The coexistence of write once read many memory and resistive memory in a single device of conjugated polymer

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**NANYANG
TECHNOLOGICAL
UNIVERSITY**

**THE COEXISTENCE OF WRITE ONCE READ MANY
MEMORY AND RESISTIVE MEMORY IN A SINGLE DEVICE
OF CONJUGATED POLYMER**

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SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

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SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

A thesis submitted to the Nanyang Technological University
in partial fulfilment of the requirement for the degree of
Doctor of Philosophy

2016

Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research and has not been submitted for a higher degree to any other University or Institution.

19/8/2016

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Date

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Nguyen Viet Cuong

Abstract

The thesis demonstrates for the first time coexistence of write once read many memory (WORM) with resistive random access memory (RRAM). This is the first time such coexistence phenomena are reported in organic materials system. Furthermore, better understanding of working mechanism in resistive switching phenomena in organic materials particularly conjugated polymer has been achieved.

Two materials systems are chosen, namely, poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT PSS) and Polyvinyl alcohol (PVA) where PEDOT PSS is a conducting polymer and PVA is an insulator polymer.

For a device with 5 μm thick PEDOT PSS sandwiched between two Au electrodes, the coexistence of WORM memory and RRAM memory can be achieved (Chapter 4). The WORM result was attributed to dedoping of the conducting PEDOT⁺ PSS⁻ segments to insulating PEDOT⁰ segments. The RRAM was explained due to Proton H⁺ conductive properties of PSS acid domains inside the film after dedoping. This points to a general feature: *resistive switching behavior of a whole device is the result of additive/summative resistive switching characteristic of its components.*

Based on this, we reveal the coexistence of RRAM memory and WORM memory demonstrated in PEDOT PSS blend with PVA (Chapter 5). The WORM memory is again attributed to PEDOT PSS while RRAM memory is attributed to the charge trapping characteristic of PVA. The device performance is improved significantly as compared to the earlier PEDOT PSS system, with more than 1000 cycling stability and much more than 10⁴ s retention for RRAM mode. Additional I-V characteristic of this device is further studied in chapter 6 which reveals a new type of WORM memory. This type of WORM memory is driven by metallic migration of Au electrodes.

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- Fig 7.2** Electrochemical transistor as a selector for RRAM devices.

Abbreviations

WORM	Write Once Read Many- i.e. Memory state can be written but cannot be erased.
RRAM	Resistive Random Access Memory- i.e. Memory states can be written, erased and re written. It is also known as FLASH or Memristor in some works in organic memory literature
PEDOT PSS	Poly(3,4-ethylenedioxythiophene) polystyrene sulfonate- i.e. a conjugated poly thiophene polymer (PEDOT) doped by polystyrene sulfonate acid (PSS H).
PVA	Poly Vinyl Alcohol- i.e. an insulative polymer, hydrophilic electret.
MEH PPV	Poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene]- i.e. a conjugated polymer without doping.
PS	Poly styrene
PI	Poly Imide
PMMA	Poly Methyl Methacrylate
PCBM	Phenyl-C61-butyric acid methyl ester- i.e. a conjugated polymer without doping
P3HT	Poly(3-hexylthiophene-2,5-diyl)- i.e. a conjugated polymer without doping
PVPy	Poly vinyl pyrrolidone
PVP	Poly vinyl Phenol
OFET	Organic field effect transistor
OLED	Organic light emitting diode
RFID	Radio Frequency Identification device
DRAM	Dynamic Random access memory
SRAM	Static Random Access Memory
MOF	Metallo Organic Framework
I-V	Current- Voltage
DI water	Deionized water

ITO	Indium tin oxide- i.e. a conducting oxide
DNA	Deoxyribonucleic acid
I-V	Current versus voltage
AFM	Atomic force microscopy
cAFM	Conducting atomic force microscopy
Write process in RRAM	large electrical applied voltage (typically 4V to 10V) to change resistive state of device from high resistive state to low resistive state
Erase process in RRAM	a reverse process of Write process
Read process in RRAM	very small electrical applied (typically 0.3V to 1.5V) to sense resistive state
Write process in WORM	large electrical applied voltage to change resistive state (either at low resistive state or high resistive state) of the device to either high or low resistive state correspondingly
Read process in WORM	very small electrical applied (typically 0.3V to 1.5V) to sense resistive state
Erase process in WORM	written resistive state cannot be erased or changed

Chapter 1

Introduction

The thesis answers the question whether coexistence of write once read memory and resistive memory can be achieved in the same device; and studies the mechanism of such coexistence. This kind of coexistence can be helpful in realizing multi-purpose memory devices for future smart sticker with memory and archive units all in the single device. In this chapter, the rationale of the dissertation will be stated and discussed briefly to provide a panoramic view on the research topic, originalities, novelties and future implications. The thesis overview and hypothesis are also provided. The key philosophy in this thesis is that resistive switching behavior of a whole device is the result of additive/summative resistive switching characteristic of its components.

1.1 Status of organic electronics devices

Solid state electronics devices such as transistor and diode have been built by Silicon process through Ultra large Silicon Integration technology (ULSI). The technology process requires high quality Silicon wafer which can only be achieved at very high growth temperature (1000°C). Furthermore, device fabrication typically requires ultra clean environment i.e. clean room facilities. Therefore, the cost of Silicon based device can be very high. Although cost can be effectively reduced through volume production of Silicon devices, stringent process conditions (doping, implantation and diffusion) still pose some difficulties in cost reduction.

On another hand, Silicon based device is brittle rendering inflexibility. Therefore, some emerging applications such as flexible display devices or wearable devices can hardly be built by Silicon based devices. On versatility aspects, Silicon has indirect band gap which makes it unable to emit photons. Other inorganic materials such as GaAs or InGaAs can be used for light emitting materials but the raw material cost is high and the processing condition is very complicated. Therefore, it is solution process technology at room temperature is desirable to fabricate devices with inherent flexibility, versatility and simple process condition for possible wearable display, memory and smart labels with real needs in the market (fig 1.1).

Among all of the candidates, conjugated polymers stand out as promising materials for cheaper and versatile electronic device. Large wealth of polymer structure ranging from semiconductor to conductor and polar to non-polar, charge trapping backbone can offer significant interesting applications from display to logic and memory devices. Liquid based process at room temperature and ambient condition can tremendously reduce the cost of device production. Inherent flexibility of polymers may offer wearable application, flexible display. Furthermore, polymers structure can be tuned to facilitate versatile multifunctional properties within single device, such as electrochromism, electroluminescence, memory phenomena and ferroelectric - magnetism responses. With inherent soft properties, polymer based electronics can offer applications in

bioelectronics. Hence, in this dissertation, we will investigate memory electronic device using polymer with particularly interesting properties for novel applications.

Fig 1.1| Applications of organic electronics. (a) (b) print roll to roll process for fabrication of organic device on plastic substrate. (c) radio frequency identification system. (e) Write once read

many memory for brand protection to avoid duplication. (f) smart label with incorporating memory, transistor, light emitting diode. Picture obtained from poly IC : <http://www.polyic.com/>

Polymer based memory electronics can be characterized into 3 groups: capacitor type, transistor type and resistor type (Also Known As organic resistive switching device) as shown in Fig 1.2 bellow [1] . Capacitor type uses localised charge stored at the electrodes to indicate memory state “1” and “0” while transistor type and resistor type use charge flowing between electrodes to distinguish the states. Capacitor type memory has an inherent problem called destructive read-out; once the state is read, it is destroyed hence rewritten is required. In transistor type and resistor type, reading process is non destructive. Comparing transistor type (Fig 1.2b) and resistor type (Fig 1.2c), one can point out the simplicity in device architecture of resistor type. In transistor type, 4 terminals, namely gate, source, drain and float gate, are required while in resistor type, only 2 terminals are required, namely top electrode and bottom electrode. The simple device of resistor type may offer ease in 3D stacking and higher density in comparison with transistor type. Therefore, in this dissertation, organic resistive switching memory phenomena in organic device are studied.

Fig 1.2| (a) capacitance based memory (b) transistor type memory and (c) resistive type memory.

1.2 Objective/ Scope and problem statement

In organic resistive switching device, vast number of phenomena concepts have been demonstrated including write once read many memory phenomenon (WORM) for data security and data archive, rewritable/ erasable resistive switching memory phenomenon for data storage with ability to modify data (RRAM), dynamic resistive switching memory (DRAM) and optically readout resistive memory device (Figure 1.3) [1]. However, possibility to have 2 device concepts within 1 device is rarely reported i.e. WORM memory phenomena and RRAM phenomena within one device. Furthermore, complex mechanism is often proposed without much understanding and further insight. Therefore, in this dissertation, I aim to realize and understand a device concept that within single device one can manifest the WORM memory phenomena and RRAM phenomena using voltage tuning Moreover, the device mechanisms are also studied to elucidate better understanding.

Figure 1.3| (a) RRAM where states can be written, erased and rewritten (b) Write once read many memory: states can be written but cannot be erased. (c) DRAM where written states cannot be maintained. (d) Optically read-out resistive switching memory where OFF state can be

distinguished with ON state by light emission. Figures are obtained from reference [2, 3]. Reuse with permission [2, 3].

1.3 Importance of the coexistence of WORM memory and RRAM memory in single device

WORM memory is important for data security and data archive or storing important tasks in computer for booting because the memory state in WORM device cannot be erased after writing. Especially in the modern intensive internet connected world, data encryption has been considered significantly important. Hence, although various works have concentrated on producing RRAM where states can be erased and rewritten, significant works are also focused on realizing WORM memory using organic or inorganic materials. Some successful companies such as Crossbar Inc also patent their own technology to produce WORM memory device for data security alongside with their very successful RRAM device [4].

Here, instead of producing WORM memory and RRAM memory separately with different methods or architectures, it is reasonable to raise question whether one can achieve both WORM memory and RRAM memory within single device and use voltage to control. The successful device concept may offer some advantages such as higher density and simpler device architecture.

1.4 Hypothesis

In the dissertation, PEDOT PSS and PVA have been used to study resistive switching with device structure metal/polymers/metal and realize the coexistence of WORM memory with RRAM memory within one device.

PEDOT PSS has been a well-known conjugated polymer that exhibits WORM memory phenomenon due to electrochemical reduction. However, possibility to obtain rewritable resistive switching memory (RRAM) phenomenon and WORM memory phenomenon in the same device based on PEDOT PSS has not been demonstrated before. Therefore, the thesis provides fresh ideas on device concept of the coexistence as well as further insights

in physical mechanisms of the coexistence phenomena. The hypothesis of the dissertation is briefly discussed below.

Hypothesis 1)

It is hypothesized that PEDOT PSS device in configuration Au/ PEDOT PSS/ Au device can exhibit coexistence of WORM and RRAM in form of switchable diode. The WORM memory can be attributed to electrochemical reduction of conducting PEDOT⁺ to non conducting PEDOT⁰. Switchable diode memory phenomenon can be revealed after electrochemical reduction. After electrochemical reduction, ions such as protons will dominate the transport. The trapped holes are proposed to induce switchable diode.

Hypothesis 2)

In the blend of PEDOT PSS with PVA, it is hypothesized that charge trapping characteristic of PVA will induce RRAM memory at low sweeping voltage while at WORM memory will be manifested at high sweeping voltage because of electrochemical reaction of PEDOT PSS.

1.5 Dissertation overview

The thesis addresses the hypothesis that whether WORM memory and RRAM memory can coexist in a single device and what are the memory mechanisms. The role of materials constituents in the memory device are highlighted in the dissertation. The research overview is summarized as follow

Chapter 1: Introduction and motivation of the research. The research problems are raised in this chapter.

Chapter 2: Literature review about RRAM memory device, WORM memory device in organics materials. The literature review will support the objective and originality of the works described in chapter 1.

Chapter 3: This chapter summarizes techniques used for the research to get fundamental insights into the complex problems of resistive switching memory device.

Chapter 4: Coexistence of WORM memory and RRAM memory in the form of switchable diode in Au/ PEDOT PSS/ Au device. In this chapter, the coexistence of WORM memory and switchable diode in Au/ PEDOT PSS/ Au device is reported and its working mechanism is studied. Phenomenological rationale will be discussed in details in conjunction with literature reports surveyed in Chapter 2.

Chapter 5: Coexistence of WORM memory and RRAM memory in Au/ PEDOT PSS blend PVA/ ITO. The device working mechanism is proposed and studied in this chapter. Phenomenological rationale will be discussed in details in conjunction with literature reports surveyed in Chapter 2.

Chapter 6: Additional WORM behavior in the blend of PEDOT PSS and PVA governed by metallic filament mechanism

Chapter 7: Summary and future outlook. In this chapter, the results are summarized and compared. Future outlook will be provided on the proposed problems.

1.6 Finding outcomes and originality

In this dissertation, the coexistence of WORM memory and RRAM memory has been revealed for the first time in material system containing PEDOT PSS. The working mechanisms of the coexistence have been studied and some main scientific understanding can be summarized as follow

- Identify the main reason for the manifestation of switchable diode in Au/ PEDOT PSS/ Au stems from adsorbed water and protons transport. Electrochemical reactions that dedope PEDOT⁺ to PEDOT⁰ are the primary mechanism for WORM memory.

- Charge trapping characteristic of PVA at low voltage leads to the RRAM memory in the blend of PEDOT PSS and PVA device (Au/ PEDOT PSS blend PVA/ ITO). Electrochemical reaction that dedope PEDOT⁺ to PEDOT⁰ comes into play for the WORM memory at higher potential.
- Metallic filamentary migration switching mechanism can take place when applying 5V for more than 1 minute in the PEDOT PSS blend PVA device. The switching is found to be permanent and irreversible, indicating a large activation barrier.

1.7 Conclusion

In short, the thesis deals with the coexistence of both WORM memory with RRAM memory in a single device. This coexistence has not been revealed before in literature and its working mechanisms required investigations as detailed in this work. Hence, the thesis will provide better understanding of organic resistive switching memory devices particularly in polymeric system contained PEDOT PSS and PVA.

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Chapter 2

Literature review

In this chapter, previous works on the topic will be surveyed in details and remarks on research gaps will be provided to uphold the rationale and novelties/ originalities claimed in Chapter 1. In details, resistive switching memory device is classified and reviewed in term of current-voltage. Switching mechanisms and switching materials are discussed. To support the novelties claimed in chapter 1, various types of novel device concepts in literature are also reviewed. The chapter indicates that one research gap is in the device concept in which coexistence between WORM and RRAM is rarely reported. Furthermore, the working mechanism of resistive switching memory devices still needs further insights.

2.1 Term and classification

Memory device operation process includes write, read and erase (see term and definition section). In organic resistive switching memory, write, read and erase processes are done by voltage where high voltages either in same polarity or opposite polarity are used to write/ erase the bits; reading process uses smaller voltage to “sense” the bits. In some cases, the bit after being written cannot be erased. In this dissertation, Resistive Random Access Memory (RRAM) is used to term memory with possibility to erase and rewrite memory while Write Once Read Many memory (WORM) is for device where bit (state) cannot be erased. Both of these memory types have been intensively researched over the past 15 years in resistive switching memory device [1]. Fig 2.1 illustrates the classification used in the dissertation. Both of these types of devices consist simply of top electrode and bottom electrode sandwich a spacer which can be insulator or semiconductor. The literature survey will cover research developments in WORM memory and RRAM memory respectively. Moreover, some research efforts on trying to realize the coexistence of different type of memory in single device will be also addressed.

Fig 2.1| Terminology of memory device used in this dissertation.

2.2 RRAM

2.2.1 General feature

RRAM **phenomenon** can also be distinguished phenomenologically through current-voltage characteristics such as unipolar memory or bipolar memory [2]. Figure 2.2 shows examples of such differentiation. In bipolar memory, the write and erase voltage are opposite in polarity i.e. if write polarity is positive 4V, the erase polarity is negative -4V. In unipolar memory, the write and erase voltage are same in polarity i.e. write polarity is positive 8V, erase polarity is also positive 4V .

Fig 2.2| ai) unipolar switching RRAM with type 1 aii) unipolar switching RRAM with type 2 b) bipolar switching RRAM.

2.2.2 Organic RRAM

2.2.2.1 Materials

Organic RRAM has been actively researched in both bulk film with thickness of 50 nm to 10 μm and ultrathin film with thickness of 1 nm to 10 nm. Initiated by many encouraging results of Yang Yang[3] et al and Scott [4] et al using nanoparticles embedded between Tris(8-hydroxyquinolino)aluminium Alq3 organic semiconductor. Since then, various materials and composites have been shown to have switching effect. Organic materials and nanoparticles (such as Ag, Au, CdSe etc) blends have shown RRAM properties demonstrated by a lot of research groups such as Ouyang [5] et al and Kim [6] et al. Some self-assembly monolayers (SAM) and bio materials based devices were also demonstrated to exhibit switching properties.

In Figure 2.3, general spacer design strategies are commonly adopted by research groups to induce RRAM properties namely employing single layer of polymer (such as Polystyrene (PS), Polyimide (PI)) (Fig 2.3c) [7], sandwiched nanoparticles between polymers layers (Fig 2.3a), randomly blend nanoparticles in polymer matrix (Fig 2.3b), heterojunction of polymer films and blending of two polymers. In Figure 2.4, typical current voltage characteristics of these designs (fig 2.4) are shown. It has also been witnessed that the same I-V shapes can be obtained even in the very different material and device set up; this fact suggests complex physical phenomena involving in the RRAM device. Furthermore, vast number of materials have shown switching RRAM properties including, inorganic oxide [2], cellulose [8], silk protein [9], Alovera [10], Egg white [11], polymers [1], plant, protein[12], DNA [13], metal organic framework (MOF) [14] etc. This vast number suggests very diverse phenomena and therefore an opportunity to study this rich switching phenomenon.

Fig 2.3| RRAM design using polymer spacer with nanoparticles embedded (a) or blended (b) and no particle (c)[7]. Reuse with permission from [7].

Fig 2.4| Typical I-V characteristic in device design of Fig 2.3 [7] reuse with permission from [7]

2.2.2.2 Working mechanisms

2.2.2.2.1 Filamentary

Filamentary mechanism seems to be the cause of ubiquitous switching phenomena in organic materials. In this mechanism, electrode materials will penetrate organic layer under electric field and form metallic bridge connecting top electrode and bottom electrode. Under larger bias or reversed bias, these metallic bridges will be broken and therefore renders the device back to the non-conducting state (OFF state). There are a number of electrode materials that are notorious for being fast electromigration such as Cu or Ag [15-17]. Fig 2.5 illustrates the electromigration of Cu or Ag based device. Under positive bias, the electrode materials will be ionized and migrate into the film where they will lose their charge and form neutral nanoparticles. Under larger voltage, the number of neutral particles will increase and connect top electrode to bottom electrode. The device will then be switched to ON state with high conductance and

metallic behavior such as Ohmic line shape. Under reverse bias, the weak point in the bridge will be ionized and breaks the bridge driving the device back to OFF state; this yields bipolar memory device. On the other hand, simply raising the voltage, the large current following the nanoscale bridge will also cause significant Joule heating and melts the bridge; this yields unipolar memory. The filamentary based mechanism can be used to explain all the switching described in literature; however, it is not very well regarded because the role of spacer is minor in this case and role of electrodes in the process is highlighted. Significant works have shown that RRAM memory in biomaterials involves filamentary using Ag electrodes; hence role of biomaterial is simply scaffold for filaments [18].

Fig 2.5| Filamentary based RRAM under electromigration of Cu [15].

2.2.2.2.2 Electrodes surface oxidation

Various types of electrodes can be oxidized during fabricating of organic layer or even simply being exposed to ambient air. The native oxide in those electrodes will also exhibit switching effect independent of the organic layer. Notoriously, Al [19] and Ti [20] are the two electrode materials that exhibit oxide driven organic RRAM memory in reported literatures. The organic layer in this device is simply current limiting layer. Figure 2.6 illustrates the situation. We can imagine the device as oxide layer in conjunction with organic layer and the switching is originated from the oxide layer. In

oxide system, switching has long been studied even dating back to Hickmott et al 1960s where Al_2O_3 has been investigated for switching[21]. Switching in various oxide materials have then been revealed; for example, TiO_2 , NiO , HfO_2 , Ta_2O_5 etc[22]. The memory switching in these oxides is often due to native defect such as oxygen vacancy. Oxygen vacancy is metallic in nature and therefore the working mechanism will be similar with electromigration (Fig 2.7 illustrates the typical situation for TiO_2). The role of oxide in organic RRAM has been investigated thoroughly by Dago de Leeuw et al, Mesker et al and Verbakel et al.

Fig 2.6 | organic RRAM device based on electrode oxide (a), typical I-V characteristic of device (b). [19] reuse with permission [19].

Fig 2.7 Oxygen vacancy migration of TiO_2 oxide [23]. Oxygen deficient conducting filament (blue balls) is formed under positive bias on top electrode.

2.2.2.2.3 Charge trapping effect

Embedding nanoparticles inside organic polymer has shown switching effect with unipolar type. The nanoparticles have trapping effect which will influence injection barrier between electrode and organic layer. When the nanoparticles are neutral, large injection barrier presents hence charge injection will be inhibited. When the nanoparticles are filled with charges, the injection barrier will be significantly distorted such that charge can easily tunnel through therefore the device state is switched to ON state with high current flowing. The concept was first proposed by Simmons and Verberder (SV)[24] and was also known as nanotraps memory. Figure 2.8 illustrates the model.

Following the embedding of nanoparticles, various other types of blending strategies were adopted such as blending of Phenyl-C61-butyric acid methyl ester (PCBM) and Poly Methyl Methacrylate (PMMA)[25], PCBM and PI [26], Poly(3-hexylthiophene-2,5-

diyl) (P3HT) and PMMA. In these blends system, PMMA or PI is insulator matrix to host PCBM or P3HT which is an organic semiconductor. The phase separation between the host and dopant will induce disorder system with dopant distribution within host. Figure 2.9 and Figure 2.10 shows I-V characteristic and concept of nanotrap polymer blends. Recent works also concentrate on using graphene as charge trapping layer. Significant works have been reported by Lee et al [26] and Kim et al [25].

Fig 2.8 (a) band-bending before switching (b) band bending after switching. After switching, band bending is more severe hence facilitates larger charge transport through tunneling [24]. Adapted from [24].

Fig 2.9 Concept of polymer blend nano traps. The red ball represents trap filled while gray ball is trap unfilled. (a) ON state where number of traps filled are much higher than unfilled trap. (b) OFF state. Reprinted with permission from [26]. Copyright (2015) American Chemical Society.

Fig 2.10 I-V characteristic and band-diagram model of polymer blend nano traps concept [26]. When traps are filled, charge transport (at 0.5V) is trap free but at 10V (after detrapping process), charge transport (at 0.5V) is suppressed. Reprinted with permission from [26]. Copyright (2015) American Chemical Society.

2.2.2.2.4 Charge transfer

By designing the polymer backbone to have donor (D) and acceptor (A) moieties, one can realize a charge transfer effect which is believed to be the working mechanisms of this system. When the charge is transferred from donor to acceptor, the device will be switched from OFF state to ON state. Simple blending of two systems of donor and acceptor also induces RRAM properties. Figure 2.11 illustrates this effect. Many works have demonstrated that by tuning of D-A interaction, various type of memory can be obtained [1].

Fig 2.11| Donor acceptor charge transfer design concept for RRAM device [1]. Reuse with permission from [1]

2.2.2.2.5 Molecular switch

Under electric field, some molecule change its structure which is accompanied by changing in electronic state between electrodes and molecule and this results in switching from On state to OFF state. For example, photochromic diarylethene molecule can switch its aryle ring with a triphenylamine group structure from ring closed structure to ring open structure by electric field. The structure switching results in electrical conducting modulation from high conducting to low conducting states.

2.2.2.2.6 Ion movement induces RRAM switching

Ions are charge species and in some polymer, ionic conduction can be large enough to facilitate ion movement. Using blends of P3HT, PEO and Li salt, Dago de Leeuw et al

have demonstrated switching due to Li ions movement which modifies injection barrier between P3HT and Al electrode [27].

Adsorbed water is another source of ions especially protons which are mobile. It shows that under 70% humidity condition, memory effect can be observed in hydrated DNA [13] due to protons movement. In this scenario, charge trapping due to electrolysis of water in DNA will force the protons to migrate to cathode; the trapping causes NDR in this system. Similarly, in hydrated ZnO nano particles, same scenario was obtained and reported [28]. Using ions movement causes the system to operate at very slow speed and ion relaxation will cause memory state relaxation. Although, there are limits, many works have reported RRAM phenomena in ionic systems including MOF [14], DNA[13], ionic liquid and ion gel . Many of these cases, memory effect will disappear when the device is tested in vacuum.

2.2.2.2.7 Ferroelectric induced RRAM

Using ferroelectric materials that have permanent polar charge, various works have shown RRAM memory relating to ferroelectric. Asadi et al have demonstrated memory device using blends of ferroelectric PVDF-TrFE with organic semiconductor such as P3HT or PFO. The working mechanism of the blend device is based on ferroelectric charge of PVDT-TrFE which reduces injection barrier between electrodes and organic layer. Advancing the concept further, Asadi et al have used light emitting materials such as PFO in the blends to produce optically read-out in organic RRAM [29].

By reducing thickness of ferroelectric layer to tunneling regime of 2 nm to 10 nm, RRAM memory based on tunneling effect can be obtained (also known as ferroelectric tunnel junction). Fig 2.12 illustrates the concept.

Fig. 2.12 Ferroelectric polarization modulates injection barrier RRAM [29]. Reuse with permission from [29].

2.3 Write Once Read Many (WORM)

2.3.1 General feature

WORM memory has been commercially used for RFID. Thanks to the capability to prevent data modification, applications in data encryption have been proposed. In WORM memory, there are two types: type I and type II WORM memory. In type I memory, device original state is in low resistance state, after writing the state is switched to high resistance state and cannot be modified (also known as fuse memory). In type II, device original state is in high resistance state, after switching the state is switched to low resistance state (also known as anti-fuse memory). Fig 2.13 illustrates these two types of WORM memory.

Fig 2.13 (a) Type I WORM memory (b) Type II WORM memory.

Various materials have been used to demonstrate WORM memory. Some of them are due to intrinsic properties of the materials while others are due to filamentary effect discussed in section above. WORM memory has been reported in organic molecules [30], inorganic oxide [31], carbon nanoparticles blend with polymer host [32, 33], graphene oxide [34] etc. In some systems, by small adjustment in organic molecule design, one can tune the device from WORM to RRAM and vice versa [35]. This suggests versatility of organic materials over inorganic system.

2.3.2 Material system

Moller et al have demonstrated the first WORM device using poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT PSS) [36]. Mechanisms of the memory were studied and attributed to the characteristic of PEDOT PSS. Subsequently, various WORM devices have been demonstrated in many D-A system. Blending of carbon nanoparticles in polymer matrix also demonstrates WORM memory. Furthermore, decorated DNA with Ag nanoparticles also shows WORM switching under UV illumination [37].

2.3.3 Working mechanism

2.3.3.1 Metallic Filamentary

Metal migration in many cases can form very thick filaments which cannot be erased. Using high compliance current, the metallic filaments are often inerasable. WORM memory mechanism in many works such as silk protein based device with Ag electrodes [9] or Pentacene based device with Fe electrodes [38] can be explained using metallic filamentary. In some cases, Aluminum filaments have been identified as major mechanism for WORM memory in PVK [39].

In other systems such as nanoparticles embedding in polymer host or DNA decorated with nanoparticle [37], WORM memory is due to percolation pathway formed by

particles dopant which is stable enough such that erasing process under voltage bias cannot break the filament. Hence, the device is switched to On state and maintained for many hours up to many years. Figure 2.14 illustrates the concept.

Fig 2.14 Silver filament induces WORM memory in Silk protein [9]. Reuse with permission from [9].

2.3.3.2 D-A charge transfer

Many designed organic molecules can offer freedom in tuning D-A interaction. When D-A interaction is designed such that charge transfer from D to A is unable to be retrieved back, the WORM memory will be revealed in these systems.

2.3.3.3 Electrochemical de doping effect and electrode delamination

Many conjugated polymers rely on counter ions such as acid PSSH to enhance its conductivity. Under electron injection and electrochemical reaction with adsorbed water, conjugated polymer $\text{PEDOT}^+ \text{PSS}^-$ gets dedoped into insulative PEDOT^0 . Subsequently, the counter ions (PSS^-) will be segregated at cathode and hinder charge transport (because of their insulative properties). As counter ions have large size and together with gas evolution due to electrochemical reaction with water, the cathode will be delaminated causing the loss of cathode; altogether results in significant reduction in current transport. This process exhibits I-V peak which is sensitive to voltage sweep rate (Fig 2.15b). The WORM memory will be in type I. Popular example of such scenario was PEDOT PSS where counter ions such as PSS H acid was employed. Figure 2.15 illustrates this mechanism [40] [41].

Fig 2.15 (a) Typical I-V of WORM in PEDOT PSS device (b) voltage sweep rate dependence of I-V. (c) Electrode delamination due to electrochemical reaction inducing WORM memory in PEDOT PSS[40] . Reuse with permission from [40].

2.4 Innovative device concepts based on resistive switching

Base on the general concept of resistive switching, various unconventional memory device concepts has been witnessed over the course of 10 years research literature of resistive switching phenomena. Various memory mechanisms can be incorporated into single memory device to realize multifunctional devices, multi-characteristics devices, multi-purpose devices or on-demand memory devices with reconfigurable properties or memory effect modulated by different stimuli such as electric field, light, magnetic field or mechanical force. This section of literature review will be dedicated to summarize research efforts in this direction.

2.4.1 Multipurpose memory device using magnetic spin valve

Magnetic field driven resistive change in ferromagnetic electrodes junction has been long investigated since the discovery of giant magnetoresistance. Using two ferromagnetic

electrodes such as Co, Ni or NiFe sandwiching an insulative spacer will induce electronic transport modulation dependence on direction of magnetization of electrodes which is also known as spin valve effect (fig.2.16). The spin valve effect has then been proposed for future MRAM or STT RAM. Recent surprising data have shown that utilising organic semiconductor spacer, one can obtain spin valve effect with even very thick organic layer up to 200 nm hence it is duped as organic spin valve. In [42], authors have utilized organic layer in conjunction with oxide Al_2O_3 sandwiched between two ferroelectric electrode such as Co and LSMO. It has been demonstrated that RRAM effect and spin valve effect can coexist in single device hence open up a new research field on marriage of RRAM and spintronics. It is then pointed out that one can even obtain multi logic state using electric field gating or magnetic field gating. Figure 2.17 summarizes research effort of this concept [42] .

Fig 2.16| Magneto resistance Random Access Memory

Fig 2.17| Coexistence of spinvalve effect and RRAM in single device. (a) device configuration (b) RRAM effect (c) MRAM effect [42]. Reuse with permission from [42].

2.4.2 Light control RRAM device

Inspired by the universal characteristic of RRAM, some authors have also utilized photons sensitive materials such as Silicon for RRAM device with light modulation of resistance states (ON state, OFF state and intermediate state). Therefore, advancing from magnetic field, one can tune resistance states with more compact stimuli such as light emission diode for advance computing concepts or multifunctional device for multipurpose applications. Since then, various light sensitive materials have been utilised for researching in this direction such as BFO, La- BFO and CeO₂. Figure 2.18 illustrates the concept [43].

Fig 2.18 | Light modulates RRAM device [43]. Reuse with permission from [43].

2.4.3 Combining OLED and RRAM

Many organic molecules or polymers can emit photons; hence it is reasonable to raise questions of whether one can obtain both OLED and memory within single device and whether one can use photons to read memory states. Yook et al have studied this multifunctional device concept by stacking OLED materials Alq₃ with inorganic layer LiF to realize multifunctional RRAM with light emission capability [44]. Ma et al have utilized light emission to read memory states by stacking vertically OLED structure and RRAM structure [45]. Many researchers have followed this innovative concept by employing different novel emissive materials such as GaN, ZnO, Silicon nanocrystals. Figure 2.19 illustrates the memoLED concept.

Fig 2.19| Organic light emitting diode RRAM multifunctional device [44] [46]. Reuse with permission from [44].

2.4.4 Mechanical force control/ tune resistance switching

Combining vertically RRAM structure with touch sensing materials, one can realize RRAM device for storing mechanical force and using mechanical force to tune memory states. Figure 2.20 illustrates the basic concept [47].

Fig 2.20| Mechanical force control RRAM device [47]. Reuse with permission from [47]

2.4.5 Transferable and stretchable RRAM

Building RRAM or WORM device on transferable conducting substrate such as graphene, one can realize transferable RRAM device on many unconventional targets such as bracelet, skin, watches or PDMS. Especially, by transferring the RRAM device on PDMS, a stretchable memory device can be realized. The works are unique as graphene electrodes can be transferred, conducting, stretched and sticking while other electrodes may not possess all of the above novel characteristics [48].

2.4.6 Reconfigurable device concept of WORM and RRAM

Wang et al have demonstrated reconfigurable device concept of WORM and RRAM in single device using silk based materials. The working principle is based on Ag migration. By controlling compliance current, thickness and number of Ag filaments can be controlled hence one can obtain both WORM and RRAM phenomena in a single device [9].

2.4.7 Reconfigurable device concept between switchable diode and RRAM

By tuning the distribution of oxygen vacancy in WO_x or TiO_x , the author can obtain both switchable diode phenomenon with short retention time and RRAM phenomenon with very long retention time. This device concept may enable synapsis activity such as long term and short term memory and storage memory tuning using voltage. Hence it demonstrates an on-demand RRAM concept (fig. 2.21).

Since then, many other oxides or heterojunction oxides have been utilized for realizing this multi-characteristics device concept. It has been witnessed significant number of research works on this direction [49].

Fig 2.21| Reconfigurable RRAM in various forms such as insulator, resistor and switchable diode. Each form can be reconfigured by voltage control [49]. Reuse with permission from [49].

2.4.8 RRAM integrated with photonics circuits

Photons have been praised as fastest particle where information can be transmitted at approximately light speed. This characteristic has been the major driver for realization of photonics circuitry and photonics computer. Hence, it is interesting to combine RRAM memory with photons read out.

Many recent works have demonstrated capability to integrate Silicon based photonics circuit with built-in RRAM for optically read out memory device. Figure 2.22 shows such concept. In brief, one side of Silicon waveguide is connected with Ag electrode and the other side is connected with Pt electrode. At OFF state, photons cannot transport in the waveguide due to localized surface plasmon. When the device is switched to ON state, Ag atoms migrate into Silicon waveguide and short-circuit the junction. The appearance of Ag atoms inside the waveguide will shift the plasmon resonance peak and hence photons transport can take place after switching to ON state.

Figure 2.23 shows another research report that fabricated Silicon ridge waveguide cladded by Ag top electrode and Si bottom electrode. By applying voltage on Ag electrode, short circuit will take place due to Ag migration and photons cannot transport. By breaking the Ag filaments, photons can then be transported in the circuit [50].

Fig 2.22| Silicon waveguide integrated with RRAM device with lateral RRAM design [50].

Fig 2.23| Silicon waveguide photonics circuit integrated with RRAM device in vertical design[51]. Reprinted (adapted) with permission from [51] Copyright (2013) American Chemical Society.

2.5 Remarks and opportunities for PhD research in context of literature

Although, RRAM and WORM in organic materials have been studied intensively in 10 years, a lot of questions can be still posed. Among them, questions on the possibility to make *highly reproducible* memory phenomena in organic materials and *mechanism* of such memory are often raised [1]. Significant amount of memory phenomena in organic materials often include working mechanism discussion and theoretical investigation by density functional theory, while providing indirect proof or direct proof is often not performed. Recently, Nau et al have raised questions in charge trapping mechanism system and attributed the mechanism to filamentary instead of electronics process such as charge trapping [52]. Therefore, it is an opportunity to study mechanism in organic materials switching device in both form of WORM memory or RRAM memory.

Moreover, ensuring highly reproducible switching devices over different batches is prerequisite for the better understanding of the mechanism.

Furthermore, in the device concepts, one research gap that has not been paid much attention is the coexistence of WORM memory and RRAM memory in single device where only single publication has been reported by Wang et al during the preparation of this dissertation. Hence, in the dissertation, we emphasize on gaining better understanding of the coexistence of WORM memory with RRAM memory phenomena in organic resistive switching device composed of conventional materials namely **PEDOT PSS, PVA blend PEDOT PSS**. In the following section, we survey the literature characteristic of PEDOT PSS, PVA to provide basic knowledge on the materials aspect of the dissertation.

2.6 Materials used for the dissertation

2.6.1 PEDOT PSS

Polymer forms from EDOT monomer in PSS H acid, the acid PSS H provides oxidation for the conjugation backbone. The oxidation removes the electrons and produces mobile charge known as polaron in conducting polymers. Numbers of ways to induce oxidation have been introduced in the past such as halogens (Br_2 and I_2) and arsenic pentafluoride (AsF_5) were used to induce oxidative doping in poly(acetylene). Numbers of acids were also a popular choice for oxidation process such as H_2SO_4 or HClO_4 [53]. In PEDOT PSS, the conjugation backbone is poly(thiophene) structure as shown in Fig .2.24. The polymer can be dispersed in water thanks to the acid PSS H which not only provides oxidation but also induces water dispersibility. In this scenario, PSS H induces oxidative doping for conjugated PEDOT to make it holes conducting material PEDOT^+ . Hence, it is possible to reduce the PEDOT^+ back to non-conducting PEDOT^0 by supplying electrons [36].

Fig 2.24 | Chemical structure of PEDOT PSS [54].

One particular interesting characteristic of PEDOT PSS is the possibility to conduct not only holes but ions as well [54, 55]. Often after being reduced, ionic conducting characteristic of PEDOT PSS will emerge due to PSS H formation which is a good ionic conducting materials. Hence, PEDOT PSS is also coined polyelectrolyte conducting polymer[56] . PSS H dopant is also hygroscopic; therefore it will uptake water from the environment until equilibrium is maintained. Protons transport in PSS H is likely the main ionic transport species as H^+ is smaller size compared with anionic counter species. Furthermore, protons can transport easily over water molecules via Hydrogen bonding network through Grotthus mechanism as shown in Fig 2.25 below [57].

Fig 2.25 | Grotthus mechanism of protons hopping transport through hydrogen bonding network of water. –

Harvesting multiple transport properties of PEDOT PSS, an electrochemical transistor device can be realized. When positive bias is applied on electrolyte, the cations will migrate into PEDOT PSS channel and the following electrochemical reaction will take place

PEDOT⁺ denotes the oxidized state and is compensated by the PSS⁻ counter ions. The PEDOT PSS film will now be ionic transport layer rather than hole transport layer. After this electrochemical reduction, channel conduction will drop accordingly with gate voltage.

It has been clearly proposed by many works that electrochemical reaction can take place in PEDOT PSS where conducting form PEDOT⁺ can be reduced back to insulative neutral form PEDOT⁰. Fig 2.26 shows such an electrochemical transistor based on PEDOT PSS as channel [54].

Fig 2.26 Electrochemical transistor based on PEDOT PSS channel(a-c). The gate is including electrolyte. (d) Typical transfer curve of the device at gate voltage changing from 0V to -0.5V [54].

2.6.2 Poly Vinyl Alcohol (PVA)

PVA is a hydrophilic charge trapping dielectric materials (electret) [58]. The chemical structure of PVA is shown in Fig 2.27 bellow. It has long been utilized in organic field effect transistor (OFET) with memory effect [59]. Charge trapping capability of PVA has been attributed many times as the main mechanism of memory effect in (OFET). Origin of the charge trapping is from oxygen group of PVA where negative charges reside. Tsai et al have provided evidence that holes in OFET can be trapped when oxygen groups are oriented toward hole transport layer (Fig 2.27c) [60].

Fig 2.27 a) PVA structure b) OFET structure using PVA as charge trapping layer c) Charge trapping mechanism of PVA due to orientation of O-H dipole. Reuse with permission from [60].

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Chapter 3

Experimental Methodologies

In this chapter, experimental techniques to investigate organic resistive switching mechanism are reviewed. The experiment methodologies include measuring I-V of the device at various controlled environments and various control experiment which will help to single out governing mechanism. Other supportive experimental methods such as Raman spectroscopy, Scanning probe microscopy are useful to understand doping state of the conducting polymer and surface morphology/ phase distribution of the polymer blend respectively. All of these techniques are useful for polymer memory device where approach from other techniques such as electrons microscopy can be invasive due to irradiation or unhelpful due to low contrast of polymer.

Throughout the dissertation, a number of experimental techniques are employed such as electrical transport measurement, Raman spectroscopy, Fourier transforms infrared spectroscopy (FTIR), scanning probe microscopy (Atomic force microscopy, conducting atomic force microscopy). The prerequisite before conducting the mechanism studies is to ensure the phenomena can be reproduced for many batches. As switching mechanism in organic materials is very complicated and in many cases reproducibility has been in question; hence replicability of result in many batches of experiments is of utmost importance before getting better insight of switching mechanism by conducting experimental methodologies. In this chapter, the methods and process flow for the investigation will be provided.

3.1 Transport measurement

Electronics transport measurements are done using semiconductor analyzer in resistor mode. This measurement will demonstrate whether or not a device can exhibit bistable memory state through current-voltage (I-V) sweep. After knowing the device is bistable memory, cycling of memory states and retention test of states are carried out. To investigate switching mechanism, one can conduct transport measurement over different condition such as in ambient or vacuum or under controlled humidity or high/ low temperature. Many hysteresis I-Vs in organic materials may be induced by water or humidity therefore performing electrical transport under different environments or control experiments will be advantageous to single out governing mechanism that drives switching effect. Device testing scheme will be shown in Fig 3.1.

Fig 3.1| Electrical transport measurement scheme.

3.2 Raman spectroscopy

Raman spectroscopy is a technique based on the inelastic scattering from a monochromatic light source such as laser diode. The photons of the light source are absorbed by the molecules in the sample and subsequently reemitted after interaction with the sample. The change in wavenumber of the reemitted photons after interaction with the sample in comparison with the original light source is termed as the Raman effect. The reemitted photons will tell us about molecule structure change or electronics structure change.

The Raman spectroscopy can be useful for study of conducting polymer to investigate charge state of conducting polymer and has been major tool to study PEDOT PSS particularly. In PEDOT PSS, PSS⁻ induced electrostatic doping of PEDOT⁺, hence when PEDOT PSS is de doped to PEDOT⁰, Raman scattering will change in comparison with doped PEDOT⁺PSS⁻ which will provide evidence of de doping effect on switching after device is applied voltage. Therefore de doping from PEDOT⁺ PSS⁻ (conducting state) to PEDOT⁰ (non-conducting state) can be probed by Raman spectroscopy [1].

3.3 Fourier transforms infrared spectroscopy

In IR spectroscopy, infrared radiation is passed through the sample. This radiation can either be absorbed by or passed through the sample. These spectra represent the molecular fingerprints of the sample relating to molecular vibration of particular group in the molecule. This procedure is termed as Fourier transform infrared spectroscopy when a mathematical technique called Fourier transformation is used to interpret the spectral information for analysis.

3.4 Scanning probe microscopy

a) Atomic Force Microscopy (AFM)

It uses sharp Silicon cantilever to sense the surface of the sample to provide morphology in nanometer range (Fig 3.2). The vertical resolution of the AFM can be up to 1nm and lateral resolution in in few tens of nanometer. The AFM working principle is based on force interaction between sample and cantilever's tip. The tip will sense the surface under constant force condition hence it will adjust its perpendicular and lateral position with surface morphology. The position change will be tracked by photo-detector with real time feedback loop [2].

There are two working modes such as contact mode and tapping mode. In contact mode, the tip will directly in contact with surface of the sample with very small distance in range of Angstrom. Hence, it is best mode to obtain direct information about sample such as electrical properties, magnetic properties. However, tip can be easily wear out and broken if sample morphology is rough. Furthermore, soft type of tip (0.6-1 N/m) should be used for contact mode to minimize sample damage due to tip interaction; but soft tip is prone to fast wear-out. Hence, it is a clear trade off.

In tapping mode, tip will vibrate on the sample surface under resonance frequency and hence limits the interaction between tip and sample. In tapping mode, tip damage is lesser as compared with contact mode. However, one cannot obtain more information such as electrical properties of sample by using tapping mode. Tapping mode tip is normally hard tip with spring constant of 42 N/m to avoid being stuck to the sample surface.

In this thesis, AFM is an important tool because it can provide information on surface morphology of polymer thin film and surface roughness which is important feedback to fabricate top electrode. In order to explain, if the film roughness is larger than 20 nm, the thickness of top electrode should be larger than 100nm so that it can fully cover the film across peak to valley roughness.

b) Conducting AFM

To obtain information about electrical properties of the sample, one needs to use contact mode AFM with electrical connection. In the set up, the AFM tip is coated with metal such as Pt or Au to induce electrical connect. The electric field will be applied between tip and sample 's bottom electrode and tip will serve as top electrode in the set up. Upon scanning the sample surface, one can identify sample morphology, conducting domains and non conducting domains using this technique. Furthermore, one can also obtain I-V characteristic of the conducting domain by sweeping the bias at particular point of interest.

Although the technique is straightforward, great care should be taken in problems of tip wear-out and tip damage. When the tip coating is lost, the connection is lost hence some wrong information can be obtained. Especially in many cases, local I-V measurement shows hysteresis because of tip wear-out artifact. Tip coating such as Au can be prone to fast wear-out therefore, coating such as Ir-Pt or diamond coating will be used in the dissertation to provide reproducible cAFM scanning of organic surface.

In this thesis, combination of AFM and cAFM will provide information about 2D phase separation of polymer blend of conducting and insulator polymer. When a phase is rich with conducting polymer, the cAFM current will be high while scanning the film surface. For phase that is rich with insulator polymer, opposite situation is obtained. Hence, this information facilitates switching mechanism understanding and insight in complex geometry of polymer blend.

3.5 Experimental flow

The experiment procedure includes mixing 2 polymers from commercially available source. The solution of polymer will be spin casted on clean substrate to form solid film with different thickness. The top electrodes are made by evaporated Au on top of the film. The device electronics transport will be measured in this two terminal configurations and under various condition ranging from vacuum to humidity control environment. Various types of control experiments are used to single out governing

mechanism. In all the experiment, device yield is ensured to be high >70- 80 % before carrying on to understand the mechanism.

Fig 3.2| Atomic force microscopy and typical AFM image. Images are obtained from www.Keysight.com

Fig 3.3| Typical cAFM set up. Both sample morphology and electrical properties can be obtained in this measurement technique. Images are obtained from [www. Bruker. Com](http://www.Bruker.Com).

Fig 3.4| Process flow for switching mechanism study in Au/ PEDOT PSS (5 μ m)/ Au junction.

Fig 3.5| Process flow for switching mechanism study in Au/ PEDOT PSS blend PVA (85 nm)/ ITO junction.

3.6 Reference

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Chapter 4

Coexistence of WORM memory and RRAM memory in a single device of micrometer thick PEDOT PSS

In this chapter, coexistence of WORM memory and RRAM is reported in a single device structure of Au/ PEDOT PSS (5 μ m)/ Au. In RRAM mode, the switchable diode I-V line shape can be observed in humid air of 60- 70% humidity and vanished in vacuum. The mechanism of such diode can be attributed to the adsorbed water in the 5 μ m thick hygroscopic film of PEDOT PSS. Charge trapping from water electrolysis and movement of protons cause the diode effect. WORM memory mechanism can be attributed to electrochemical properties of PEDOT PSS film under bias. The results provide phenomenology basis for further works in Chapter 5 and 6.

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4.1 Rationale

PEDOT PSS is a conducting polymer containing conjugated polymer PEDOT⁺ that is doped (oxidized) by PSS⁻ acid. Because it contains hydroscopic acid PSS H, this conducting polymer can conduct both electronics charges such as holes and ionic charges such as protons H⁺, cations such as Na⁺ and K⁺ (see literature review). PEDOT PSS is well-known for its WORM memory. On the other hand, organic acid PSSH provides medium for protons transport when electronics transport is suppressed. The ionic transport has been reported many times as the origin of I-V hysteresis in DNA or metallo-organic framework (MOF) materials. Hence, it is hypothesized that the thick film of PEDOT PSS may facilitate both WORM memory and RRAM memory by utilizing each of these components in the system.

4.2 Introduction and Motivation

Organic materials offer some special properties such as low cost processing and inherent flexibility for electronics device applications such as memory and transistor. This class of materials has been proposed many times for cheap electronics devices, disposable devices and wearable devices for ubiquitous usage of mankind in the same way that plastics have been utilized in daily activities.

Recent concept of two terminals resistive switching memory devices offers another exciting field for employing organic materials. Such simple device structure coupling with low raw materials cost of organic materials has been envisioned for many applications in future disposable radio frequency identification devices (RFID) [1]. Guided by this motivation, two terminal memory devices using organic materials have been fabricated and studied. Wide range of phenomena and mechanisms have been witnessed for the last 10 years such as Dynamic Random access memory (DRAM) [2], Static Random Access Memory (SRAM) [3], Write Once Read Many Memory (WORM) [4] and Rewritable memory (FLASH or RRAM or memristor) [5]. The complex mechanisms which strongly depend on the top electrode materials or deposition condition

hinder better understanding in this class of device. There are various mechanisms suggested for resistive switching phenomena in organic materials namely, donor-acceptor charge transfer complex [3], charge trapping due to redox reaction [6] and modulation of dopant in conjugated polymer [7] or electrode metal migration [8, 9].

In this chapter, resistive switching phenomena was studied in conducting polymer poly (3,4-ethylene-dioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) where poly styrenesulfonate acid PSS H provides doping for conjugated polymer poly (3,4-ethylene-dioxythiophene) PEDOT and makes it water dispersible. The modulation of dopant PSS H and redox reaction cause WORM memory characteristic of PEDOT : PSS [10]. Recently, Polyaniline doped with PSS acid has been found to exhibit WORM memory characteristic as well [11] ; this suggests universal memory behavior of conjugated doped by organic acids. PEDOT PSS has also been utilized for other electronics such as rewritable memory (RRAM) /synapsis activities [12-14]. In most cases [12-14], memory function was complicated by oxide formation between PEDOT PSS film and sensitive electrode such as Ti or Ta. This oxide formation may be originated from residue acid PSS H.

Here, switchable diode effect and WORM memory can be observed in micrometer thick PEDOT PSS film. Charge trapping and protons movements are attributed to be the main cause for the observed switchable diode while WORM memory can be originated from electrochemical active PEDOT PSS where redox reactions can dedope conducting PEDOT⁺ to insulative PEDOT⁰.

4.3 Experimental section

PEDOT PSS and Poly(4-styrenesulfonic acid) (PSS H) was purchased from Sigma Aldrich. The solution was filtered through 0.5 μm PTFE membrane to filter out big particles and dusts; after that it was diluted in HCl and Deionized water for 1 day to further purify. The solution was casted on Au substrate fabricated on Silicon wafer with

2nm Titanium layer to get thickness of 5 μ m. The film was dried in air at about 60% humidity without heating. 60 μ m thick Film from PSS H was made by the same way.

Transport measurement was conducted using Keithley 4200 semiconductor analyser using bended gold metal probes with thickness of 300 μ m and curvature arc of 40 μ m pressing on the PEDOT PSS or PSS H film as top electrode to study the physics of the memory switching phenomena. This avoids the interference of sputtered electrodes on resistive switching of the film. The contact area was approximately 0.00005 cm². Raman spectroscopy was used to investigate WORM memory before and after switching. Experiments were conducted at 60 % humidity and ambient condition.

4.4 Results and Discussion

4.4.1 I-V feature

The Au metal probe was pressed on PEDOT PSS film on Au substrate to make counter electrode for I-V measurement as shown in Fig 4.1a. At original state, Ohmic I-V was obtained in I-V measurement in low bias regime (from 0V to -0.5V). By sweeping to higher voltage from 0V to -5V, the current transported through the device is suppressed significantly. The I-V line shape is very similar to previous works in PANI PSS [11] and PEDOT PSS observed by Bhansali et al [15]. Conducting state probed at -0.5V shows lower value compared with the original state. This process is irreversible hence demonstrates a write once read many memory phenomenon. State retention of the device was monitored at -0.5V for 5000 s and shows no degradation in both OFF state (written state) and ON state (original state). After 3 months, the states were monitored again and are still clearly distinguishable.

After voltage sweep from 0V to -5V, the original high conducting state is suppressed irreversibly. After this suppression, rewritable memory (RRAM) arose in the form of switchable diode. These two effects namely WORM and switchable diode can be correlated. Voltage sweep from -1V to 1V and from -5V to 5V was applied to the pristine

film independently to attain the correlation between WORM and switchable diode. Fig 4.2a shows the I-V characteristic of the pristine film after voltage sweeping from -1V to 1V and voltage sweeping from -5V to 5V. When voltage was swept from -1V to 1V on pristine film, the I-V characteristic has Ohmic conduction at low bias (0.5V). However sweeping from -5V to 5V applied on pristine film independently shows bistable hysteresis and almost zero current at low bias (0.5V). At very low voltage regime (-50mV to 50mV) after voltage sweep from -1V to 1V is applied on the pristine film, Ohmic properties are presented with the I-V curve crosses the axis origin. After voltage sweep from -5 to 5V is applied on the pristine film, the I-V curve does not cross axis origin as shown in inset of Fig 4.2a. As seen from Fig 4.2a, the switchable diode effect arises after biasing from -5V to 5V. Two current peaks at positive and negative bias regime were observed when the voltage was swept from -5V to 5V which are the characteristics of negative differential resistance (NDR). Using a rectangular pulse width of 0.1s and amplitude of 5V or -5V, the switchable diode was obtained as shown in Fig 4.2b. We can see reversible rectification using smaller reading voltage sweep from -1.5V to 1.5 V. For pulse of 5V, rectification ratio $I(-1.5V)/I(1.5V)$ is 10 while for pulse of -5V, rectification ratio $I(1.5V)/I(-1.5V)$ is 3.5.

Fig 4.1| (a) Configuration to investigate I-V transport of PEDOT PSS film (b) WORM I-V sweep shows irreversible suppression of current (c) long retention of OFF state and ON state

Fig 4.2| RRAM phenomenon in form of switchable diode effect

Unlike the similar phenomenon in ferroelectric diode [16] where no NDR was observed, in this case the switchable diode effect is accompanied by two NDR regions. Furthermore, in Fig 4.2b, the diode forward polarity is opposite to the writing pulse polarity which is in contrast with the similar phenomenon reported in ferroelectric diode where the diode forward direction follows the writing pulse polarity [16]. It is the first time the switchable diode effect was observed in a conducting polymer system such as PEDOT PSS.

The states retention and write/ erase cycles were shown in Fig 4.3. States retention of ON state and OFF state was recorded at -1.7V after applying voltage of 5V and -5V for 60 seconds respectively. ON and OFF states can be switched for more than 50 times and resistive states can be maintained for more than 3000 seconds. Fig 4.3b shows data retention decay which replicates the short term memory discussed largely in memristive systems such as WO_3 and SnO_2 [17, 18]. Similar trend of state retention was also observed in switchable diode of WO_3 and SnO_2 [17, 18].

Fig 4.3| Cycling stability of the junction and retention characteristic

4.4.2 Physical mechanism

4.4.2.1 WORM memory mechanism

WORM mechanism in PEDOT PSS film has been a well-known phenomenon and has been attributed many times to redox reactions that reduce PEDOT^+ to PEDOT^0 in the bulk film [10]. Optical image of the pristine PEDOT PSS film and after biasing -5V was recorded as shown in Fig 4.4a. It is shown that the region with bias -5V is darker than pristine areas. Raman spectroscopy is employed to probe the region after biasing compare to the pristine region. Intensities of Raman peak at 1267 cm^{-1} and band shape near 1450 cm^{-1} which is correspondent to ring (C=C) breathing modes can be a useful indicator of doping and dedoping of PEDOT PSS [19, 20]. Investigation by Raman spectroscopy shows disappearance of peak at 1267 cm^{-1} and the shoulder peak at 1400 cm^{-1} in darker region subjected to bias -5V which indicates that the biased region has been reduced. Furthermore, the current peak near -2V is sensitive to rate of voltage sweep which is another indicator of electrochemical roles in the reduction of this conducting polymer film. As the rate of voltage sweep is increased, current peak level at -2V will also

increase as shown in Fig 4.4c. All these characteristics are fingerprint of electrochemical roles in reducing process of PEDOT PSS which gives rise to WORM memory phenomena [21].

Fig 4.4| (a) Optical image of pristine area and area after being bias -5V (b) corresponding Raman spectra of each area (c) I-V sweep at different sweep rate.

4.4.2.2 Switchable diode mechanism

In this section, the mechanism of switchable diode will be investigated by control experiments. The junction was further tested in vacuum at 10^{-4} Torr to gain better insight into the mechanism of this switchable diode effect. In Fig 4.5, I-V in vacuum and right after breaking vacuum are shown. Inside vacuum, an almost straight line can be seen when voltage was swept from -5 to 5V; the lack of nonlinearity and hysteresis inside vacuum indicates the role of water molecules in this observed diode effect. The junction was tested again right after breaking vacuum with I-V sweep from -5V to 5V; the hysteresis and nonlinearity regained at this test are in similarity with Fig 4.2a. Therefore, we deduce that the adsorbed water molecules are possibly the main reason for switchable

diode effect in Fig 4.2a and 4.2b. Water molecules have also been pointed out as the reason for hysteresis in field effect transistor using carbon nanotubes (CNT) as channel or hygroscopic SiO_2 as gate dielectric [22, 23]. In the same manner, CNT based or hygroscopic SiO_2 based field effect transistor shows hysteresis in humid air but non-hysteresis in vacuum or N_2 environment.

As pointed out above, water contained inside hydroscopic materials will cause hysteresis, it is then reasonable to investigate junction made of PSS H acid as a control sample. We performed control experiments to validate this rationale. In Fig 4.6a, the I-V sweep from -5V to 5V of PSSH is shown. Similar I-V shape with Fig 4.2a was observed in this PSSH system. Hence, we deduce that the observed switchable diode phenomenon arises from the PSSH phase separated regions inside the film of PEDOT PSS. However, the unipolar I-V sweep from 0V up to -15V of PSSH pristine film did not display hysteresis as shown in Fig 4.6b which suggests that the WORM phenomenon observed in Fig 4.1b is not originated from the PSSH regions but from the dedoping process of PEDOT PSS.

It is observed that diode forward directions in Fig 4.2b is antiparallel to the writing voltage polarity hence it cannot be explained by model of voltage modulating injection barrier adopted by some publications [17, 18]. Following a model discussed by Xie et al and Du et al, the following working mechanism can be proposed [24, 25]. Holes trapping can be facilitated by electrolysis of water as PEDOT PSS is a hygroscopic material due to the PSS H acid content. As holes are trapped at anode, protons H^+ will move to cathode to complete the circuit. The non-crossing to axis origin of IV curve after voltage sweeping from -5V to 5V shown in Fig 4.2a inset indicated the presence of cation H^+ movements. After applying -5V, holes are injected from bottom electrode and get trapped at the interface near the anode and protons H^+ will be transported to cathode. The charges are trapped and protons are transported via the water molecules within the PEDOT PSS film through Grotthus mechanism where protons will be transported from one water molecule to another water molecule through Hydrogen bonding [26]. It is noteworthy that electrolysis of water in the film and the acidic PSS H in PEDOT PSS film are the possible sources of protons. At small voltage sweep from -1.5V to 0V (applied to top

electrode), trapped holes hinder further injection which results in reverse-bias-like I-V in Fig 4.2b. When voltage was swept from 0V to 1.5V, holes will be injected from anode and trapped holes were extracted at the cathode; this results in forward-bias-like I-V in Fig 4.2b. The above discussed charge transport events occurred in the PSSH phase separation regions of PEDOT PSS film as revealed by control experiment Fig 4.6a.

Fig 4.5 (a) I-V of Au/ PEDOT PSS (5 μ m)/ Au in vacuum and (b) right after breaking vacuum

Fig 4.6 (a) bipolar I-V sweeping of pristine PSSH film (b) unipolar I-V sweep of pristine PSSH film.

Similar I-V characteristic can also be observed in water- redox based memory device of metal organic framework (MOF) [27] and hydrated/ Nickel decorated DNA [28]. However, WORM memory cannot be achieved in MOF or DNA. Hence, the results described in this chapter are the unique culmination of PEDOT PSS.

4.5 Conclusion and outlook for next chapter

In this chapter, coexistence of WORM memory and RRAM memory in the form of switchable diode was studied in device structure Au/ PEDOT PSS (5 μm)/ Au. Initially the device is in high conducting state when measured at -0.5V. By applying -5V to the top electrode, the device switches to low conducting state with low current at -0.5V; WORM memory arises after this negative -5V bias. After the device is switched to low conducting state by irreversible process, switchable diode arises. The diode effect is explained as charge trapping due to electrolysis and protons H^+ movement facilitated by adsorbed water inside hygroscopic PEDOT PSS thick film. It is highlighted that this coexistence is unique for PEDOT PSS.

Based on previous rationale, one may expect in a complex system containing blend of two materials together will exhibit memory phenomena associated with each component. This chapter shows the case for thick PEDOT PSS where WORM memory is originated from dedoping of PEDOT^+ to PEDOT^0 and switchable diode RRAM is originated from ionic properties of PSS H acid. For the next chapters, this rationale can be further upheld. Chapter 5 shows that the blend of PEDOT PSS and Poly vinyl Alcohol (PVA) will exhibit both WORM memory and RRAM memory in a single device where RRAM memory is originated from charge trapping of PVA and WORM memory is originated from PEDOT PSS. Chapter 6 shows additional behavior of devices in chapter 5 in which WORM memory can be induced by metallic migration mechanism.

The outcomes revealed in this chapter, however, pose some shortcomings. The WORM memory in this case occurs before the switchable diode RRAM. From application viewpoint, WORM memory is an irreversible process, it is preferred to have WORM

memory activated at higher bias compared to RRAM memory so that one can utilize both memory modes in a single device.

Furthermore, retention time of RRAM switchable diode should be improved for possible applications in disposable memory devices which may require longer retention time of 24 hours. Cycling time should also be enhanced in the future chapter.

4.6 Reference

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Chapter 5

The coexistence of write once read many memory (WORM) and RRAM in a single device of poly(3,4-ethylenedioxythiophene): polystyrene sulfonate (PEDOT PSS) and Polyvinyl Alcohol (PVA) blend

In this work, the coexistence of write once read many memory (WORM) and RRAM can be achieved in a single device of poly(3,4-ethylenedioxythiophene): polystyrene sulfonate (PEDOT PSS) and Polyvinyl Alcohol (PVA) blend. In RRAM mode, the cycling of the device can be more than 1000 times. The device state can be switched to a permanent high resistance state by applying -8V and it cannot be restored back to lower resistance states. The RRAM effect is attributed to stem from the charge trapping characteristics of PVA, while the WORM effect can be explained by the electrochemical characteristic of PEDOT PSS. In contrary to chapter 4, the appearance of WORM memory occurred after RRAM memory, which is desirable for practical single device integration. Furthermore, the performance of the RRAM mode has been significantly improved with lower switching voltage (-3V to 2.5V), almost 1000 cycling times and much more than 10^4 s in retention.

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5.1 Rationale

PEDOT: PSS has been a well-known example of WORM memory device in organic resistive switching research. On the other hand, PVA has also been another candidate for organic charge trapping flash memory thanks to the capability to trap charge in OFET design. Here, it is hypothesized that by blending two materials together, a coexistence of WORM and RRAM can be achieved where WORM can be originated from PEDOT PSS while RRAM can stem from charge trapping characteristic of PVA.

5.2 Introduction and Motivation

Due to its inherently flexible and cost-effective in processing, organic materials have been paid much attention in solution processable devices such as transistor or memory for future disposable and wearable electronics. Organic materials for flexible and novel applications have been utilized for interesting investigation in both industrial purpose as well as basic research [1, 2]. Recent concept of two -terminal resistive switching device has renewed interests in utilizing organic materials for future memory devices with higher storage density and simplicity in fabrication. Many interesting resistive switching memory phenomena in polymer and composites have been reported so far such as Dynamic Random access memory (DRAM)[3], Static Random Access Memory (SRAM) [4], Write Once Read Many Memory (WORM) [5] and Rewritable memory (also known as FLASH or RRAM or memristor) [6]. Although device structure is simple, physical mechanisms behind these memory phenomena are often very tangled. Many mechanisms have been proposed for resistive switching phenomena in organic materials namely, donor-acceptor charge transfer complex , charge trapping [7]and modulation of dopant in conjugated polymer [8] or electrode metal migration [9]. Looking at large variety of resistive switching phenomena in very different organic materials raises an intriguing question that whether two (or more) resistive switching modes (for examples WORM and RRAM modes) can be obtained in a single device through active manipulating voltage bias and therefore facilitate a reconfigurable device concept.

Although switching characteristics of organic materials was the main research activities, many recent works have also concentrated on water based organic materials resistive memory for biocompatible and environmental friendly applications [10]. Biocompatible and biodegradable resistive switching memory [11] in some natural macromolecules such as protein, DNA and silk based materials have been demonstrated recent years. In addition, using water soluble polyurethane and organic semiconductor blends with various ratios, Sun et al have realized many resistive memory modes such as write once read many memory or rewritable (Flash or RRAM) memory for particular blend ratio [12]. In this work, the coexistence of WORM and RRAM in a single device using blend of Poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT PSS) and Poly Vinyl Alcohol (PVA) will be demonstrated. Both materials are biocompatible and water soluble/dispersible. Although PEDOT PSS has been well-known in resistive memory device, memory phenomena associated with blend of PEDOT PSS and PVA is limited. Furthermore, coexistence of WORM memory and RRAM in a single device has not been reported before in organic resistive memory device research field. It is envisaged that the concept demonstrated in this chapter can be expanded into synthesizing new single polymers (rather than blends) resistive switching device that can exhibit various modes of switching (such as RRAM, DRAM and WORM) using electrical stimuli as well as photonics stimuli. This concept may provide new angle of research into functional devices with active tuning stimuli using organic materials.

5.3 Experimental section

PVA (code name 363103 Alrich) and PEDOT PSS (code name 483095 Alrich) were purchased from Sigma Aldrich. The blend of PEDOT PSS and PVA weight ratio of 1 PEDOT PSS to 10 PVA was prepared in DI water. The commercially available ITO coated glass electrode was cleaned by detergent and subsequently by acetone/ IPA mixture in ultrasonicator bath; the ITO was treated with oxygen plasma to induce hydrophilicity. The solution in 13 mg/ ml blend of PEDOT PSS and PVA in DI water was spin coated at 1500 rpm to get nominally 75 nm thick films. The films were annealed at 120°C in Ar filled glovebox for 2h. The top gold electrodes were evaporated through

shadow mask using thermal evaporator at 1×10^{-4} Pa and deposition rate at 0.005 nm/s using in-situ crystal quartz. Using gold electrodes, we avoid complicated oxide interface between PEDOT PSS and reactive metal electrodes such as Titanium or Aluminum [13], [14]. Such oxide interface has been pointed out many times as the main or contributing factor for resistive switching in organic materials (see chapter 2 literature survey). Atomic force microscopy (AFM) was used for investigating surface morphology and conducting Atomic force microscopy (cAFM) was used to identify conducting domains and insulative domains. The AFM is model P8 NT-MDT; we used diamond coated tips with radius of 50nm and spring constant of 2- 10 N/m for imaging electrical transport. Control film of PVA (75 nm) and PEDOT PSS (90 nm) were made on cleaned ITO coated glass for comparison; devices were completed by gold evaporation as described above. Electrical bias was applied on top electrodes while bottom electrode was grounded. Film thickness was determined from surface profiler meter KLA TENCOR. The measurement was performed at 60% humidity and ambient condition unless separately noted. Circular electrode with size of 0.2 mm in diameter was used throughout this chapter unless noted separately. Switching time was obtained by Keithley 4200 pulse mode for pulse width larger or equal to 16ms at 5V and by Radiant ferroelectric tester to apply pulse width smaller or equal to 5ms at 5V.

5.4 Results and discussion

The structure of device is shown in Fig 5.1a. In Fig 5.1b and c, the AFM and conducting AFM image of the film are shown. The AFM image shows aggregations domains. The corresponding cAFM (at 0.2V tip biased) at the same location shows that those aggregations can conduct electrical current. It is therefore possible to assign those aggregations as PEDOT PSS rich domains where charge can transport through conjugated bonds of conducting polymer PEDOT PSS. Non- conducting area is possibly PVA- rich matrix where insulator property of PVA hinders electrical transport.

Fig 5.1 (a) device structure of the blend PEDOT PSS : PVA device, (b) and (c) AFM image and corresponding cAFM image of the blend respectively (d) cAFM and AFM of PVA film (left panel is AFM image).

5.4.1 Coexistence of WORM memory and RRAM memory: I-V measurement

The current voltage characteristic of the device in the ratio 1:10 is shown in Fig 5.2. The reversible self-crossing I-V characteristic can be seen in voltage range of -3V to 4V with state 1 and state 0 being noted. The original state of the device is in state 0, by applying threshold positive voltage of 4V; the state 0 was abruptly switched to state 1. The state 1 can be switched back to state 0 by applying -3V. The device resistance states can be cycled for more than 1000 times by writing at 4V, erasing at -3V and reading at 0.3V as shown in Fig 5.3a.

In Fig 5.3b, the replication of the memristor characteristic of 8 devices randomly chosen from 3 different batches is shown; this demonstrates consistency of the observed phenomenon. In Fig 5.2, after sweeping from 0 to -10V, the resistance of the device stays at high resistance state (denoted as state *WORM*) and cannot be restored back to state 1 or state 0 by opposite voltage sweep from 0V to 10V. WORM memory characteristic was unveiled after this sweep where state *WORM* cannot be restored back to state 1 or state 0. Switching time can be as fast as 5ms at 5V as shown in Fig 5.3c, pulse width of 1ms at 5V yields unstable switching; switching energy is then calculated as $E = I \cdot V \cdot t = 0.75 \text{ mJ}$. Hence, in a single device, through controlling of voltage bias, one can obtain both memristor and WORM memory. Here, WORM memory is in type 1 while RRAM memory is bipolar (see literature review chapter).

5.4.2 Mechanism study and discussion

5.4.2.1 Excluding the metallic filament mechanism from governing working mechanism

As pointed out earlier in Chapter 2 literature survey, ubiquitous discovery of RRAM memory in different kind of materials is due to metallic filaments migration from electrode. In this kind of sub 200 nm thin film, metallic particles incorporated during electrode evaporations can also produce switching and complicate the understanding. Hence, it is important to rule out metallic filaments mechanism and highlight the role of polymer in this case. Better understanding and working mechanisms can be drawn after

ruling out metallic filaments as governing mechanism. Control experiments are performed to serve this purpose.

Fig 5.2 Coexistence of RRAM and WORM. When voltage was cycled between -3V and 4V, RRAM is unraveled. After sweeping toward -8V (arrow 6, 7), the device's state will be switched to WORM memory (state_{WORM}) and unable to be restored back to state 0 or 1 (arrow 8, 9).

Fig 5.3 (a) Cycling and (b) cumulative probability of 8 random devices from 3 different batches. Current was extracted at 0.5V. (c) Successful switching of the device by 5V pulse with pulse width of 5ms. Pulse width of 1ms at 5V yields unstable switching. Inset of (c) is voltage pulse scheme.

5.4.2.1.1 Control experiments with PVA and PEDOT PSS respectively

The I-V of PVA and PEDOT PSS control film are shown in Fig 5.4a and b respectively. Clearly seen in Fig 5.4a, current level of PVA film is in micro Ampere range which indicates insulator properties of this film compared to blend film; no threshold voltage or memory switching was found in PVA film alone. Metallic filaments mechanisms can be ruled out in this control experiment and resistive switching mechanism can be attributed to the blend of PEDOT PSS and PVA. While applying higher voltage (up to -10V) to PVA control device, WORM characteristics are absent. WORM memory characteristic without RRAM occurrence is observed in I-V plot of Au/ PEDOT PSS/ ITO. Hence, RRAM effect of the device can be attributed to PVA and PEDOT PSS blend rather than any of its individual material; WORM effect can be attributed to PEDOT PSS. WORM memory in PEDOT PSS has been explained extensively as redox reactions which dedope conducting PEDOT^+ to non-conducting PEDOT^0 [15]. Furthermore, the top electrode contact and PEDOT PSS 's conduction pathways can be distorted due to electrochemical characteristics of PEDOT PSS (including migration of PSS chains) in which suppression of electrical transport and hence a WORM memory phenomenon can be obtained [16, 17].

Fig 5.4| (a) I-V characteristic of Au/PVA/ ITO (b) I-V characteristic of Au/ PEDOT PSS/ ITO. Inset of (b) shows Ohmic line shape I-V at small voltage (-1V to 1V) of pristine Au/ PEDOT PSS/ ITO device

5.4.2.1.2 Blend ratio dependence of I-V

To gain clearer understanding on the controlling mechanisms of the RRAM mode, spurious effect from metallic filaments mechanism from electromigration of top or bottom electrodes must be excluded. It is argued that if metallic filaments are the main mechanism, qualitatively the same switching should be observed in any blend ratio or even in control experiments with PVA. Further control experiments are performed to elucidate/ exclude role of electrodes or electrodes' filaments in the RRAM mode of the blend. PEDOT PSS to PVA blend ratio of 1: 5, 1: 10 and 1:30 was used to study the effect of blend ratio. All the samples were fabricated at the same batch to avoid spurious effects of electrode fabrication. It is seen from Fig 5.5, due to the insulative properties of PVA, the current level will be reduced with increasing PVA content. Filament mechanism from electrode metal migration can be excluded based on the current level dependence on the polymer blend ratio.

Fig 5.5| I-V of Au/ blend PEDOT PSS and PVA/ ITO with different blend ratio

5.4.2.2 Working mechanisms

After excluding the spurious effect of metallic filaments, in this section, the working mechanism can be proposed with further control experiments and qualitative observations. Comparing with existing literatures will also facilitate better understanding.

5.4.2.2.1 WORM memory mechanism

WORM memory in PEDOT PSS based system has been many times attributed to the electrochemical reactions of PEDOT PSS. The electrochemical reaction can be evidenced by gas evolution from the reactions that distort the top electrode (also see Fig 2.15). The electrochemical reaction can de-dope the conducting PEDOT⁺ to non-conducting PEDOT⁰. Furthermore, the electrochemical reaction can distort top contact and percolation path way of PEDOT PSS film. Such distortion can suppress electrical transport in PEDOT PSS and hence gives rise to WORM memory.

In Fig 5.6, observation of top electrode of Au/ blend 1 PEDOT PSS to 10 PVA/ ITO after -8V shows significant bubbles, distortion and delamination. Such “electrode-blown-up” can be observed in both vacuum and air (Fig 5.6a and b). This observation is also consistent with many observations found on PEDOT PSS based device research in literature (see Fig 2.15). Similarly, “electrode-blown-up” has also been observed in many oxide based system such as TiO₂ and Ta₂O₅ where oxygen vacancy forming reaction causes gas evolution [18] which in turn causes the delamination and distortion of top electrode

Comparing with the control sample of PEDOT PSS, similar distortion can be seen (fig 5.6c). Furthermore, for PVA based device, electrode distortion is very minor (after -10V). In case of small sweeping voltage (-3V to 4V), electrode distortion is hardly observed. The following reactions are proposed to take place

(a)

(b)

(c)

(d)

Fig 5.6| Optical microscope observation of top electrode after biasing (left panel) and pristine device (right panel) of (a) PEDOT PSS blend PVA (ratio 1:10) in air after -8V (b) PEDOT PSS blend PVA (ratio 1:10) in vacuum after -8V (c) PEDOT PSS (d) PEDOT PSS blend PVA (ratio 1: 10) at small voltage sweep -3V to 4V (e) PVA after -10V to 4V sweep. (f) Electrode distortion in case of Al/ PEDOT PSS (80 nm)/ Al from reference [19] for convenient comparison purpose. Electrode size is approximately 0.2 mm in diameter.

Comparing with Fig 5.4, Fig 5.6 shows that WORM memory mechanism can be attributed to PEDOT PSS in the blend. Furthermore, very similar I-V has been obtained between WORM memory of PEDOT PSS blend PVA and PEDOT PSS. In case of PVA, WORM memory as well as the severe “electrode-blown-up” are not observed as compared with PEDOT PSS blend PVA device. As the charge transport in PEDOT PSS is relied on conductive percolation pathway of conducting PEDOT⁺, therefore the electrochemical reactions, which have distorted this percolation pathway, will suppress

electronic transport in this film. The observations and arguments are in accordance with literature report of PEDOT PSS based devices.

5.4.2.2.2 Working mechanism of RRAM memory

Comparing with WORM memory mechanism which is a well-known topic, the RRAM memory mechanism in PEDOT PSS based devices is still a topic of debate and discussion. The RRAM memory occurs at small voltage sweep of -3V to 4 V. As observed earlier, this small voltage sweep does not cause irreversible electrode distortion (Fig 5.6b).

The device was tested in vacuum. Switching can still be observed unlike results in chapter 4 where RRAM behaviour vanished in vacuum. Therefore, we can exclude water molecules as the governing origin of I-V hysteresis. Figure 5.7 shows the I-V characteristics of the polymer blend PEDOT:PSS/PVA with ratio 1:10 in vacuum.

Fig 5.7| I-V of blend device 1 PEDOT PSS : 10 PVA in vacuum at 10^{-4} Torr

In figure 5.8, the retention characteristic of the device is tested in air and vacuum (at 10^{-4} Torr). For vacuum test, the device was sustained in vacuum for 3 weeks before testing. In both cases, the retention shows power law decay with $I \propto t^{-\beta}$ for low resistance state (ON state). This decay characteristic is in accordance with reports of resistive switching memory device with charge trapping as the main mechanism. Similar I - t relation can also be obtained in OFET memory device using PVA or organic self-assembly monolayer as charge trapping layer where current decays in power law [20, 21]. The similarity points to the fact that the governing mechanism of the device is the charge trapping by PVA. It is observed that a longer retention can be obtained while testing the device in vacuum. This suggests that water molecules have an important role in charge de-trapping; interestingly this is in accordance with OFET charge trap flash memory using hydrophilic electret such as Poly vinyl phenol (PVP), PVA and poly(2-vinyl pyridine) (PVPyr) [22, 23]. Hence it is possible to minimize the negative effect of adsorbed ions on the retention time by recording the retention in low temperature such as 243K. Figure 5.8c shows that I - t decay can be significantly minimized.

Fig 5.8 Retention characteristic of Au/ Blend 1 PEDOT PSS : 10 PVA/ ITO a) in vacuum b) in air. In (c) retention characteristic of device at 243 K is shown, I - t decay is significantly minimized.

Fig 5.9 shows the I-V characteristic of Au/ PEDOT PSS blend PVA/ ITO in ratio 1 :10 on ITO electrode with air plasma treatment and without air plasma treatment. It is clearly shown that devices on ITO without air plasma treatment show lower current level although switching can still be observed. This result further upholds the fact that metallic filaments are not a main mechanism because filament formation will only depend on conductivity of electrodes rather than electrodes' interface properties. It is well-known that air plasma treatment of ITO will reduce carbon contamination and enhance the work function while keeping conductivity unaffected.

Fig 5.9| I-V of Au/ PEDOT PSS blend PVA/ ITO with ratio of 1 : 10 on ITO electrodes with air plasma treatment and without air plasma treatment.

Model of traps induced resistive switching discussed extensively in literature can be adopted to elucidate the RRAM mode of PEDOT PSS blend PVA. In this model, conducting dopant in system such as Poly(3-hexylthiophene-2,5-diyl) (P3HT) or Phenyl-C61-butyric acid methyl ester (PCBM) doped Polyimide (PI) matrix or Poly Methyl Methacrylate (PMMA) matrix [24] [25] can trap charges injected from cathode or anode

into organic layer. This charge trapping phenomenology model has successfully described the I-V hysteresis observation in the blend systems above (PCBM blend PI) . Here, some modifications of the charge trapping model proposed by Lee 's and Kim 's [24-26] are proposed as the working mechanism to capture the essential information of the observations. Figure 5.10 shows the modified model for the PEDOT:PSS blend PVA system.

Fig 5.10| PEDOT PSS blend PVA system charge trapping model

For Au/ PEDOT PSS blend PVA/ ITO device, traps filling due to holes injection can switch the device to ON state. After traps filling, charges can also be trap-free transported and less scattered [24, 26]. In the proposed mechanism model, traps are originated from PVA. Using PVA as gate dielectric of organic field effect transistor (OFET), large hysteresis transfer curve can be obtained due to charge trapping of PVA. It was suggested

that dipoles from the OH groups of PVA can be the origin of traps[22, 27]. The device can be switched back to OFF state by applying negative voltage on Au top electrode, the trapped charges are extracted back and the device state will be back to OFF state or original state for ITO bottom electrode devices. This phenomenology model qualitatively explains the observation in Fig 5.9. To test this model, it is expected that by lowering down the device to around 100 K, switching should be deteriorated due to charge trapping frozen- out in electrets. The experimental observation shown in Fig 5.10 upholds this expectation. In similarity, OFET charge trapping memory device with PVA as gate electret also shows significant degradation of transfer curve when temperature is reduced to below 170K. Furthermore, charge trapping resistive memory using blend of PCBM and PS also shows diminished I-V when device is tested at 200 K [28].

Fig 5.11 | I-V measurement comparison at 297 K and 100K.

Tsai et al showed that the hysteresis in the transfer curve of OFET device with PVA electrets as charge trapping gate dielectric can be significantly reduced when the device is soaked in humid air [27]. It is explained that the dipole of waters trapped inside the film will reduce the charge trapping capability in PVA electrets. Hence, it is expected that

similar observation can be obtained in this work. It is shown in Fig 5.8 that the retention time can be significantly reduced when the devices are tested in ambient condition hence this result upholds the role of water in the stability of the hysteresis I-V in the devices of PEDOT PSS blend PVA. Fig 5.11 shows the I-V obtained after soaking device in 90 % humid air for 1 day. It is clearly seen that I-V hysteresis is deteriorated. LRS (state 1) can no longer be retained as seen in the second voltage sweep. The situation can be remedied by heating the device in Ar filled glove box at 120°C for hours.

Fig 5.12 (a) I-V characteristics of device after being soaked in humid air 90 % RH for 1 day (b) after annealing the device in Ar glove box at 120°C.

After carefully excluding metallic migration mechanism from the governing mechanism, it is now possible to fit I-V curve at ON state and OFF state to further prove the trapping mechanism. The I-V fitting has been utilized for mechanism identification purpose in a

number of works [29-31]. Here, the charge transport can be fitted to trap charge limited current (TCLC) at the OFF state. The TCLC is a modified model of space charge limited current (SCLC) in Mott-Gurney law and Child law to include effect of traps[32] . In TCLC model, effect of traps can be included. The TCLC model qualitatively is given by for shallow traps

$$I \propto 9/8 \epsilon \mu \theta V^2 / d^3 \quad (1)$$

Where ϵ , μ , d and θ are permittivity, hole mobility, film thickness and traps concentration in the film. When traps are filled, I-V characteristic deviates from the square law and enters trap filling regime with power law of I-V and power index $n > 2$ [32, 33]. After traps are fully filled, abrupt jump in I-V can be observed. This situation has been described many times in resistive switching memory literatures [29-31] as well as organic single crystal literatures[34]. In the ON state, the I-V can be fitted to Poole-Frenkel (P-F) emission model ($\ln(I/V) \propto V^{0.5}$) where charge can transport without being trapped [26]. The Fig. 5.13 shows the fitting.

Fig 5.13| Fitting of I-V in Au/ PEDOT PSS blend PVA/ ITO device (a) ON state (b) OFF state

5.4.2.2.3 Predictions

After improving the understanding of the mechanism, possible qualitative predictions can be exercised based on the rationale proposed previously to realize memory effects in system of PEDOT PSS and composites (see section rationale). PVA has been a well-known water soluble electret (also known as charge storage dielectric). To further test the hypothesis that PVA is the trap site, control sample using polyvinylpyrrolidone (PVPy) (instead of PVA), a well-known charge storage electret material, was fabricated [35]. It is predicted that the blend of PEDOT PSS and PVPy in ratio 1: 10 may also exhibit coexistence of memory switching of RRAM effect and WORM effect. Here PVPy was chosen because of the compatible solvent with PEDOT PSS; both of them can be dissolved in DI water, this fact may facilitate better film formation. The charge trapping centers, in this case, are possibly originated from polar carboxyl groups $C=O$.

I-V sweep of blend PEDOT PSS and PVPy in ratio 1 to 10 is shown in Fig 5.14. In voltage window from -4 V to 4V, observable hysteresis can be seen (Fig 5.14a). This demonstrates direct evidence of the RRAM effect in the blend of PVPy with PEDOT PSS. WORM memory can be observed by applying -8V or 8V (Fig 5.14b). Even though possible complications can arise due to difference in phase separation between different kinds of blend (PEDOT PSS blend PVA and PEDOT PSS blend PVPy), yet trace of memory hysteresis still can be observed.

Fig 5.14 (a) RRAM and WORM effect of Au/ blend 1 PEDOT PSS to 10 PVPy/ ITO . Right panel is PVPy chemical structure.

The results of PVA and PVPy blends have pointed to the importance of charge storage dielectric materials on the manifestation of RRAM effect. It is then predicted that blending of PEDOT PSS and other polymers containing polar groups such as organic acids will also facilitate observable RRAM and WORM memory. Here, Poly(2-acrylamido-2-methyl-1-propanesulfonic acid) was used by blending with PEDOT PSS in ratio 10 to 1 in DI water. The device structure of Au/ blend/ ITO has been fabricated and the memory characterization was carried out. The charge trapping center can arise from negative SO_3^- groups in this organic acid (see chemical structure in Fig 5.15).

Fig 5.15 RRAM and WORM memory in the single device of blend Poly(2-acrylamido-2-methyl-1-propanesulfonic acid) and PEDOT PSS in ratio 10 : 1 in DI water. The device structure is Au/ blend/ ITO. Upper panel is chemical structure of Poly(2-acrylamido-2-methyl-1-propanesulfonic acid).

5.5 Conclusion and chapter outlook with discussion

In conclusion, the coexistence of WORM memory and memristor in blend of PEDOT PSS with PVA has been reported. The RRAM mode is bipolar and WORM memory is in type I. At low voltage from -3V to 4V, the device exhibited RRAM characteristic with self-crossing I-V. Furthermore, the HRS (state 0) and LRS (state 1) could be cycled for more than 1000 times with states retention of much more than 10^4 s. After negative voltage of -8V, the device's resistance state was switched permanently to state WORM which is smaller than both state 0 and state 1. The coexistence of these two resistive switching modes may facilitate future reconfigurable memory device with highly secured data storage options.

Furthermore, better understanding on the mechanisms has been achieved for RRAM mode. RRAM mode was not observed in Au/ PEDOT PSS/ ITO and Au/ PVA/ ITO devices. Here, using PVA blend with PEDOT PSS in ratio 1 to 10, one can obtain RRAM mode. This fact points toward the important role of charge storage polymer in realizing RRAM effect in PEDOT PSS based composites and further validates previous results in OFET based flash memory.

It has been further predicted and demonstrated that sizable RRAM and WORM memory can also be observed in blend of PEDOT PSS and PVPy as well as blend with other polymers containing polar groups. In all of the above systems (blend PEDOT PSS with PVA, PVPy and organics acids), RRAM mode appears as bipolar and WORM memory appears as type I WORM memory (see literature review chapter for definitions and classifications). The possibility to make predictions suggests great improvement in the understanding of resistive switching phenomena in PEDOT PSS based blend systems, which have been pointed out as a complicated topic.

Unlike various works in literature, Au electrodes and ITO electrodes were used for the investigation of resistive switching phenomena in this PEDOT PSS based blend systems. This experimental set-up avoids complication of oxide interface between organic films

and active electrodes such as Ta or Al or Ag which has been a matter of debate and discussion especially for PEDOT PSS based systems (see for examples [14, 36]). Hence, it is a better step to understand resistive switching phenomena in PEDOT PSS and its blends.

Nevertheless, memory phenomena observed here add-on another intrigued aspect of PEDOT PSS which is rich in complicated yet interesting physics such as Luttinger liquid behavior [37], electrochromism [38], thermoelectricity [39], piezoresistive, long-live spin- transport, anisotropic charge transport and Shklovskii transport behavior [40]; to name a few.

On a broader outlook, the chapter does not only demonstrate coexistence of WORM memory and RRAM memory but provides better understanding as well. Here, some degree of correlation can be seen between what have been observed in OFET based charge trapping using PVA as gate dielectric and what have been demonstrating in this chapter using RRAM based charge trapping with PEDOT PSS blend PVA. This interesting correlation may suggest some further predictions. For example, much better retention and ON- OFF ratio has been observed in OFET charge trapping using *hydrophobic* electret gate dielectric such as Poly-Styrene (PS) [20]. Hence, it is predicted that blend containing a conducting (semi-conducting) polymer blended with *hydrophobic* electret such as PS may facilitate much longer retention time for RRAM mode. Recent work of Kim et al has shown very good retention characteristic of PS blend with PCBM in ratio of 7 to 1 in resistive switching device[41] . The results of Kim et al qualitatively uphold the prediction; however, more works should be done to clarify clearly the role of phase separations in their charge trapping resistive switching devices. Furthermore, PCBM is an electron transport layer which is not electrical active like PEDOT PSS hence coexistence of WORM memory cannot be observed in work of Kim et al.

Therefore, future work can be on synthesizing new polymer that can exhibit WORM switching and can be dissolved with PS in a common solvent. In this scenario, possible coexistence of WORM memory and high performance RRAM can be achieved in a single device. Much broader outlooks shall be provided in the last chapter.

5.6 References

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Chapter 6

Additional WORM behavior in blend of PEDOT PSS and PVA governed by metallic filament mechanism

Chapter 5 has shown possibility to obtain both WORM memory and RRAM memory in a single device of Au/ PEDOT PSS blend PVA/ ITO. However, some questions still arise for example: can WORM memory be triggered at positive voltage ? or can metallic migration alter the I-V shape of the WORM or the RRAM ? In this chapter, additional behaviour of WORM memory is investigated. It is shown that WORM memory can also be triggered at a large positive voltage (6V) applied on Au electrode. Furthermore, once the WORM memory is triggered, subsequently a longer voltage application time (approximately 1min) can switch the device state to another permanent low resistance state. This low resistance state has linear I-V shape over -2V to 2V which suggest metallic migration mechanism. Fuse type WORM (type 1) has been converted to anti fuse type (type 2) after this very long voltage application time.

6.1 Introduction and Motivation

Metallic filaments have long been suggested for the ubiquitous observation of organic resistive memory device. Through TEM analysis with dedicated sample preparation, Kwan et al have shown metallic filaments inside organic materials based resistive memory devices [1]. Recently, TOF SIMS scanning techniques have provided another evidence of metal filaments inside organic films [2].

In the metallic filament mechanism, positive voltage applied from metallic top electrodes will drive metal ions from electrodes into the film and precipitate there. Larger voltage stress time will increase the number of metal particles inside the film and creates metallic connection between top electrode and bottom electrode. When negative voltage is applied on top electrode, it drives back metal ions hence metal bridge is broken and the device state will return to OFF state. Most of the switching mechanism based on metallic filaments requires a forming voltage which takes place at very high voltage (10V) and/or at very long stress time with lower voltage (5V). In this forming procedure, current compliance is applied so that the device does not break down. Control of this forming process is difficult.

In this chapter, the role of metallic filaments on WORM device is studied. It is shown that after WORM transition (described in chapter 5), the device can be switched back to low resistance state by stressing the device between -5V and 5V for approximately 1min. This new low resistance state is inerasable and permanent for at least 1 day without decay. Hence, fuse type WORM memory (type 1) obtained in chapter 5 can be transformed into anti fuse type (type 2) WORM memory by this long voltage stress time.

6.2 Experimental Section

In this chapter, blend of PEDOT PSS and PVA in ratio 1 to 10 was used for the study. The bottom electrode was commercially available ITO coated glass and the top electrode was Au. The top electrodes were made by thermal evaporation at 10^{-4} Pa. Measurements

were carried out using probe station and semiconductor analyser for I-V trace. Film thickness is approximately 75 nm measured by surface profiler meter. Detail of experiments can be found in chapter 5.

6.3 Result and discussion

Figure 6.1a shows WORM memory triggered by a -8V (Figure 5.1). This WORM memory is fuse type (see literature review for classification). Similar effect can be obtained when applying 6V, the current transport is suppressed by 6V. Figure 6.1b shows such observation.

This fact is reasonable and can be explained by dedoping of PEDOT PSS after being injected by electrons from cathode (chapter 5) discussed intensively in references. Electrode distortion was also observed at 6V WORM transition in similarity with case of -8V (chapter 5).

From this point onward, the WORM memory mentioned is one that is triggered by -8V. Figure 6.2a shows I-V at voltage sweep from -5V to 5V after WORM transition voltage – 8V in Fig 6.1a. After approximately 2 sweeps (-5V to 5V) with timing of approximately 1 min, switching from state WORM to another low resistance state can be seen and this state is permanent and cannot be erased by applying another negative voltage as seen from Figure 6.2a.

This low resistance state is permanent for at least 1 day without any decay. This transition suggests anti fuse type of WORM memory where current transits from low value to high value. Another procedure was carried out with another device. Here, the switching voltage is at negative voltage side as seen in Figure 6.2 b. This fact points to the stochastic nature of this process.

(a)

(b)

Fig 6.1 (a) coexistence of WORM and RRAM with WORM memory is triggered at -8V (b) WORM memory triggered at 6V.

(a)

(b)

Figure 6.2 (a) device 1 switching from state WORM to new low resistance state (b) device 2. Color of the arrows is correspondent to color of the curves.

Using current compliance, the possibility to erase state is expected. It is shown in Figure 6.3 that such expectation is reasonable. However, the device in cycle 2 shows again stochastic characteristic and the device is again not rewritable. Observation of I-V of the device in voltage range of -2V to 2V shows linear Ohmic shape with $I \propto V$ (Fig 6.4b).

This fact points to metallic filament mechanism of this transition. To further elucidate the mechanism, temperature dependence study was conducted for low resistance state (branch 6 of Fig 6.2a). As seen in Fig 6.4c, resistance versus temperature shows positive coefficient which is signature of metallic transport.

Fig 6.3 Compliance control induces erasable process.

Fig 6.4 (a) plot of RRAM mode and anti fuse type WORM of device in Fig 6.2a (b) zoom in voltage range of -2V and 2V plotted in linear range (c) Temperature dependence of sweep 6 in Fig 6a.

Fig 6.5 (a) Pristine device (b) device after WORM transition at -8V, air pockets are created inside the film (c) Au migration in Fig 6.2 can occur at the pockets sides to connect top and bottom electrode and switches the device from OFF state to ON state.

Some works in literature have shown the role of Au to form filament in organic resistive switching device especially when the Au top electrode is biased positively [3, 4]. In inorganic materials, Au diffusion has also been noted. In this chapter, the filament is possibly induced by Au diffusion driven by voltage. It is conjectured that Au migration is more likely than ITO migration because the ITO bottom electrodes are flatter (RMS 2.6 nm) hence electric field concentration will be less as compared to Au top electrode (RMS 7.6 nm) that is evaporated on the film. Furthermore, this is corroborated with the evidence from cAFM analyses. Scanning the film (scan time of 74s) without Au top electrodes by cAFM applied at 10V did not show switching hence it is unlikely that the filament originates from ITO (Fig 6.6). Figure 6.5 illustrates the working mechanism.

Although the results in this chapter may be against the applicability of chapter 5 for data security and archive (because state WORM can be modified by long voltage application), it is emphasized that the switching observed in chapter 6 is different from chapter 5, it can only be achieved at very long voltage stress time. Therefore, possible circuit design may eliminate this problem by limiting access time. Furthermore, it is able to discern

state 1 (see Fig 6.1a or Fig 5.1) with the new switching state by considering nonlinearity. The I-V (from -2V to 2V) associated with state 1 has some degree of nonlinearity while I-V associated with the new switching state is linear (Fig 6.4b). Moreover, the current level of the new switching state is higher than state 1 as seen from Fig 6.4b. Another way to mitigate this unwanted switching is by using high A.C voltage. Under large frequency for 1 minute (500 kHz driving voltage 0.1V), the portion of Au top electrode is completely blown-off as seen in Fig 6.7. This may be due to large frequency induced heating of trapped water inside the film.

Fig 6.6| (a) morphology (b) current mapping by applying 10V on cAFM scanning over $2 \times 10 \mu\text{m}$ for 74s on PEDOT PSS: PVA/ ITO using conducting tip as top electrode, no switching is obtained.

Fig 6.7| Au electrode blown off after testing the device at 500 kHz with AC voltage of 0.1V.

6.4 Conclusion

In this chapter, role of metallic filament is discussed. After WORM transition at - 8V, the device can still be switched to new lower resistance state by applying voltage stress time in the range of 1 minute. The new state is also permanent and inerasable. This low resistance state has linear I-V shape over -2V to 2V which suggests metallic migration mechanism. Fuse type WORM (type 1) has been converted to anti fuse type (type 2) after this very long voltage application time.

6.5 References

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Chapter 7

Thesis conclusion and general outlook

In this chapter, novelty of the work is discussed. Future works and outlook on research directions can be drawn. In detail, the thesis demonstrates for the first time the coexistence of WORM and RRAM in a single device containing conjugated polymer. The mechanisms behind this coexistence are identified and further insight has been obtained. Basing on the understanding, better performance devices can be obtained and new polymers can be synthesized to achieve this coexistence.

7.1 Scientific significance

7.1.1 Uniqueness of the phenomena described in the thesis

The thesis studies the coexistence phenomena of WORM memory with RRAM memory in conjugated polymer within a single device of PEDOT PSS and PEDOT PSS blend PVA . It is the first time such phenomena are discussed and unveiled. Here, some degrees of similarity between the results in the thesis and work of Wang et al were noted. Wang et al [1]demonstrated coexistence of WORM and RRAM in a single device made of silk based materials by controlling current compliance (c.c), hence it requires some changes in circuit design in order to facilitate c.c change. In this thesis, current compliance was fixed at either 0.1 A or 0.05A therefore no change in external circuit design is required. In comparison with thorough literature survey in chapter 2, the uniqueness of the works described in this thesis is evident. The coexistence of two types of memory behaviour may find applications in future wearable/ disposable electronics devices for data security, data storage.

7.1.2 Better insight into RRAM working mechanism of PEDOT PSS based devices

Alongside with the new phenomena discussed above, the thesis provides some better insights in understanding the working mechanism of PEDOT PSS based materials for resistive switching devices (chapter 4 and 5). Using Au electrode or ITO electrode for investigating memory phenomena of PEDOT PSS offers much better understanding compared with literature data which employed active electrodes (Ti, Al, Ta for examples see motivation of chapter 4 and 5) that can be easily oxidized even in air. In the data obtained in literature using those active electrodes (Al or Ti), RRAM can be obtained but WORM memory is not reported, possibly because the governing mechanism now is driven by electrodes rather than the polymer itself. Furthermore, RRAM obtained by employing active electrodes exhibits complicated behaviour with many different I-V characteristics which were reported to be unipolar in some publications [2] but bipolar in other publications [3].

7.2 Thesis conclusion and discussion

The thesis describes for the first time coexistence of WORM memory with RRAM memory.

Chapter 4 describes coexistence of WORM memory and RRAM memory in the form of a switchable diode with device structure Au/ PEDOT PSS (5 μ m)/ Au. The work is based on the rationale that each component of PEDOT PSS namely the holes conducting PEDOT⁺ PSS⁻ chains and the ionic conducting PSS H acid can exhibit memory behavior of its own. It is well known that hole conducting PEDOT⁺ PSS⁻ can exhibit WORM memory due to dedoping of PEDOT⁺ back to PEDOT⁰ by receiving electrons. Furthermore, it is also understood that the polymer containing ions can also facilitate I-V hysteresis due to ionic movement. Hence, this argument forms the rationale basis for not only chapter 4 but as well as chapters 5 and 6.

The coexistence of WORM memory and RRAM memory in blend of PEDOT PSS and PVA on ITO substrate has been validated to be due to the combination of PEDOT PSS and PVA (chapter 5) . The rationale in chapter 5 was motivated by chapter 4 results. In this scenario, WORM memory can be obtained from PEDOT PSS while RRAM memory can be originated from charge trapping of PVA. By control experiment with blend ratio, metallic filament can be excluded from the governing mechanism. The switching mechanism can be proposed due to trap filling from PVA traps. The switching effect is seen to be deteriorated at 100 K due to traps freeze-out which is in consistency with results from OFET flash memory using PVA as trapping medium. Using this understanding, it is further shown that RRAM memory and WORM memory can be obtained in the same device using blend of PEDOT PSS and some typical electret polymers. These facts point the important role of electret materials on the switching. This is the main chapter of the thesis.

The WORM memory of Au/ PEDOT PSS blend PVA/ ITO induced by metallic migration from electrodes (chapter 6) has been established and differentiated from the

WORM induced by dedoping of PEDOT PSS (chapter 4 and 5) This WORM memory, however, is not desired. Hence, remediation is proposed based on I-V shape differentiation and AC voltage application.

In the thesis, clear role of water in resistive switching memory device is discussed in chapter 4 and 5. In chapter 4, trapped water causes I-V hysteresis with I- t decay (Fig 4.2a and Fig 4. 3b). In chapter 5, water is not the main cause of I-V hysteresis but has negative effect on states retention where I-t decay (Fig.5.8b) is again observed in similarity with chapter 4 (Fig 4.3b). A method to minimize the negative effect of water is anticipated and demonstrated by measuring the device in vacuum and lowering down the measuring temperature to 243 K. Although the thesis demonstrates the feasibility and nonvolatility of WORM and RRAM memory in PEDOT PSS blend PVA, ultimate performance can only be obtained at low temperature and in vacuum; this fact hinders real practical application of the results. However, better understanding has been achieved in this system hence it will guide future developments of the concept. Basing on various predictions in chapter 5, one of the possibilities to enhance performance is to employ hydrophobic electrets such as PS blend with conducting and electrical active polymers to achieve WORM memory and RRAM memory in a single device with high performance.

In general view point, it is noted in literature that organic materials are prone to degradation, humidity affections and temperature stability. Hence, many challenges involved in organic materials are about stability and repeatability. Furthermore, manufacturing techniques for organic devices are also not completely mature or wide-spreading adopted. Therefore, organic materials devices still need more research into novel device concept (to open new market needs), better synthesized raw materials (to obtain better performance devices) and novel/ effective manufacturing technique with good yield and stability (to manufacture device for industry applications).

7.3 Future work

7.3.1 Toward functional cross bar array of organic resistive memory

The results described in this thesis are focused on discrete devices. However, for active matrix, one needs to integrate device with a selector such as diode or transistor. Figure 7.1 illustrates the situation where crossbar arrays of 4 devices does not have selector such as diode. When it is in absence of selector, leakage current can be a detrimental issue which can lead to error read out of memory state.

To facilitate wearable memory devices or disposable memory devices, the selectors should be flexible and cheap in manufacturing. Furthermore, the selector must be compatible to solution process or printing process which is still a challenge for fully printing RRAM memory. One recent example reported is the printable diode made from Niobium Silicide [4] ink for printing process.

Another way to integrate selector and RRAM device is through utilizing electrochemical transistor properties of PEDOT PSS or WO_3 . Figure 7.2 illustrates the device configuration. In electrochemical transistor, the channel current is initially high (ON state). By applying positive voltage that drives lithium ions inside electrolyte migrating into PEDOT PSS channel, the channel current can be turned off due to Li^+ and PSS-electrostatic interaction which dedopes PEDOT^+ to PEDOT^0 .

Currently, there is no research paper about fully print RRAM device with selectors. Hence, this concept will be made significant interest in both academic and industry.

7.3.2 Toward better performance coexistence of RRAM and WORM memory in a single device

As predicted in chapter 5, much better performance in RRAM mode can be realized using hydrophobic electret materials to blend with electro-active conjugated polymer which can exhibit WORM memory. In chapter 5, the electro-active material is PEDOT PSS while electret is hydrophilic PVA. One of the challenges is to synthesize an electro-active polymer which can be dissolved in common solvent with hydrophobic electret such as Poly styrene (PS).

Fig 7.1 (a) cross bar array with 4 devices without selector (b) with selector such as diode. Reuse with permission from [5].

Fig 7.2 Electrochemical transistor as a selector for RRAM devices.

7.4 References

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Appendix table: Comparison table between work in the thesis and other organic resistive memory devices

Comparison parameter	Literature	Literature	Literature	Literature	Literature	Literature	Literature	Literature	Best device of the thesis
	Single layer polymer (pentacene, P3HT, PMMA, MEH PPV, Alq ₃ , Rose Bengal) [1, 2, 3, 4 and 5)	Blend of Semiconductor and insulator (blend PI-PCBM, PMMA-P3HT) [6, 7]	Blend of Semiconductor and nano particles or 2D materials [8, 9]	Conducting polymer (PEDOT PSS, PANI PSS) [10, 11]	Blend of Semiconductor and Ferroelectric polymer [12]	Ion conducting material (MOF, PEO+Li, electrolyte gel, Hydrated DNA) [13, 14, 15]	Organic semiconductor / Inorganic Junction [16]	Organic donor acceptor [17]	Au/PEDOT : PSS blend PVA/ITO
Mode of exhibited resistive switching	Mix results: RRAM or WORM depending on specific condition	RRAM or WORM depending on condition	RRAM	WORM	RRAM	RRAM	RRAM	RRAM or WORM depends on molecule	RRAM and WORM
ON-OFF ratio	80-1000	100-1000	100-1000	100-1000	1000	10-50	10-200	>100	10
Cycling	100-1000	100	10 ⁵	NA	1000	10-50	20	50	1000
Retention (s)	>10 ⁴ (s) to 1 year	10 ⁴ (s)	10 ⁵ (s)	>10 ⁴ s	>10 ⁴ s	50 s to 10 ⁴ s	> 1000s	>10 ⁴ s	>10 ⁴ (s)
Mechanisms	Metallic filaments or oxidation of top electrode or traps at electrode/organic film interface	Trapping detrapping of carrier at semiconductor-insulator interface	Charge trapping at nano particles or 2D materials	Dedoping	Ferroelectric induced Schottky barrier tuning	Ionic motion of protons or Li	Memory comes from Inorganic materials	Donor-acceptor charge transfer	Dedoping for WORM mechanism and charge trapping at PVA for RRAM mechanism
Mechanism remarks	Metallic filaments are thought to be main mechanism evidenced by TEM	Still under development	Still under development					Still under development	
Additional functions	Light emitting diode and memory in same device	NA	NA	NA	Light emitting diode and memory in same device	Environmental friendly	NA	NA	RRAM and WORM
Switching times	1 μ s to 500ns	1 μ s to 5ms	500 ns to 5ms	5ms to s	1ms	10 ms to 1s	100 ns to 1 μ s	NA	5ms
Switching energy	2.5nJ	10 ⁻⁶ J	0.02nJ	0.06mJ	0.002mJ	24J	3.6nJ		0.75mJ

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