section for Pt/ TaON/ TiN(TEM)



(a)



(b)

Figure 3-2 (a)Pt/Cu/TaON/TiN device's schematic diagraph
(b) The image of cross section for Pt/ Cu/TaON/ TiN(TEM)

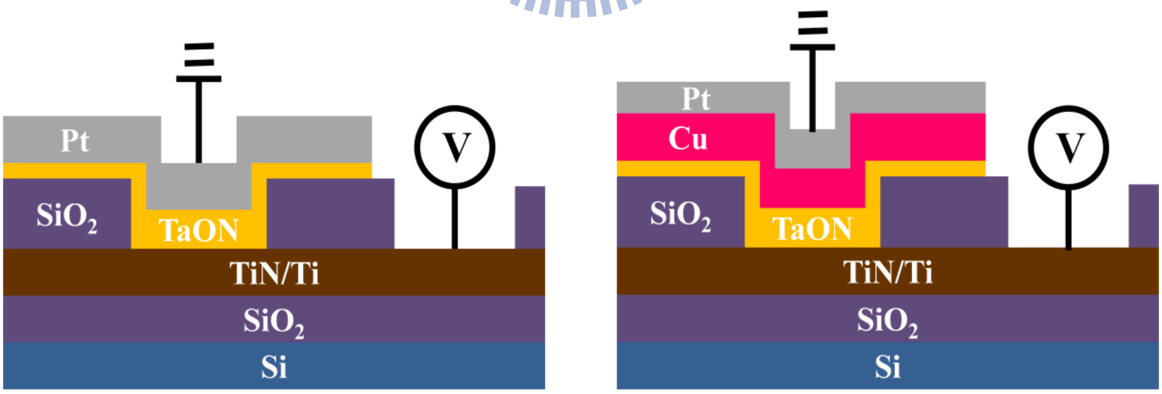
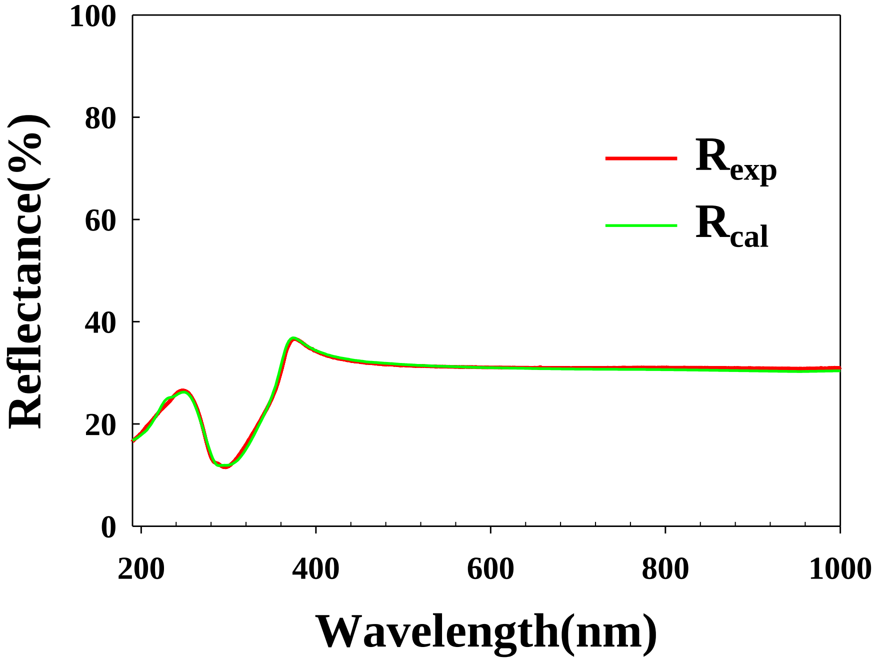
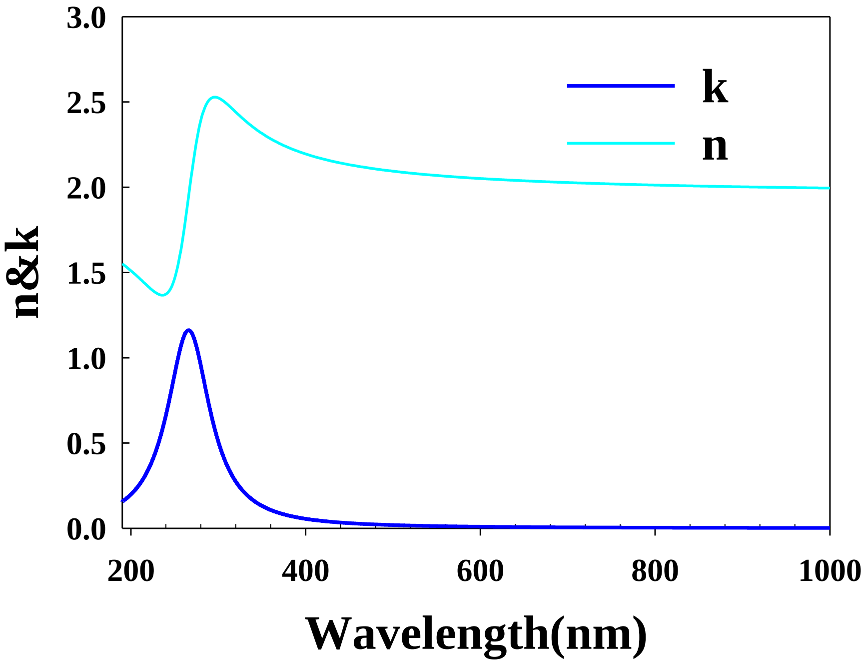


Figure 3-3 electrical measurement schematic diagraph



(a)



Eg(V)=2.84eV
Thinkness(nm)=20.593nm

(b)

Figure 3-4 The material analysis of N&K(a) the fitting of reflective wave (b) n&k

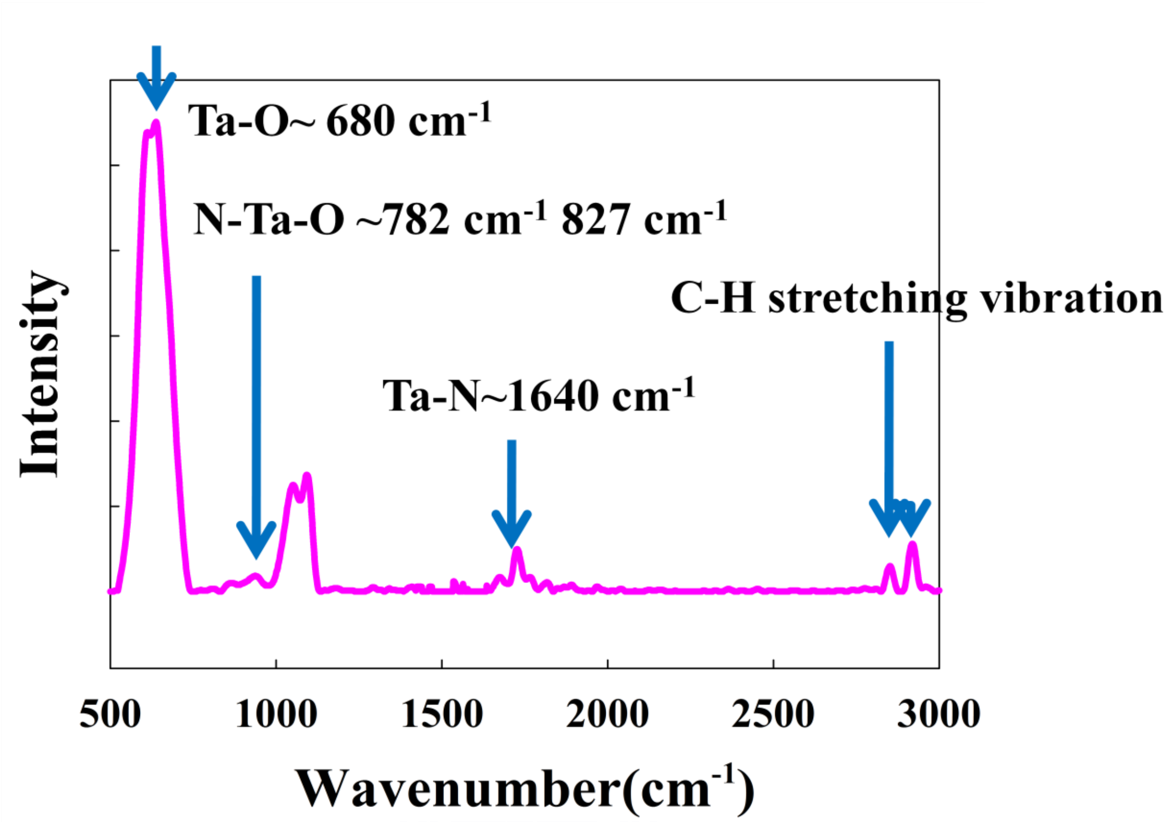
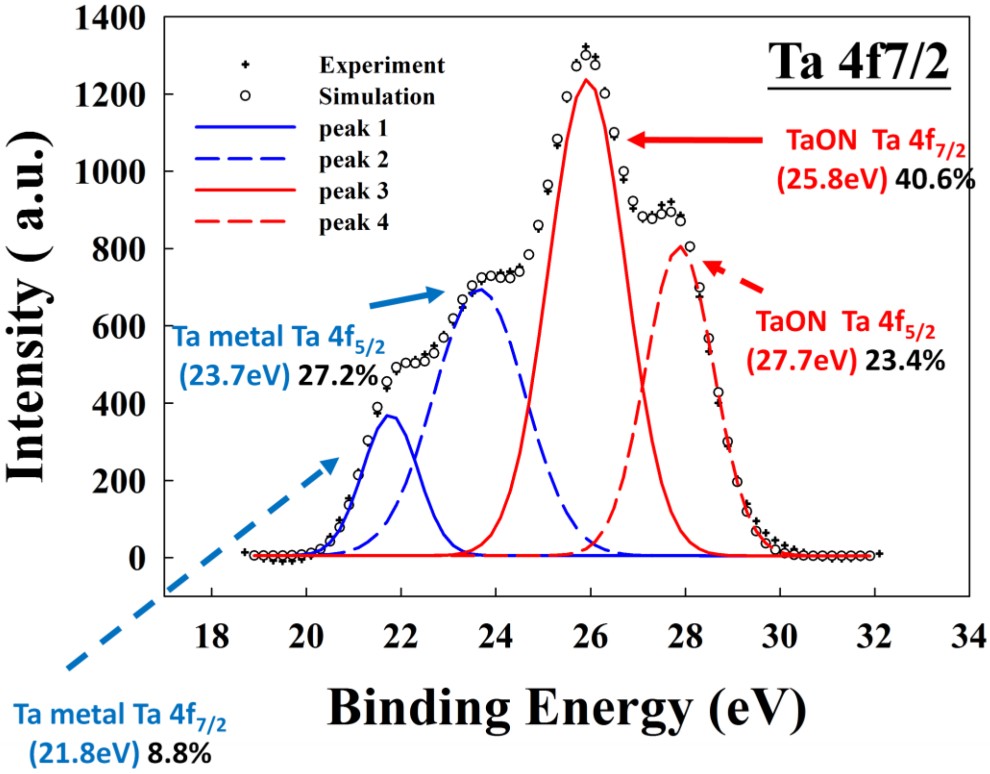
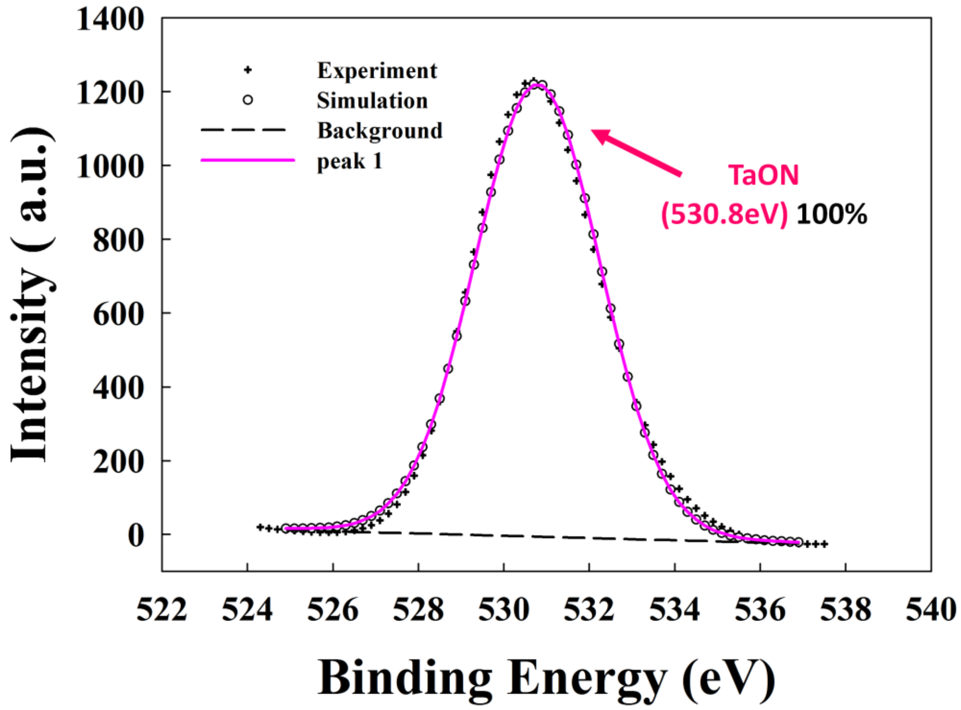


Figure 3-5 The material analysis of Mid-IR



(a)



(b)

Figure 3-6 The material analysis of XPS (a) Ta 4f7/2 spectra
(b) O 1s spectra

Chapter 4

Results and Discussion

4-1 The Resistive Switching Features of Different Top Electrode

In the section, first, we discuss primarily that the different two top electrodes (Cu,Pt) affect the resistive switching characteristics. So we fixed the thickness of the insulator, TaON, 20nm and the bottom electrode TiN. We discuss the mechanism of resistive switching by the two devices. Because we know that Cu's redox is easier than Pt's, our inference is that the one device (Cu top electrode) has the resistive switching by Cu cations redox and migration in the film and the other (Pt top electrode) has the resistive switching by oxygen anions migration (oxygen vacancy remains) in the film.

4-2 Bipolar Resistive Switching Fature of Pt / TaON / TiN Structure

4-2.1 Current-Voltage characteristics

We introduce our electrical measurement at first. For our structure Pt/TaON/TiN, it is at high resistance state original before it is processed Forming. "Forming" is the initial applied large voltage process which can produces large electric field in the insulator and makes the insulator TaON produce impact ionization. We calls this process soft break down .When soft break down happens, device's resistance will become low. Therefore, the large current will pass through the TaON. But soft break down which can recover from low resistance to high resistance differs from hard break down. Like **Figure 4-1(a)**, we choose one device that bottom electrode TiN is applied positive DC sweep from 0V to 10V with voltage step increasing 10mV and top electrode is common. We can observe TaON film break down when the voltage value is 6V which is Forming voltage. Due to avoiding the insulator TaON causing the permanent destruction, we have to set the current compliance (I_{comp}) about 5mA.Then, we choose another device that bottom electrode TiN is applied negative DC sweep from 0V to -10V with voltage step increasing 10mV and top electrode is common and also set current compliance like **Figure 4-1(b)**. We observe that the negative Forming is successful as well. After Forming, we can operate the devices with bipolar method.

Figure 4-2 is the operating devices current-voltage characteristics. We give the bias to bottom electrode and top electrode is common. The figure shows when the positive bias sweeps from 0V to 2V, the current suddenly increases to current compliance which we set is the same as Formig . In that time, the resistance state of the device switches from high to low which is "set" and the voltage which lets current increase suddenly is "set voltage" .When bias sweeps from 2V back to 0V, the resistance state keep in low. The negative bias sweeps from 0V to -1.6V, we can find about 0.6V afterward that the current doesn't increase along with voltage increasing, but the current decreases instead. In the end, the resistance state of the device switching from low to high is "reset" process and the voltage which begins to make the current decreased along with voltage increasing is "reset voltage". The positive bias Forming has the same operation as the negative bias Forming.

4-2.2 Reliability

The reliability of any memory is very important, because we don't want to our data loss or change. Thus, we have to operate our devices and understand our devices' fundamental characteristics. We will measure devices' endurance, retention, and multi-level. We hope that our devices can be operated more times, memorized data for a long time, and have a large capacity.

4-2.2.1 Endurance

Endurance is how many times device can be operated. We wouldn't program and erase wrong. In the memories, endurance is very important. So we also apply DC bias and AC pulse to device's (Pt/TaON/TiN +Forming) bottom electrode and top electrode is common.

In DC endurance test, we apply DC sweep and read the current values of 0.2 V, and then calculate the resistance. The **Figure 4-3** is the current-voltage curve of DC sweep 100cycles. The **Figure 4-4** shows the resistance of the 100 times DC sweep cycles at 0.2V. We can observe the on state resistance (low resistance) / off state resistance (high resistance) have about 2 orders and is stable for 100 times. In order to measure our device whether can endure more operation times or not, we use AC pulse.

AC Pulse is faster operation than DC sweep, so device is operated more times per second. In AC endurance test, first, we must measure condition what pulse can "set" or "reset" the device. Giving a positive bias pulse to device which is at the high resistance state so as to make switch to low resistance state .In order to make sure the device's state, we apply a small voltage sweep from 0V to 0.2V to make sure the device "set" successfully. Afterward we give a negative bias pulse to the same device and apply a small voltage sweep from 0V to 0.2V to make sure the device "reset" successfully. In addition, avoiding wasting time, in one time applying 1000 times continuous positive bias pulses and negative bias pulses. This process is like operating the device ”set” and “reset” 1000 times .Repeating to apply 1000 times continuous positive bias pulses and negative bias pulses one hundred times that means we will operate the device’s “set” and “reset” 100,000 times.

The **Figure 4-5** is a signal we set. “Set” pulse width is 10us, and voltage is 2.2V. “Reset” pulse width is 18us, and voltage is -2V. The **Figure 4-6** is AC endurance at room temperature. We observe the on/off ratio about 1.5 orders.

4-2.2.2 Retention

Another important feature of memories is retention. Retention is how long can the memory memorize and no datum losing. Of course we hope that memorial time is longer and longer. At retention test we maintain device (Pt/TaON/TiN +Forming) at high or low resistance state . We measure the device’s resistance value by 0V~0.2V sweeping at the time passing about 1s, 30s, 100s, 300s, 1000s, 3000s, 5000s, 7000s, 9000s, 10000s at 85^{0}C.In that way ,we can check out device’s resistance state changed or not after long time passes. In **Figure 4-7**, we see the device maintain the on/off ratio about 2.5 orders after 10,000 seconds.

4-2.2.3 Multi-level

Multi-level is the important feature of memory. Due to smaller and smaller memory technology, we hope that the memory can be stored more and more data in a finite space. If one device can save one over data, we don’t need many devices to save data. Thus, we can save space and miniature memories.

We can operate two methods to get multi-level. The one is changing the current compliance and the other is changing voltage stop. The two methods make on/off ratio order under control in order to increase the density of storage. The method which is changing current compliance to operate multi-level is in **Figure 4-8(a)**. We control the current compliance (I_{comp}) at 1 mA, 5 mA, and 10mA. From **Figure 4-8(b)**

20cycs per current compliance, we observe the on/off ratio orders changed from 1 to 2. Although the high resistance state value doesn't be changed, the low resistance state value is decreased along with current compliance increasing. The other method which is changing voltage stop to operate multi-level is in **Figure 4-9(a)**. We control the voltage stop (V_{stop})at -1.1V, -1.6V, and -1.9V. From **Figure 4-9(b)** 20cycs per voltage stop, we get the one result instead which is the high resistance state value increased along with voltage stop increasing and the low resistance state value is not changed. The other result in **Figure 4-9(c)** 20cycs per voltage stop is that the "set" voltage (V_{set}) distribution is increased by voltage stop increasing.

4-3 The Bipolar Resistive Switching Mechanism Discussion of the Structure Pt/ TaON/ TiN

After we are familiar with our device characteristic, we can construct some models to explain these phenomena. Due to some unusual phenomena, published resistive switching mechanism didn't explain. So we propose some suit mechanism explanation for our data.

4-3.1 Forming of bipolar

The RRAM is the structure of MIM (metal /insulator/ metal). There is not any RRAM characteristic before Forming process. Thus, we have to apply Forming bias which is the first step to break down the insulator. So that electrons can be conducted easily in the insulator via the conductive path which is constructed by the breaking down. However, general break down is not revivable. The breaking down is called Soft break down which can be recovered and is the key phenomenon in our device. In the other word , when our device is operated Formig, device's state is switched from high resistance state to low resistance state, and then device can be operated "reset" from low resistance state to high resistance state.

In the **Figure 4-10**, we set current compliance about 5mA and apply DC sweep to bottom electrode and top is common. In positive Forming process, we give DC sweep from 0V to 10V. Beginning the current keeps in very small value about 10^{-13}A~10^{-12}A. However, the current elevates abruptly from 10^{-12}A to current compliance (5mA) at the Forming voltage about 6V. The phenomenon we can specify with schematic diagram. The **Figure 4-11(a)** is device initial state. In the **Figure 4-11(b)** when we apply a large positive bias on bottom electrode, there is upward electric field produced in the insulator. The electric field has large strength will make the weakest place of insulator soft break down. Once the soft break down happens, the tantalum-oxygen bonds and the nitrogen-oxygen bonds will be broken. Then, oxygen will be ionized and is charged negative charge. Since the ionized oxygens are anions, they will drift along with reverse direction of electric field and be stored in the TiN electrode which is the nice oxygen ions storage tank (from Gibb's free energy TiO 672.4kj/mol). Therefore, there are many oxygen vacancies left in the insulator. Those oxygen vacancies are just like a conductive filament which electrons hopping via. In that time, the large current pass through insulator, so we know that the device's resistance state is switched from high to low.

In **Figure 4-10**, we set current compliance about 5mA and apply DC sweep to bottom electrode and top is common. In negative Forming process, we give DC sweep from 0V to -10V. We also find out the negative bias Forming is successful and forming voltage value is the almost same as positive bias Forming. The phenomenon we explain in **Figure 4-12(a)** and **(b)**. Due to electric field direction downwards, the only special thing is that oxygen anions drift towards top electrode .The Pt electrode isn't the nice oxide storage tank (Gibb free energy PtO is 391.6 kJ/mol), and oxygen anions will run away by Pt's grains. However, the soft break down needs adequate oxygen anions to be recovered. This moment the insulator's oxygen anions are not enough to rebound the insulator. Thus, observing **Figure 4-13** 100 times DC sweep endurance can let us know that the positive bias Forming operation is more stable than the negative bias Forming operation. Due to the oxygen anions running away, insufficient oxygen anions fill the oxygen vacancies in negative bias Forming. The condition make the high and low resistance state value smaller in negative bias Forming process than in positive bias Forming process .

4-3. 2 I-V Feature of bipolar

We know that the resistance of the device will change from high to low by Forming process. But we can't conclude the device which is workable. The most important thing of all we hope Forming process is soft break down rather than hard break down. Therefore, We must make it's resistance from low to high by "reset" and then from high to low by "set" many times.

In the **Figure 4-14(a)**, we successfully let the device "reset" (resistance state from low to high) ,maintain resistance state in high state. In the "reset", we apply the DC sweep from 0V to -1.6V. The -1.6V is voltage stop which we can set to change the high resistance state of our device like multi-level. Now we focus on about -0.6V. We find that the current value become smaller and smaller from about -0.6V to voltage stop -1.6V. That is the unusual condition. Thus, we think the condition is the resistive switching from low resistance to high resistance. In order to explain the condition, we construct the model. The resistive switching is related with ionized oxygen moving. The electrons hopping by oxygen vacancies forming conductive filament causes insulator conductible. After the positive bias Forming process, the conductive filament appears. In that time, the oxygen ions(negative charges) move towards TiN electrode by the electric field (upwards) reverse direction. In the "reset" process , applying negative bias to bottom electrode produce the downwards electric field , and then oxygen ions move back to the insulator filling the oxygen vacancies which is produced by Forming process like **Figure 4-14(b)** . The oxygen vacancies filled by oxygen ions makes the conductive filament vanish and electrons can’t hop via oxygens vacancies. Therefore, the device’s resistance state switches from low to high. Besides, the resistance state still stays in high when the DC sweeping back to the 0V.

If we set different voltage stop, the high resistance state is also different like multi-level. Because of the oxygen vacancies filled probably by electrons, the oxygen vacancies are filled by oxygen ions difficultly. So setting different voltage stop can make different number of electrons go away from oxygen vacancies. More voltage stop can drive away more electrons. In addition, more oxygen vacancies are filled by oxygen ions and device’s resistance state is lower**[15]**.

After “reset” process, the device’s resistance state is high. In order to switch back to the low resistance state, we must operate “set”. In the **Figure 4-15(a)**, we give the DC sweep from 0V to 2V to the device. We focus on about 1.2V the current increases abruptly to current compliance (5mA). In other word, the device’s resistance state switching from high to low is “set”. The current compliance is that we prohibit the device from hard break down happening. We also construct the model to explain “set” process. In **Figure 4-15(b)**, when we apply a positive bias to bottom electrode, the soft break down happen again. The enough electric field make oxygen ionized. The oxygen ions move toward TiN and the oxygen vacancies are left. The conductive filament appears again .When DC sweeping back to 0V, the device’s resistance state maintains at low.

In **Figure 4-10 and 4-15(b)**, we are aware that Forming voltage (about 6V) is more than “set” voltage (about 1.2V). We also find the same phenomenon in multi-level operation **Figure 4-9**. Along with voltage stop larger, “set” voltage becomes larger. We know that electric field in the resistive switching layer equals crossed voltage divided by crossed interface layer's(the resistive switching layer is near bottom electrode TiN) thickness(E=V/d). Because Forming is the first step to produce a complete conductive path connecting top and bottom electrodes and using the law of partial voltage the voltage almost is crossed at high resistance ,we must apply voltage crossed whole insulator to produce a electric field which is large enough to ionize oxygens like **Figure 4-16(a)**. After Forming process, the conductive path is produced in insulator. However, according to your giving voltage stop from large to small, the layer's thickness is changed from thick to thin and high resistance state's resistance value will be switched from large to small like **Figure 4-16(b) (c) (d)**. Thus, "set" only needs voltage crossed interface layer (the resistive switching layer) near bottom electrode to produce a electric field to ionize oxygens in the interface layer. The interface layer's thickness become thicker with voltage stop larger, so "set" voltage becomes larger for maintaining enough large electric field to ionize oxygens. Besides Forming (the resistive switching layer's thickness is whole insulator) needs more voltage than "set".

4-3.3 The mechanism discussion the first Reset of positive and negative Forming

From basic I-V operation process of device Pt/ TaON/ TiN**,** we can find the structure has bipolar electrical characteristic. The bipolar characteristic is that applying bias to bottom electrode positive for "set" and negative bias for "reset". The mechanism of bipolar resistive switching is discussed in above section. In addition, when we apply positive Forming, the oxygen anions moving to TiN and leaving the oxygen vacancies make device's resistive state switch from high to low. Then, giving the first negative bias in order to let the oxygen anions go back and fill the oxygen vacancies that will make device's resistive state switched from low to high. Above explanation is polarity method .However , we can't explain why the device's resistive state can be switched from high to low by negative Forming and can be switched from low to high by the first negative bias "reset" with the polarity method. We find the leakage current in Forming process **Figure 4-10** and the first "reset" I-V curve **Figure 4-17** is different between positive and negative Forming.

First of all, we explain different leakage current with band diagram. In **Figure 4-18(a)**, we know that the work function of Pt(5.65eV)is more the TiN(4.8~5.3eV).Therefore ,when entering insulator ,the elections see that the barrier's height of positive Forming **Figure 4-18(b)** is higher than of negative Forming **Figure 4-18(c)**. Electrons enter from TiN is easier than from Pt. So positive Forming has lower leakage current than negative Forming has.

Next, we construct the model to explain the first "reset" I-V curve phenomenon in positive and negative Forming. The first "reset" of negative Forming is heat and diffusion method .When negative Forming producing downwards electric field make oxygen anions move to top electrode Pt and produce conductive filament. Because Pt affects oxygen difficultly, the oxygen anions moving to top electrode is free. In that time, applying a negative bias smaller than Forming make conductive filament produce heat. Besides, we know although the producing downwards electric field makes oxygen anions still pushed to Pt electrode, the oxygen anions can be diffused to fill the oxygen vacancies in bulk by the oxygen anions' concentration gradient like **Figure 4-19**.The diffusion ability is stronger than drift ability. When oxygen anions are diffused, the heat produced by conductive filament will give energy to oxygen anions and make oxygen anions repair insulator defect (oxygen vacancies is also defects) like **Figure 4-20(a)**. When the defects are repaired, the conductive filament making of oxygen vacancies disappear as well. Finally, the device's resistance state becomes high. After operating the first "reset" of negative Forming, the operation process resistive switching mechanism which is the same as positive Forming's is polarity method. Furthermore, the first "reset" is in **Figure 4-20(b)**, after positive Forming, oxygen anions are accumulated together and bonded with TiN. Thus, as applying negative bias, oxygen anions are pushed back to insulator and fill up the oxygen vacancies. In this moment the device's resistance state is switched from low to high.

4-4 Bipolar Resistive Switching Feature of Pt/Cu/TaON/TiN Structure

After discussing the mechanism of the structure Pt/TaON/TiN, we replace the Pt top electrode with Cu top electrode in advance. We believe the structure perhaps has completely different feature and resistive switching mechanism. We not only construct another model to explain the different feature but also use many experiments to prove our options. In order to clarify the different mechanism, our insulator's thickness and process condition are the same between structure Pt/TaON/TiN and Pt/Cu/TaON/TiN.

4-4.1 Current-Voltage characteristics

First, we still do the electrical measurement. The **Figure 4-21(a)** is negative bias Forming I-V curve. We apply negative bias to bottom electrode and top electrode is common. The applied bias is DC sweep from 0V to -10V, step increasing is 10mV, and then we have to set the current compliance (I_{comp}) at 5mA so as to let the device alive. The soft break down happened rather than hard break down. We observe that the current value increase abruptly at about -4V, so the -4V is Forming voltage. We also can apply positive bias from 0V to 10V, step increasing is 10mV, and then we have to set the current compliance (I_{comp}) at 5mA to bottom electrode and top electrode is common. Form **Figure 4-21(b)**, we find out the Forming voltage is about 6V. After Forming process,we start to operate the device.

Figure 4-22 is a current–voltage characteristic curve. The major discovery is that the structure Pt/Cu/TaON/TiN’s polarity is different from the structure Pt/TaON/TiN’s. In other word, the structure Pt/Cu/TaON/TiN’s operation process is negative bias “set” and positive bias “reset” , but the structure Pt/TaON/TiN’s is contrary. We give bias to bottom electrode and top electrode is common. In “set” operation process, we apply the DC sweep from 0V to -1.3V, step is 10mV, and then set the current compliance at 5mA. We find out the current value raising suddenly to current compliance meaning resistance switched from high to low at about -0.6V is “set voltage”. When we apply the DC sweep back to 0V, the resistance is kept in low state. In “reset” operation process, we give the DC sweep from 0V to 1.1V, step is 10mV. Then, we observe the current decreases slowly at sweeping voltage from about 0.4V to 1.1V.At 0.4V “reset voltage” device’s resistance state beginning to be switched from low to high. When we apply the DC sweep back to 0V, the resistance is kept in high state. The positive Forming’s “set” and “reset” operation process is same as negative Forming’s.

4-4.2 Reliability

The device is workable .We discuss the structure Pt/Cu/TaON/TiN’s device basic characteristic briefly in DC endurance and room temperature retention. We also can compare Pt electrode with Cu electrode in basic characteristics.

4-4.2.1 Endurance

We measure structure Pt/Cu/TaON/TiN DC sweep endurance. **Figure 4-23** is drawn that we operate the device Pt/Cu/TaON/TiN 100times and **Figure 4-24** read resistance value at 0.2V. We can observe the on state resistance (low resistance) / off state resistance (high resistance) have about 1.5 orders and on state resistance is stable for 100 times.

AC Pulse is faster operation than DC sweep, so device is operated more times per second. In AC endurance test, first, we must measure condition what pulse can “set” or “reset” the device. Giving a negative bias pulse to the high resistance state device so as to make switch to low resistance state .In order to make sure the device’s state, we apply a small voltage sweep from 0V to 0.2V to make sure the device “set” successfully. Afterward we give a positive bias pulse to the same device and apply a small voltage sweep from 0V to 0.2V to make sure the device “reset” successfully. In addition, avoiding wasting time, in one time applying 1000 times continuous positive bias pulses and negative bias pulses. This process is like operating the device ”set” and “reset” 1000 times Repeating to apply 1000 times continuous positive bias pulses and negative bias pulses one hundred times that means we will operate the device’s “set” and “reset” 100,000 times.

The **Figure 4-25** is a signal we set. “Set” pulse width is 12us, and amplitude is -1.3V. “Reset” pulse width is 30us, and amplitude is 1.8V. The **Figure 4-26** is AC endurance. We observe the on/off ratio about 1 orders.

4-4.2.2 Retention

Retention is the time of the data storing in the device. In that time, we keep the temperature at 85^0C. First, we let device operate “set” and keep at low resistance state. We measure the device’s resistance value by 0V~0.2V sweeping at the time passing about 1s, 30s, 100s, 300s, 1000s, 3000s, 5000s, 7000s, 9000s, 10000s.Next ,we let device operate “reset” and maintain at high resistance state. We also measure the device’s resistance value by 0V~0.2V sweeping at the time passing about 1s, 30s, 100s, 300s, 1000s, 3000s, 5000s, 7000s, 9000s, 10000s. In **Figure 4-27**, we see the device maintain the on/off ratio about 1.5 orders after 10,000 seconds. Moreover, the experiment shows not only device Pt / TaON / TiN but also Pt / Cu/ TaON / TiN has good retention.

4-5 The Bipolar Resistive Switching Mechanism Discussion of the Structure Pt/ Cu/ TaON/ TiN

After discussing the mechanism of structure Pt/TaON/TiN, we observe different phenomenon of structure Pt/Cu/TaON/TiN. Because the operation process is completely different, we consider the resistive switching dissimilar as well.

4-5.1 Forming of bipolar

Forming is a method to establish a conductive path in the insulator. However, we view the conductive path as different composition between positive and negative Forming. First, we observe the I-V curve **Figure 4-28** positive and negative Forming. In positive Forming, we set current compliance about 5mA and apply DC sweep to bottom electrode and top is common. The DC sweep from 0V to 10V. Beginning the current keeps in very small value about 10^{-12}A~10^{-11}A. The current elevates abruptly at the Forming voltage about 6V. In negative Forming process, we give DC sweep from 0V to -10V at current compliance about 5mA and applying DC sweep to bottom electrode and top is common. Strangely, the Forming voltage in negative Forming is about -4V.However, the phenomenon doesn't happen in structure Pt/TaON/TiN (in **Figure 4-10** , the Forming voltage is the same).So we think that the mechanism of producing conductive path is different in positive and negative Forming process.

First, we can specify positive Forming in the **Figure 4-29(a)**. When we apply a large positive bias on bottom electrode, there is upward electric field producing in the insulator. The electric field has large strength will make the weakest place of insulator soft break down, so the Forming voltage is equal with structure Pt/TaON/TiN. In that time, the oxygens are ionized and drift along with reverse direction of electric field to bottom electrode leaving oxygen vacancies in the insulator, so the resistance is switched from high to low.

Next, we detail the conductive path produced in negative Forming. We apply negative DC sweep to bottom electrode and top electrode is common. In **Figure 4-29(b)(c)(d)**, when we give a negative bias to bottom electrode ,the downwards electric field is produced. The electric field make the copper atoms on the top electrode interface oxidized into copper ions. Because of the copper ions charged positive, they drift along with the direction of electric field and are restored in bottom electrode. Once more and more copper cations are restored into copper atoms, they link together and become a conductive path connecting top with bottom electrode. Thus, the resistance is switched from high to low.

From the **Figure 4-30** 100 times DC cycles' set voltage distribution, we know the negative Forming has more concentrated V_{set} distribution than positive Forming. For the reason the Forming process is important. Looking **Figure 4-31(a)**, after negative Forming, the conductive path composed of copper atoms previously have confined the resistive switching layer in a small region. On the contrary, there are only oxygen vacancies produced after positive Forming. In operation process, copper cations moving by oxygen vacancies are produced random conductive path and resistive switching region is distributed randomly like **Figure 4-31(b)**.So the negative Forming has more excellent operation process stability than positive Forming.

4-5. 2 I-V Feature of bipolar

The resistive switching mechanisms of operation process are the same after applying negative or positive Forming. After Forming, we also operate "reset". Now, the method we operate device Pt/Cu/TaON/TiN is different from the method we operate structure Pt/TaON/TiN. In **Figure 4-32(a)**, “reset” process, we apply DC sweep from 0V to1.1V to the bottom electrode. The 1.1V is voltage stop, and then the device start to switch resistance from low to high about 0.4V. The reason we explain why the device can switch resistance .In the **Figure 4-32(b)**, we consider the resistive switching is related with electron migration and heat. When we give a positive bias to bottom electrode to produce a large current flowing the filament, the current make the heat produced. Due to heat disturbance, the electrons will hit the copper atoms out easily. More and more copper atoms hit makes linking conductive filaments are broken. Then, the resistance state is switched from low to high. Besides, the resistance state still stays in high when the DC sweeping back to the 0V.

After “reset” process, the device’s resistance state is high. In order to switch back to the low resistance state, we must operate “set”. In the **Figure 4-33(a)**, we give the DC sweep from 0V to -1.3V to the device. We focus on about -0.6V the current increases abruptly to current compliance (5mA) .The voltage is “set voltage”. The resistance switched from high to low is related with copper redox, too. In **Figure 4-33(b)**, when we apply a negative bias to bottom electrode, the downwards electric field is produced. In that time, copper atoms are oxidized into cations in top electrode and moved to the tip of the filament due to electric focusing on it. The copper cations are restored into atoms. More and more copper atoms accumulated and nucleated are linked to construct conductive filaments. Due to conductive filament connecting top with bottom electrode, the device’s resistive state is switched from high to low. When DC sweeping back to 0V, the device’s resistance state maintains at low .When operating the device “set” or “reset”, these phenomenon happen again and again.

4-6 The Current Fitting of Structure Pt / TaON / TiN and

Pt/Cu/ TaON / TiN

In order to verify our resistive switching mechanism model in structure Pt/TaON/TiN and Pt/Cu/TaON/TiN, we fit the I-Vcurve of operation process. Finding out conduction mechanism matches with our resistive switching mechanism explanation.

We use a stable I-V curve to do the current fitting at first. We know that the different conduction mechanism s have different appearance of line. Thus ,we can judge whether every part of operation process I-V curve fitted in any conduction mechanism is linear relationship or not and we can check line's slope correct or not. Doing above method we can find out conduction mechanism of every part in I-V curve.

4-6.1 Current-Voltage curve fitting of structure Pt/TaON/TiN

We begin to do the device Pt/TaON/TiN's current fitting. In **Figure 4-34**, we focus on "set" process. When we apply DC sweep from 0V to 2V, the resistance state is switched from high to low. At the high resistance state we fit the conduction mechanism which the DC sweep about from 0.02V to 0.1V is the Ohmic conduction mechanism , from 0.12V to 0.36V is the Schottky conduction mechanism , from 0.38V to 0.48V is the Poole-Frenkel conduction mechanism ,and from V 0.54to 1.08V is the space charge limit current(SCLC) conduction mechanism. When we apply DC sweep back to 0V, the resistance state is maintained low. We can fit the Ohmic conduction mechanism in whole I-V curve.

Next, we focus on "reset" process. In **Figure 4-34**, when we apply DC sweep from 0V to -1.6V, the resistance state is switched from low to high. At the low resistance state we can fit the Ohmic conduction mechanism in whole I-V curve. When we apply DC sweep back to 0V , the resistance state is maintained high. At the high resistance state we fit the conduction mechanism about from -0.016V to -0.08V is the Ohmic conduction mechanism, from -0.096V to -0.224V is the Schottky conduction mechanism, from -0.24V to -0.592V is the Poole-Frenkel conduction mechanism, from -0.608V to -1.232V is the space charge limit current (SCLC) conduction mechanism, and from -1.28V to -1.424V is the Tunneling conduction mechanism. After positive or negative Formung, the operation has the same current fitting.

4-6.2 Current-Voltage curve fitting of structure Pt/Cu/TaON/TiN

In order to understand the conduction mechanism whether there are difference between structure Pt/TaON/TiN and Pt/Cu/TaON/TiN, we do Pt/Cu/TaON/TiN's current fitting **Figure 4-35** as well. Strangely, the current fitting of Pt/Cu/TaON/TiN is little different from the current fitting of the other.

Thank to still the Ohmic conduction mechanism of low resistance state, we only observe the conduction mechanism of the high resistance state. At high resistance state of "set" process we only fit the conduction mechanism which the DC sweep about from -0.013V to -0.182V is the Ohmic conduction mechanism , from -0.195V to -0.546V is the Schottky conduction mechanism. At high resistance state of "reset" process we still only fit the conduction mechanism which the DC sweep about from 0.011V to 0.121V is the Ohmic conduction mechanism , from 0.154V to 0.847V is the Schottky conduction mechanism. There is so special current fitting that we can prove the mechanism explanation of resistive switching indirectly above section. Next section, we will explain why we can fit out those conduction mechanism. After positive or negative Formung , the operation has the same current fitting .

4-7 The Conduction Mechanism of Structure Pt / TaON / TiN

and Pt/Cu/ TaON / TiN

After we finish doing the current fitting of two devices, we still have to explain why we can get these conduction mechanism .Besides , the most important thing is why we can get completely different conduction mechanism of two device's high resistance state. The above-mentioned will be explained by band diagram.

4-7.1 Conduction mechanism of structure Pt / TaON / TiN

First of all, we explain the "set" process. When we don't give any voltage to the device, the bend diagram is like **Figure 4-18(a)**. The platinum has work function about 5.65 eV and titanium nitride has work function about 4.8 eV~ 5.3 eV. Then, we apply bias to bottom electrode titanium nitride and platinum is common .At the beginning, giving a very small positive bias to TiN. Due to the positive bias, the Fermi energy of TiN will be decreased slightly and make electrons which are excited to the TaON's conduction band by the heat flowed into bottom electrode TiN like **Figure 4-36**, so we can fit out the Ohmic conduction mechanism. Later, we add higher bias than beginning, but we observe another conduction mechanism Schottky. Like **Figure 4-37**, because of the Fermi energy of TiN will be more decreased and TaON conduction band is more sloped. In that time, electrons in top electrode platinum accepting thermal energy can jump over the barrier height near platinum side. Next, increasing bias continuously not only make Fermi energy of TiN more decreased but also let TaON conduction band more sloped continuously. In addition, the electrons hop with traps like **Figure 4-38**. So at larger voltage we can fit out the Poole-Frenkel conduction mechanism. Finally, Fermi energy of TiN will be more decreased and TaON conduction band is more sloped. A large number of electrons enter TaON's conduction band from top electrode. Because the entering electrons see some electrons left in the traps and are repulsed like **Figure 4-39**, we fit out the space charge limited current (SCLC) conduction mechanism. When soft break down happen, the electrode hopping with oxygen vacancies make device conductive. Thus, we can fit out the Ohmic conduction mechanism naturely.

Second, we explain the "reset" process. At the beginning, TiN bottom electrode is given a very small negative bias. Due to the negative bias , the Fermi energy of TiN will be raised slightly and make electrons which are excited to the TaON's conduction band by the heat flowed into top electrode Pt like **Figure 4-40**, so we can fit out the Ohmic conduction mechanism. Later, we add higher bias than beginning, but we observe conduction mechanism Schottky. Like **Figure 4-41**, because of the Fermi energy of TiN will be more raised and TaON conduction band is more sloped. In that time, electrons in bottom electrode titanium nitride accepting thermal energy can jump over the barrier height near titanium nitride side. Next, increasing bias continuously not only make Fermi energy of TiN more raised but also let TaON conduction band more sloped continuously. In addition, the electrons hop with traps like **Figure 4-42**. So at larger voltage we can fit out the Poole-Frenkel conduction mechanism. Fermi energy of TiN will be more increased and TaON conduction band is more sloped. Then, finally, a large number of electrons enter TaON's conduction band from bottom electrode. Because the entering electrons see some electrons left in the traps and are repulsed like **Figure 4-43**, we fit out the space charge limited current (SCLC) conduction mechanism.

4-7.2 Conduction mechanism of structure Pt /Cu/ TaON / TiN

In the device Pt/Cu/TaON/TiN, we see different phenomenon. First, we also explain the "set" process. When we don't give any voltage to the device, the bend diagram is like **Figure 4-44**. The copper has work function about 4.65 eV. Then, we apply bias to bottom electrode titanium nitride and copper is common. At the beginning, giving a very small negative bias to TiN . **Figure 4-45** is that electrons conduction schematic diagram of “set” process. Due to the negative bias , the Fermi energy of TiN will be raised slightly and make electrons in the insulator TaON conduction band flowed into top electrode Cu like **Figure 4-46**, so we can fit out the Ohmic conduction mechanism. Later, we add higher bias than beginning, so some electrons can jump over the barrier near TiN at room temperature. Thus, we observe the conduction mechanism Schottky .Because in that time copper cations are driven into TaON and restored near TiN, the part of insulator near TiN has smaller cross-voltage and the part of insulator near Cu has larger cross-voltage. The energy band diagram is like **Figure 4-47**

Why don’t We fit out the the Poole-Frenkel conduction mechanism? Because the conductive path is made of copper atoms just like that the top electrode Cu is extended into the insulator TaON and relative barrier height is near interface layer at TiN side. Moreover, the thickness of thickness becomes thin, because of copper atom driven. Therefore, there are few defects in TaON. The Poole-Frenkel conduction mechanism doesn’t happen.

Figure 4-48 is that electrons conduction schematic diagram of “reset” process. The conduction mechanism of “reset” process is symmetrical with “set” process. The voltage sweeping from small to large is Ohmic **Figure 4-49** and Schottky **Figure 4-50**. The low resistance state is just like a small resistance, so naturally the conduction mechanism is Ohmic .

4-8 Temperature Method Explains Copper Conduction Filament in TaON

We use current fitting to prove there are different conductive mechanism in the device Pt/TaON/TiN and Pt/Cu/TaON/TiN. But this method is not enough. Thus, we use actual equipment to prove this thing.

First, we use DC sweep to measure two devices in different temperature. We measure that two devices' high resistance state and low resistance state are changed with temperature changing. Thus , we maintain two devices' resistance state at high , and then apply DC sweep from 0V to 0.2V step 10mV to bottom electrode and common to top electrode respectively . Measuring two devices is at 25^{o}C, 40^{o}C, 60^{o}C, 80^{o}C, 100^{o}C, 120^{o}C, 130^{o}C and 140^{o}C, as well as, reading is at 0.2V like **Figure 4-51(a)** and **Figure 4-51(b)**. We can find out simultaneously that the measured current values are larger (resistance are smaller) with temperature increased at high resistance state in two devices. Because of TaON having energy gap about 2.4eV, we can recognize that the two devices' high resistance state is semiconducting state.

Next, we also use DC sweep to measure two devices in different temperature. But now we maintain two devices at low resistance state. Fortunately, we observe the different phenomenon in **Figure 4-52(a)** and **Figure 4-52(b)**. Due to increased current values with temperature increasing, the **Figure 4-52(a)** means the low resistance state of device Pt/TaON/TiN is semiconducting state as well. However, as current values are decreased (resistance are increased) with temperature increasing, the **Figure 4-52(b)** means the low resistance state of device Pt/Cu/TaON/TiN is metal like state. Therefore, we can prove in advance that the conductive path in device Pt/Cu/TaON/TiN is made of copper atoms.

4-9 Sampling Method to Prove the Devices of Top Electrode Cu's Resistive Switching Mechanism

Above section, we use temperature to prove copper filament is the conductive path in device Pt/Cu/TaON/TiN. In the section, we research deeply the copper filament in device Pt/Cu/TaON/TiN. We are aware that the device Pt/Cu/TaON/TiN has a polarity which applying negative bias to bottom electrode is “set” process and positive bias is “reset” process. Since there are copper filaments in insulator and copper filaments are keys to make the device switched resistance ,and then “reset process” is mainly related with thermal effect, we think we also can use joule-heating and electro-migration method in negative “reset” bias to let the copper filaments to be broken in order to switch device’s resistance from low to high. The joule-heating uses heat to break the copper filament .The electro-migration is the phenomenon that electrons flowing results copper atoms to move .The electrons flowing produces large momentum to affect copper filaments. Thus, we use sampling method to do that.

We use constant current sampling which we apply a constant current to device and observe what time does the device be switched. First of all, we let our device Pt/Cu/TaON/TiN to be maintained at low resistance state. And then, we apply a constant current sampling to bottom electrode. From the **Figure 4-53(a)**, the sampling condition is constant positive current 9mA, and we can observe that the device is switched from low to high in the **Figure 4-53(b)**. And then, another sampling condition is set negative current 9mA, because we think we can “reset” with joule-heating or electro-migration as well. In **Figure 4-54(a)**, we observe the sensor device voltage’s absolute value becoming larger abruptly from 0.62V to 0.72V which means the device are switched from low resistance state to high resistance state. (R=V/I (I=constant)).After we check DC sweep again ,the device has been switched undoubtedly like **Figure 4-54(b)**.In order to reduce thermal interference, another equipment is measured at temperature 77K and can get obvious result in **Figure 4-55(a) (b)**. Thus, those equipments (joule-heating or electro-migration is not related with polarity) prove again that the copper filaments are made of copper atoms and are keys in resistive switching of device Pt/Cu/TaON/TiN different from Pt/ TaON/TiN.

4-10 Another Resistive Switching Characteristic of Pt/ TaON/ TiN Structure

After discussing the bipolar resistive switching characteristic, we find out another resistive switching characteristic in the device Pt/TaON/TiN. Another resistive switching feature is unipolar which the device is operated by applying negative or positive bias in “set” process and “reset” process to the same electrode. We can give negative bias not only let resistance of device to be switched from high to low but also have resistance of device to be switched from low to high. The unipolar can switch resistance state in the same polarity, so we think the mechanism of unipolar is different from the mechanism of bipolar.

4-10.1 Current-Voltage characteristics

The same step with bipolar operation, first, we have to operate Forming process. The Forming makes the device produce soft break down and conductive path appear simultaneously. We choose one device that bottom electrode TiN is applied positive DC sweep from 0V to 10V with voltage step increasing 10mV and top electrode is common. We can observe TaON film break down when the voltage value is 6V which is Forming voltage. Due to avoiding the insulator TaON causing the permanent destruction, we have to set the current compliance (I_{comp}). In addition, we can operate negative bias Forming process as well.

After operating Forming process, we can operate the device with unipolar method. The **Figure 4-56** is unipolar resistive switching I-V characteristic diagram. We give the DC sweep from 0V to -3V to bottom electrode and top electrode is common .When the negative bias at about -1.9V, the current suddenly increases to current compliance which we set 5mA. In that time, the resistance state of the device is switched from high to low which is “set” and the voltage which lets current increase suddenly is “set voltage”. We don’t let bias sweep from -3V back to 0V, because the conductive path produced in “set” process will be broken like **Figure 4-57**. And then we apply the negative DC sweeps from 0V to -1V. In the process we find about -1V afterward that the current doesn’t increase along with voltage increasing, but decrease instead. In that time the resistance state of the device is switched from low to high which is “reset” and the voltage is “reset voltage”. The positive bias Forming has the same operation as the negative bias Forming.

4-10.2 DC endurance

The **Figure 4-58(a)(b)** are the DC sweep cycle 50 times I-V curves after operating positive bias Forming. The **Figure 4-59(a)(b)** are the DC sweep cycle 50 times I-V curves after operating negative bias Forming The **Figure 4-60(a)** is the DC sweep endurance cycle 50 times after operating positive bias Forming reading at 0.2V. Because the unipolar operation is unstable and have the device die easily, we only operate 50 times DC sweep in other to confirm our device having the unipolar resistive switching feature of negative bias “set” and negative bias “reset”. The on/off ratio is 2.5orders before the thirtieth cycle, and then only 1 order after the thirtieth cycle. The **Figure 4-60(b)** is the DC sweep endurance cycle 50 times after operating negative bias Forming reading at 0.2V. The on/off ratio is 3orders before the tenth cycle, and then only 1 order after the tenth cycle. The uniploar operation has poor feature.

4-10.3 Retention

The **Figure 4-61** is the unipolar operation retention at 85^0C temperature. We also measure the device's resistance value by 0V~0.2V sweeping at the time passing about 1s, 30s, 100s, 300s, 1000s, 3000s, 5000s, 7000s, 9000s, 10000s.Next ,we let device operate "reset" and maintain at high resistance state. We also measure the device's resistance value by 0V~0.2V sweeping at the time passing about 1s, 30s, 100s, 300s, 1000s, 3000s, 5000s, 7000s, 9000s, 10000s .This device maintains the on/off ratio about 2 orders after 10,000 seconds.

4-10.4 The discussion of resistive switching mechanism

4-10.4.1 Forming of unipolar and the first Reset

The positive and negative bias Forming and their first "reset" mechanism has been said in the section **4-3.1** and **4-3.3**. However, we find out the different phenomenon in the **Figure 4-60(a)(b)** the DC endurance at 0.2V of positive and negative Forming and I-V curve of "reset" process **Figure 4-58(b)** and **Figure 4-59(b)**. In **Figure 4-60(a)** DC sweep operation after positive Forming, the high resistance state value is higher before the thirtieth cycle than after. However, in **Figure 4-60(b)** DC sweep operation after negative Forming, the high resistance state value is higher before the tenth cycle than after. Why does the high resistance state value changing happen earlier in negative Forming than in positive Forming? Because when we apply a large positive or negative bias on bottom electrode, there is electric field producing in the insulator. The electric field has large strength will make the weakest place of insulator soft break down. Once the soft break down happens, the tantalum-oxygen bonds and the nitrogen-oxygen bonds will be broken. Then, oxygen will be ionized and is charged negative charge. Since the ionized oxygens are anions, they will drift along with reverse direction of electric field .Applying positive bias Forming produces upwards electric filed and applying negative bias Forming produces downwards electric filed. In positive Forming process oxygen anions will be drifted to bottom electrode and be stored in the TiN electrode which is the nice oxygen ions storage tank **Figure 4-62(a)**. In negative Forming process oxygen anions will be drifted to top electrode and run out insulator easily by Pt's grains **Figure 4-62(b)**. Thus, there are less oxygen anions to fill the oxygen vacancies after negative Forming than after positive Forming , so making resistance of device switches from low to high more and more difficultly and the high resistance state value changing happen earlier in negative Forming than in positive Forming

4-10.4.2 I-V Feature of unipolar

From **Figure 4-56** we find the unipolar resistive switching. We also consider the resistive switching is related with ionized oxygens moving due to electrons hopping by oxygen vacancies forming conductive filament causing insulator conductible like bipolar feature of device Pt/TaON/TiN in "set" process. However, the only different thing is that the "reset" process.

We can observe "set" process first. When we give the DC sweep from 0V to -3V to bottom electrode, the resistive switching of device from high to low happen at about -1.9V like **Figure 4-63(a)**. When the negative bias is applied to TiN, there is a downwards electric field produced. In that time, the oxygens ionized become oxygen anions and leave oxygen vacancies. The oxygen anions are moved to top electrode Pt by electric field. Because Pt produce bond with oxygens very difficultly (Gibb free energy of PtO is 391.6kJ/mol), the oxygen anions not only are free near Pt but run away by Pt's grains. Owing to the oxygen anions driven to Pt, electrons moving by left oxygen vacancies lets insulator conductible like **Figure 4-63(b)**.

Next, we discuss the "reset" process. After "set" process, the some free oxygen anions have been accumulated near top electrode. When we apply negative bias again from 0V to -1V to bottom electrode like **Figure 4-65(a)**, the oxygen anions don't recover the oxygen vacancies. Because electric field direction is still downwards, oxygen anions are accumulated continuously near Pt. However, the oxygen anions diffused by oxygen anions' concentration gradient is stronger than the oxygen anions drifted by the electric filed like **Figure 4-64**. Besides, the bias makes oxygen vacancies produce heat to enhance oxygen anions to fill up the oxygen vacancies. The heat lets free oxygen anions become active. Thus, the conductive path is broken like **Figure 4-65(b)**, so resistance is switched from low to high. No matter how polarity Forming process, the operation resistive switching mechanism is the same. Why can't we apply positive bias in "set" process and positive bias in "reset" process? Because the bottom electrode TiN will bond with oxygen anions, so the oxygen anions are captured by TiN. As "reset" process, the captured oxygen anions can't diffuse. Therefore, we can't operate device with above method.

4-11 Another Resistive Switching Characteristic of Pt/Cu/ TaON/ TiN Structure

4-11.1 Current-Voltage characteristics

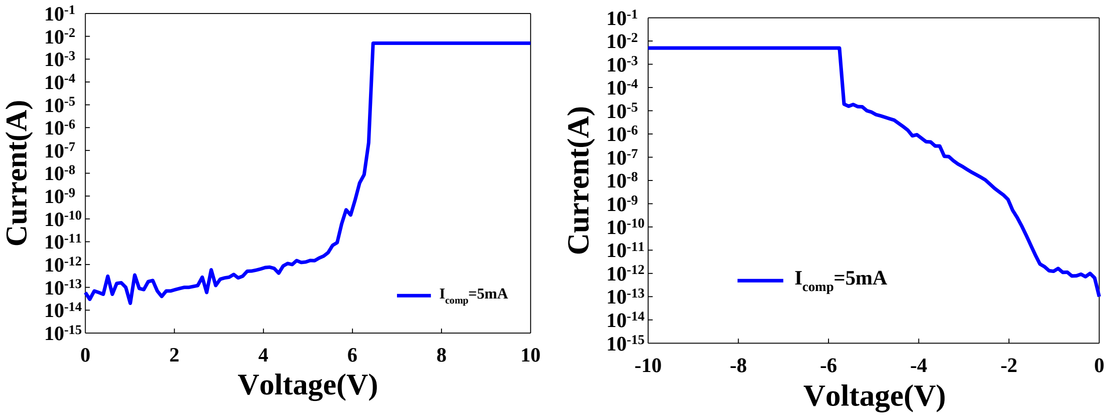
After the sampling operation, we have already understood the conductive path is made of copper atoms. Because "reset" process is mainly associated with the electron migration, one thing which bipolar operation is unnecessary can be expected. Thus, we think that another resistive switching must exist.

The **Figure 4-66** is resistive switching I-V characteristic diagram. In "set" process, we give the DC sweep from 0V to -1.2V to bottom electrode and top electrode is common. When the negative bias is swept to about -0.9V, the current suddenly increases to current compliance 5mA. In that time, the resistance state of the device is switched from high to low which is "set" and the voltage which lets current increase suddenly is “set voltage”. And then we apply the negative DC sweeps from 0V to -0.9V. In the “reset” process we find about -0.5V afterward that the current doesn’t increase along with voltage increasing, but decreases instead. In that time the resistance state of the device is switched from low to high which is “reset” and the voltage is “reset voltage”. So we can operate negative bias “set” and negative bias “reset”.

4-11.2 The discussion of resistive switching mechanism

In the **Figure 4-66** “set” process, we give the DC sweep from 0V to -1.2V to the device. We focus on about -0.9V the current increases abruptly to current compliance (5mA) .The voltage is “set voltage”. The resistance switched from high to low is related with copper redox, too. In **Figure 4-67(a)**, when we apply a negative bias to bottom electrode, the downwards electric field is produced. In that time, copper atoms are oxidized into cations in top electrode and moved to the tip of the filament due to electric focusing on it. The copper cations are restored into atoms. More and more copper atoms accumulated and nucleated are linked to construct conductive filaments. Due to conductive filament connecting top with bottom electrode, the device’s resistive state is switched from high to low.

In the **Figure 4-66**, “reset” process, we apply DC sweep from 0V to-0.9V to the bottom electrode. The -0.9V is voltage stop, and then the device start to switch resistance from low to high about -0.5V. The reason we explain why the device can switch resistance .In the **Figure 4-67(b)**, we consider the resistive switching is related with electron migration. When we give a negative bias to bottom electrode to produce a large current flowing the filament, the electrons will hit the copper atoms out. More and more copper atoms hit makes linking conductive filaments are broken. Then, the resistance state is switched from low to high.



(a) (b)

Figure 4-1 Pt/TaON(20nm)/TiN current-voltage curve bias on TiN
(a) positive bias Forming (b) negative bias Forming

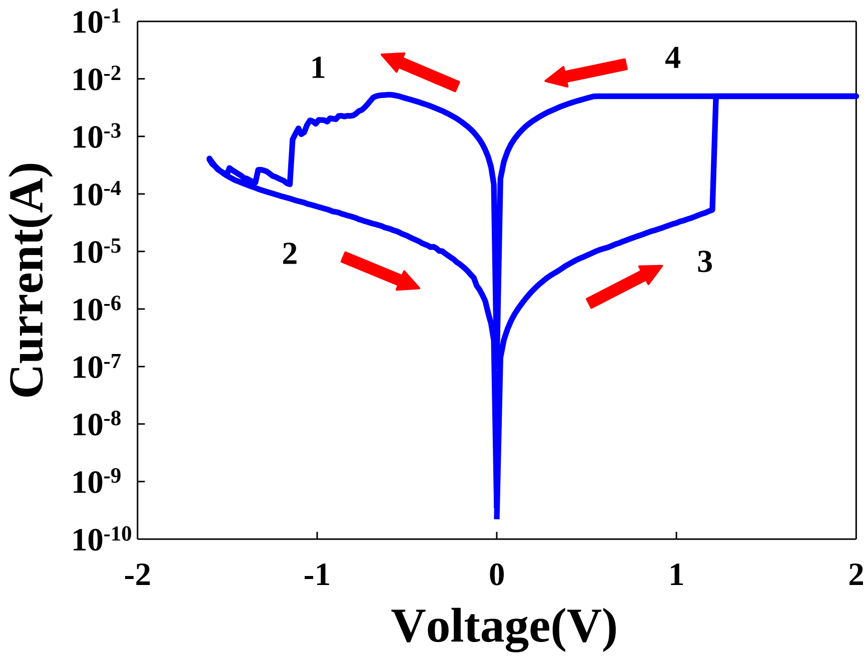


Figure 4-2 Pt/TaON(20nm)/TiN current-voltage characteristic operation curve

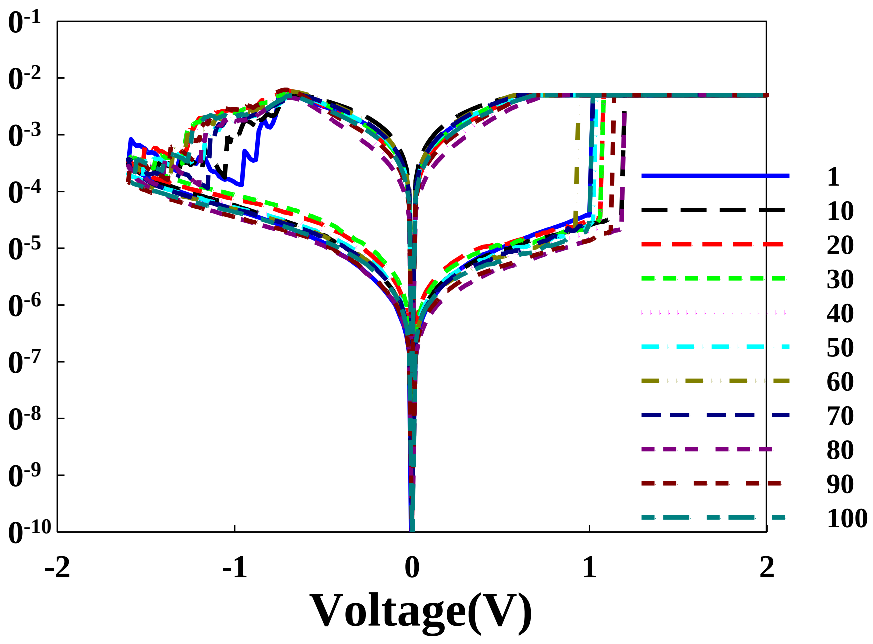


Figure 4-3 Pt/TaON(20nm)/TiN current-voltage operation curve DC sweep 100 times

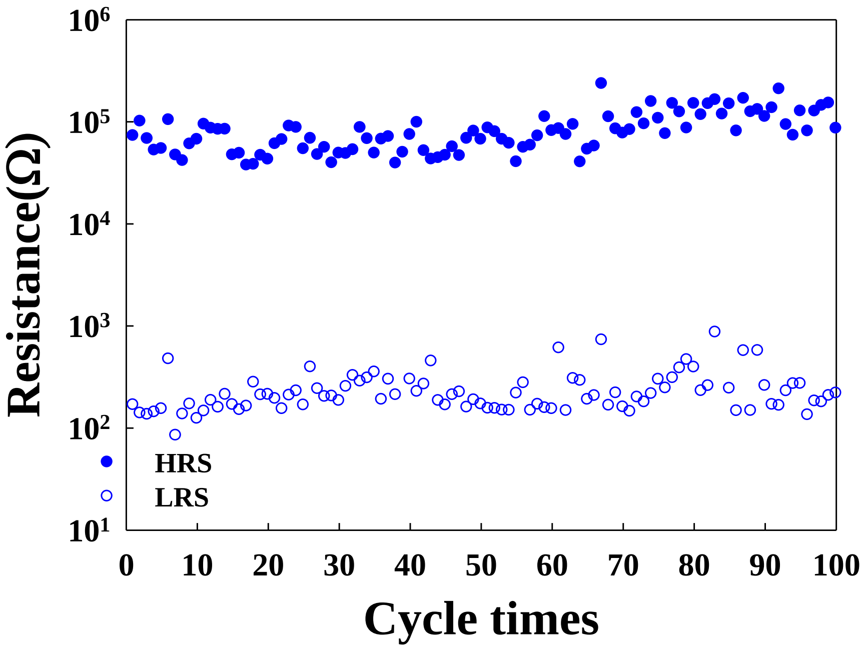


Figure 4-4 Pt/TaON(20nm)/TiN device DC endurance @0.2V

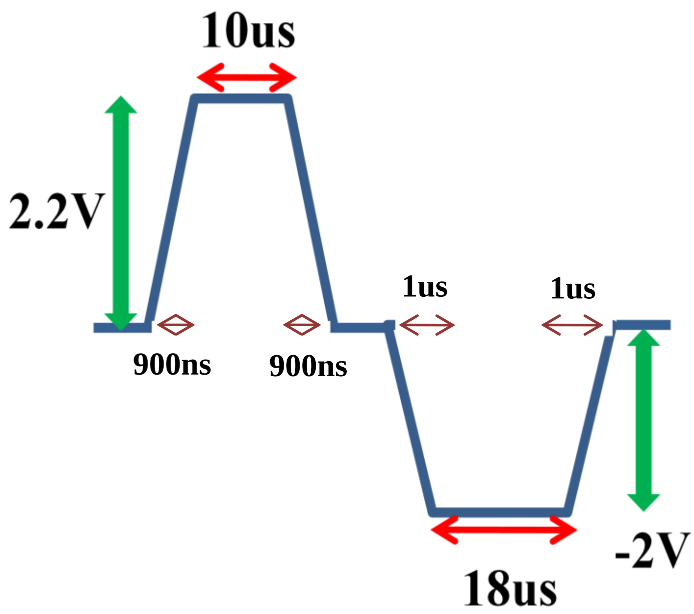


Figure 4-5 Pt/TaON(20nm)/TiN AC endurance SET pulse and RESET pulse operation

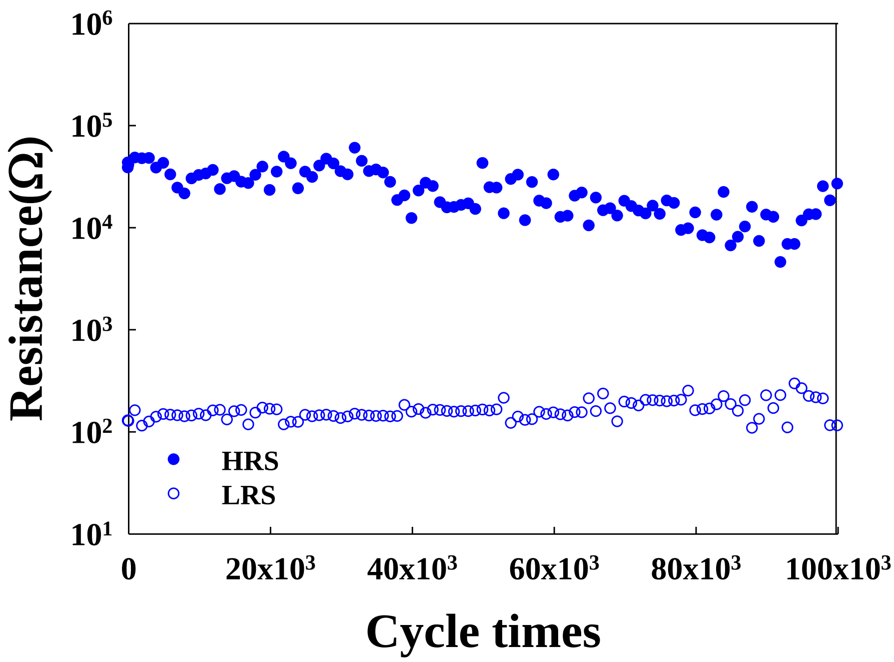


Figure 4-6 Pt/TaON(20nm)/TiN device AC endurance @0.2V

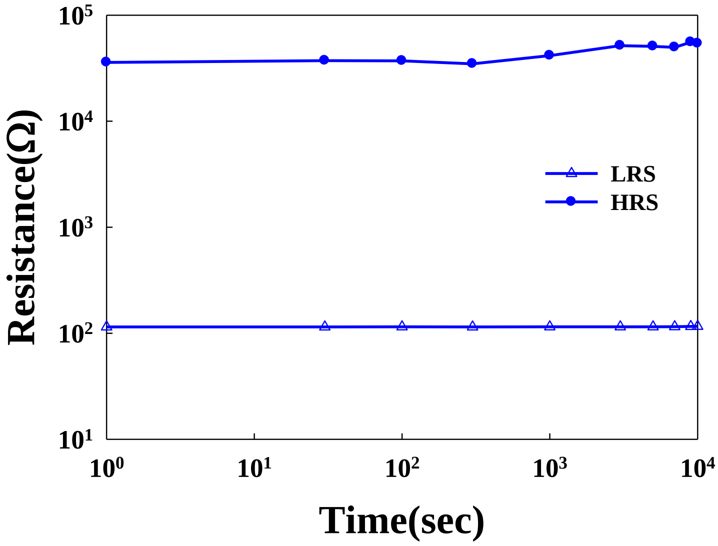
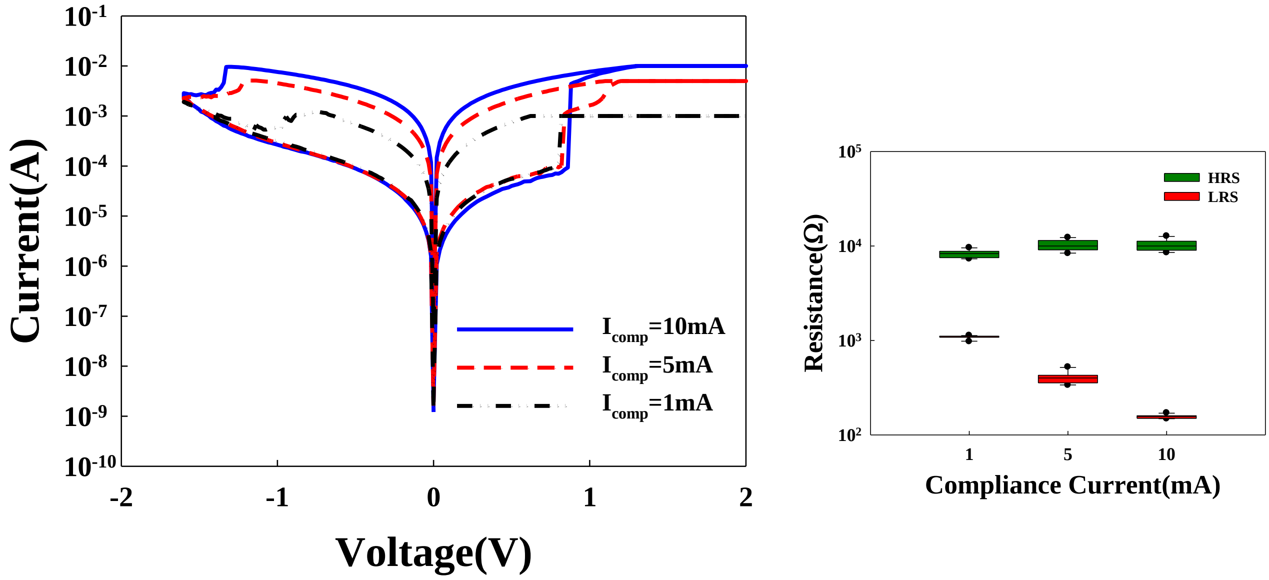
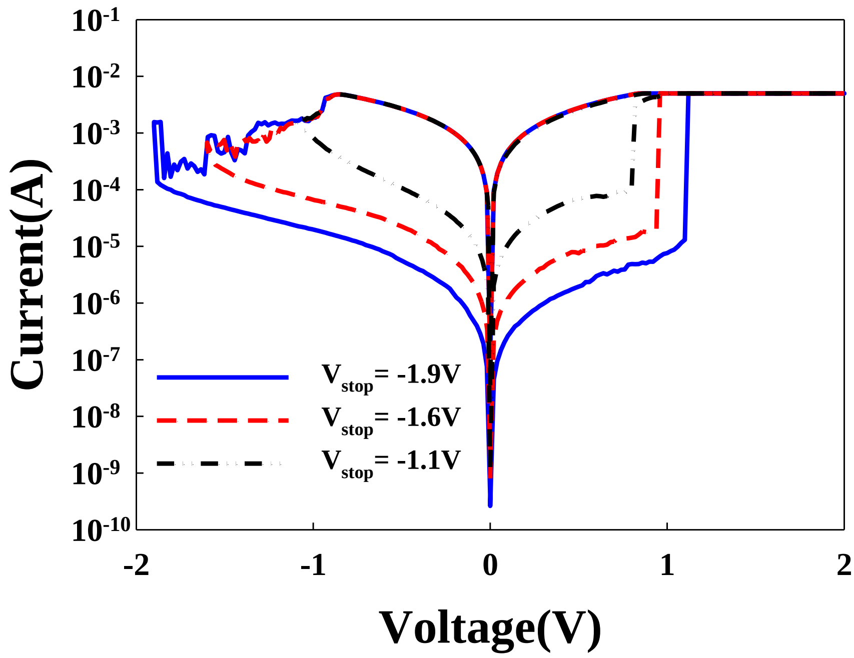


Figure 4-7 Pt/TaON(20nm)/TiN device at temperature 85^{0}C retention @0.2V

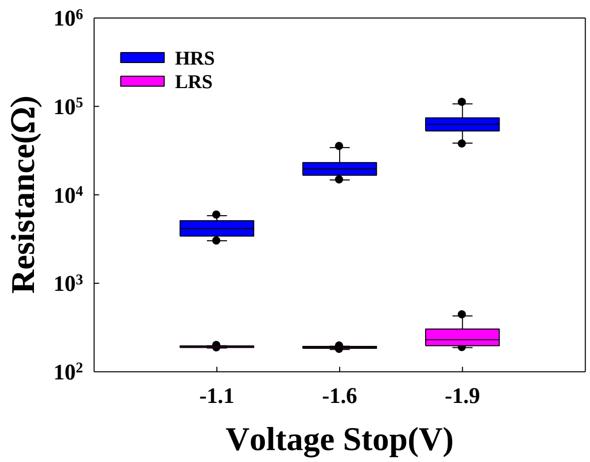


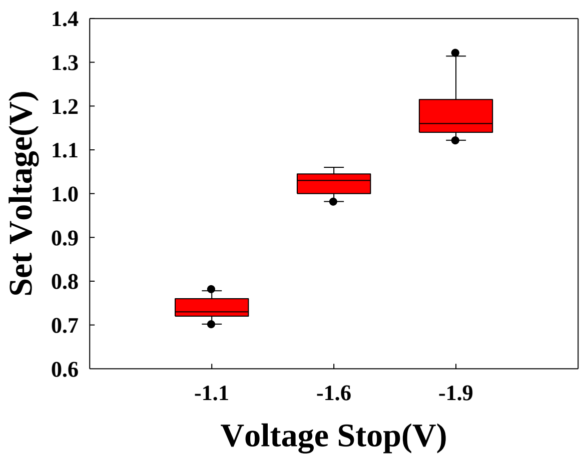
(a) (b)

Figure 4-8 Pt/TaON(20nm)/TiN device multi-level change current compliance (a) I-Vcurve (b) on/off ratio @0.2V



(a)





(b) (c)

Figure 4-9 Pt/TaON(20nm)/TiN device multi-level change voltage stop (a) I-Vcurve (b) on/off ratio @0.2V (c) V_{set} distribution of different V_{stop}

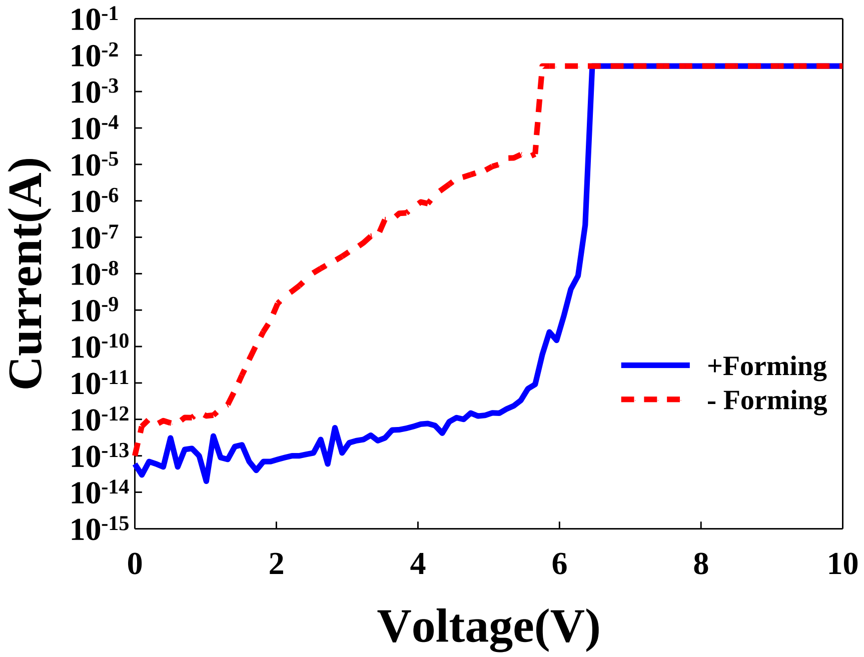


Figure 4-10 Pt/TaON(20nm)/TiN device +Forming and –Forming overlap I-V curve

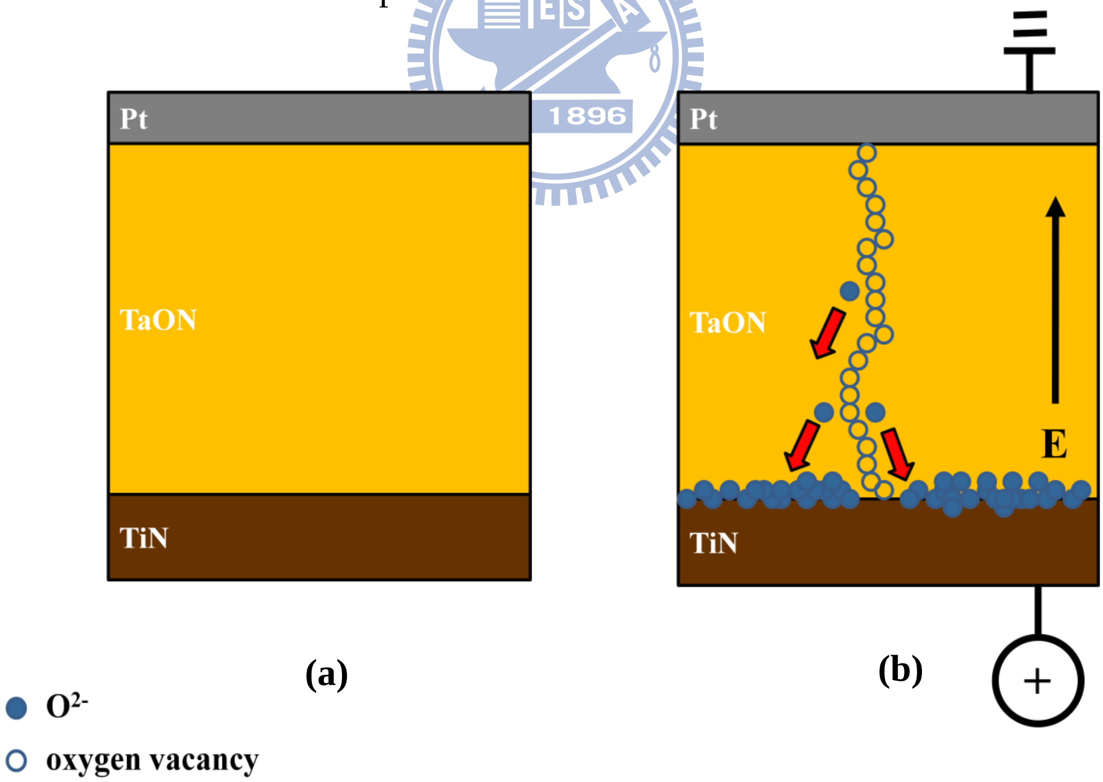


Figure 4-11 Pt/TaON(20nm)/TiN device positive Forming schematic diagram (a) Initial (b) Forming process

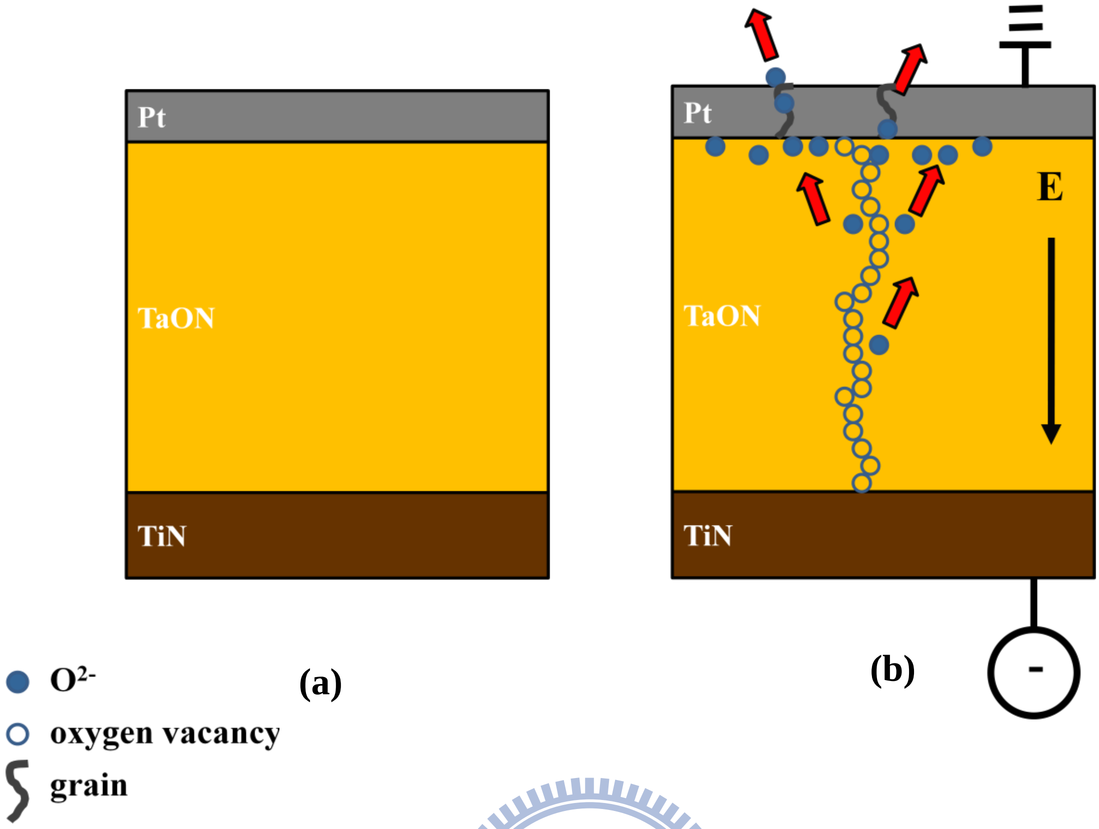


Figure 4-12 Pt/TaON(20nm)/TiN device negative Forming schematic diagram (a) Initial (b) Forming process

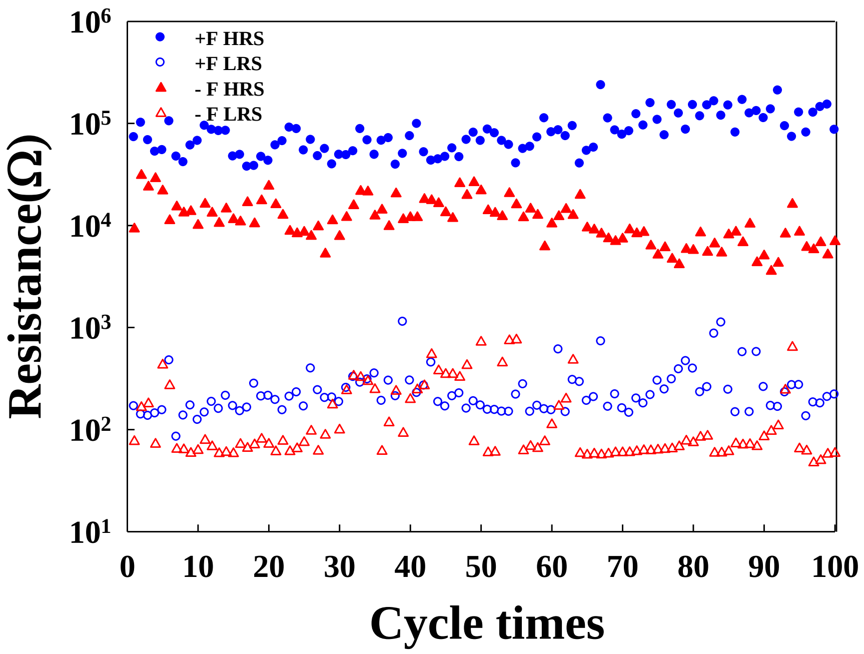


Figure 4-13 Pt/TaON(20nm)/TiN device DC endurance overlap @0.2V after operating positive Forming and negative Forming

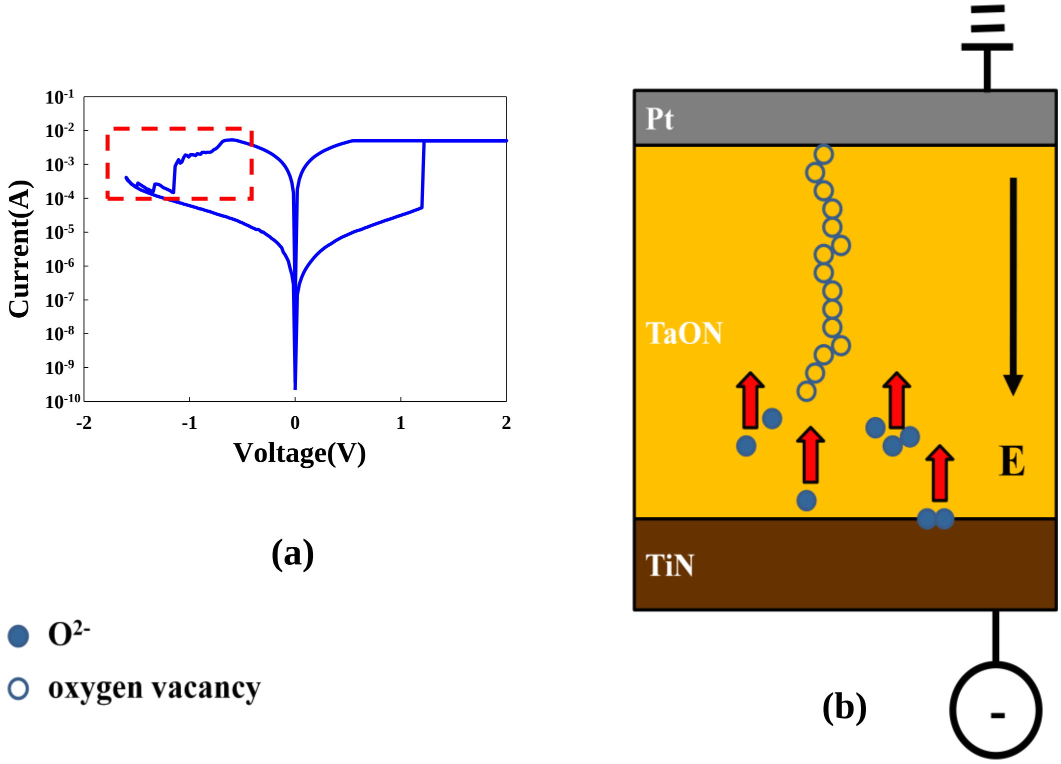


Figure 4-14 Pt/TaON(20nm)/TiN device operation
(a) I-V curve (b) “reset” process schematic diagram

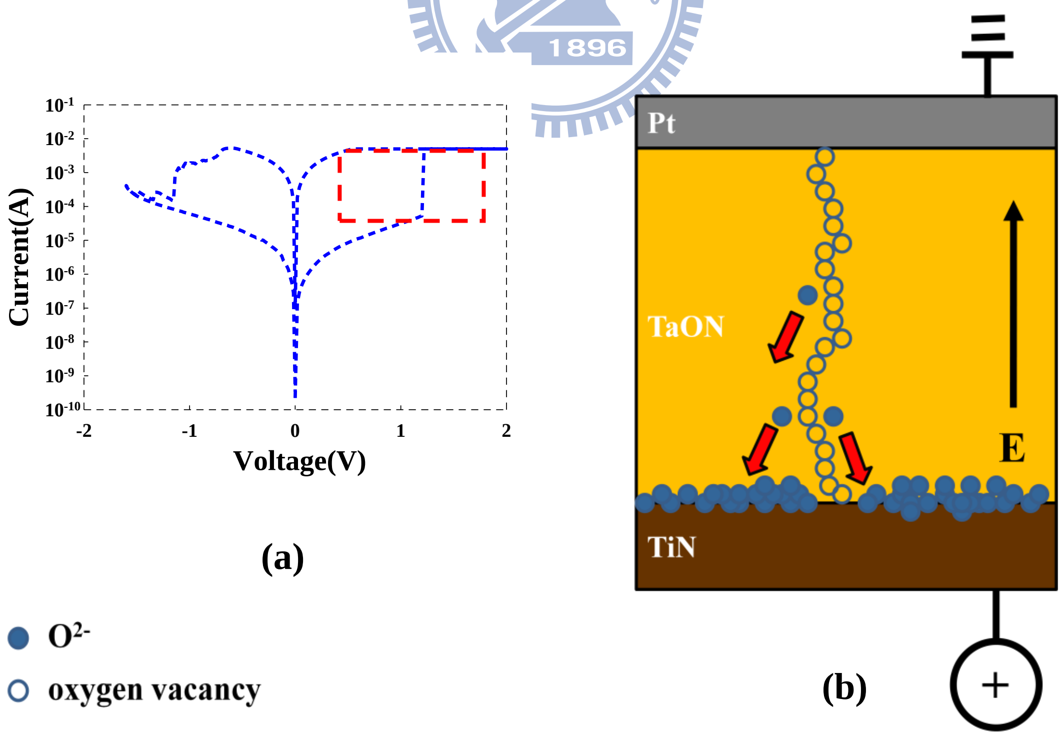


Figure 4-15 Pt/TaON(20nm)/TiN device operation
(a) I-V curve (b) “set” process schematic diagram

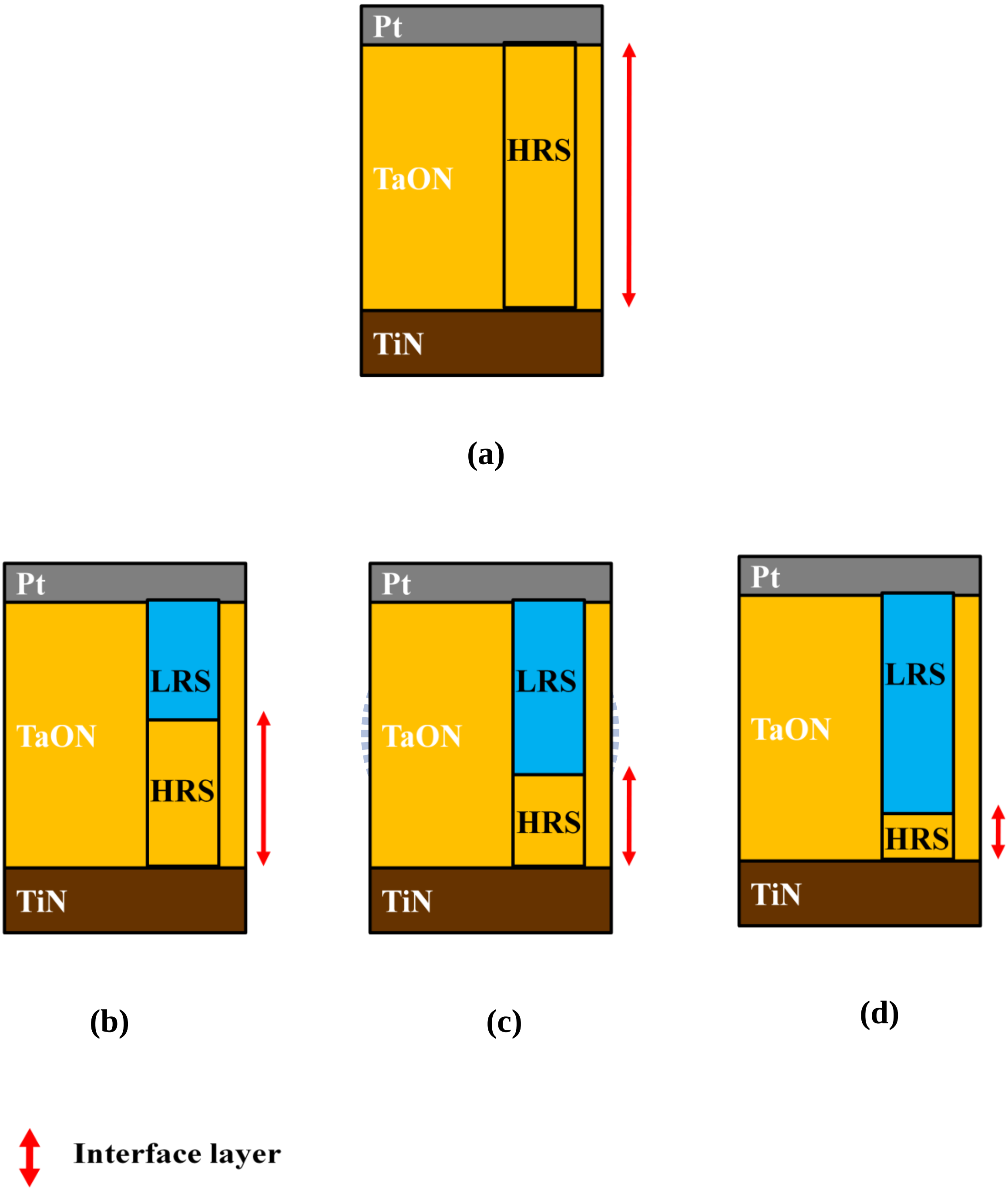


Figure 4-16 Pt/TaON(20nm)/TiN device operation schematic diagram (a) Before Forming (b) After -1.9V "reset" (c) After -1.6V "reset" (d) After -1.1V "reset

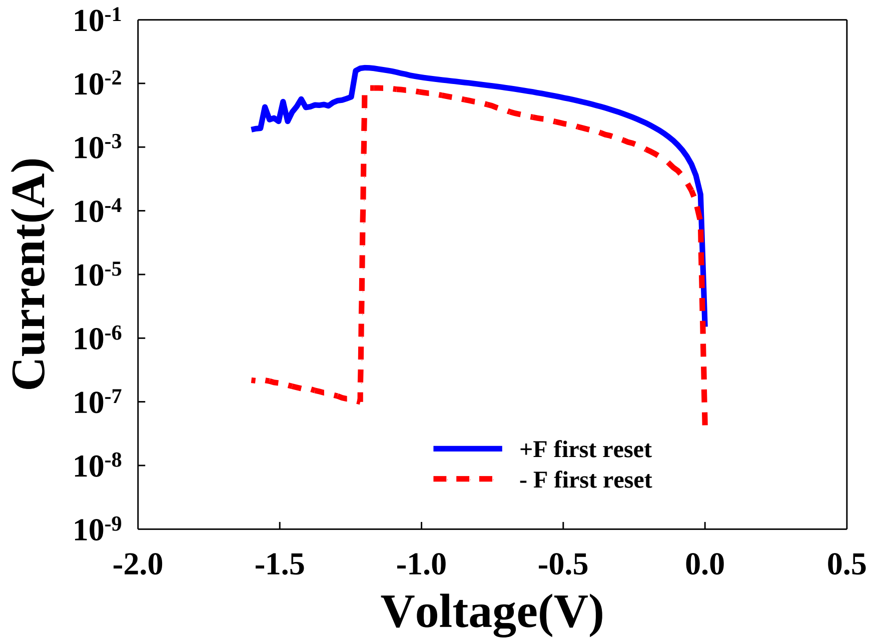


Figure 4-17 Pt/TaON(20nm)/TiN device +Forming and –Forming first “reset” overlap I-V curve

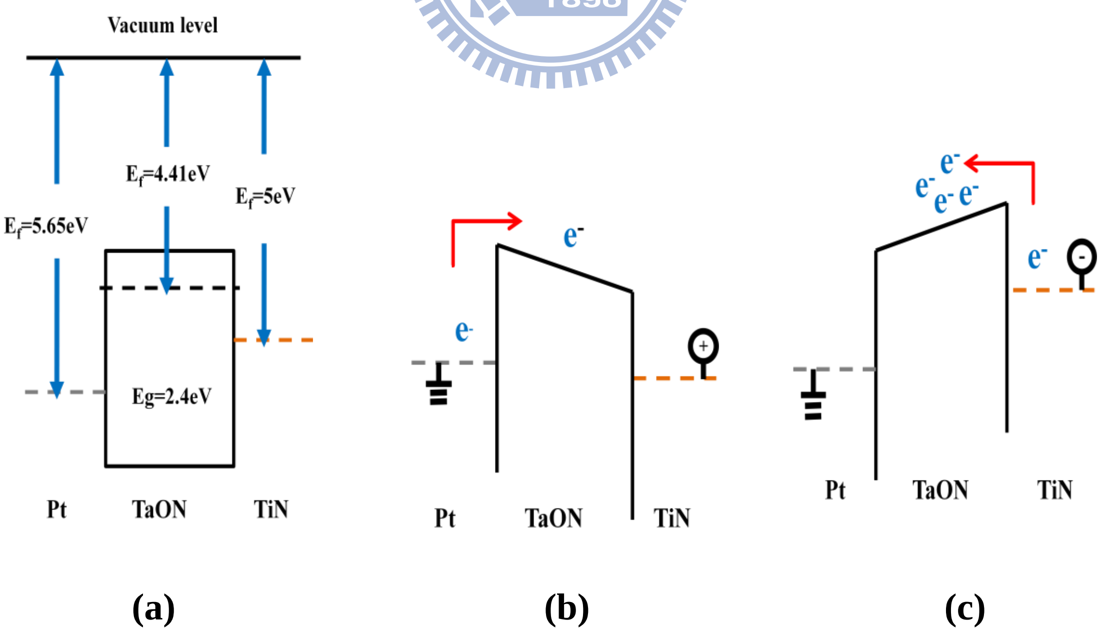


Figure 4-18 Pt/TaON(20nm)/TiN device band diagram (a) no bias (b) +Forming (c) -Forming

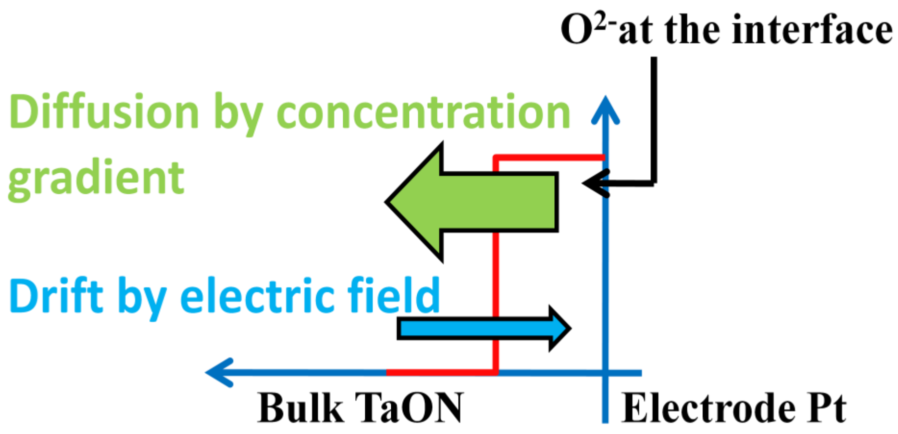


Figure 4-19 the schematic diagram of oxygen anion moving in the first “reset”

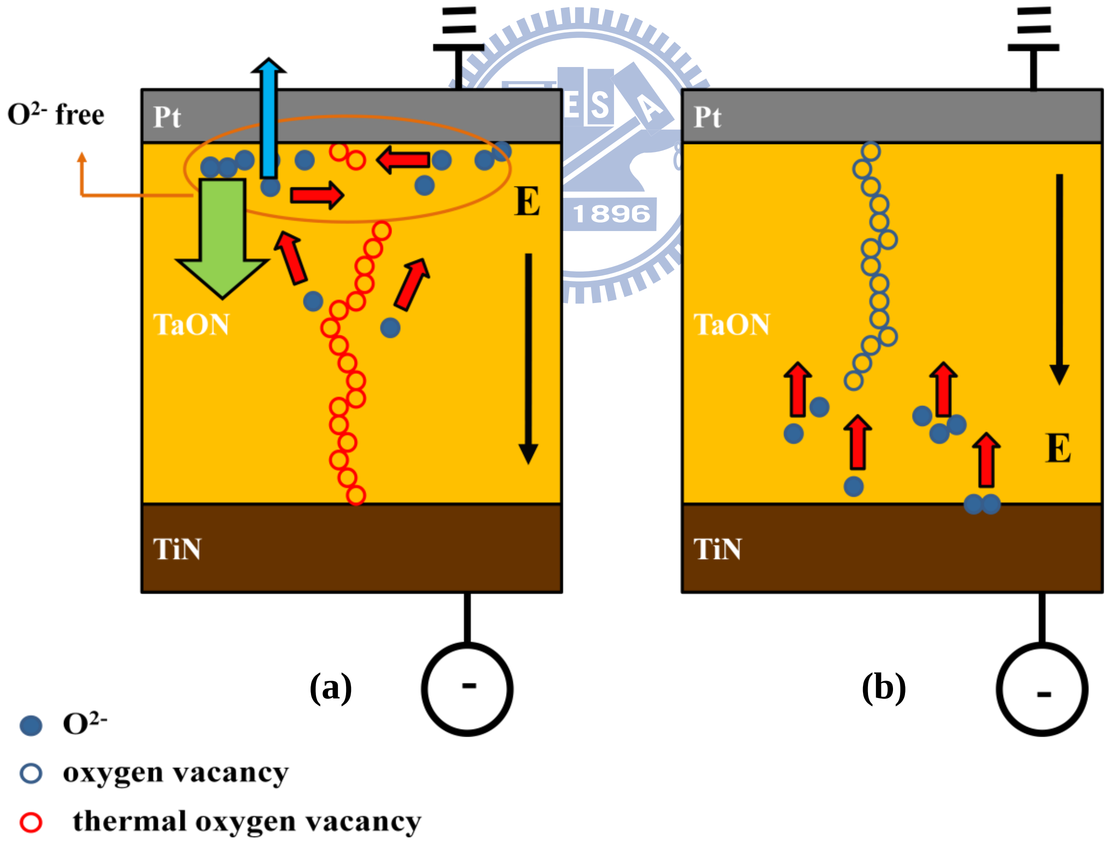
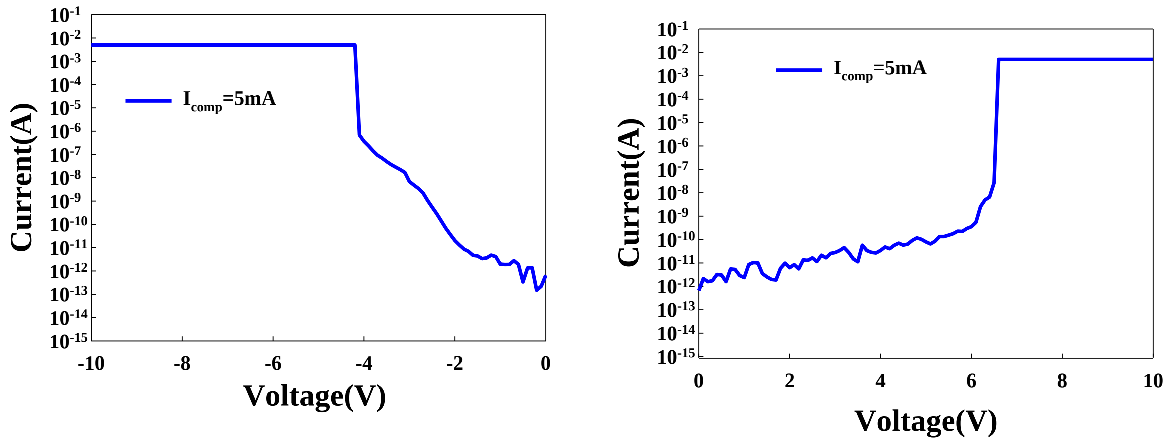


Figure 4-20 Pt/TaON(20nm)/TiN device schematic diagram
(a) first “reset” after -Forming (b) first “reset” after +Forming



(a) (b)

Figure 4-21 Pt/Cu/TaON(20nm)/TiN current-voltage curve bias on TiN (a) positive bias Forming (b) negative bias Forming

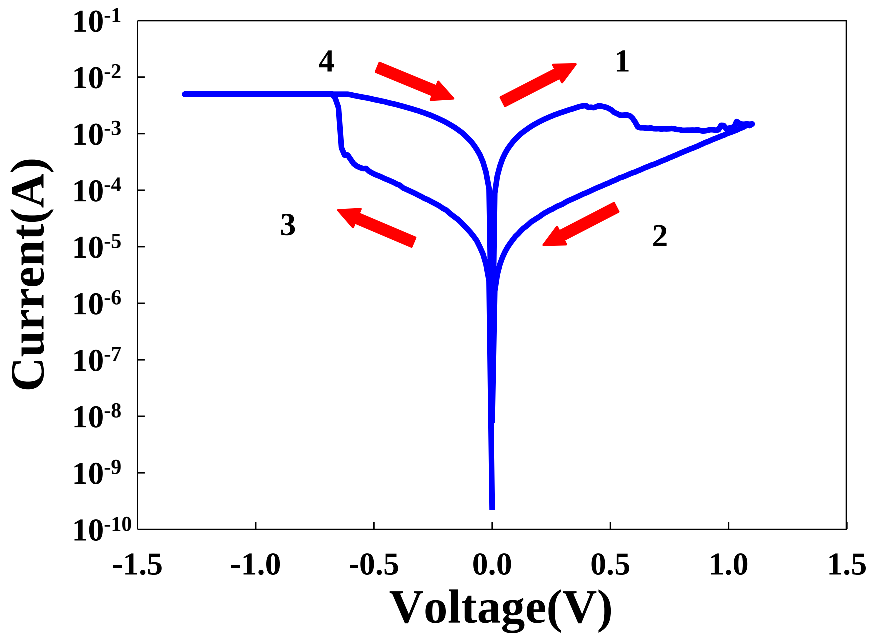


Figure 4-22 Pt/Cu/TaON(20nm)/TiN current-voltage characteristic operation curve

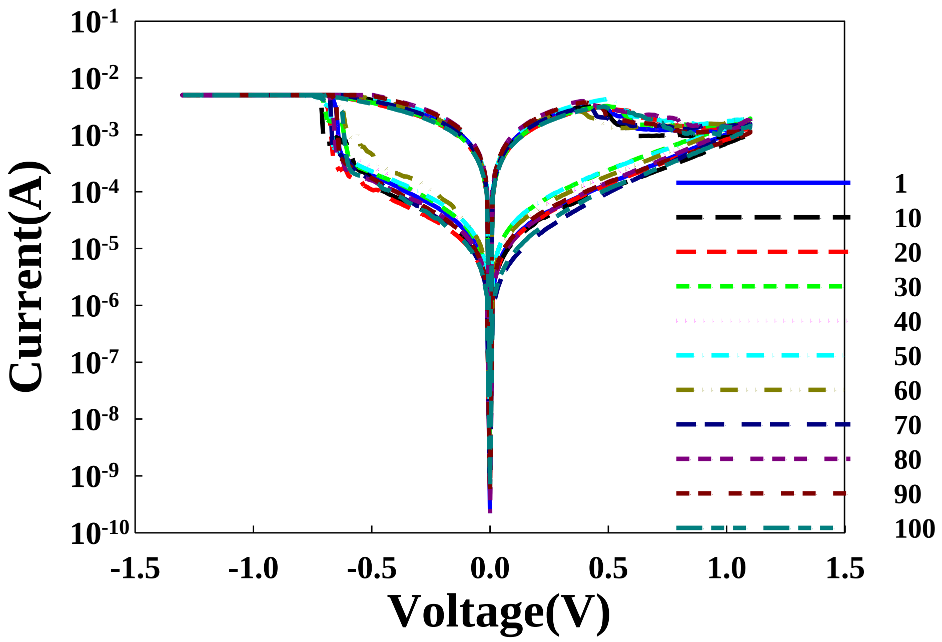


Figure 4-23 Pt/Cu/TaON(20nm)/TiN current-voltage operation curve DC sweep 100 times

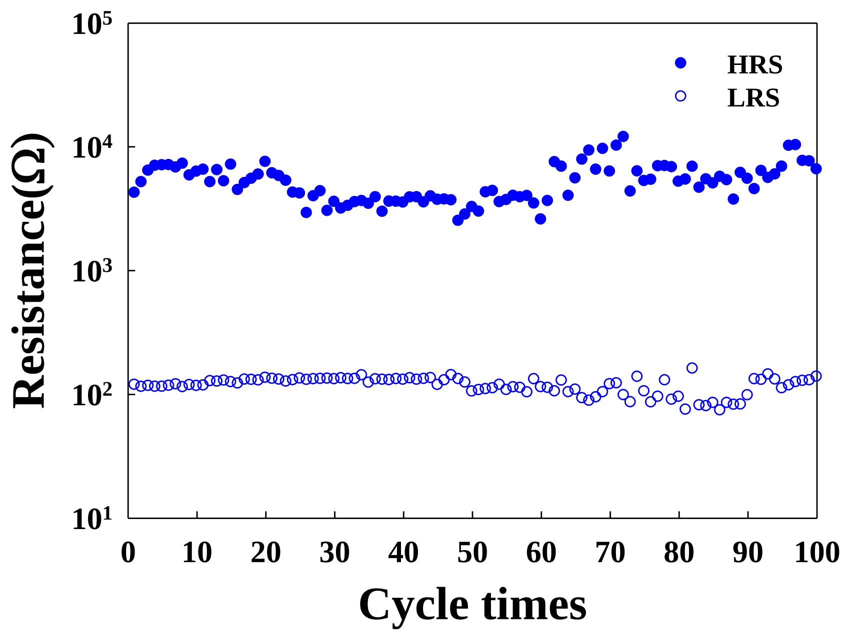


Figure 4-24 Pt/Cu/TaON(20nm)/TiN device DC endurance @0.2V

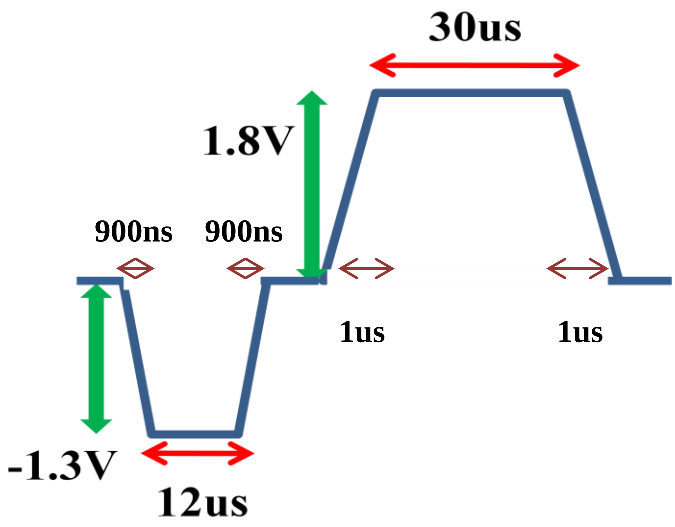


Figure 4-25 Pt/Cu/TaON(20nm)/TiN AC endurance “set” pulse and “reset” pulse operation

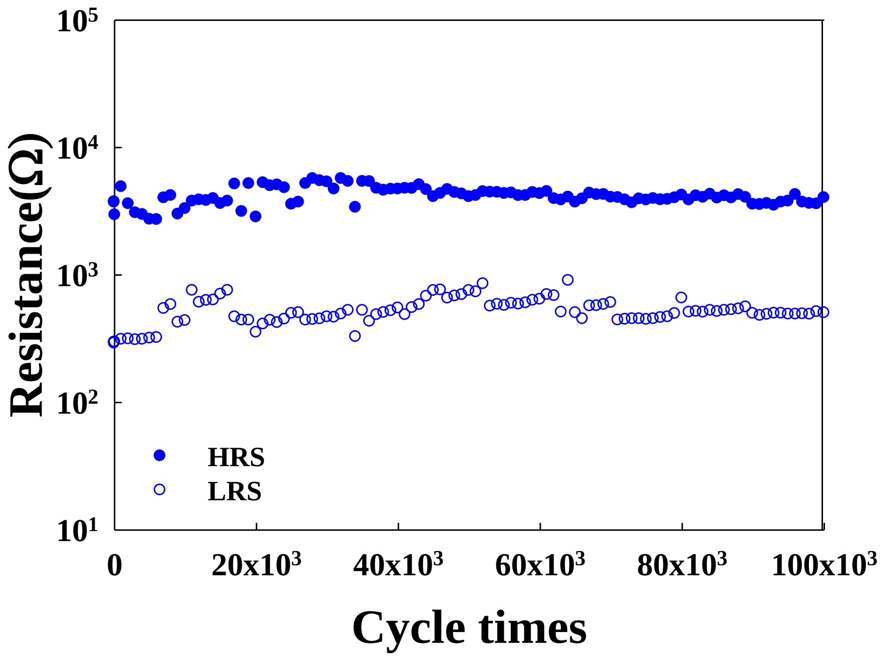


Figure 4-26 Pt/Cu/TaON(20nm)/TiN device AC endurance @0.2V

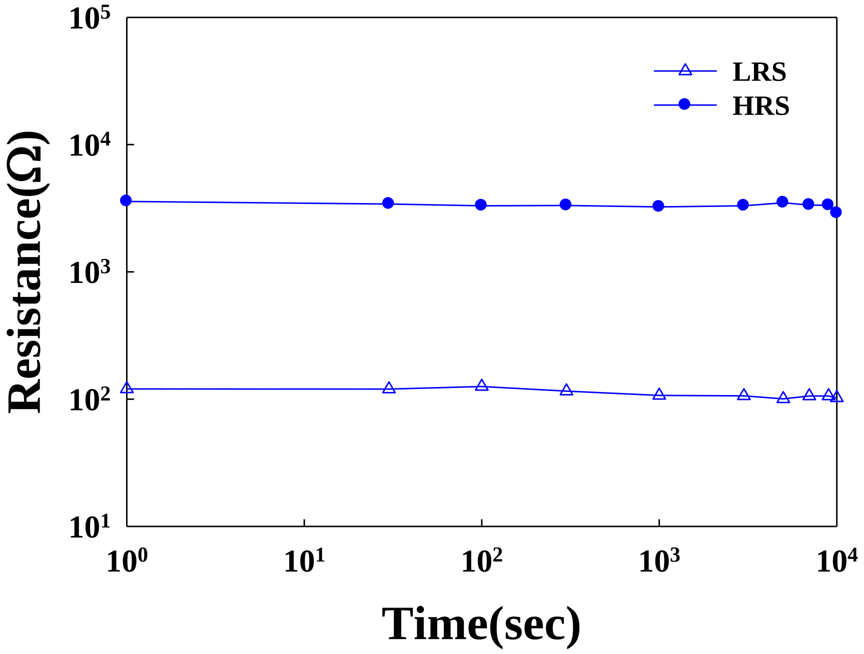


Figure 4-27 Pt/Cu/TaON(20nm)/TiN device room temperature retention @0.2V

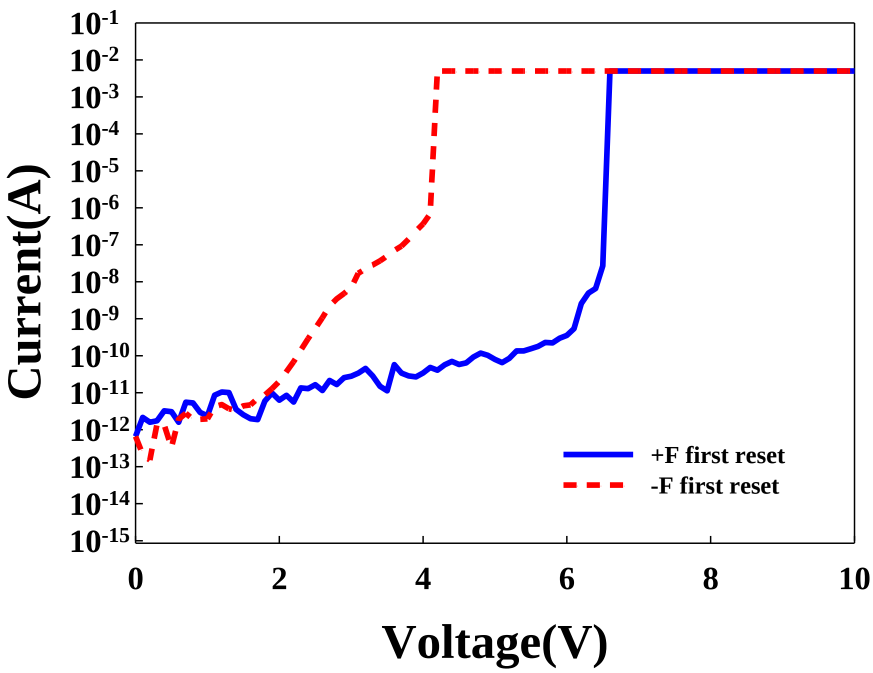


Figure 4-28 Pt/Cu/TaON(20nm)/TiN device +Forming and –Forming overlap I-V curve

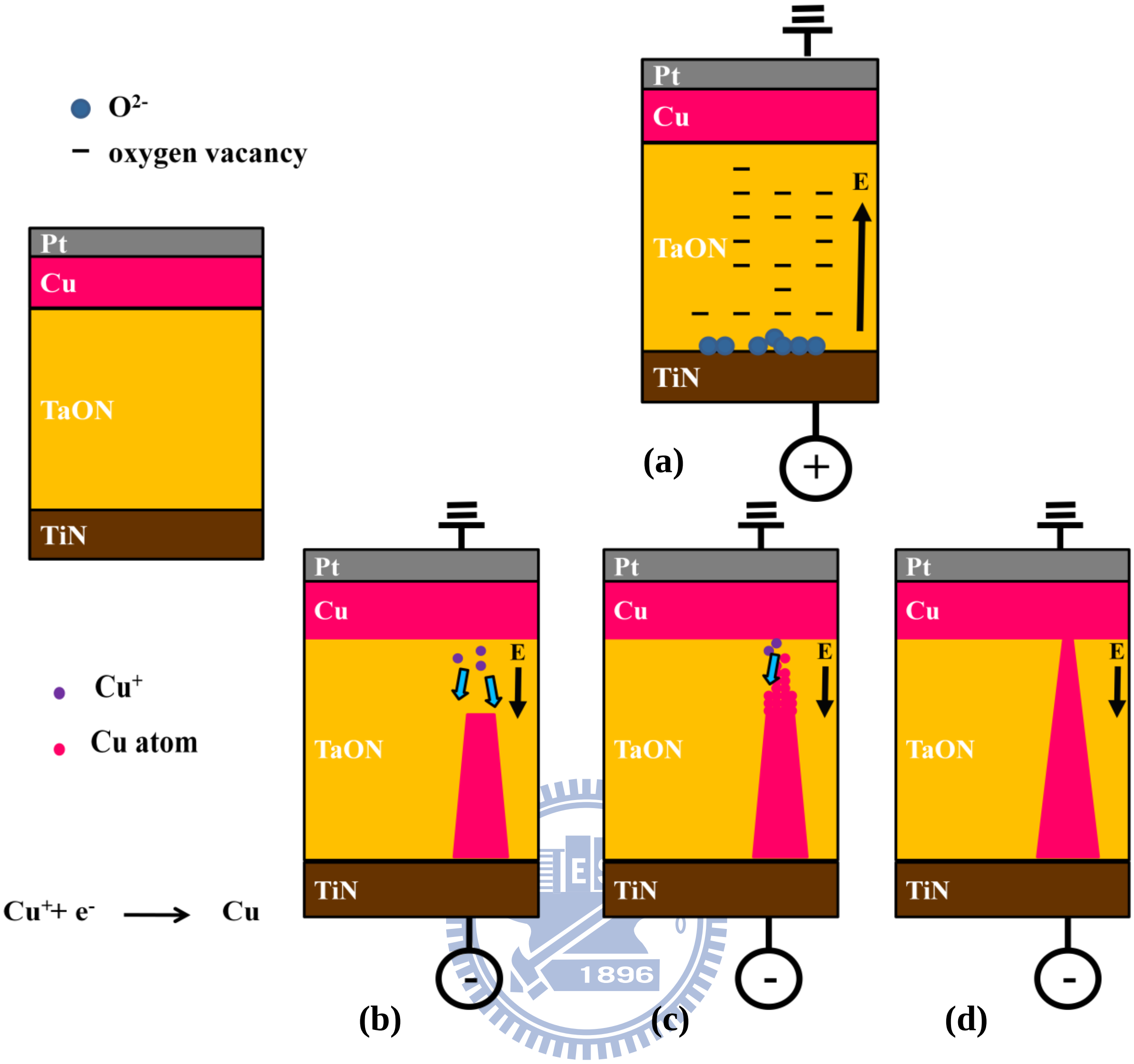


Figure 4-29 Pt/Cu/TaON(20nm)/TiN device schematic diagram
(a) +Forming process (b)(c)(d) – Forming process

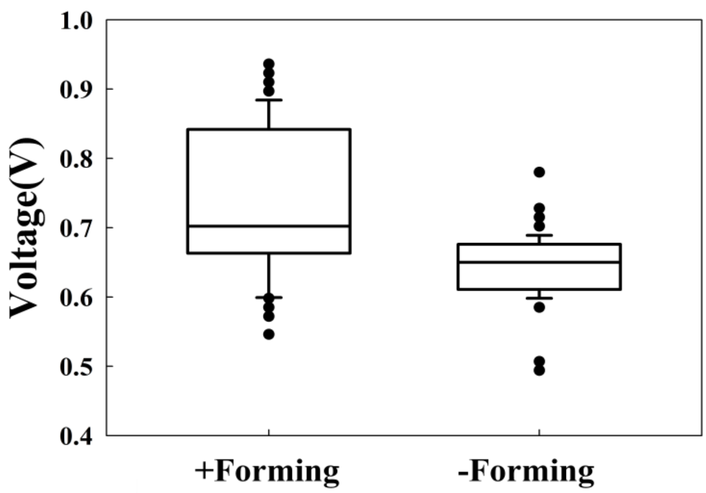
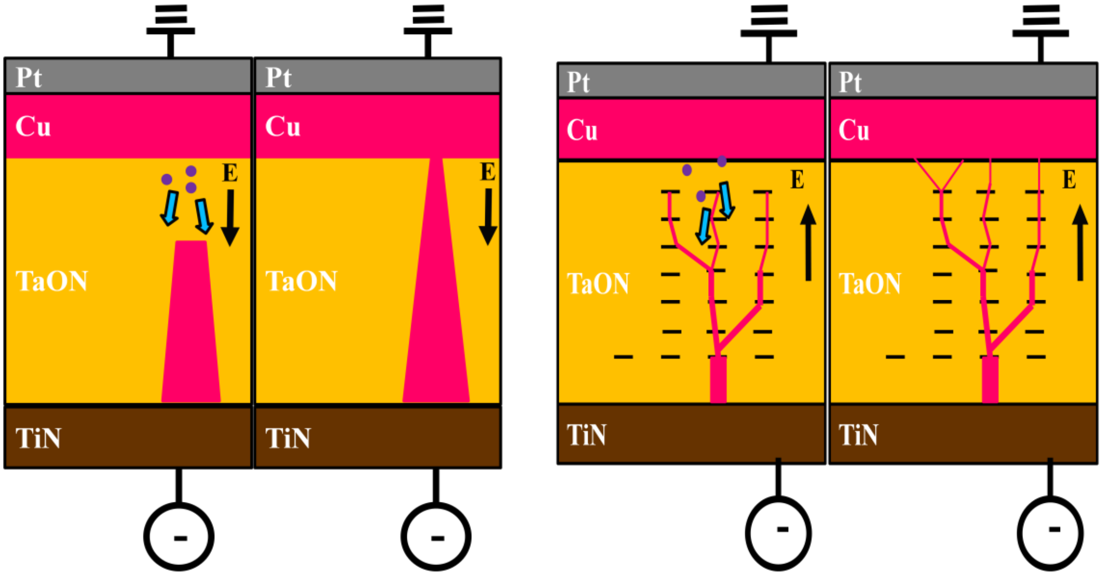
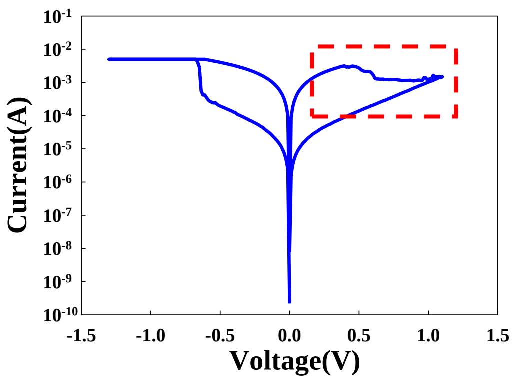


Figure 4-30 Pt/Cu/TaON(20nm)/TiN device DC sweep 100 times cycle V_{set} distribution after +Forming or - Forming

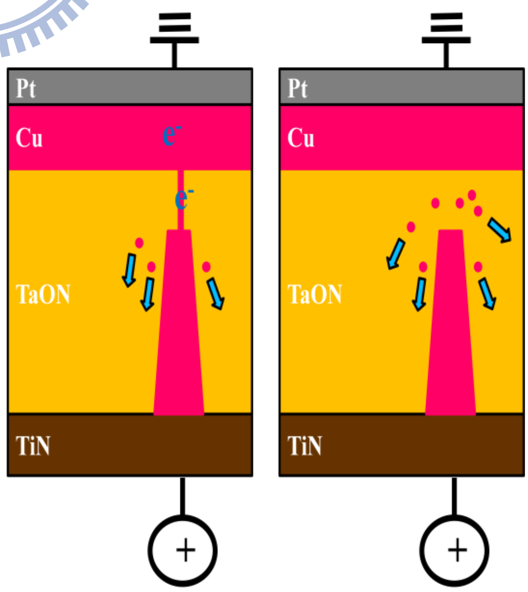


(a) (b)

Figure 4-31 Pt/Cu/TaON(20nm)/TiN device schematic diagram operation process after Forming (a) -Forming (b)+ Forming

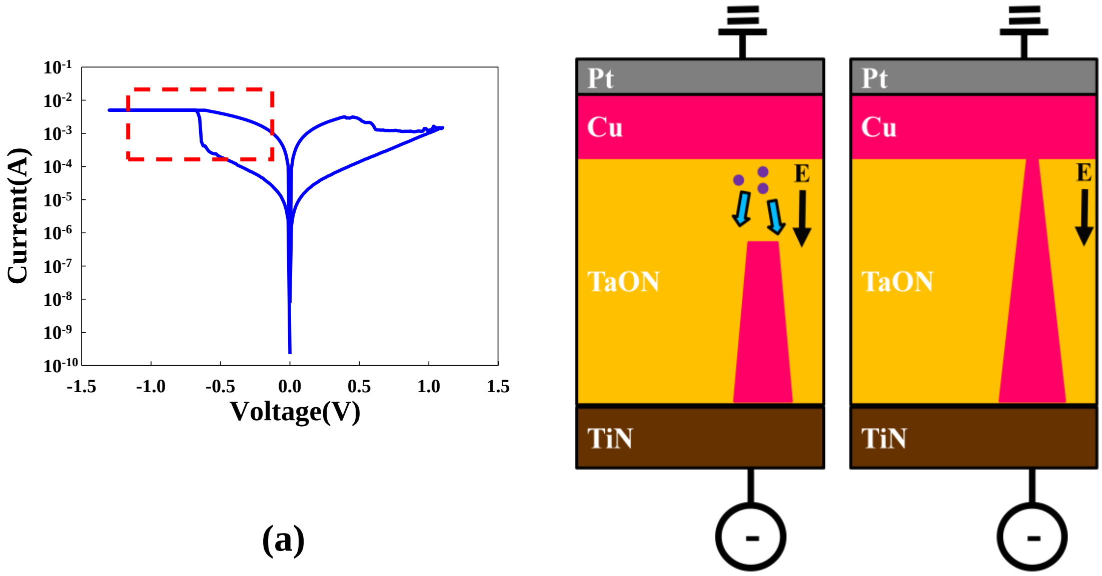


(a)



(b)

Figure 4-32 Pt/Cu/TaON(20nm)/TiN device operation
(a) I-V curve (b) “reset” process schematic diagram



(a)

(b)

Figure 4-33 Pt/Cu/TaON(20nm)/TiN device operation
(a) I-V curve (b) “set” process schematic diagram

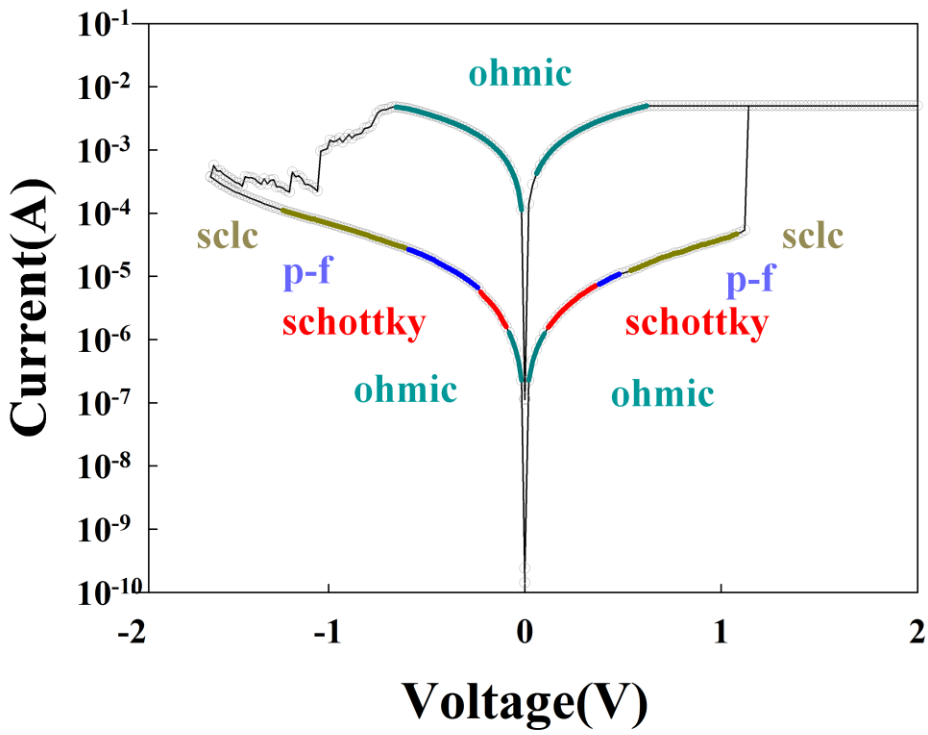


Figure 4-34 Pt/TaON(20nm)/TiN device operation process current fitting

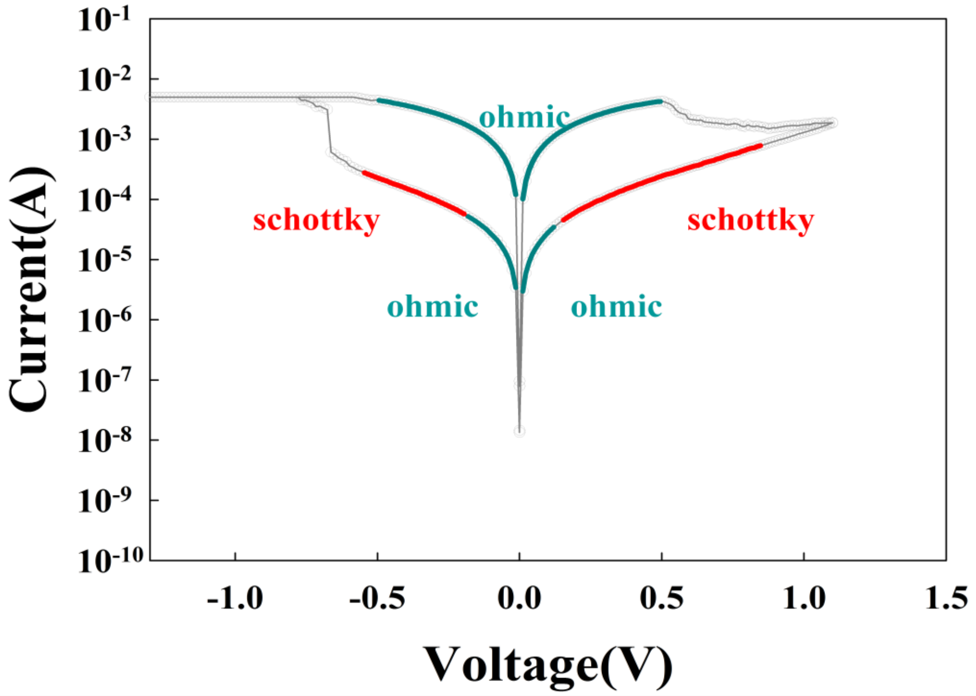


Figure 4-35 Pt/Cu/TaON(20nm)/TiN device operation process current fitting

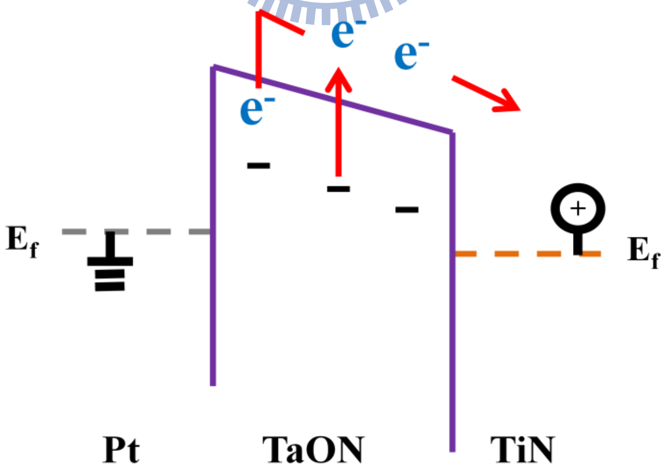


Figure 4-36 Pt/TaON(20nm)/TiN device energy band diagram for the high resistance of “set” process [Ohmic]

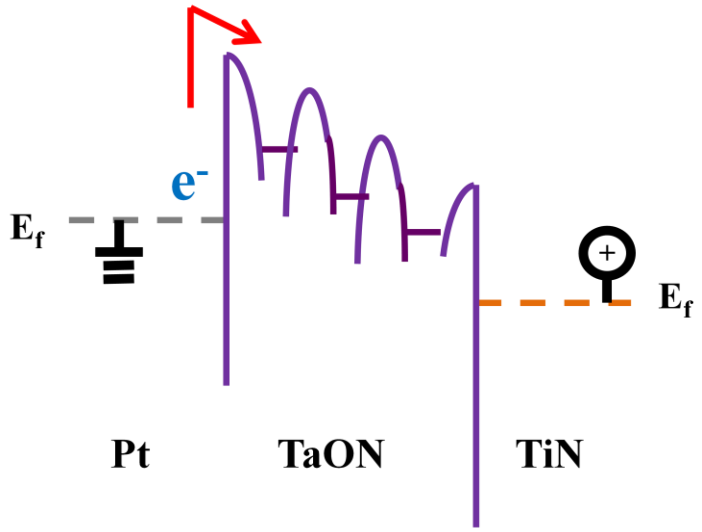


Figure 4-37 Pt/TaON(20nm)/TiN device energy band diagram for the high resistance of "set" process [Schottky]

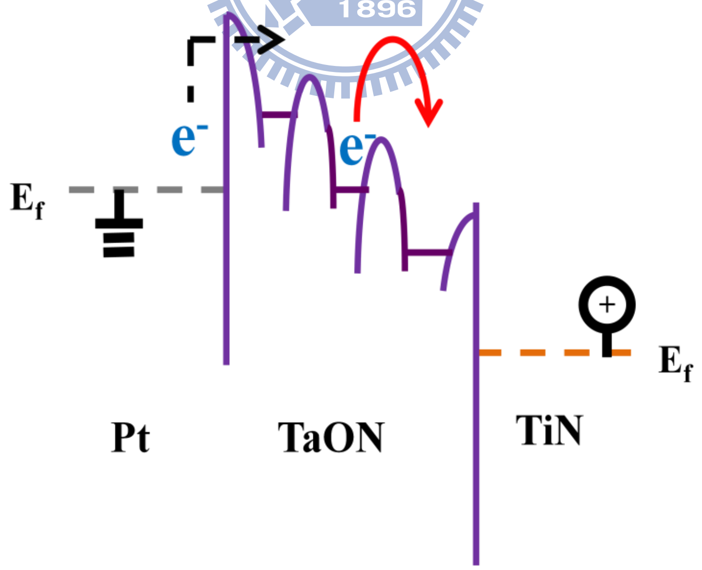


Figure 4-38 Pt/TaON(20nm)/TiN device energy band diagram for the high resistance of "set" process [Poole-Frenkel]

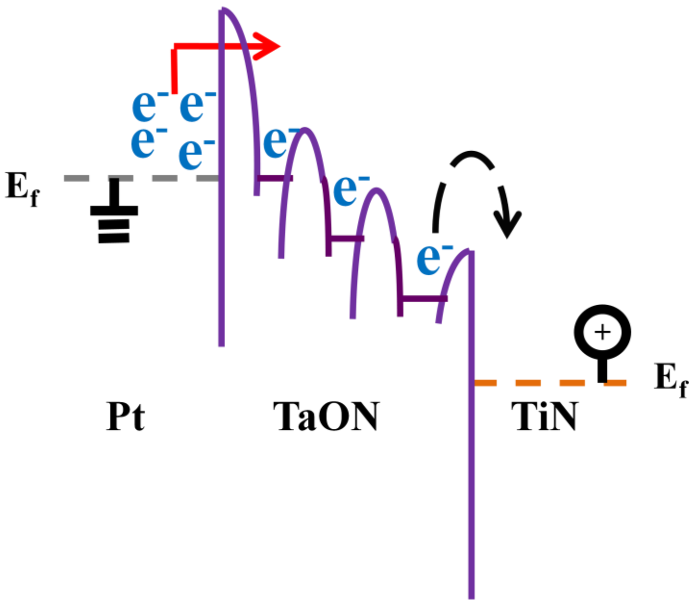


Figure 4-39 Pt/TaON(20nm)/TiN device energy band diagram for the high resistance of “set” process [SCLC]

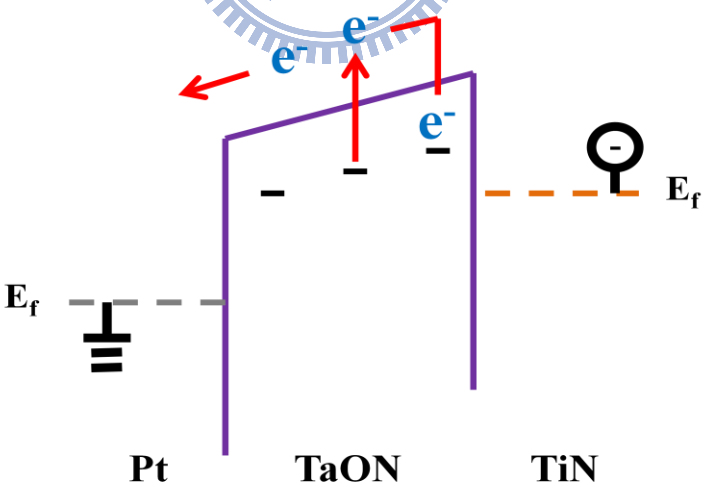


Figure 4-40 Pt/TaON(20nm)/TiN device energy band diagram for the high resistance of “reset” process [Ohmic]

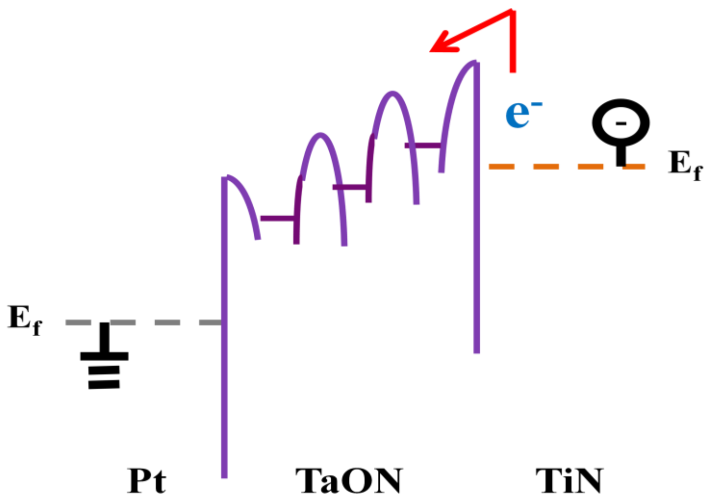


Figure 4-41 Pt/TaON(20nm)/TiN device energy band diagram for the high resistance of “reset” process [Schottky]

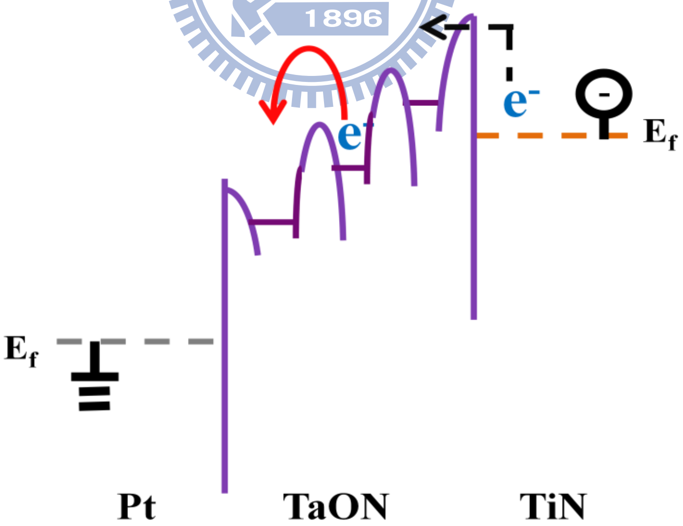


Figure 4-42 Pt/TaON(20nm)/TiN device energy band diagram for the high resistance of “reset” process [Poole-Frenke]

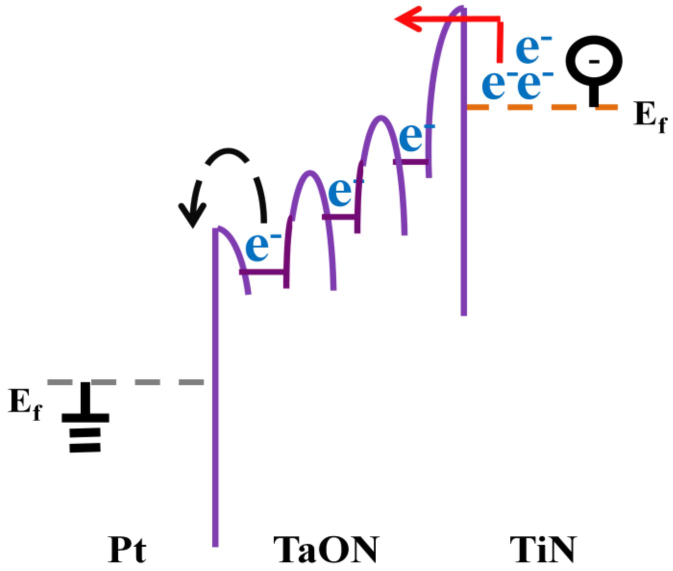


Figure 4-43 Pt/TaON(20nm)/TiN device energy band diagram for the high resistance of "reset" process [SCLC]

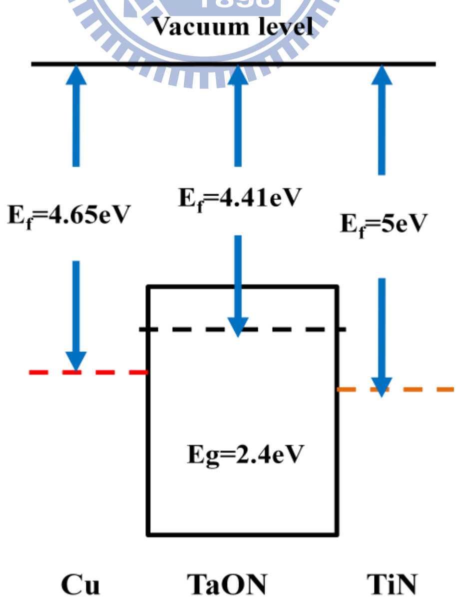


Figure 4-44 Pt/Cu/TaON(20nm)/TiN device no bias energy band diagram

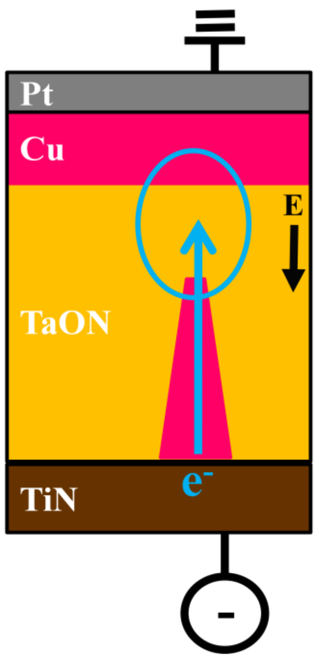


Figure 4-45 Pt/Cu/TaON(20nm)/TiN device electrons conduction schematic diagram of “set” process

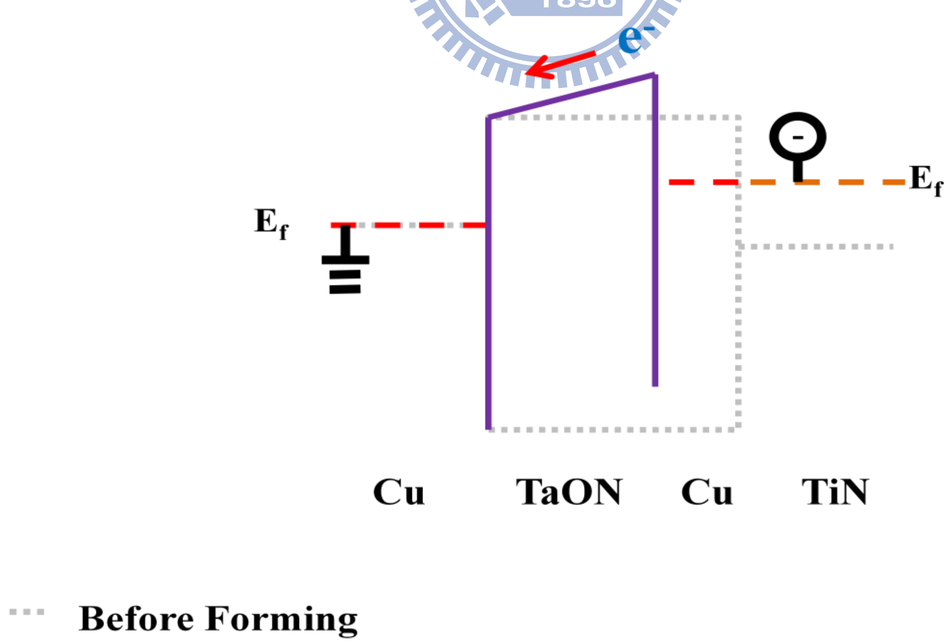


Figure 4-46 Pt/Cu/TaON(20nm)/TiN device energy band diagram for the high resistance of “set” process [Ohmic]

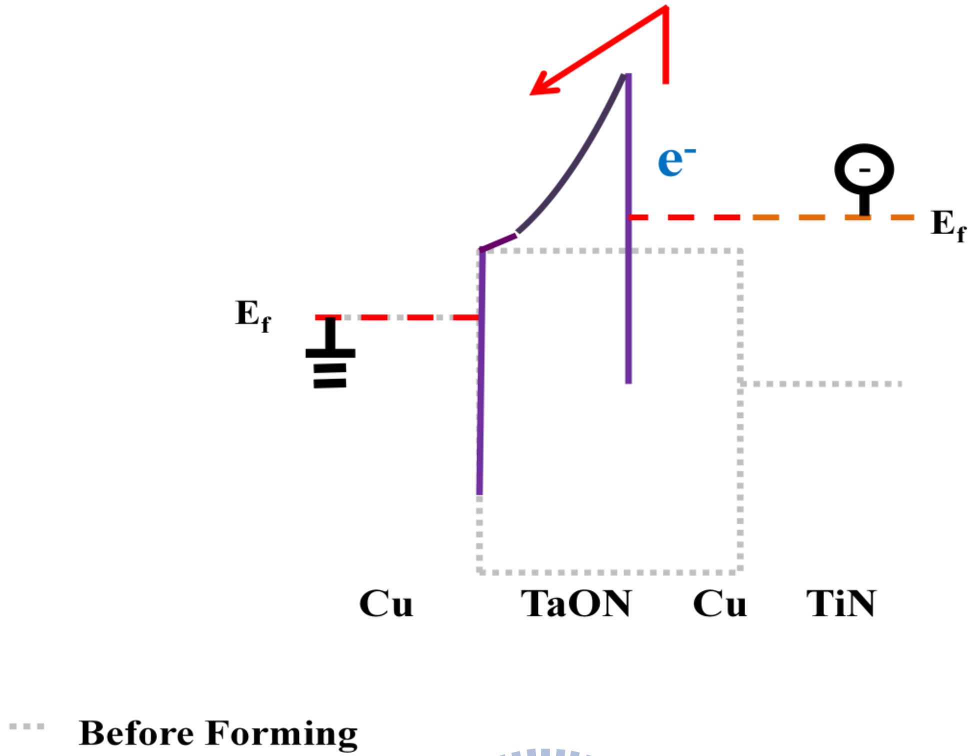


Figure 4-47 Pt/Cu/TaON(20nm)/TiN device energy band diagram for the high resistance of "set" process [Schottky]

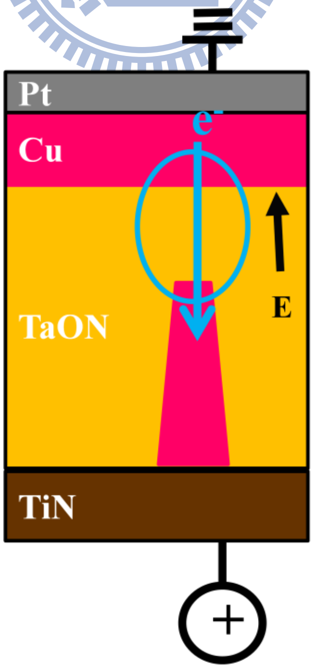


Figure 4-48 Pt/Cu/TaON(20nm)/TiN device electrons conduction schematic diagram of "reset" process

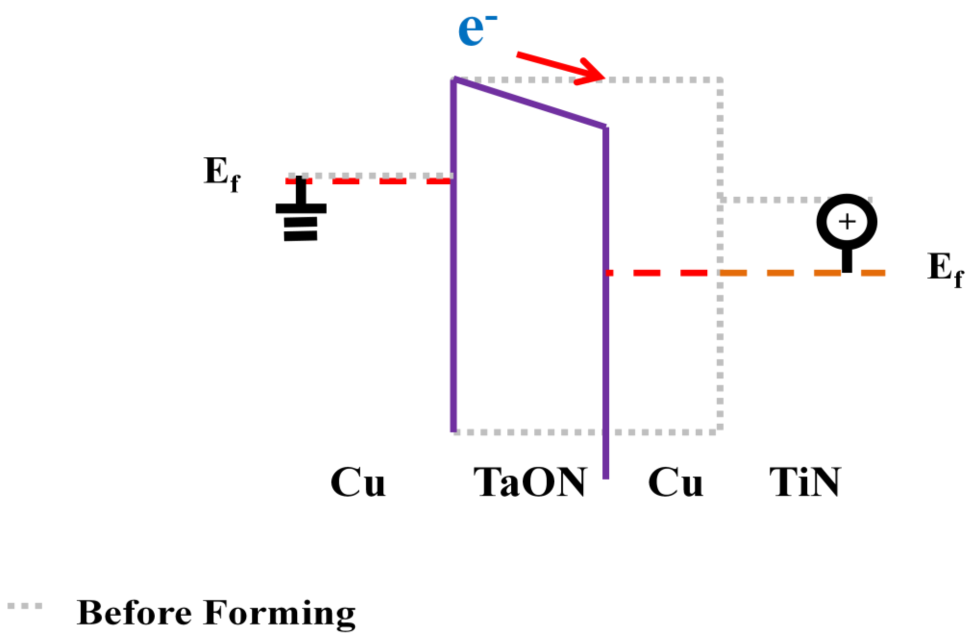


Figure 4-49 Pt/Cu/TaON(20nm)/TiN device energy band diagram for the high resistance of "reset" process [Ohmic]

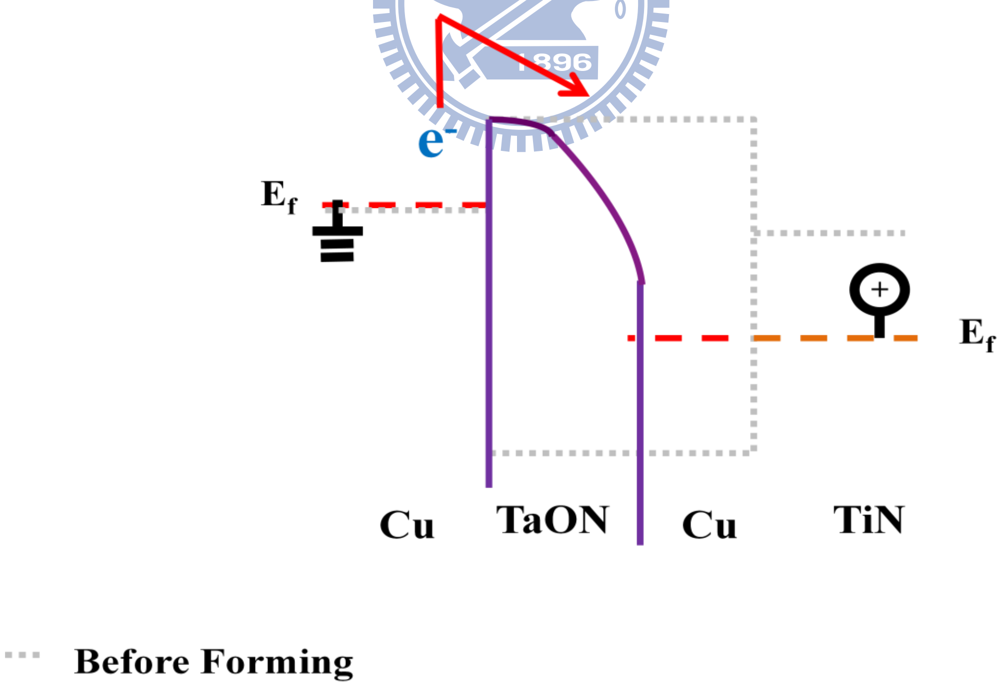
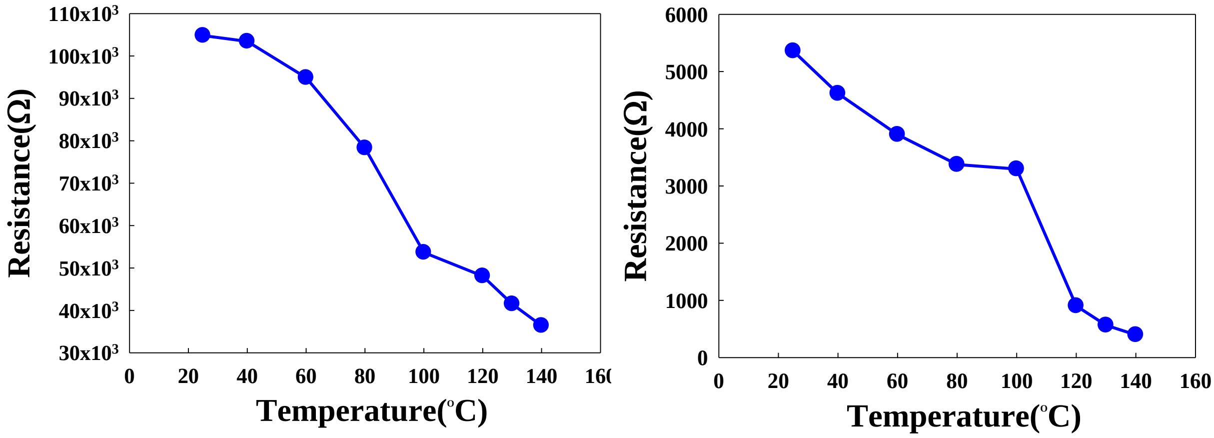
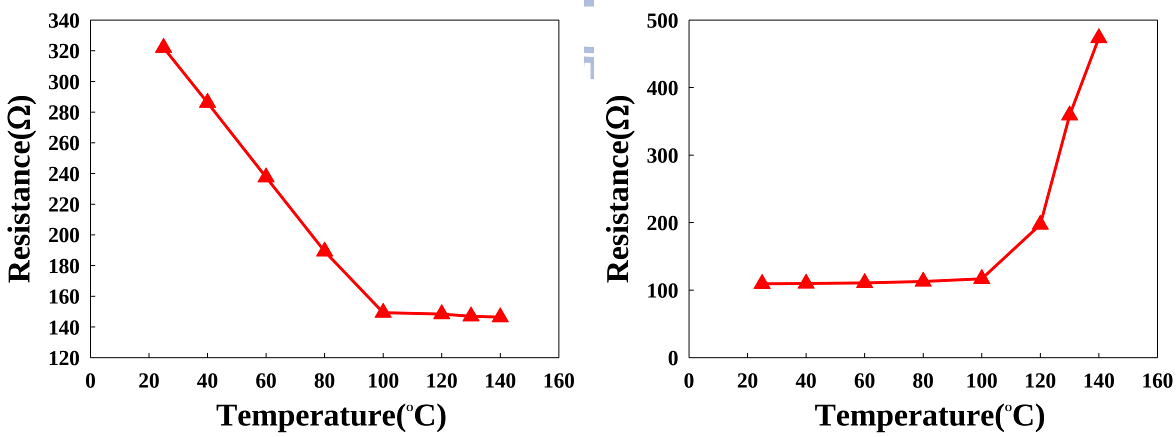


Figure 4-50 Pt/Cu/TaON(20nm)/TiN device energy band diagram for the high resistance of "reset" process [Schottky]



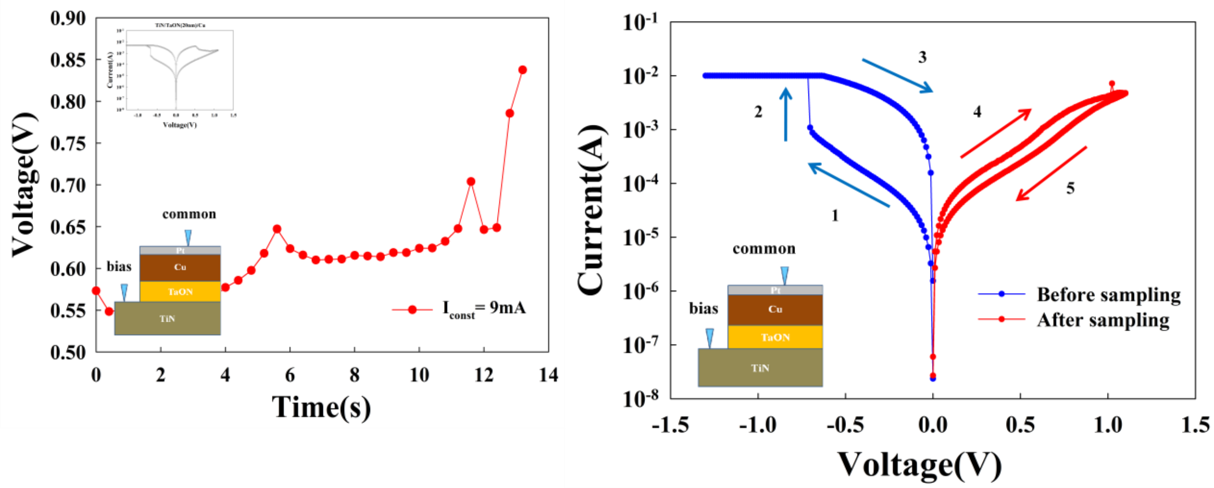
(a) (b)

Figure 4-51 Temperature measurement at high resistance state @0.2V
(a) Pt/TaON(20nm)/TiN (b) Pt/Cu/TaON(20nm)/TiN



(a) (b)

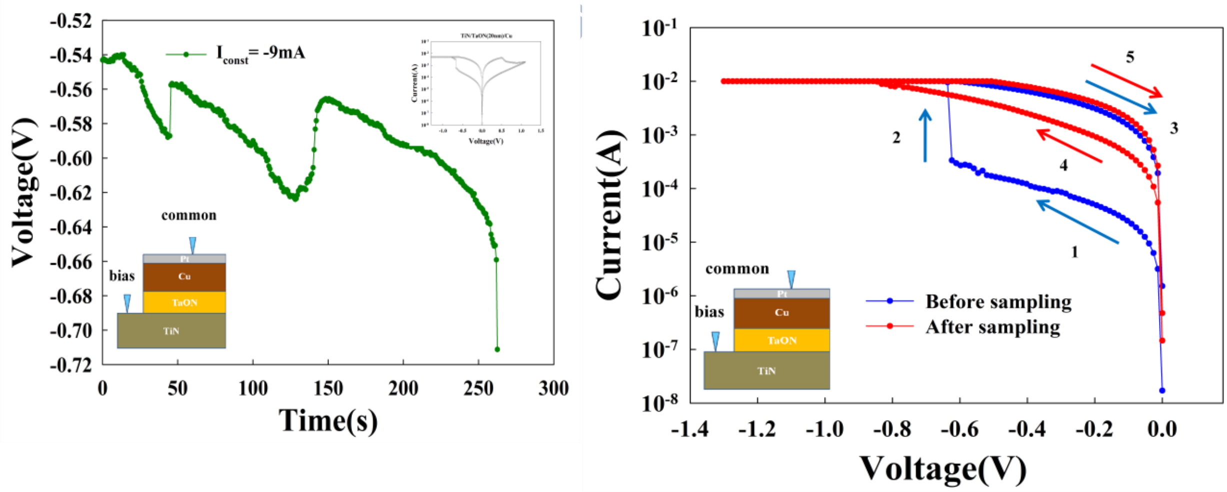
Figure 4-52 Temperature measurement at low resistance state @0.2V
(a) Pt/TaON(20nm)/TiN (b) Pt/Cu/TaON(20nm)/TiN



(a)

(b)

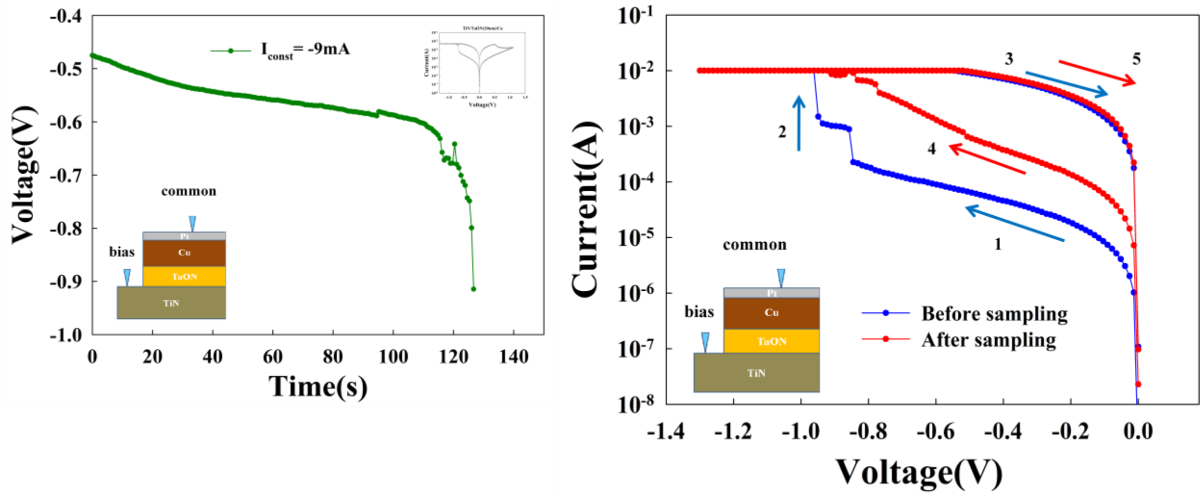
Figure 4-53 use CCS(constant current sampling) to switch device's resistance at temperature 300K
(a) Positive CCS (b) before and after CCS I-V curve



(a)

(b)

Figure 4-54 use CCS(constant current sampling) to switch device's resistance at temperature 300K
(a) Negative CCS (b) before and after CCS I-V curve



(a)

(b)

Figure 4-55 use CCS(constant current sampling) to switch device's resistance at temperature77K
(a) Negative CCS (b) before and after CCS I-V curve

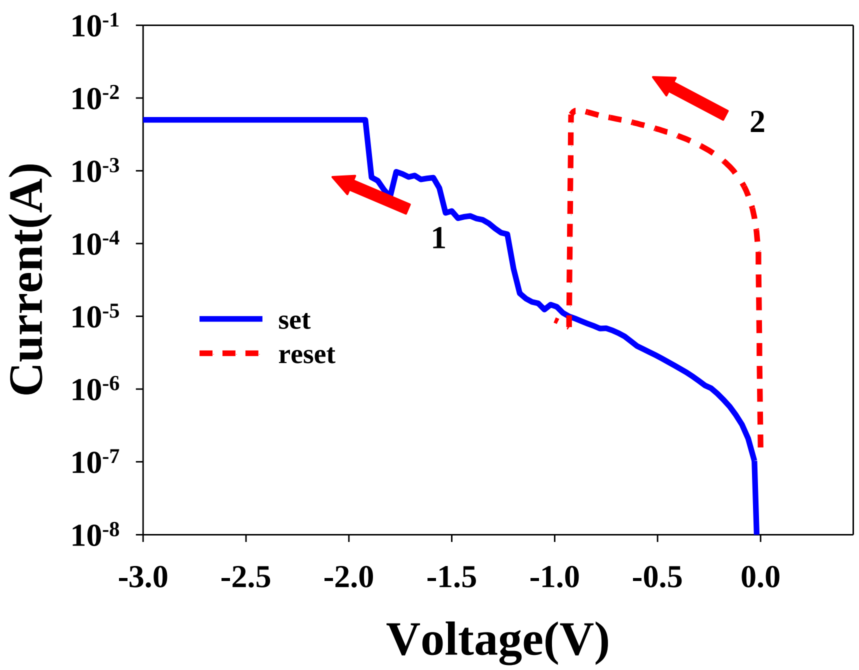


Figure 4-56 Pt/TaON(20nm)/TiN unipolar current-voltage characteristic operation curve

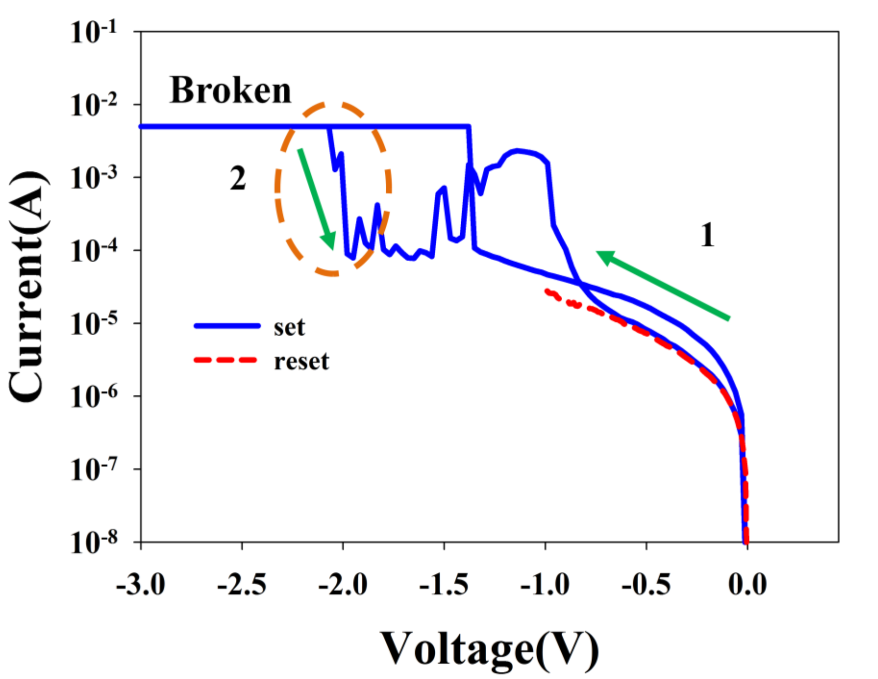
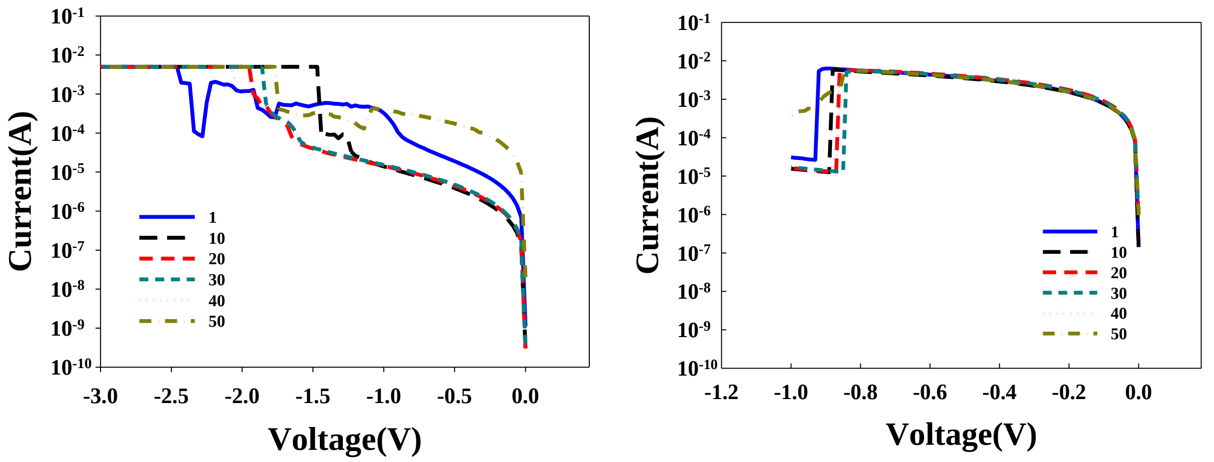
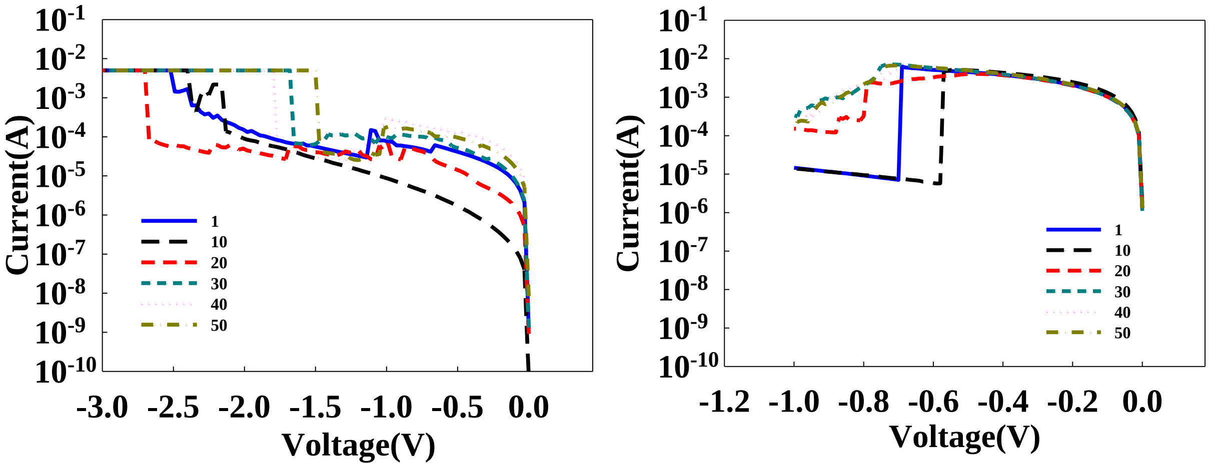


Figure 4-57 Pt/TaON(20nm)/TiN unipolar current-voltage
“set” process double 0~ -3 and -3~0



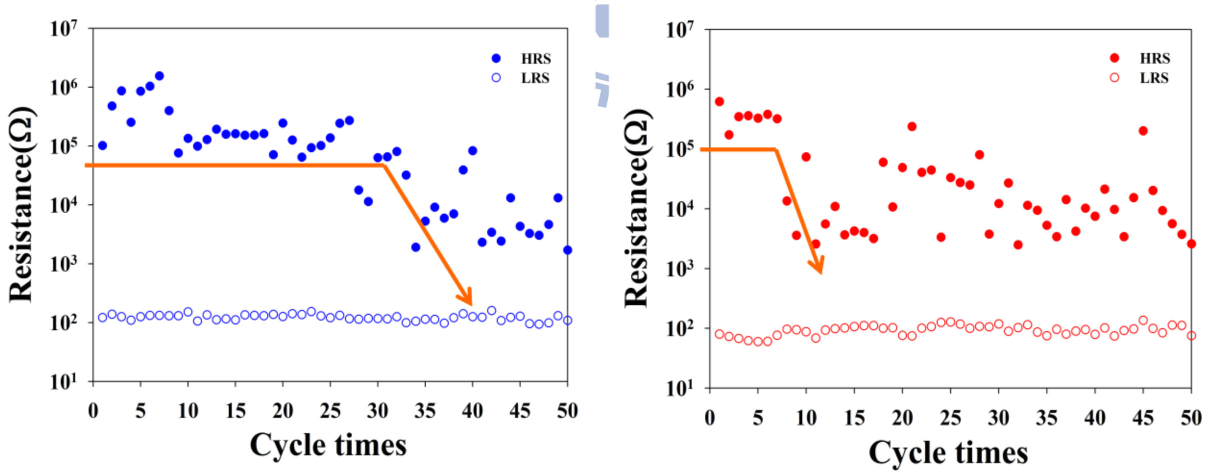
(a) (b)

Figure 4-58 Pt/TaON(20nm)/TiN unipolar current-voltage operation
curve DC sweep 100 times after +Forming(a) “set” (b) “reset”



(a) (b)

Figure 4-59 Pt/TaON(20nm)/TiN unipolar current-voltage operation curve DC sweep 100 times after -Forming(a) “set” (b) “reset”



(a) (b)

Figure 4-60 Pt/TaON(20nm)/TiN device unipolar operation DC endurance @ 0.2V(a) after +Forming (b) after - Forming

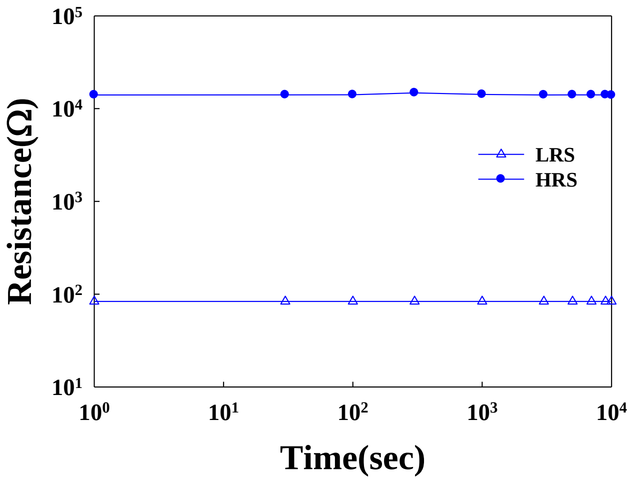


Figure 4-61 Pt/TaON(20nm)/TiN device unipolar operation retention at $85^{0}C$@ 0.2V

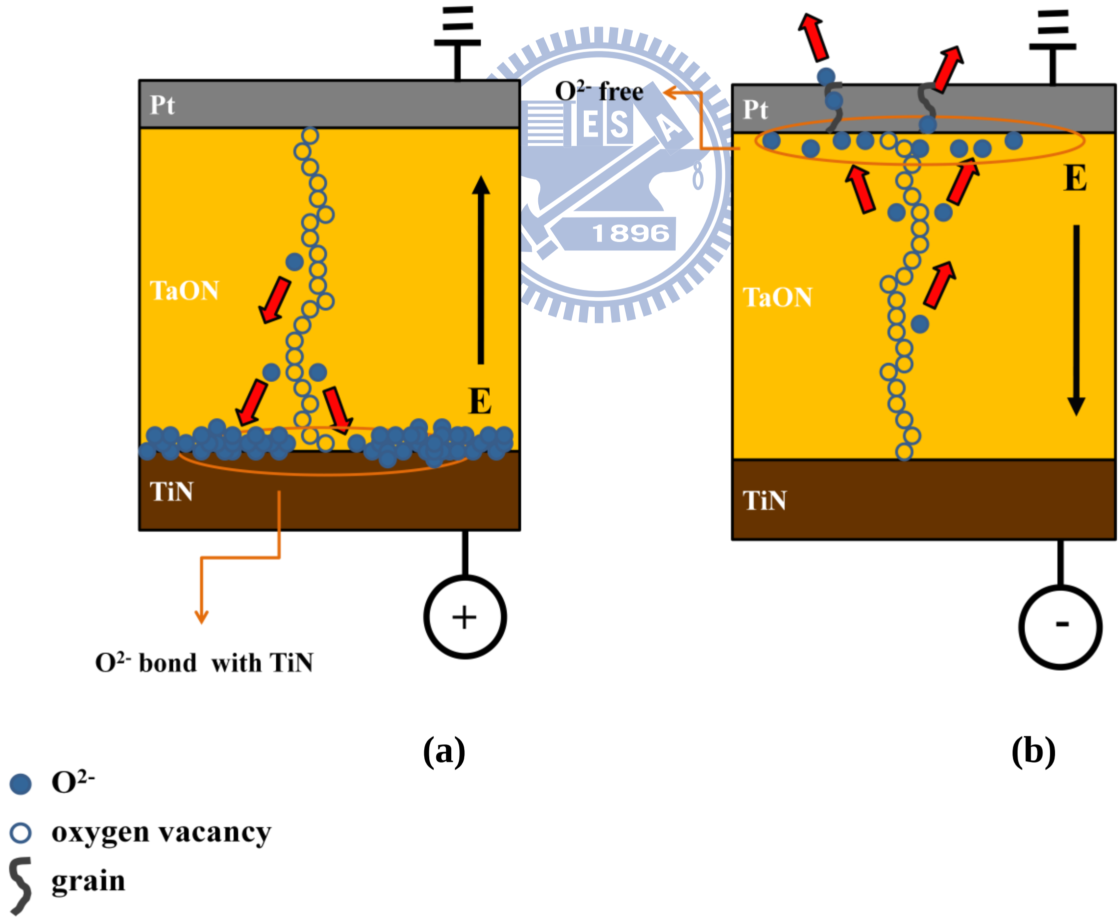


Figure 4-62 Pt/TaON(20nm)/TiN device Forming process schematic diagram (a) positive bias (b) negative bias

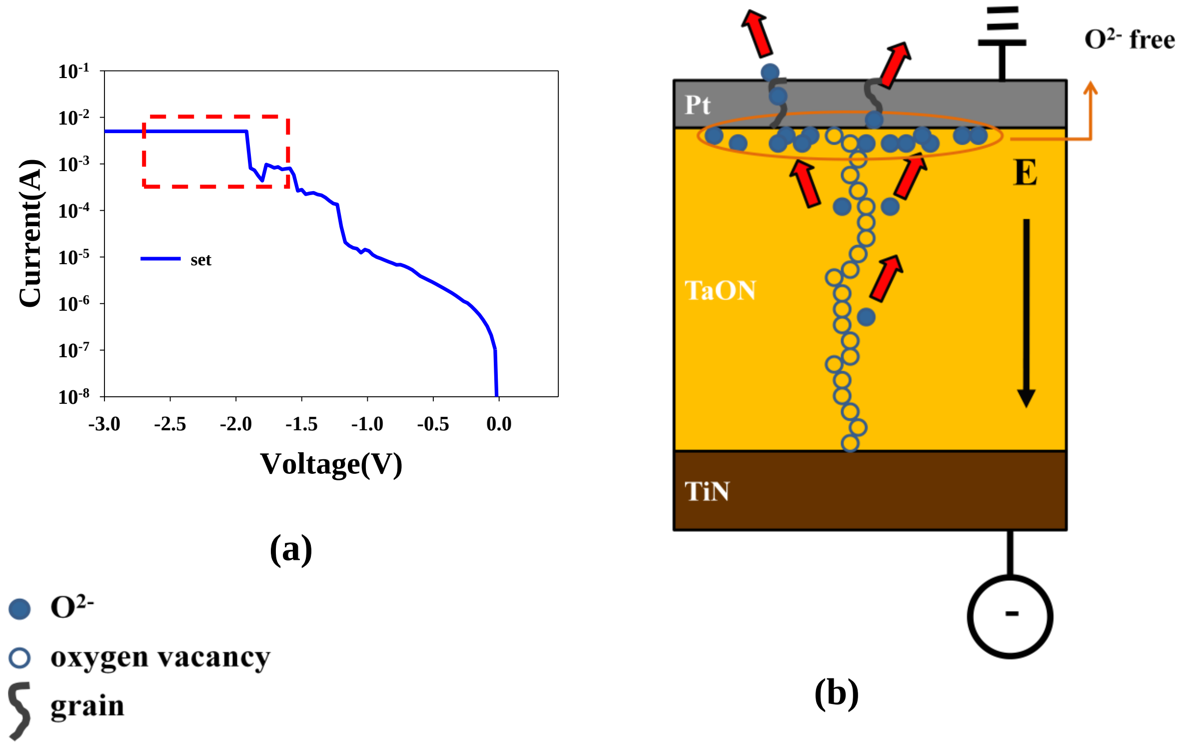


Figure 4-63 Pt/ TaON(20nm)/TiN device operation
(a)I-V curve (b) "set" process schematic diagram

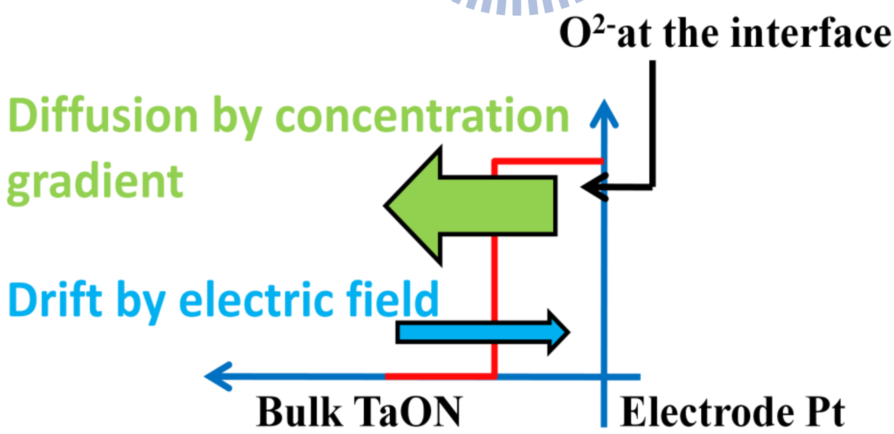


Figure 4-64 the schematic diagram of oxygen anions moving during "reset" process

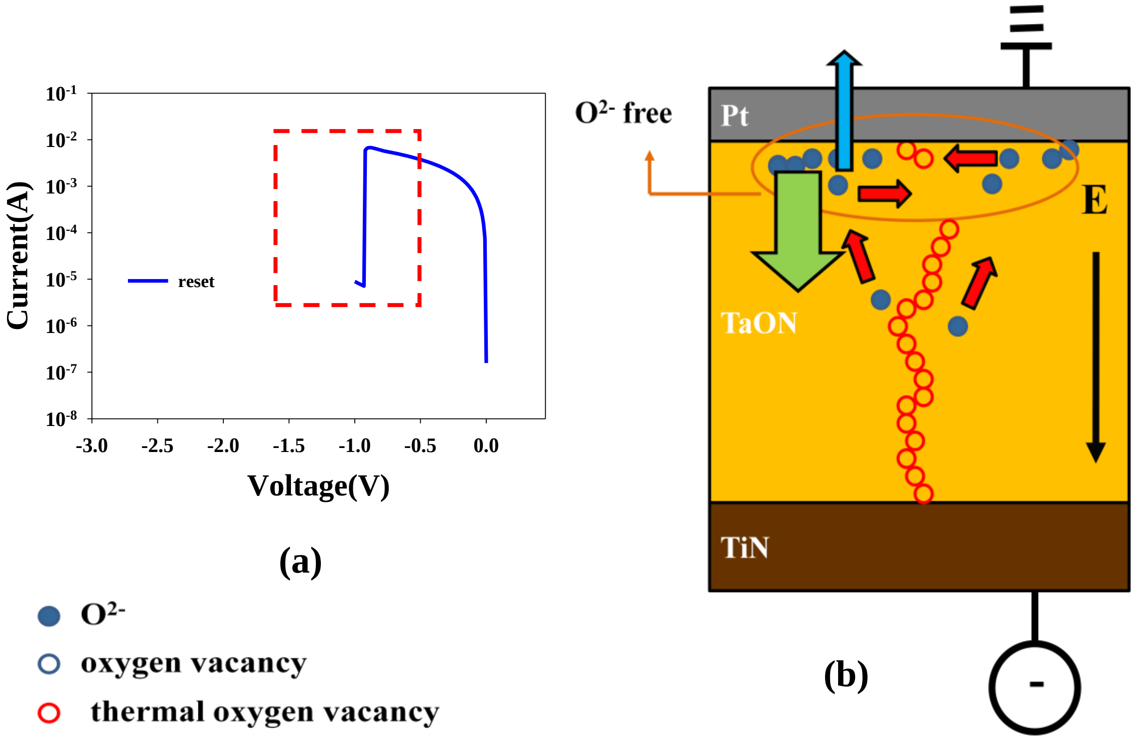


Figure 4-65 Pt/ TaON(20nm)/TiN device operation (a)I-V curve (b) "reset" process schematic diagram

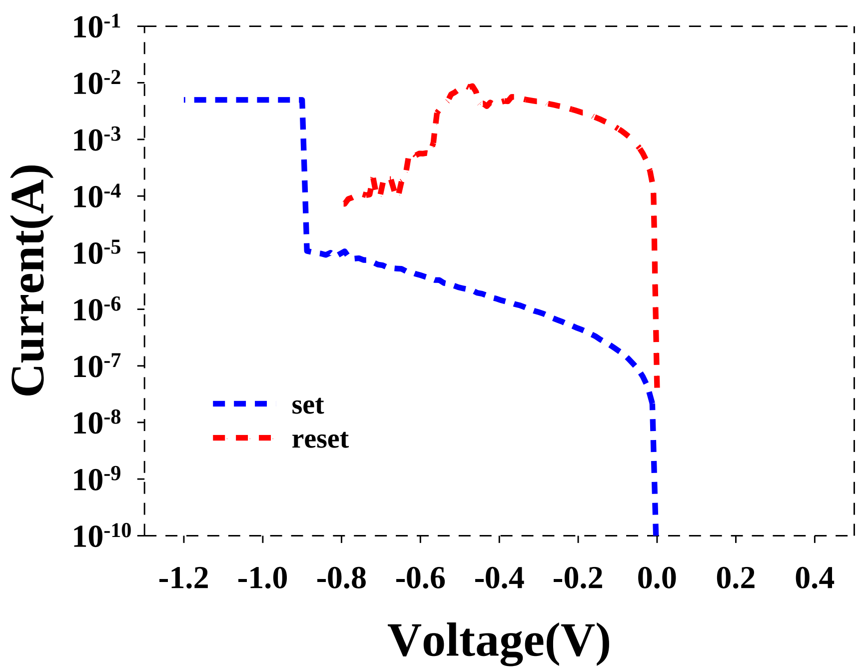
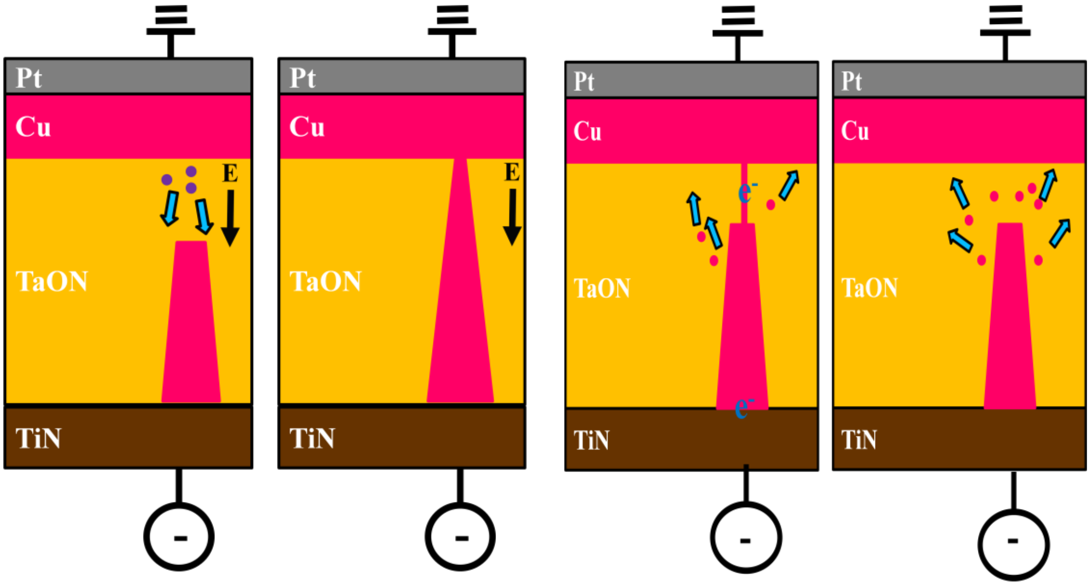


Figure 4-66 Pt/Cu/TaON(20nm)/TiN unipolar current-voltage characteristic operation curve



(a) **(b)**

Figure 4-67 Pt/ Cu/TaON(20nm)/TiN device operation process schematic diagram (a) “set” (b) “reset”

Chapter 5

Conclusion

The structure of Pt/TaON/TiN are successful for resistance switching memory. The device Pt/TaON/TiN could be operated more than 10^5 times and maintain the stable on/off ratio about 1.5 orders. Besides, the data could be stored more than 10^4 seconds and the on/off ratio was held 2.5 orders without data losing. Ultimately, the device could be operated multilevel which could increase density of storage and was good characteristic for memory application.

We have investigated the Forming and resistive switching behaviors of Pt/TaON/TiN memory devices and compared their electrical properties with devices of Pt/Cu/TaON/TiN. First, from Forming voltage and I-V curve we have found out significantly different behaviors of two structures. The bipolar conduction mechanism of structure Pt/TaON/TiN is related with oxygen redox and the bipolar conduction mechanism of structure Pt/Cu/TaON/TiN is related with copper redox and thermal effect. We also have used many methods which were current fitting, changing temperature measurement, and CCS to prove copper ions playing a important role in determining the switching behavior.

Due to the resistive switching characteristic of structure Pt/TaON/TiN, the positive Forming and negative “reset” corresponding with positive “set” and negative “reset” operation polarity have been explained easily by oxygen redox .However, the negative Forming and negative “reset” not corresponding with positive “set” and negative “reset” operation polarity have been explained by thermal effect which increases oxygen vacancies to be recovered.

We measure that the structure Pt/TaON/TiN has the unipolar feature of negative “set” and negative “reset and the structure Pt/Cu/TaON/TiN has the same feature.

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