Chapter 1 Introduction

1.1. Introduction

By the coming of 21th Century, people want their communication electronic product and multimedia tools to become lighter, smaller, environment-friendly, energy-saving, speed, and low-cost information storage and communication function as the mean direction of application through popularization of the knowledge and high-speed information circulation. Most of personal digital products (such as mobile phone, personal digital assistant, digital camera, and MP3 player, etc.) are memory device. Generally, memory device is divided into two types, the volatile memory and the non-volatile memory. In computer system, although, nonvolatile memory could storage data forever, but write-read speed is slower than DRAM or SRAM. Therefore, the computer system needs two types of memory device.

1.1.1. Volatile Memory

According to the memory devices which can maintain the data or not after turning off the power, we can divide them into two parts: volatile and non-volatile memory. In volatile memories operation, data information will not maintain in the device after turn off the power. The familiar volatile memories are DRAM (dynamic random access memory) and SRAM (static random access memory).

DRAM (dynamic random access memory) is a type of random access memory that stores each bit of data in a separate capacitor within an integrated circuit. Since real capacitors leak charge, the information eventually fades unless the capacitor charge is refreshed periodically. Because of this refresh requirement, it is a dynamic memory as opposed to SRAM.

SRAM (static random access memory) is a type of semiconductor memory where the word static indicates that it, unlike dynamic RAM (DRAM), does not need to be periodically refreshed, as SRAM uses bistable latching circuitry to store each bit. SRAM exhibits data remanence,[1] but is still volatile in the conventional sense that data is eventually lost when the memory is not powerNonvolatile Memory.

The advantage of DRAM is its structural simplicity: only one transistor and a capacitor are required per bit, compared to six transistors in SRAM. This allows DRAM to reach very high density. Like SRAM, it is in the class of volatile memory devices, since it loses its data when the power supply is removed. Unlike SRAM however, data may still be recovered for a short time after power-off. But SRAM was read faster than DRAM.

1.1.2. Nonvolatile Memory

1.1.2.1 Flash Memory

Flash memory is the most popular memory device nowadays. The structure of flash memory uses floating gate to storage charge, as shown in the figure 1-1. The floating gate, poly-silicon, is covered by insulator. Then, the charge at floating gate can not be released without bias. The information can be stored in the flash memory. The charge in the floating gate is defined "0", without "1".

The operation speed and rewritable times should be confined, due to the tunneling effect in programmed process. As release-rewrite many times, insulator would breakdown. Hence, the flash memory device can be rewritten about 10^6 times.

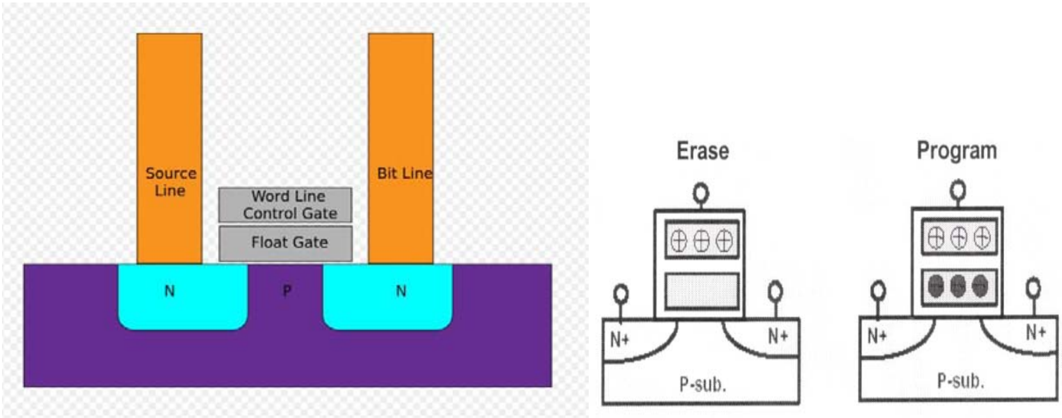


Fig. 1-1: The structure of Flash memory.

1.1.2.2 FeRAM (Ferroelectric Random Access Memory)

For the purpose of improve the drawbacks of Flash memory (such as high program and erase-voltages, slow program speed, write-erase endurance that is limited to ~10^5 cycles). Among all new memories, ferroelectric random access memory (FeRAM) is the first device for application in our life. But it has some problems that are limited reading about 10^{12} times for us to overcome.

Writing is accomplished by applying a field across the ferroelectric layer, forcing the inner atoms "up" or "down" (depending on the polarity of the charge), thereby defined as "1" or "0". In reading process, however, is somewhat different than in DRAM. When reading process, using reads in “1” forcefully to differentiate “1” or “0”. Since this process overwrites the cell, reading FeRAM is a destructive process, and requires the cell to be re-written if it was changed. In comparison, FeRAM requires far less power to flip the state of the polarity, and does so much faster.

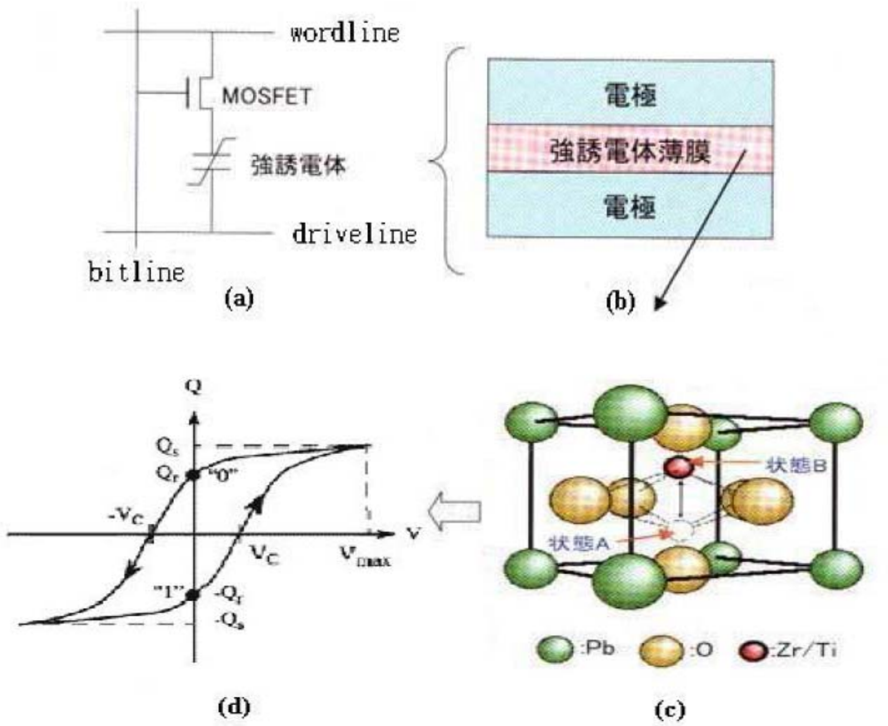
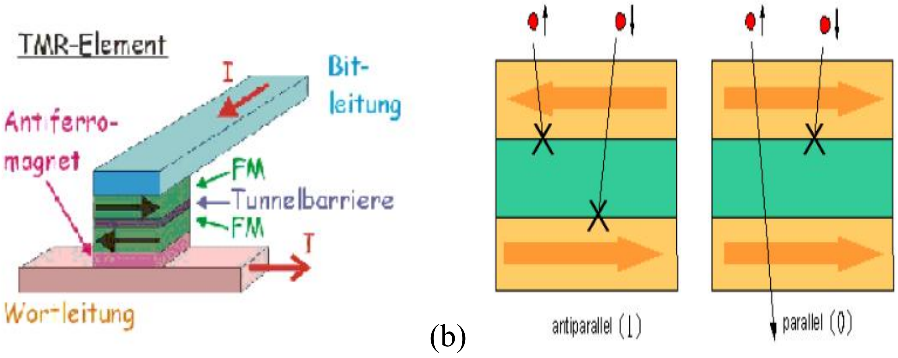


Fig. 1-2: The principle instruction of FeRAM

1.1.2.3 MRAM (Magnetic Random Access Memory)

Magneto-resistive Random Access Memory (MRAM) is a non-volatile computer memory technology, which has been under development since the 1990s. Unlike conventional RAM chip technology, in MRAM data is not stored as electric charge or current flows, but by magnetic storage elements. The elements are formed from two ferromagnetic plates, each of which can hold a magnetic field, separated by a thin insulating layer. One of the two plates is a permanent magnet set to a particular polarities, the other's field will change to match that of an external field. Typically if the two plates have the same polarity this is considered to mean "0", while if the two plates are of opposite polarity the resistance will be higher and this means "1".



(a) (b)

Fig. 1-3: (a) The structure of the MRAM. (b) The principle of the memory.

Furthermore, MRAM has infinity write-read-erase cycle times, this is the best advantage of all non-volatile memory. But the high current consumption is the most problem for MRAM in the present. So it should be improved better in the future.

1.1.2.4 OUM (Ovonic Unified Memory)

Ovonyx's phase-change memory (also known as Phase Change memory, PRAM) may be emerging as one of the leaders. On 28 December 2005, Ovonyx Inc. and Samsung Electronics announced that they have entered into a long-term license agreement relating to Ovonic Unified Memory (OUM) thin-film semiconductor memory technology. OUM is one of the most advanced applications of the science of disordered materials that was invented and pioneered by ECD Ovonic' cofounder Standford R. Ovshinsky. Whereas conventional silicon memory relies on the conductive properties of silicon due to the inherent order of its crystals, OUM uses a layer of an alloy called chalcogenide formed on regular silicon chips that can change from a disordered or amorphous state to a crystalline state with a highly ordered atomic structure, with the application of heat. Such phase changes brought about by bursts of electric current can be used to generate the "1s" or "0s" needed for digital products. The technology is also versatile enough to display not only filly amorphous and fully crystalline states, but also intermediate states that some day may be used to make multi-state memories.

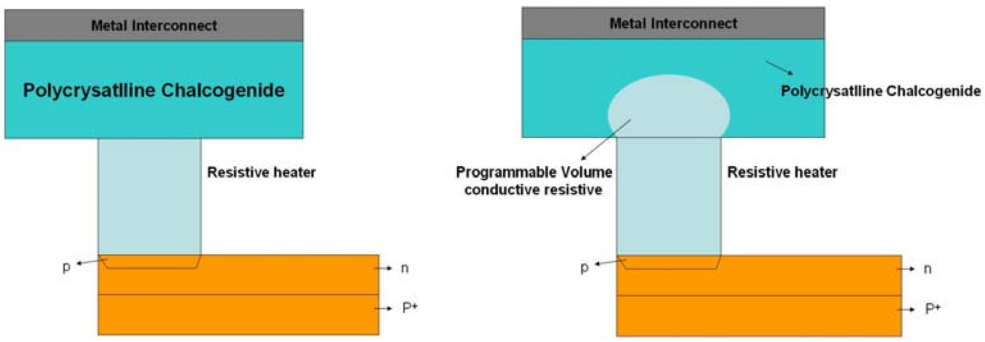
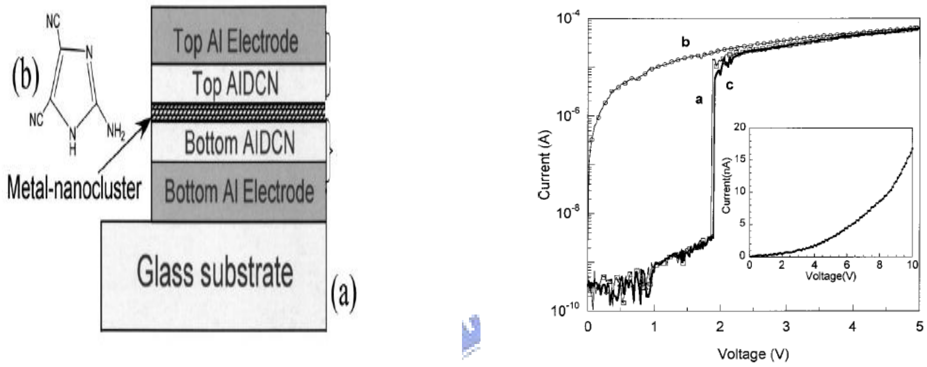


Fig. 1-4: The basic structure of Phase-Change memory (OUM).

1.2. Organic Bistable Memory Device

Organic memory devices are generally realized by interposing thin film layers containing organic materials between two electrodes and have caused much attention due to their potential advantages of flexibility, easy processing, low cost, and larger area fabrication by printing techniques. Generally, electrical bistablility means there are two electrical states for a device, i.e., the high-conductance state (ON state) and the low-conductance state (OFF state), and the device can exist at either state for a prolonged time (retention time); under some applied condition, the device can be switched from one state to the other, which is ideal for rewritable nonvolatile memory application.

The first organic bistable device was issued in the organic photoelectric research laboratory of UCLA in 2002 Component, as shown in Fig. 1-6. The organic semiconductor material is not only developed to some extent in the photoelectric field but also in semiconductor Field. The UCLA organic photoelectric research laboratory issued organic memory device that uses the organic layer, AIDCN (2- amino-4,5 imidazoledicarbonitrile), it is the single crystal structure, as shown in Fig. 1-. The structure of organic bistable device is five layers. (Fig.1-), its component structures have two metal electrode inserted for “organic layer / intermediate level /organic layer” sandwich structure.



(C)

Fig. 1-5: (a) the structure of the organic bistable device which was fabricated by the UCLA organic photoelectric research laboratory. (b) The chemical structure of AIDCN. (c) The basic structure and Current-Voltage characteristic of organic bistable Memory.

1.3. Motivation

Organic field effect transistors, organic light emitting diodes, organic photovoltaic cells have attracted considerable attention during the last several years due to their envisioned applications in low-cost, flexible, large area and lightweight organic electronics. However, another important device, the organic memory, has received scarce attention, despite its important role in the electronic circuitry. Carchano *et al*. had found the first effect of the organic electronic bistable in 1971. Y. Yang *et al*. had published the first non-volatile organic bistable memory device in 2001, and L.P. Ma *et al.* has published the non-volatile organic memory device (OBD) to combine with the polymer light emitting diode (PLED) in 2002, that fabricate the bistable lighting device. The organic light emitting diode is controlled by the switch which the organic bistable memory device at the bottom. It has attracted lots of attentions and there are more and more scientists throw themselves into the domain of the organic thin film bistable effect, and to use the effect at the non-volatile memory. But, there are some questions in the organic memory device, for example, the electronic measurement still can optimize and the memory device is still at read only state. Consequently, there is commercial product nowadays.

In this work, we try to investigate an organic light emitting diode with logical function by combining with an organic electrical bistable device. We fabricate the structure of the OBDs is ITO-electrode / organic layer / metal-electrode that the structure is usually used. And the characteristic of the OBDs has measured. Moreover, we interpose the metal film between the organic layer in order to enhance the characteristic of the electric bistable effect. However, the performance of the OBDs based on the ITO-substrate is non-uniform. The roughness of the ITO-substrate is too larger than an inner metal film and to avoid the roughness to affect the performance of the OBDs. Thus, replace the ITO-substrate by Au.

Another, our OBDs erases the data hardly after writing. The elements of the inner metal film play the important role. Y. Yang *et al.* evaporate the inner metal, as they vent the oxygen into the chamber in order to form oxide. But, we use the oxygen-plasma to control the elements of the inner metal film. Our method can avoid the organic layer to react with oxygen that this is different from Y. Yang *et al.* that the way saved time. In this way, we can surely confirm the principle of the electronic bistable effect, and we successfully solve the question which the data of the OBDs is not erased.

Chapter 2 Organic Bistable Memory Devices

2.1. Introduction

In this work, we fabricate an organic electrical bistable device that combine with organic light emitting diodes. We report an organic bistable memory made of a single organic layer embedded between two electrodes. And, we also fabricate the device that interposes the thin metal film, Al. The electrical bistable characteristic is improved. The current-voltage characteristic in this structure will be presented, too. And discuss the re-writing behaviors. We replace ITO-electrode by Au so as to avoid the roughness of the ITO-substrate to affect the inner metal layer.

2.2. Material

In the experiment, the purity and the quality of the material should be considerate well. The materials used in this experiment are as follows: The organic layer is Tris (8-hydroxyquinoline) aluminum (Alq_3), which is one of the well-known organic electron transfer semiconductor materials, as shown in Fig. 2-1. This material, $Alq_{3,}$ is made and purified by the Seachent CO. LTD, and the purity is 95%. The metal electrodes are aluminum (Al) and gold (Au), they are produced by Sumitomo and Tanaka Company, respectively, and the purity are of both up to 99.999%.

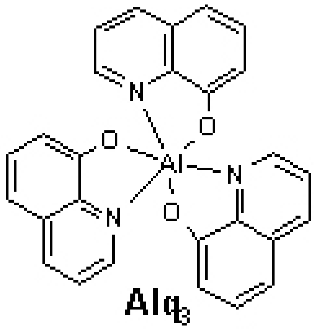


Fig. 2-1: The chemical structure of Alq3.

2.3. Thermal Instrument

Many organic materials are deposited by the thermal evaporation at present. Using thermal evaporation to deposit organic thin film has the following advantages: first of all, heated by the resistance wire, so the temperature can be perfectly controlled; in addition, the material is heated in the wide area, hence it could be heated uniformly without overheating problem. Moreover, there are several sources, so we can co-evaporate different material together; finally, the structure of thermal coater is very simple and the cost could be dropped down. Therefore, to use thermal coater to deposit the thin film in my research and use metal hard mask to define the pattern of the device.

There are five tungsten boats to heat the material and two quartz oscillators to record the thickness of the thin film. Before depositing the thin film, it should pump out the air lower than $7.56x10^{-2}$torr by the machine pump. And then use cryo-pump to drop down the vacuum lower than $3x10^{-6}$torr. Afterward, begin to heat the boat to fabricate the thin film. The thermal deposition instrument is shown in Figure 2-2.

Fig. 2-2: The thermal deposition instrument.

2.4. Fabrication of the OBDs with ITO Substrate

In the experiment, there are several layers in the organic bistable device. During the evaporation procedure, any pollutant or particle will influence the device's performance and yield. Hence, the substrate surface is clean or not will to play an important role. The substrate is cleaned by follow step. The first step of the ITO-glass substrate is sonicated in the detergent about 5 minutes; second, scrub by hand for minutes then wash with de-ionized water for 3 minutes. Finally, using N_2 to blow the water away and put it on hat-plant to bake for minutes, then subsequently treated with UV ozone, prepare to deposit the organic film later.

The device is based on ITO-glass substrate, as shown in Fig.2-3(a). The organic material is sandwiched between two metal electrodes with or without the thickness inner metal layer. During the thermal evaporation procedure, the shadow mask was used to pattern the top Al electrode and define the device area. The top Al electrode was thermally evaporated with area of 4 mm^2 through a shadow mask, so as to define an active cross area.

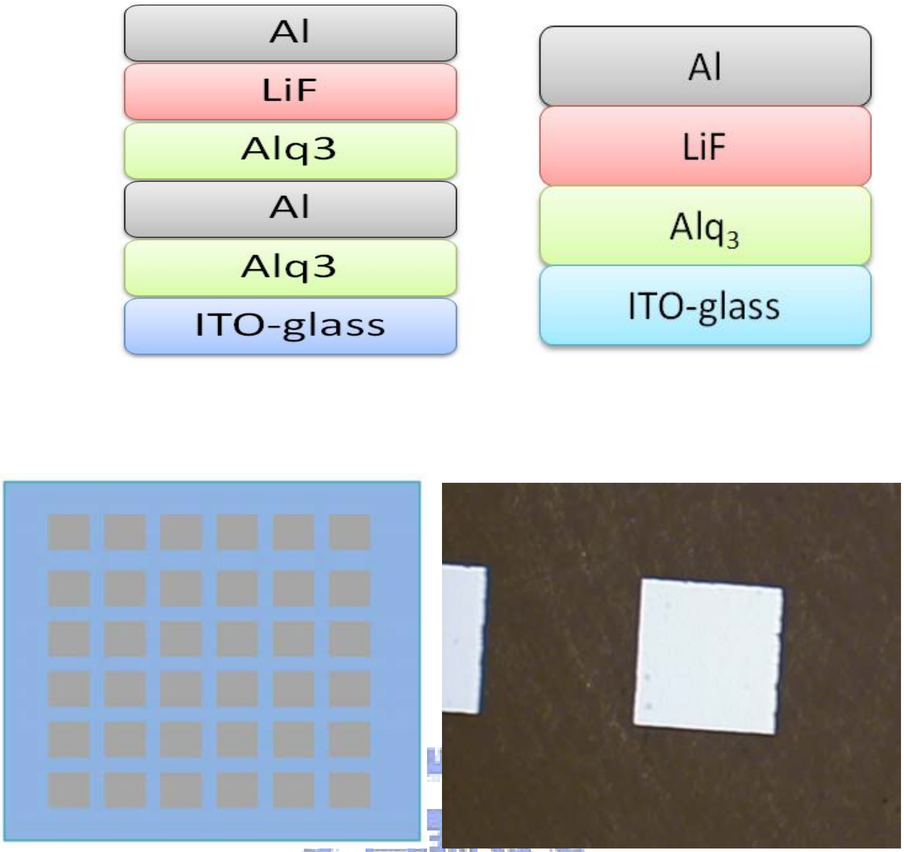


Fig. 2-3: (a) The structure of the two kind of our device. (b) The top view of the device.

The active layer of the organic bistable memory device (OBD) consists of organic multi-layer structure interposed between an anode and a cathode, as shown in the Figure 2-3(a). The structure of our OBD was fabricated through the following process: first of all, the 45nm Alq_3 organic layer is thermally evaporation, 0.25nm/sec on the pre-cleaned glass substrate at a pressure of approximately 6×10^{-6} Torr. Then, an Al thin film was deposited on top of the organic layer by thermal evaporated deposition. The thickness of this Al thin film is 1 nm, 0.03nm/s. Afterward, the second 45nm Alq_3 organic layer was deposited, 0.25nm/sec by thermal evaporation at a pressure of 6×10^{-6} torr without breaking vacuum of chamber. Then, the material of LiF, was deposited on the top of the second Alq3 layer. Finally, breaking vacuum to pattern the top Al electrode by using metal mask and define organic bistable memory device area. The structure of the OBD is fabricated, as show by 4156b in Figure 2.3(b). The thickness of each layer is monitored by quartz crystal calibrate. Every fabrication parameter is shown in Table 2-1.

Table 2-1: The parameter of fabrication process

	ITO	Organic	Metal	Organic	Top electrode
Vacuum Value	$6x10^{-6}$ torr.				
Thickness		45nm	1nm	45nm	200nm
Evaporated rate		0.3nm/s	0.02nm/s	0.3nm/s	0.3nm/s

Fig. 2-4: The HP-4156B.

2.5. Electrical Characteristic Measurement

Current-voltage (*I-V*) characteristics reported here is measured with a HP 4156B, as show in Figure 2-4, where voltage is changed at stepping rate of 0.1 V/sec. All electrical characteristic are measured in ambient condition. A typical current–voltage (*I–V*) curve for an OBD is shown in Figure 2-5. It distinctively displays two conducting states. Reading of the device conductance state is done with an applied voltage below a certain critical threshold voltage (V_{th}). With an applied voltage on the device, the device is stable and the current increases slowly with the voltage, the current remains low. The current is in the range of 10^{-11}A at 1V. This is the low conductivity state (we define it as "OFF" state). When the applied voltage is increased further to ~1.8 V, a sharp increase in the current is observed (we define the voltage is threshold voltage, V_{th}), indicating the device transition from the low conductivity state (the OFF-state) to a high conductivity state (we define it as "ON "state). This transition from the OFF-state to the ON-state serves as the programming process for the memory device. For the programmed device, the device shows a higher current as the voltage applied. The current density at 1V is about 10^{-5}A. At next bias, the device is still hold at high conductance state. The ON/OFF current ratio is six orders of magnitude.

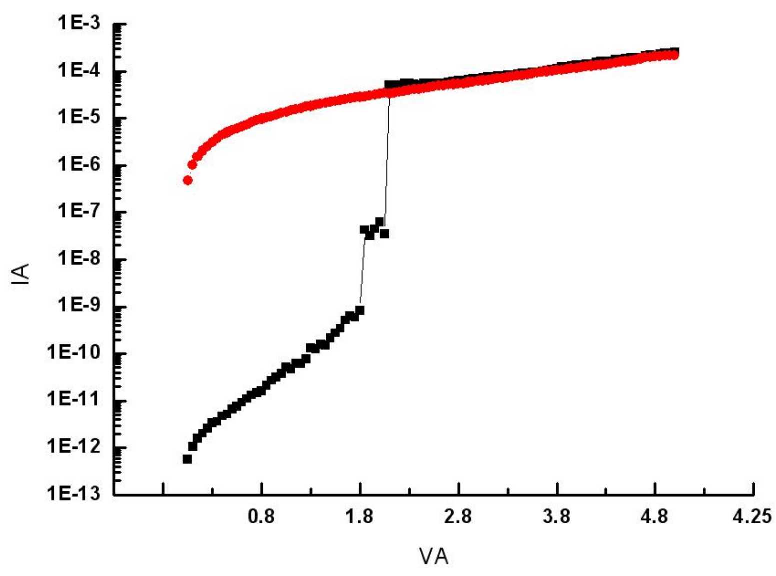


Fig. 2-5: *I-V* characteristic of ITO/Alq_3/Al. Current is expressed in absolute value. An abruptly jump in the low-current was observed on the way to the ON/OFF state transition around 1.8V. The bias is swept from 0 to 5 V, and swept back 0 to 5 V.

The figure 2-6 shows the ratio of ON-state to OFF-state current as a function of the applied voltage. In the voltage ranging from 0 to 2 V, we can applied a low voltage (e.g., 1.0V) to discriminate the “ON” or “1” state and the “OFF” or “0” state from the current. Therefore, the ON/OFF ratio of the OBD is enough to avoid the reading error rate. The retention time is about 300sec (not show here).

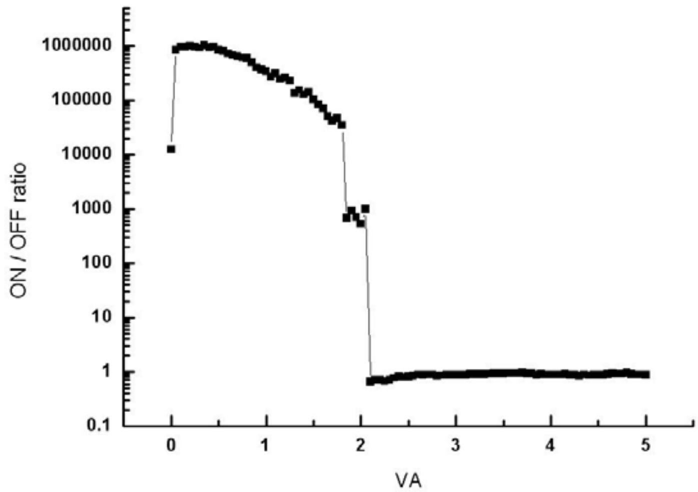


Fig. 2-6: The ON / OFF current ratio as a function of applied voltage.

Organic bistable memory devices are generally realized by interposing metal thin film layers within organic materials between two electrodes in order to improve the electrical bistable effect. We also fabricate the same memory device structure. This device shows the bistable characteristics, too. A current-voltage (*I-V*) characteristic of an organic bistable memory device is shown in Figure 2-7.

The first forward bias scan form 0 to 5 V, the device shows a very low current state about 10^{-11}A (we define it as “OFF” state) until at a critical voltage about 1.8 V (threshold voltage, V_{th}), where it switches from low current state to high current state about 10^{-2}A (we define it as “ON” state). As bias is swept back from 5 to 0 V, the device remains in the high conductivity state (the ON-state), indicating bistable memory effect. This current is eight orders of magnitude higher than that in the OFF state. The retention time is above 1200sec, this show in Figure 2-9.

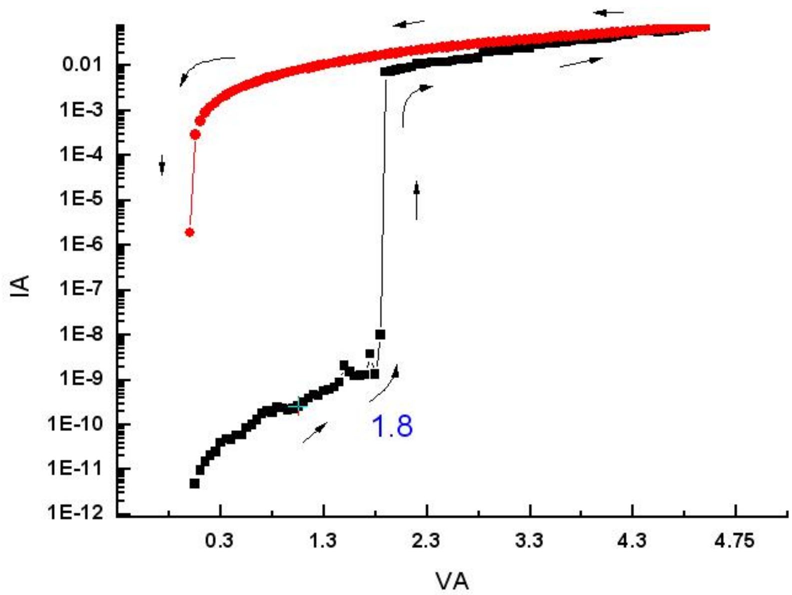


Fig. 2-7: *I-V* characteristics of ITO/Alq_3/Al/Alq_3/Al. An abruptly jump in the off-current was observed on the way to the off/on transition around 1.8V.

The Fig. 2-8 shows the ratio of ON-state to OFF-state current as a function of the applied voltage. In the voltage ranging from 0 to 1.8 V, we can applied a low voltage (e.g., 1.0V) to discriminate the “ON” or “1” state and the “OFF” or “0” state from the current. Therefore, the ON/OFF ratio of the OBD is enough to avoid the reading error rate.

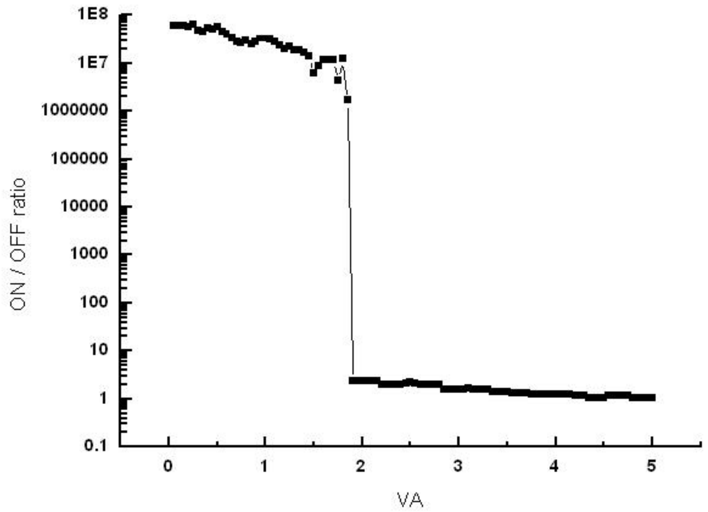


Fig. 2-8: The ON / OFF current ratio as a function of applied voltage with inner metal film.

At the same time, the state retention ability under a bias was evaluated in a continuous bias as show in Fig. 2-9. The voltage (+1.0 V) is continuously applied in the OFF-state and ON-state and the current is read at 60s intervals, at ambient conditions. It is found that no detectable degradation of the ON and OFF states is observed at least over 1400 seconds, the result of the OFF and ON states are not transient states.

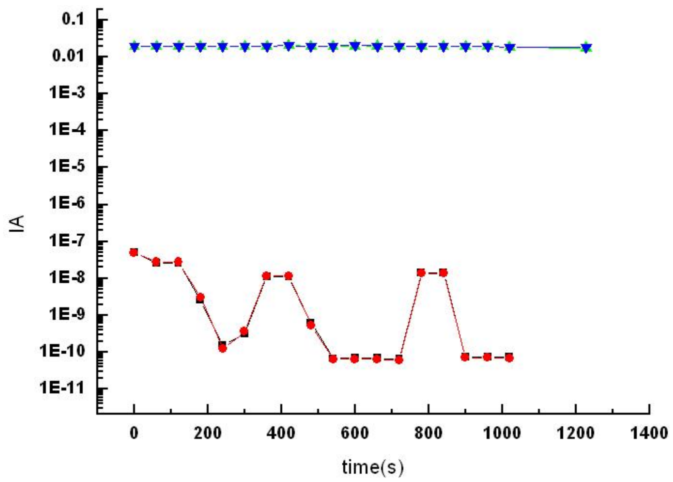


Fig. 2-9: The Stability test on ITO/Alq_3/Al/ Alq_3/Al device in both ON and OFF states under applied voltage of +1V continuously. The retention time is over 1200sec.

2.6. Mechanism and Discussion

The detail mechanisms involved in the OBD is still under investigation. However, L. Ma *et al.* have reported a principle of the organic bistable memory which the embedded the thin metal layer. When the applied bias to the device is high enough, free electrons in the metallic cores of the nanoclusters tunnel through the barrier against the applied electric field direction, resulting in the Al-nanocluster layer being polarized. Subsequently, the charge is stored at both sides of the middle Al-nanoclusters layer, as shown in Fig 2-10. This is similar to the formation of a conducting channel in a transistor. When the bias is removed, because of the oxide barrier layers between the middle metal layers, the polarized charges cannot recombine, and they remain at the two ends of the middle metal layer. This causes the nonvolatile memory effect. It is realized that only a reverse bias in the device to the low-conductance.

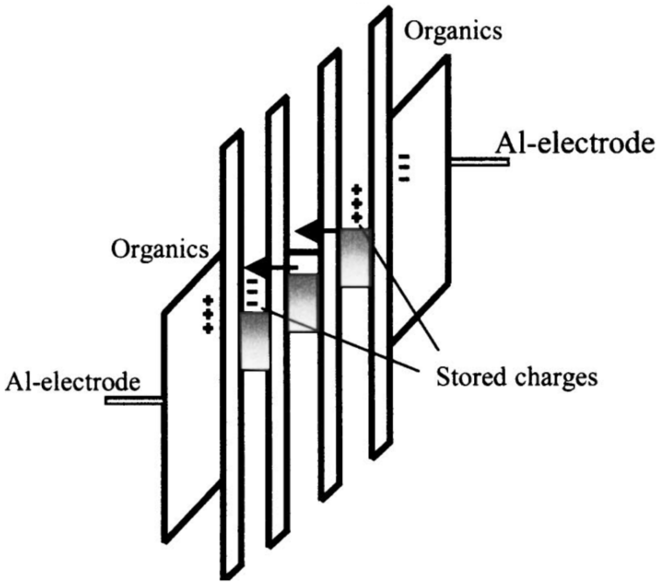


Fig. 2-10: Schematic illustrations of the possible bistable behavior mechanism (at the middle metal layer)

Besides, P.T. Lee et al. have reported the electronic bistable effect of the Al/Alq3 based OBDs are caused by interface traps, as shown in Fig. 2-11. At the first, the current is very small with low bias because electrons are obstructed by a barrier formed between the Al and Alq_3. Thus, only a few electrons can be injected into the organic active layer. Then most of them are further trapped by the defects in the bulk Alq_3 thin film. As a result, the device stays at high resistance. By applying a voltage above the threshold, the barrier can be overcome, and this enables numerous electrons to be injected into the active layer and the defect can be filled. Accordingly, electrons are transported easily into the active layer and drift unobstructed towards the other end of the device. At the next bias, the device exhibits a resistance-like characteristic when the reading voltage is larger than the energy barrier Al and Alq_3, that is, Ohmic relation. Thus, the ON-state can be obtained for any reading voltage. Fig. 2-11 shows in blow.

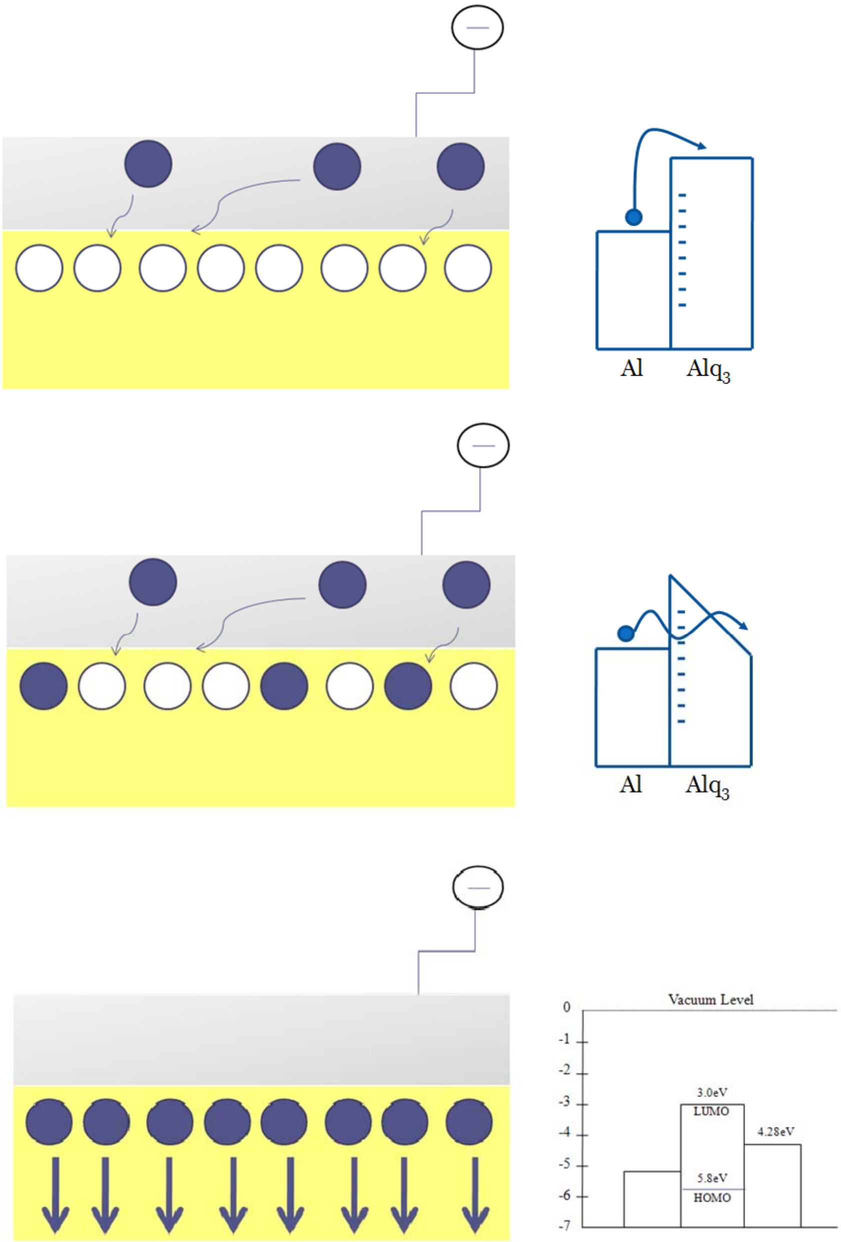


Fig. 2-11: Schematic illustrations of the possible bistable behavior mechanism at the interface.

The switched state with high conductivity can be turned back to its original state with low conductivity by applying a negative pulse. Figure 2-12 displays the re-writing electrical behaviors after applying electrical erasing voltage pulses. First, the device with high conductance state after writing process is given an electrical erasing voltage pulse and then a re-writing bias scan is applied on the OBD (corresponding to the blue curve in Figure 2-12). The threshold voltage 1.8V shifts to 1.2V and the on/off ratio $3.33x10^5$ drops to $1x10^2$ raising greatly the reading error rate.

An electrical erasing voltage pulse is a way that the memorized state can be switched back to its beginning state. This is also a significant parameter in the memory. In the reported device, the high conductivity can be simply changed to low conductivity. Unfortunately, the on/off current ratio varies randomly and the threshold voltage shifts as well. Consequently, there is an influence on the reliability of the device due to these unexpected results.

The results from two electrical erasing pulse cases might be subject to the defect formation at the interfaces because of electric field stressing, and disequilibrium between trapped carriers at the writing stage and released carriers at the erasing stage. The traps in the reported device can be formed from process fabrication and electrical measurement. There must be defect formation at the interfaces during process fabrication owing to imperfect junctions. Figure 2-13 shows the AFM image of the Alq_3 thin film deposited onto the ITO-substrate. It is clear that the surface of the Alq_3 thin film is not flat.

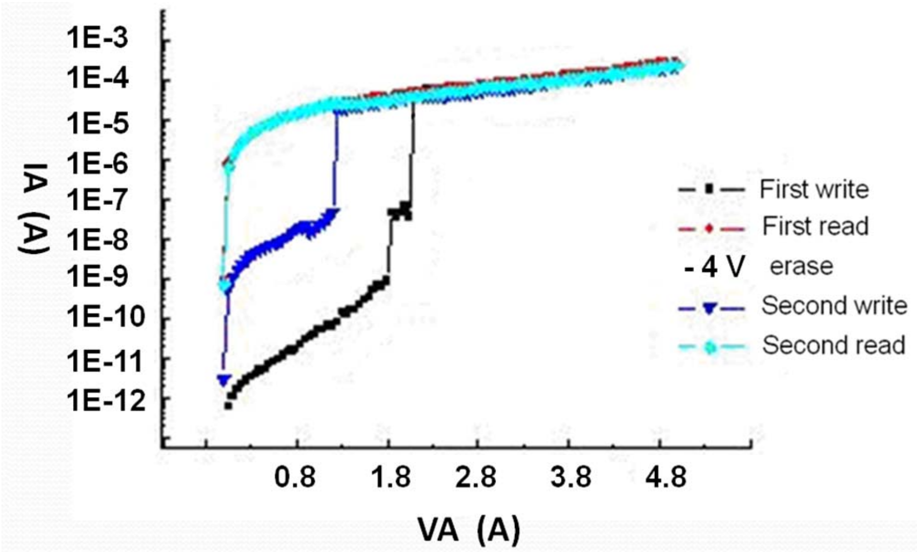


Fig. 2-12: The device was indicated rewritability of the device.

We fabricate two kinds structure of the OBDs. One of the metal layer is interposed between the organic layer and the other is the tri-layer that the organic layer between the electrodes. There are some different electrical characteristic. At the threshold voltage, the device with inner metal layer is 1.8V, the same as the tri-layer device. However, the ON-state current is 1×10^{-2}A with the metal layer device that is larger than the tri-layer device, 1×10^{-5}A. So the ON/OFF current ratio is enhanced from six orders to eight orders that decrease the reading error rate. And, the retention time is above 1200 seconds with the metal layer device that is also larger than the retention time with the tri-layer device, 300 seconds. We extend the stored data time. But, the only tri-layer device displays the re-write effect after apply the reverse bias in this device that discuss in the above section. Because the inner metal layer is not covered well to cause by the roughness of the ITO-substrate that the same as nano-particle at the organic layer. The faction of the inner metal layer leads to many interface traps.

Our processed information, the electronic bistable effect, is shown in Table 2-2. We compare the two kinds of the organic bistable memory device, which there is a thin film or not, Al, between the organic layer. The process needs some time with an inner metal film interposed between organic layers. We obtain the better performance, such as the ON/OFF ratio, the retention time.

Table 2-2: The information of the OBDs

	V_{th}(V)	ON/OFF Ratio	ON state current(A)	OFF state current(A)	Retention Time(s)	Erase
Without Al	1.8	6	1E-5	3E-11	~300	yes
With Al	1.8	8	1E-2	2E-10	>1200	no

The OBDs based on ITO-substrate is displayed the electronic bistable effect, but the performance is non-uniform. We suppose that the ITO-substrate is too roughness to be covered well with the inner metal layer. The inner metal layer is only 1nm, but the roughness of the Alq_3 deposit on the ITO-substrate is about 3.5nm, measure by AFM, as show in Figure 2-14, Table 2-3. The inner metal layer is not covered well, that the same as nano-particle at the organic layer. The faction of the inner metal layer leads to many extra interface traps due to the roughness of the ITO-substrate. This affects the electronic bistable effect that the OBDs don't erase. And, the main principle of the inner metal film device is not clean. To prove our suggestion, the bistable effect in the inner metal film device is attributed to the inclusion of traps at the Al/Alq_3 interface during the evaporation of the top electrode. The proof is that we have not observed a bistable effect in our device if the Alq_3 is directly and gently contacted by a mechanical contact ingot, as shown in Fig. 2-13.

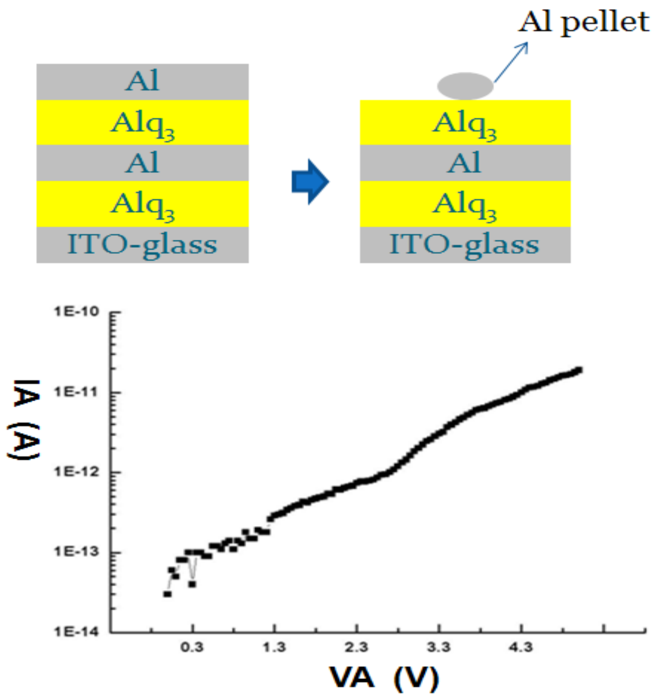


Fig. 2-13: I–V curve without the top Al electrode and mechanically contacted with a small Al tablet (the off-current is lower because the contact area in that case is smaller than with the evaporated Al contact). No switching has been observed for applied bias up to 5 V.

In order to solve the question that is not erased, we replace the ITO-substrate by Au. ITO and Au are both high work-function, and the roughness of the Au deposit on Si-substrate is better than ITO-substrate. When the ITO-substrate is treated with UV ozone, the work-function of the ITO-substrate is enhanced to about 5.1 eV. The point of the work-function is not discussed here.

Table 2-3: The compare of the two kinds of the OBDs.

	ITO-Substrate	Au
Work-Function (eV)	Over 5.0 eV (UV)	5.1 ev
Roughness (before) (nm)	5.557	3.198
Roughness (after) (nm)	3.285	0.527

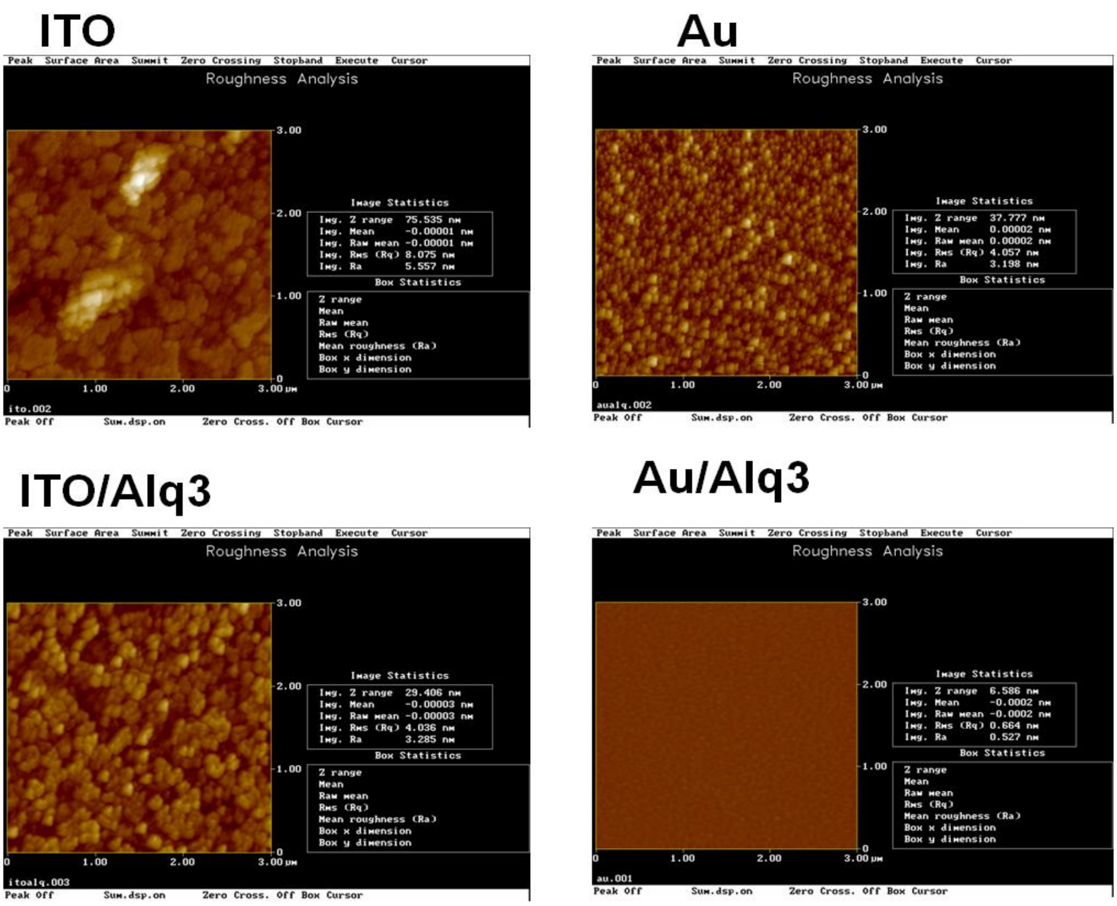


Fig. 2-14: The AFM image of the roughness of ITO and Au.

2.7. Conclusion

In this chapter, we have fabricated the structure of the OLEDs of the organic bistable memory device embedded the inner metal layer or not. We also account for the operated mechanism of the two kinds of the OBDs. One of them is the inner metal film is polarization that the OBD interpose the thin metal film. The other is caused by interface traps that the OBD is tri-layer. We compare the two kinds of the organic bistable memory device. The better performance is obtained with measurement that the inner metal layer device, such as the ON/OFF ratio from six orders to eight orders, the retention time is extended about 300 seconds to over 1200 seconds. And the threshold voltage is not increase.

The switched state with high conductivity can be turned back to its original state with low conductivity by applying a negative voltage pulse. And the tri-layer device displays re-writing electrical behaviors. The threshold voltage 1.8V shifts to 1.2V and the on/off ratio 3.33×10^5 drops to 1×10^2. Because of electric field stressing and disequilibrium between trapped carriers at the writing stage and released carriers at the erasing stage.

In order to avoid the roughness of ITO-substrate to affect the inner metal film, we replace the ITO-substrate by Au. Then, we will discuss the characteristic in the next chapter.

Chapter 3 Al/Alq$_3$/Al/Alq$_3$/Au Bistable Memory Devices

3.1. Introduction

With great advance in the field of organic materials, numerous organic semiconductor materials have been proposed for electronic and opto-electronic devices, such as organic thin film transistor (OTFT), organic light emitting diode (OLED), and organic solar cell, etc. However, in despite of intensive progress in various organic devices, research development in organic electronic memory is far behind. Recently, several groups also pay close attention to this important electronic application, organic bistable device (OBD) which exhibits two different conductivities at the same applied voltage. Due to the advantages of cost effective, light weight, and flexibility, organic bistable device is one ideal candidate compatible with silicon based rewritable nonvolatile memories.

In this chapter, we replace the ITO-substrate with Au. There are several thickness of the inner metal layer is treated with oxygen-plasma for different time. Our method avoids the organic layer to react with oxygen, immediately. This is different from Y. Yang *et al.* that they evaporates the inner metal, at the same time, they pass the oxygen into the chamber in order to form oxide. The method saves time of the fabrication. Our device exhibits two different conductive states at the same applied voltage and it is found to exhibit distinct bistability with an ON/OFF current ratio up to 10^7. And the performance of the electronic bistable effect is uniform. Furthermore, this device shows over 2100s data retention time. We also change the state from high-conductance to low-conductance state when we apply an erase voltage. Hence, we believe that the inner metal has formed oxide or not that affects the characteristic of the OBDs.

3.2. Fabrication of the OBDs with Au-electrode

In this experiment, the structure of the OBDs is the same as above chapter. There is only one different, that the ITO-substrate replace with Au on Si-substrate, as shown in Fig 3-1. During the evaporation process, any pollutant or dust will destroy the device's performance and yield. Hence, the Si-substrate surface which is clean or not will plays an important role. The washing steps of the substrate are as follows: first of all, dip in the DI water about 5 minutes; second, immerse in the H_2SO_4:H_2O_2 about 10 minutes at 75~85^{o}C to decompose the oxidation, then dip in DI water about 5 minutes. Afterward, dip into diluted HF to remove chemical oxide. Again, dip into DI water. Finally, I use N_2 to blow the water away and prepare to deposit the film later.

The fabrication process of the device is described below. First, a 100-nm-thick Au is deposited on a pre-cleaned n-type silicon wafer by thermal deposition method at a vacuum about 6×10^{-6} torr at room temperature as electrode. Second, a 45 nm-thick Alq_3 is deposited on the Au-electrode, followed, a thin metal film deposited on organic layer. The thickness of the thin metal film is 10 nm, 20nm, 50nm. Then, break the chamber so as to treat with oxygen-plasma for 30 seconds, 1 minute, 4 minutes. The follow evaporation is Alq_3 and LiF. Finally, the shadow mask is used for the purpose of define the device area. The top Al electrode is thermally evaporated with area of $800 \times 800\mu m^2$ through a shadow mask. The current-voltage (*I-V*) characteristic is measured by Hewlett Packard 4156A semiconductor parameter analyzer at ambient environment. Every fabrication parameter is shown in the Table 3-1.

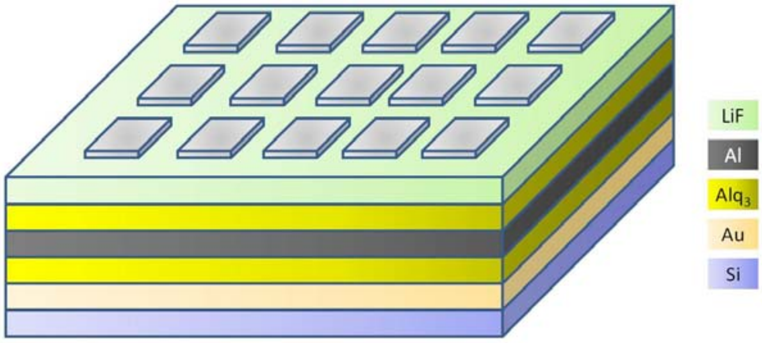


Fig. 3-1: The structure of the OBDs based on Au-electrode.

Table 3-1: The parameters of fabrication process.

	Au	Organic	Metal	Organic	Top electrode
Vacuum Value	$6x10^{-6}$ torr.				
Thickness	100nm	45nm	10,20,50nm	45nm	200nm
Evaporated rate	0.1nm/s	0.3nm/s	0.02nm/s	0.3nm/s	0.3nm/s

3.3. Electrical Characteristic Measurement

Typical current-voltage (*I-V*) characteristic of the OBDs are shown in Fig. 3-2. The device exhibits two states of the different electrical conductivity at the same voltage. During the first bias scan (black-curve), a low current is observed for the device in a bias range for 0 to 3.6 V. A sharp increase in the current, from 10^{-6} A to 10^{-1} A, take place at around 3.6 V, indicating the transition of the OBDs from a low conductivity state (OFF state) to a high conductivity (ON state). After the transition, the OBDs remained in the ON state, as shown in the subsequent voltage scan (red-curve). The conductivity of the OBDs in the ON state is more than six orders of magnitude larger than that in the OFF state. The low conductivity state can be recovered by simply applying a negative bias, as show in next 3.5.

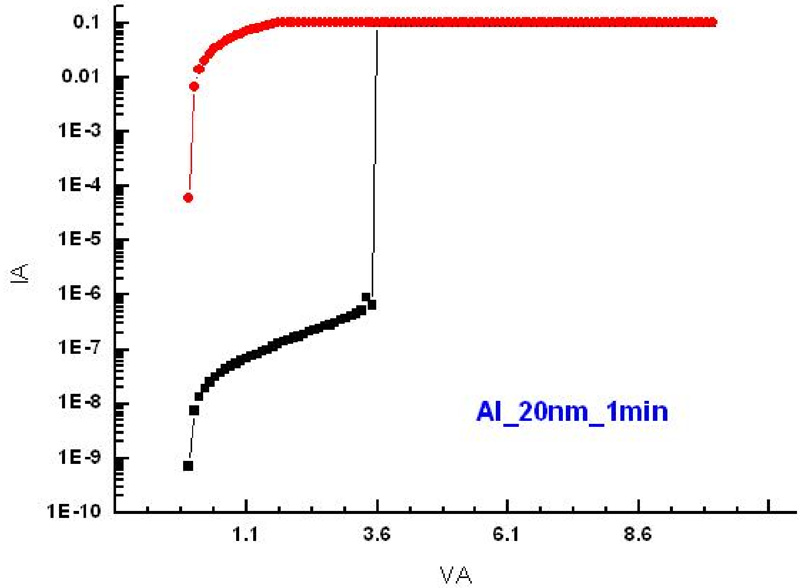


Fig. 3-2: Typical current-voltage (*I-V*) characteristic of the OBDs.

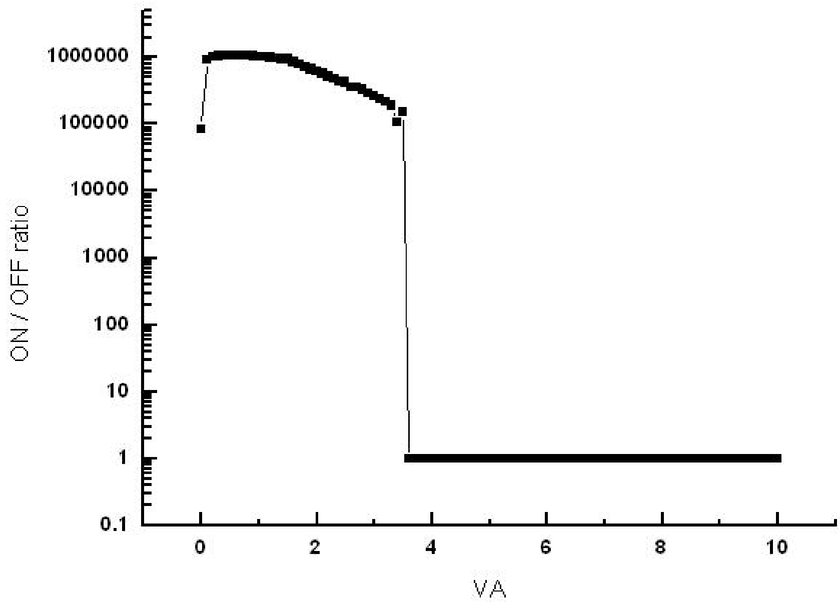


Fig. 3-3: The ON/OFF current ratio as a function of applied voltage.

The high ON/OFF ratio up to six orders is shown in Fig. 3-3. In the voltage rang from 0 to 3.6 V, we can applied a low voltage (1.0V) to discriminate the “ON” or “1” state and the “OFF” or “0” state from the current. Therefore, the ON/OFF ratio of the OBD is large enough to avoid the judgment error.

The retention ability of the OBDs under a bias stress is shown in Fig. 3-4. It is found that no detectable degradation of the ON states is observed at least over 2000 second, The result of the indicates that the ON states are not transient states for a long time.

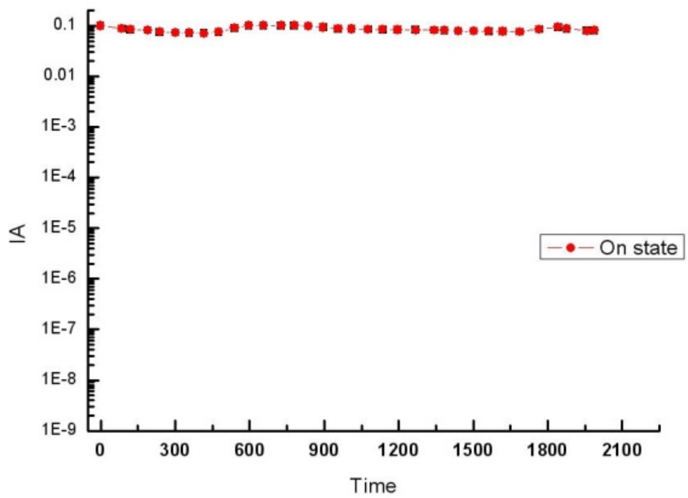


Fig. 3-4: The Stability test on $Au/Alq_3/Al/Alq_3/LiF/Al$ device in both ON and OFF states under applied voltage of +1V continuously.

3.4. Investigation of Thickness and Oxygen-plasma Time on the Inner Metal Film.

In this section, we will discuss the effect of the different Oxygen-plasma time in the inner metal film on the device's characteristic. In the report, the inner metal film is treated with the Oxygen-plasma for 30 seconds, 1 minute and 4 minutes, separately. And the thickness of an inner metal film is 10nm, 20nm and 50nm, separately. The parameter of the oxygen-plasma is shown in Table 3-2. The rest fabrications are the same as present process that mentioned before. In the current-voltage (*I-V*) curve of the OBDs that the thickness of the inner metal film is 20 nm, as shown in Fig. 3-5. The device exhibited low conductivity state at the low voltage (corresponding green and black curves). They transit to high conductivity state as the voltage pass threshold voltage (3.0 V for 30 seconds, 3.6 V for 1 minute). Then, the voltage sweeps back from 10 V to 0 V, the device still hold at high conductivity state. The devices both display electronic bistable effect. But, the device is treated for 4minutes with oxygen-plasma time that don't display electronic bistable effect.

Table 3-2: The parameters of the Oxygen-plasma.

Power	Pressure	Vent O_2	T (chamber)	T (substrate)
100 W	650 mtorr	900 sccm	100^{o}C	250 ^{o}C

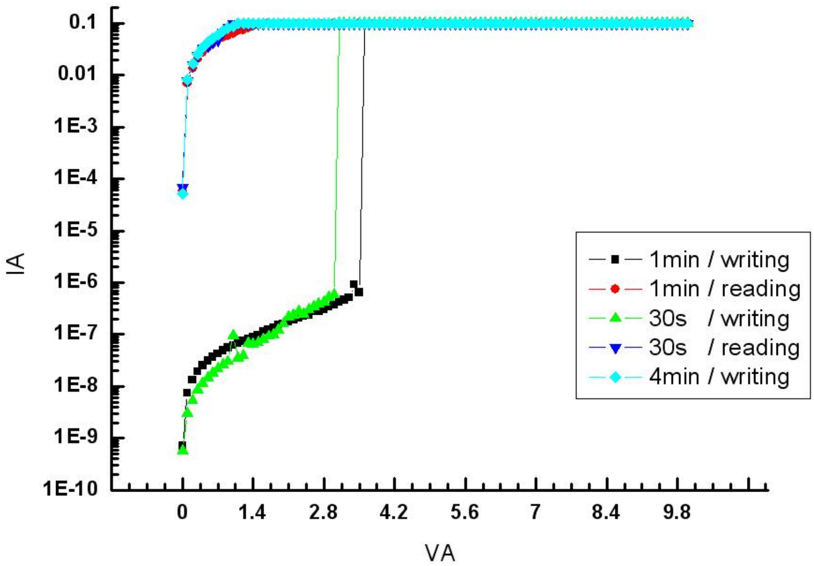


Fig. 3-5: *I-V* curve of the oxygen-plasma time (30 s, 1 min and 4 min, respectively) with the same inner metal thickness, 20 nm.

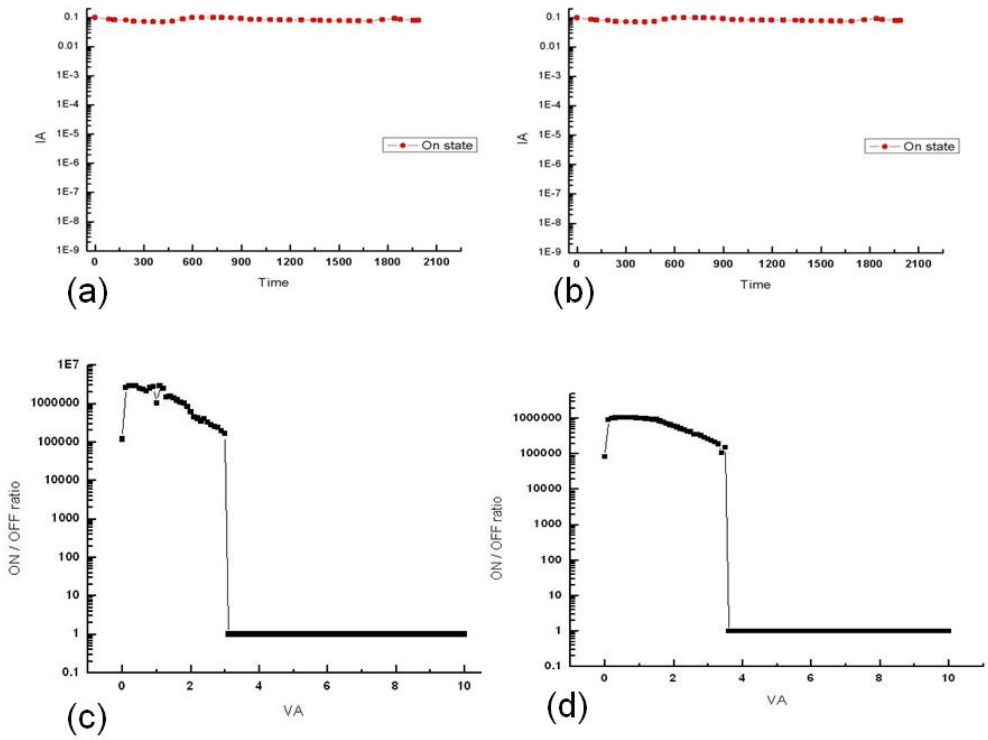


Fig. 3-6: (a) Retention time of the device treats plasma with 30s. (b) The retention time of the device treats plasma with 1min. (c) The ON/OFF ratio of the device treats plasma 30s. (d) The ON/OFF ratio of the device treats plasma 1min.

The Fig. 3-6 shows the ratio of ON-state to OFF-state current as a function of the applied voltage. There are six orders in the 30s device and seven orders in the 1min device. Therefore, the ON/OFF ratio of these OBDs is enough to avoid the reading error rate. At the same time, the state retention ability under a bias was evaluated in a continuous bias as show in Fig. 3-6. The voltage (1.0 V) is continuously applied in the ON-state and the current is read at 60s intervals at ambient conditions. It is found that no detectable degradation of the ON states is observed at least over 2100 seconds separately with the different oxygen-plasma time.

Fig. 3-7 shows the transmittance spectrum of the different oxygen-plasma time with a thin metal film is 20 nm. The different transparency of the different simples treated with the Oxygen-plasma is obtained. The simple is deposited on ITO-glass substrate by thermal evaporation. These metal films are the partial-oxide, oxide and over-oxide, separately. The Al-oxide is transparent, so the transparency is increasing with the oxygen-plasma time increase. However, the transparent of the blue-curve is over 100%, as shown in Fig. 3-7, because of the oxygen-plasma destroy the metal film, Al. Even, the ITO on the glass-substrate is also destroyed. The red and green curve is similar. Then, this is maybe a metal film completely oxide. There is a switch at the about 870nm because of the grating in the instrument.

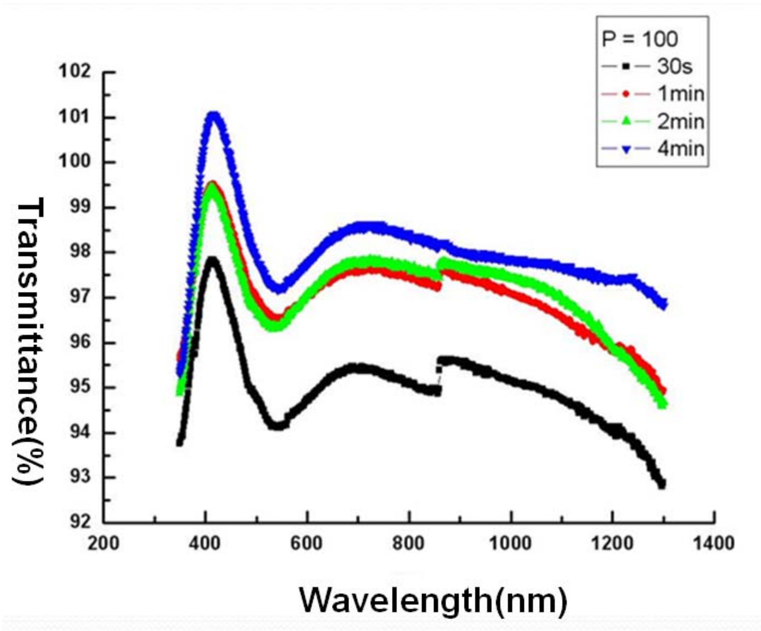


Fig. 3-7: The absorb spectrum of the different oxygen-plasma time with an inner metal film is 20 nm.

The Fig. 3-7 is also explained why there are some different electronic bistable effects from these OBDs in Fig. 3-5. The oxide thickness of the 1-minute device is thicker than 30-second device. Then, the electrons need more energy to pass through a oxide layer. The threshold voltage is larger than 30-second device (3.0 V for 30 seconds, 3.6 V for 1 minute). The structure of the 4-minute device is maybe destroyed by oxygen-plasma and there is no electronic bistable effect. And the current is over 0.1 A.

The Fig. 3-8 shown the *I-V* curve of the OBDs of the different oxygen-plasma time with an inner metal film is 10 nm. There is no electronic bistable effect. The inner metal film formed an oxide film that it is too thin to avoid oxygen to react with organic layer. The oxygen-plasma is not only destroyed the inner metal film, but also destroyed the first organic layer. The thickness of a device is less and less. The current is increasing with the oxygen-plasma time increases.

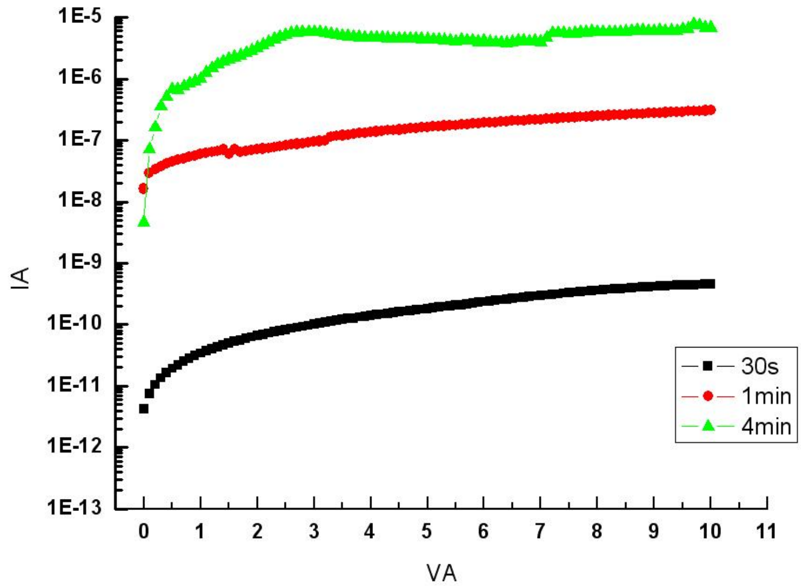


Fig. 3-8: *I-V* curve of the oxygen-plasma time (30 s, 1 min and 4 min, respectively) with the same inner metal thickness, 10 nm.

The Fig. 3-9 shown the *I-V* curve of the OBDs of the different oxygen-plasma time with an inner metal film is 50 nm. All of them don't display electrical bistable characteristic. The electronic conductivity of the inner metal is larger than two-sided organic layer. The 30-second device form oxide layer is too thin that lead to a large of carriers pass through with the bias on the device. So, the current is large. The 1-minute device formed enough oxide thickness to block the bulk of the carrier pass. Therefore, the current is smaller than the 30-second device. The thickness of an oxide layer is more and more thickness with the oxygen-plasma time increase. Consequently, the device that is treated with oxygen-plasma for 4 minutes doesn't also display electrical bistable characteristic.

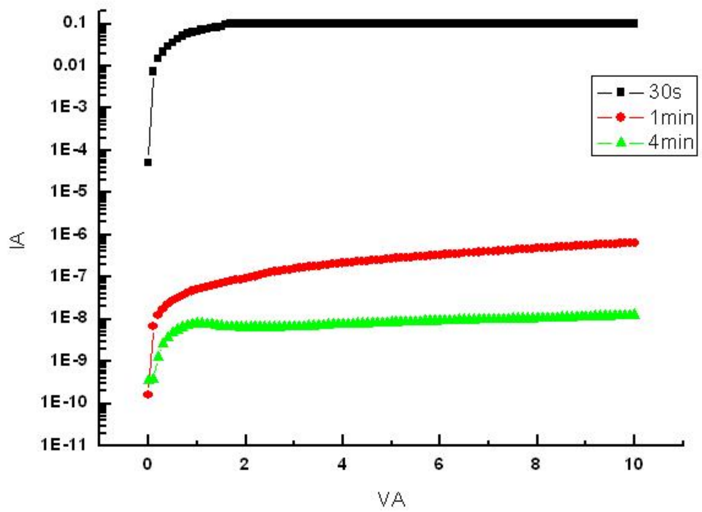


Fig. 3-9: *I-V* curve of the oxygen-plasma time (30 s, 1 min and 4 min, respectively) with the same inner metal thickness, 50 nm.

3.5. The Re-writing Characteristic of the OBDs with Oxygen-plasma

The switched state with high conductivity can be turned back to its original state with low conductivity by applying a negative voltage pulse. The current-voltage characteristic, as shown in Figure 3-10, display the re-writing electrical behaviors after applying electrical erasing voltage pulses. During the first forward bias scan from -10 to 10 V, the device shows a very low conductance state (negative bias is for the purpose of making sure that the device is at the OFF-state) until at a critical voltage (around 5 V), where it switches from the OFF-state to the ON-state. As the bias is swept back from 10 to 0 V, the device remains in the ON-state, indicating memory effect. As it is swept further to the negative voltage, the device is recovered to the OFF-state at about -2 V, indicating re-writability of the device.

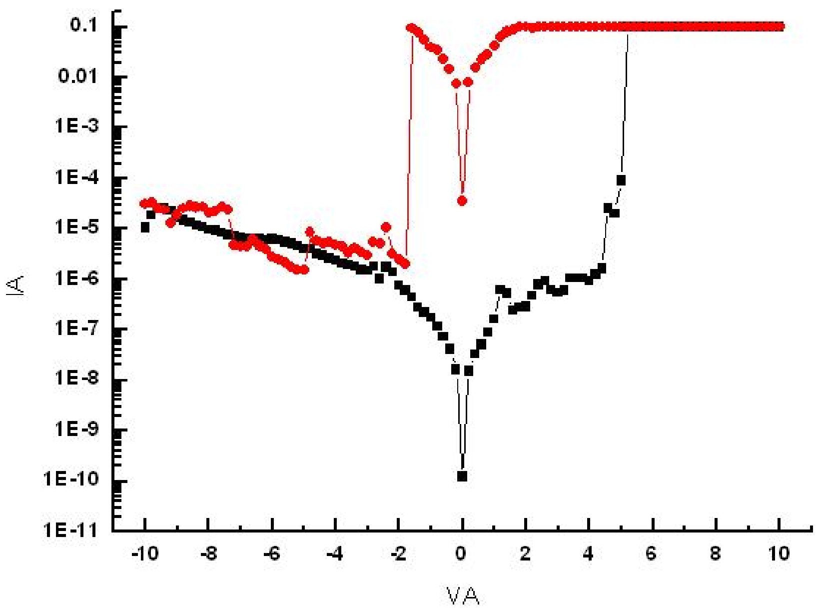


Fig. 3-10: The indicating re-writability of the device.

Electrical switching between the low and high conductance states is performed numerous times, as demonstrated in the Fig. 3-11. A 5 V pulse induced the device to be in the ON-state. This ON-state could be read by a 1 V pulse with a current of about 10^{-1}A. A negative bias of -5 V erases this ON-state, to produce the OFF-state. The OFF-state could be detected by a 1 V pulse the OFF-state with a current of about 10^{-8}A. The electrical bistability of the device could be precisely controlled by applying as appropriate voltage pulse numerous times without any significant device degradation.

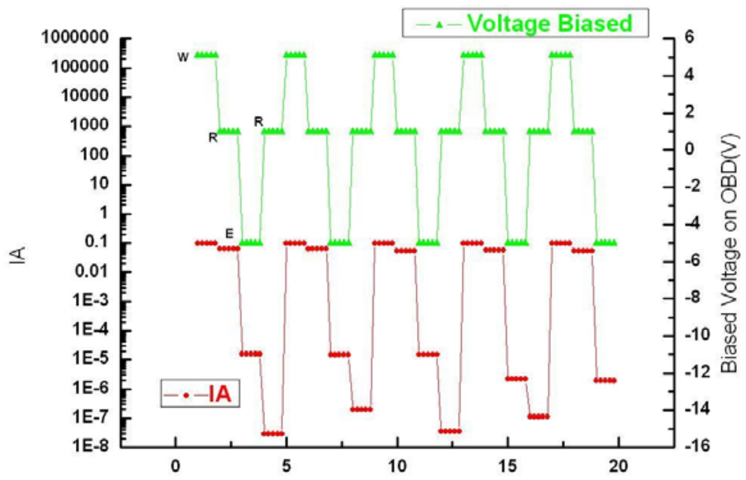


Fig. 3-11: Write-read-erase cycles of the device. In the bottom curve indicate the device in the high and low conductance states.

The threshold voltage is less and less with the re-writing times increase. Because the electrons doesn't discharged from trap site with applied an erase pulse completely. The on/off ratio is still about six orders to decrease the reading error rate. There are four write-read-erase cycles with the OBDs that treated oxygen-plasma. The relative parameters of the device for three cases are listed in Table 3-3.

Table 3-3: The relative parameters of the reported organic bistable device.

	After first pulse	After second pulse	After third pulse	After fourth pulse
Threshold voltage (V)	5.0	4.0	2.1	1.6
ON/OFF ratio	2.82×10^{6}	4.14×10^{5}	2.32×10^{6}	7.15×10^{5}

3.4. Conclusion

In this chapter, we replace the ITO-substrate with Au. And the inner metal layer that avoids the organic layer to react with oxygen immediately is treated with oxygen-plasma. The device exhibits two different conductive states at the same applied voltage and it is found to exhibit distinct bistability with an ON/OFF current ratio up to 10^{7}. Furthermore, this device shows over 2100s retention time. The state is changed from high-conductance to low-conductance state with an erase pulse. There are four write-read-erase cycles.

The electrical bistable characteristic of the OBDs is affected by an inner oxide film. In the same oxygen-plasma time, there is only device with a 20nm inner metal film displays electrical bistable effect. There is no electrical bistable effect when the inner metal film is too thick or thin. The inner metal film formed an oxide film that it is too thin to avoid oxygen to react with organic layer and destroy the device. The device formed thick oxide layer to block the bulk of the carrier to pass.

Chapter 4　Conclusions and Future Work

4.1. Conclusions

In my thesis, we introduced several kinds of memory about volatile or non-volatile in the first chapter.

In second chapter, we compare the two kinds of the organic bistable memory device. The better performance is obtained that the inner metal layer device. And, the roughness of ITO-substrate affects the inner metal film. The inner metal layer is not covered well, that the same as nano-particle at the organic layer. The switched state with high conductivity can be turned back to its original state with low conductivity by applying a negative voltage pulse.

Last, we replace the ITO-substrate with Au. And the inner metal layer that avoids the organic layer to react with oxygen immediately is treated with oxygen-plasma. There is only device with a 20nm inner metal film displays electrical bistable effect. There is no electrical bistable effect when the inner metal film is too thick or thin. The state is changed from high-conductance to low-conductance state with an erase pulse. There are four write-read-erase cycles.

4.2. Future Work

In the report, there are still some problems to improve about the electrical bistable characteristic. These problems are listed below:

1. The multi-state with OBDs.

   There are multi-metal-layers interposed between the organic layers in order to product the multi-state. As shown in below.

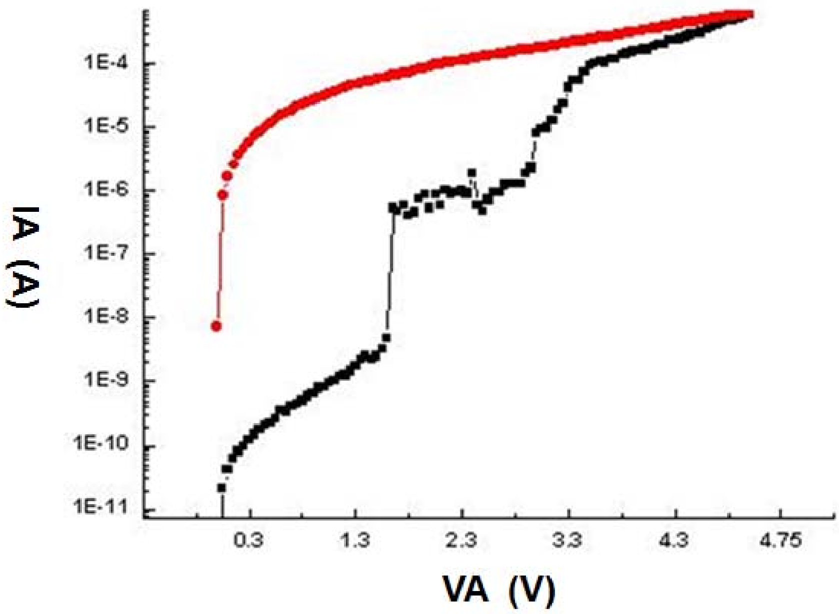


Fig. 4-1: The organic multi-state memory device.

2. The logical organic light emitting diode.

We will combine organic memory into OLED. This device display optic bistable effect. The characteristic is shown in below.

Table 4-2: The device display optic bistable effect.

	10.5(V)	11.5(V)	12.5(V)	13.5(V)	14.5(V)	15.5(V)
First	Off	Off	Off	Off	Off	2.07
Second	Light	0.03	0.14	0.31	0.49	0.49

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Vita

Ming-Hsi Wang was born at 24 April, 1984 in Taipei City, Taiwan. He received the B.S. degree from Department of Physics, National Central University, Taiwan in 2006. The M.S. degree will be received from Department of Photonics and Display Institute, National Chiao Tung University, Hsinchu, Taiwan in 2008. His research includes OLED and the analysis and fabrication of organic bistable memory device.