SCHOOL OF MATERIALS AND MINERAL RESOURCES ENGINEERING
UNIVERSITI SAINS MALAYSIA

EFFECT OF FULLERENE (C_{60}) IN PECTIN POLYSACCHARIDE THIN FILM FOR RESISTIVE SWITCHING CHARACTERIZATION

by

CHEONG YI HUAN

Supervisor : Prof. Ir. Dr. Cheong Kuan Yew

Dissertation submitted in partial fulfillment
of the requirements for the degree of Bachelor of Engineering with Honours
(Materials Engineering)

Universiti Sains Malaysia

AUGUST 2022

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September 2021

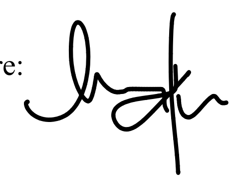
DECLARATION

I hereby declare that I have conducted, completed the research work and written the dissertation entitled 'Thesis Title'. I also declare that it has not been previously submitted for the award of any degree and diploma or other similar title of this for any other examining body or University.

Name of Student: **CHEONG YI HUAN** Signature: 

Date: 11/8/2022

Witness by

Supervisor: PROF. IR. DR. CHEONG KUAN YEW Signature: 

Date: 11/8/2022

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LIST OF ABBREVIATIONS

NVM	Non-Volatile Memory
RRAM	Resistive Random Access Memory
CMOS	Complementary Metal Oxide Semiconductor
C_{60}	Fullerene
ITO	Indium Tin Oxide
HRS	High Resistive State
LRS	Low Resistive State
AFM	Atomic Force Microscopy
SPA	Semiconductor Parameter Analyzer
FTIR	Fourrier Transform Infra-Red
FeRAM	Ferroelectric Random Access Memory
SRAM	Static Random Access Memory
DRAM	Dynamic Random Access Memory
PCM	Phase Change Memory
MRAM	Magnetoresistive Random Access Memory
STT-RAM	Spin-Transfer-Torque Random Access Memory
FeFET	Ferroelectric Field Effect Transistor
FTJ	Ferroelectric Tunnel Junction
NP	Nanoparticle
PVK	Poly(N-vinylcarbazole)
PEDOT	Poly(3,4-ethylenedioxythiophene)
MWCNT	Hybrid nanostructures made of carbon nanotubes
PCL	Polycaprolactone

LIST OF SYMBOLS

Ω/cm	Ohm per centimeter
I	Current
V	Voltage
cm	Centimeter
µm	Micrometer
°C	Degree Celsius
V_{set}	Set voltage
V_{reset}	Reset voltage
mA	Milliampere
wt%	Weight percentage
%	Percentage
g	Gram
Hz	Hertz
s	Second
mN	Millinewton
m	Meter

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ABSTRAK

Sisa elektronik yang berkembang pesat telah menjadi salah satu isu global utama dalam era elektronik. Rintangan pertukaran ialah salah satu teknologi memori yang paling menjanjikan kerana mempunyai ketumpatan storan yang tinggi, struktur ringkas dan penggunaan kuasa yang rendah. Pektin telah diperkenalkan untuk dibuat sebagai lapisan penebat peranti Memori Akses Rawak Resistif (RRAM) yang mempamerkan ciri rintangan yang sangat baik. Walau bagaimanapun, ia tidak mencukupi untuk mengalahkan bahan bukan organik yang konvensional. Ia didapati bahawa fullerene (C_{60}) boleh meningkatkan daya tahan dan kestabilan pengekalan peranti RRAM kerana sifat penerimaan elektronnya. Di sini, kepekatan C_{60} yang berbeza telah diadun dengan pektin untuk menghasilkan peranti RRAM (Au-Pd/pectin-C_{60}/indium tin oksida (ITO)) untuk melihat kesannya. Ujian kebolehbasahan telah dijalankan dengan menggunakan goniometer, kekasaran permukaan diperhatikan dan ditentukan dengan menggunakan Atomic Force Microscopy (AFM), Fourrier Transform Infra-Red (FTIR) spectroscopy pula digunakan untuk menentukan kompaun, dan Semiconductor Parameter Analyzer (SPA) digunakan untuk menentukan sifat elektronik. Penambahan C_{60} ke dalam prekursor pektin telah mengurangkan kebolehbasahan prekursor dan menyebabkan kekasaran permukaan filem. Peranti mempamerkan nisbah ON/OFF yang baik (>10), penambahan C60 mengurangkan nilai V_{set}. Tambahan pula, ia boleh mengurangkan tetingkap memori baca. Oleh itu, kajian ini memberikan perbandingan menyeluruh tentang tingkah laku fizikal dan elektronik peranti RRAM berasaskan pektin selepas penambahan C60 ke dalam filem nipis. Walaupun penambahan C_{60} telah menyebabkan penurunan prestasi peranti RRAM, C_{60} masih memegang janji untuk aplikasi yang berpotensi untuk peranti NVM.

ABSTRACT

The rapidly growing electronic waste had become one of the major global issues in the electronic eras. Resistive switching is one of the most promising memory technologies due to its high storage density, simple structure, and low power consumption. The biocompatible pectin extracted from citrus peel had been introduced to be fabricated as the insulating layer of the Resistive Random Access Memory (RRAM) devices which exhibits excellent resistive switching characteristics. However, it is insufficient to beat the conventional inorganic materials. It is discovered that fullerene (C_{60}) had improved the endurance and retention stability of the RRAM devices due to its electron-accepting nature. Herein, different concentrations of C_{60} were be blended with pectin to fabricate RRAM devices (Au-Pd/pectin-C_{60}/indium tin oxides (ITO)) to see the effects. Wettability test had been conducted by using goniometer to determine the surface tension of pectin-C_{60} liquid precursors and the contact angle of the precursor with ITO surface, surface roughness observed and determined by using the Atomic Force Microscopy (AFM), Fourrier Transform Infra-Red (FTIR) spectroscopy to determine the functional groups and the electronic properties by using Semiconductor Parameter Analyzer (SPA). Addition of C_{60} into the pectin precursors had decreased the wettability of the precursors and caused the thin films surface roughness to increase. The devices exhibit good ON/OFF ratio (>10), the addition of C_{60} reduces the V_{set} values, lower energy is required to operate the devices. Furthermore, it had reduced the read memory window. This study thus provides a comprehensive comparison of the physical and electronic behavior of the pectin-based RRAM devices after the addition of C_{60} into the thin film. Although C_{60} had caused the downgrade of RRAM devices, it still holds promise for potential applications for NVM devices.

CHAPTER 1:

INTRODUCTION

1.1 GENERAL INTRODUCTION

In recent years, the demand of artificial intelligence had led to the emerging of Non-Volatile Memories (NVM) in the nanoelectronics field (Plonus, 2020). The NVM is a memory that retains its values to prevent memory loss of data when the power is disconnected. It is used as a cache to hold the instructions by the computer. There are several types of NVMs such as the flash memory, Ferroelectric Random Access Memory (FeRAM), Phase Change Memory (PCM), Magnetoresistive Random Access Memory (MRAM), Spin-Transfer-Torque Random Access Memory (STT-RAM), ferroelectric memory, and Resistive Random Access Memory (RRAM).

One of the NVM widely studied is the Resistive Memory (RRAM) for its interesting properties such as its good compatibility with the Complementary Metal Oxide Semiconductor (CMOS) technologies, having high storage density, low power consumption, simple structure and a strong cost competitiveness (Akinaga & Shima, 2012; Y. Li et al., 2020). ReRAM consists of the Metal/Oxide/Metal (MOM) structure which is the sandwiched of functional-oxide layer (acting as switching layer) by two metal electrodes (top electrode and bottom electrode), this can form as an array of memory in (Akinaga & Shima, 2012).

Normally, the memory device can switch between the high resistance state (HRS, “OFF” state) and low resistance state (LRS, “ON” state) when voltage is applied beyond set (Vset) or reset (Vreset). The HRS and LRS are equivalent to "0" and "1" binary conversion respectively. This concept allows the increase of storage capacity within one memory cell as the multibit storage can be expected in more than 2 resistance states of a material. The former cannot be erased, when a certain voltage sweep is applied, it will switch from HRS to LRS which the LRS will not change the memory but can only be reprogrammed under the opposite voltage pulse (Akinaga & Shima, 2012).

However, the functional-oxide layers are normally made of inorganic materials which take a very long period to degrade. While the disposal of electronic gadgets and components including the memory components increases extensively due to the human behaviour of frequently changing new devices to follow the latest trend instead of the malfunction of the electronic devices. The increase of the disposal of memory components while having long degradation period will eventually create a very high number of electronic wastes, this had become one of the major global issues in this era (Cheong et al., 2021).

To overcome this global issue, there is an urgent for the current RRAM devices to develop a 'green' electronic device, bio-organic materials that originate from plants, viruses, non-living, living or once-living things are introduced to replace the engineering materials currently using for resistive switching memory applications. The bio-organic materials are expected to be degradable easily, decomposable, abundant and are safe for human use (Cheong et al., 2021). Under the bio-organic materials, there are several categories which are polysaccharide, polypeptide, virus, and plant extract. In the recent studies also, some biomaterials such as pectin, chitosan and protein had been explored as an attractive building block for resistive switching memory application (J. Xu et al., 2019). In this study, pectin polysaccharide from the polysaccharide group is the focus for the project, the advantages of this material are such as its good solubility and fast metal ions transport (J. Xu et al., 2019).

Pectin is a complex polysaccharide which consists mainly of methoxy esterified α, D-1, 4-galacturonic acid units. It can be classified into high methoxy pectin or low methoxy pectin depending on the speed of formation of gel (J. Xu et al., 2019). Pectin consists of the functional groups such as O-H, C-O-C and C-O-H, when it is sandwiched by metal electrodes, metal ions can migrate through it by interacting with these functional groups (Cheong et al., 2021; J. Xu et al., 2019). This indicates that pectin enables the migration of ions and is applicable for developing the resistive switching memory as it can act as an ionic conductor. However, the study about pectin polysaccharide for this application is still very limited and is needed to be studied further (J. Xu et al., 2019).

Meanwhile, several studies had revealed that the blending of organic molecules with inorganic compounds can be useful for the resistive switching memory applications. Fullerene (C_{60}) is proposed to be the electron trapping sites as a floating gate because of its electron-accepting nature and had improved the endurance and retention stability, it is efficient as a blending component for resistive switching application (Aneesh & Predeep, 2013; Y. Li et al., 2020). It acts as the electronic conductivity type organic semiconductor (Dolzhenko et al., 2019). Fullerene C_{60} is a nanostructured allotrope of carbon in ball shape structure which contains 60 carbons and consists of five-membered rings and six-membered rings. It owns a unique physical and chemical properties which allows it to have high resistivity which can reach to about 10^8 Ωcm depends on the degree of crystallinity and acts as a charge storage medium (Dolzhenko et al., 2019). The degree of crystallinity increases, the conductivity increases (Dolzhenko et al., 2019).

1.2 PROBLEM STATEMENT

The memory devices play a very important role in the electronics world due to the continuous emerging of electronics and technologies in this era which requires high storage. Non-Volatile Memory (NVM) became more and more important to retain the memory for long term even if the power supply is disconnected. One of the widely studied NVMs is the Resistive Memory due to its interesting properties such as high storage density and low power consumption. By considering the global concern of electronic wastes, organic materials had been reported to emerge as a potential candidate in electronic and optoelectronic applications such as the memory devices. Generally, organic memory devices normally consist of organic/nanoparticles/organic sandwich structures. Pectin polysaccharide is introduced as a bio-organic material for the resistive switching memory application. There are also some studies revealing that the blending or organic molecules with inorganic compounds can be useful for this application. Fullerene (C_{60}) was proposed to be the floating gate to improve the endurance and retention stability of this application. Recently, there are several investigations that had been done to investigate the effects in organic materials fabricated utilizing C_{60} fullerene molecules dispersed in bio-organic thin film such as polycaprolactone, poly-vinyl-phenol, poly(N-vinylcarbazole), poly(3,4-ethylenedioxythiophene) etc. However, there are still no studies about the effect of C_{60}

in pectin polysaccharide in resistive switching memory application. Thus, few characterization methods need to be conducted to understand the effect of C_{60} concentration towards the resistive switching memory properties when blended into pectin polysaccharide.

1.3 RESEARCH OBJECTIVES

This research is aimed to study the effect of C_{60} concentration in pectin thin film for resistive switching characterization. Research objectives of this project are:

- to characterize and compare the resistive switching properties of pectin thin film with different concentration of C_{60}.
- to determine the physical properties of the pectin precursor and thin films when blended with different C_{60} concentrations.

1.4 SCOPE OF RESEARCH

In this study, different concentrations of fullerene (C_{60}) had mixed into pectin thin film, the Au-Pd/pectin-C_{60}/ITO device had been fabricated out too to understand the effect of C_{60} in terms of the physical properties of the thin film and the resistive switching properties of the bio-organic based RRAM device.

The wettability of the pectin-C_{60} precursors on the ITO surface was determined using the goniometer by determining the surface tension of the precursors and the contact angles of the precursors on the ITO surface. While the functional groups of the as-received powders (both pectin and C_{60}), the pectin-C_{60} precursor, the thin film and the device were analyzed by using the Fourrier Transform Infrared (FTIR) Spectroscopy to determine the purity of the as-received powders and understand the effects of the functional groups that can affect the physical properties of the thin film and electrical properties of the devices. Furthermore, the surface roughness of the thin films was determined by using the Atomic Force Microscope (AFM). While the resistive switching performance such as the V_{set}, V_{reset}, read memory window and the ON/OFF ratio of the device were determined from the I-V characteristics graph and Log I-V graph analyzed by the Semiconductor Parameter Analyzer (SPA).

CHAPTER 2:

LITERATURE REVIEW

2.1 INTRODUCTION

Prior to the study about the effect of C_{60} concentration in pectin thin film for the RRAM applications, it is crucial to understand the applications and functions of each element and how they had contributed to the RRAM industry. In the literature review section, the non-volatile memories (NVM) and RRAM devices are introduced to understand how they had contributed to the memory devices. In addition, the resistive switching mechanism were also discussed to understand how bio-organic thin film can aid in the resistive switching memory applications. Furthermore, the contribution of bio-organic thin films had also discussed below as well as the role of C_{60} as a promising candidate for the RRAM applications.

2.2 NON-VOLATILE MEMORIES (NVM)

The NVM is the secondary memory that retains its values to prevent memory loss of data when the power is disconnected. NVMs covers ferroelectric random-access-memory (FeRAM), phase change memory (PCM), magnetic random-access-memory (MRAM) and spin-transfer-torque RAM (STTRAM) (A. Chen, 2016). It is normally based on the floating gate configuration, which also relates to two-terminal switching elements which can contribute to high-density memory architectures, such as the crossbar arrays. Among the NVMs, designed Flash memories such as NOR and NAND Flash memory is considered as the most important products that can be electrically erased and reprogrammed and are the baseline of NVMs due to some of their properties such as the high operation speed of NOR and high density for large data storage applications of NAND.(Meena et al., 2014) The materials used for NVM including ferroelectrics dielectrics, metal oxides, ferromagnetic metals, chalcogenides, carbon materials, etc (A. Chen, 2016). The NVM applications have emerged in various industries such as transportation, enterprise storage, mobile phones, smart cards and mass storage (Meena et al., 2014).

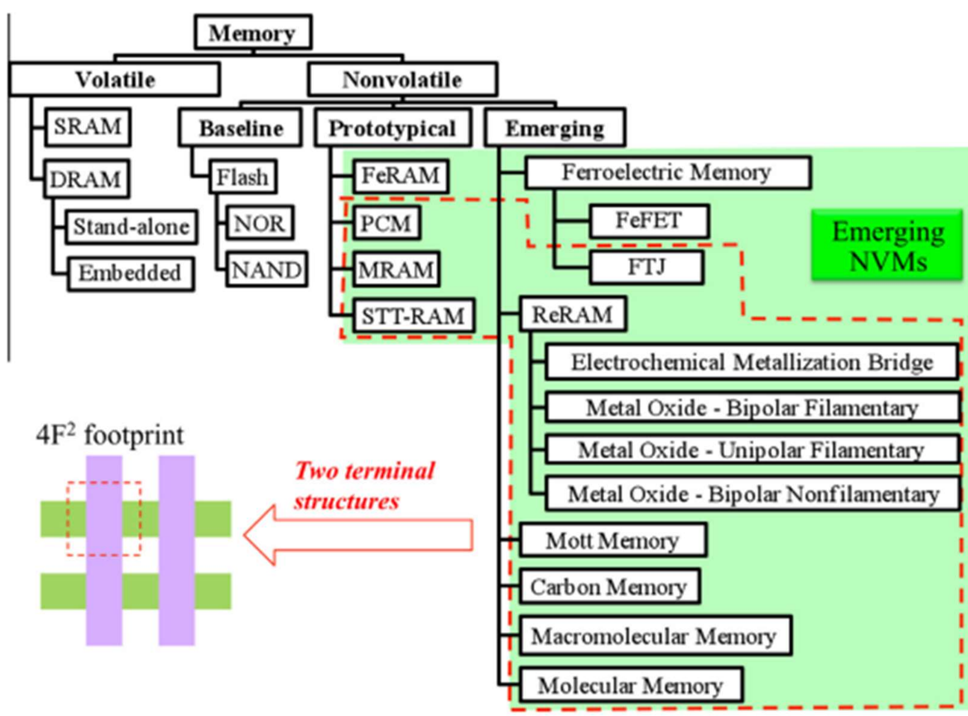

Figure 2.1: The NVMs that have simple two terminal structures (A. Chen, 2016).

SRAM: Static Random Access Memory

DRAM: Dynamic Random Access Memory

FeRAM: Ferroelectric Random Access Memory

PCM: Phase Change Memory

MRAM: Magnetoresistive Random Access Memory

STT-RAM: Spin-Transfer-Torque Random Access Memory

FeFET: Ferroelectric Field Effect Transistor

FTJ: Ferroelectric Tunnel Junction

2.3 RESISTIVE RANDOM ACCESS MEMORY (RRAM)

RRAM is one of the newly and emerging memory devices that has a different read/write/retention/endurance characteristic compared to the conventional SRAM, DRAM, and Flash. It is a disruptive technology that can revolutionize the products performance in various areas including the consumer electronics, personal computers, automotive, medical, military and space industries (Meena et al., 2014). The RRAM device is attractive due to its compatibility with the conventional semiconductor processes and has the potential of being a universal memory technology, (Xu et al. 2019) have also mentioned that RRAM is considered to be the most promising because it can operate faster than perfect chalcogenide random-access-memory (PCRAM) while having a simpler and smaller cell structure than magnetic memories such as the MRAM or spin-transfer torque random-access-memory (STT-MRAM) (Meena et al., 2014)(J. Xu et al., 2019). It is potentially cheap and simple that it could compete across the whole digital memories' spectrum (Meena et al., 2014).

The RRAM structure is basically a simple, two-terminal metal-insulator-metal (MIM) device which is an insulating layer (functional oxide layer) sandwiched by two metal electrodes, top electrode (TE) and bottom electrode (BE).(Akinaga & Shima, 2012; Meena et al., 2014) The MIM structure of RRAM can form an array of memory.

Figure 2.2 below shows the schematic diagram of the unit cell of RRAM and an array of crossbar structure of the memory devices.

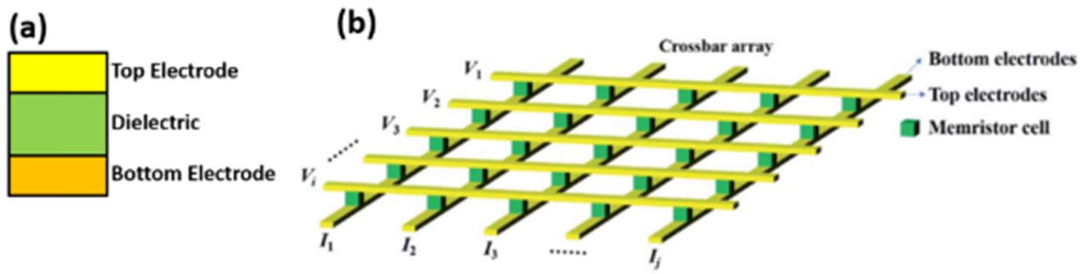

Figure 2.2: Schematic diagram of (a) a unit cell of RRAM and (b) an array of crossbar structure with voltages (V) and current (I) applied and measured (Cheong et al., 2021).

2.3.1 The Technical Glossaries of RRAM

RRAM can exist in two distinct conductivity states and can switch between at least two distinct resistance states call the high resistance state (HRS, "OFF") and low resistance state (LRS, "ON"), equivalent to "0" and "1" respectively, by applying voltages to the electrodes. It is revealed that when the voltage applied increases from 0 V to a critical point call the set voltage (V_{set}), the current level will increase from HRS to LRS, this process is called the SET process; In vice versa, when voltage applied in another direction and reaches the reset voltage (V_{reset}), the current level will decrease from LRS back to HRS, this is called as the RESET process.

The SET and RESET process will be carried out repeatedly by sweeping the gate voltage between LRS and HRS to show a non-volatile resistance change (Akinaga & Shima, 2012; Meena et al., 2014). It is important to take note that, the sample initially will be in the high initial HRS state, thus for the first set of the SET process, a higher voltage is needed to apply than that of the SET process to soft breakdown the MIM structure, this process is called as the 'Electroforming process', or simply the 'Forming process' (Akinaga & Shima, 2012; Prakash et al., 2013). The SET and RESET process are normally presented in the I-V characteristic curve as shown in Figure 2.3.

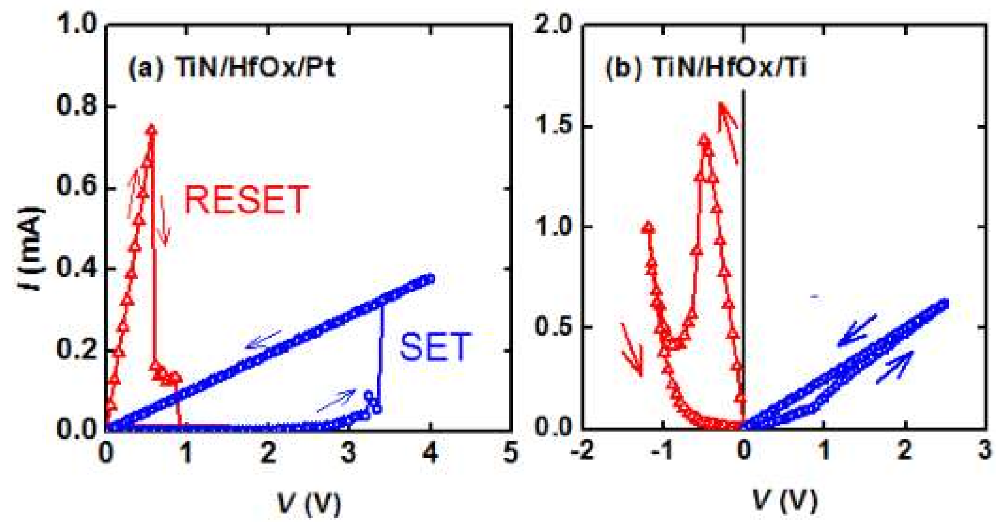

Figure 2.3: I-V characteristics of two operation modes of RRAM. (a) Unipolar and (b) bipolar modes. The arrows represent the sweep direction, red lines represent RESET while blue lines represent SET processes (Akinaga & Shima, 2012).

The resistive switching effect of the RRAM operation can be classified according to the I-V curve too. As shown by the I-V curves at Figure 2.3, the switching modes of the RRAM devices can be classified as unipolar (nonpolar) and bipolar (Prakash et al., 2013). There are several types of resistive switching effect, which is the memory type and the threshold type. The memory type of the resistive switching effect is normally utilized by the RRAM. Figure 2.4 shows the example of resistance switching effects observed in the Pt/CoO/Pt MIM structure. In the I-V curve, there exists three processes which is the Forming process, RESET process and SET process (Akinaga & Shima, 2012).

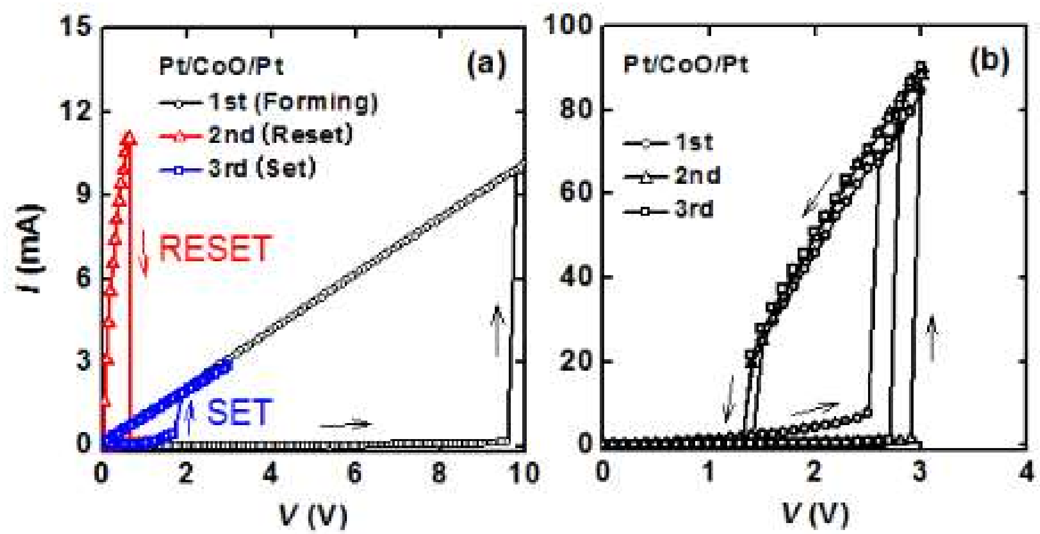

Figure 2.4: Resistance switching of Pt/CoO/Pt MIM structure (Akinaga & Shima, 2012).

2.3.2 Read Memory Window

The read memory window is the voltage range of voltages between the V_{set} and V_{reset}. A wide read memory window is desired in RRAM devices to permit more flexibility in designing the probe circuitry, the states of the devices will be much stable and will not be altered easily with a wider range of voltage provide to the devices to determine the status of the RRAM devices (Tayeb et al., 2021). However, it is crucial to control the read memory window too, read memory window which is too wide will need more power to operate the memory devices which is undesirable as it needs to consume higher energy and will increase the cost (Tayeb et al., 2021).

2.3.3 ON/OFF Ratio

The ON/OFF ratio of a memory device is the ratio of ON-state current and OFF-state current without voltage applied on the gate terminal. It indicates the current leakage of the devices, such as high ON/OFF ratio indicates that the device has low leakage current which will cause read errors. Higher ON/OFF ratio is required in memory devices to obtain sufficient ON/OFF window to store data in longer period, although a ratio of 1.2 is sufficient, it still need to be more than 10 the evade the errors effectively in differentiating the resistance states (Tayeb et al., 2021). Prior to determine the ON/OFF ration of the devices, the read voltage (V_{read}) needs to be determined, the V_{read} is the voltage to read as input, normally it is determined between 0.01 V to 0.7 V (Tayeb et al., 2021).

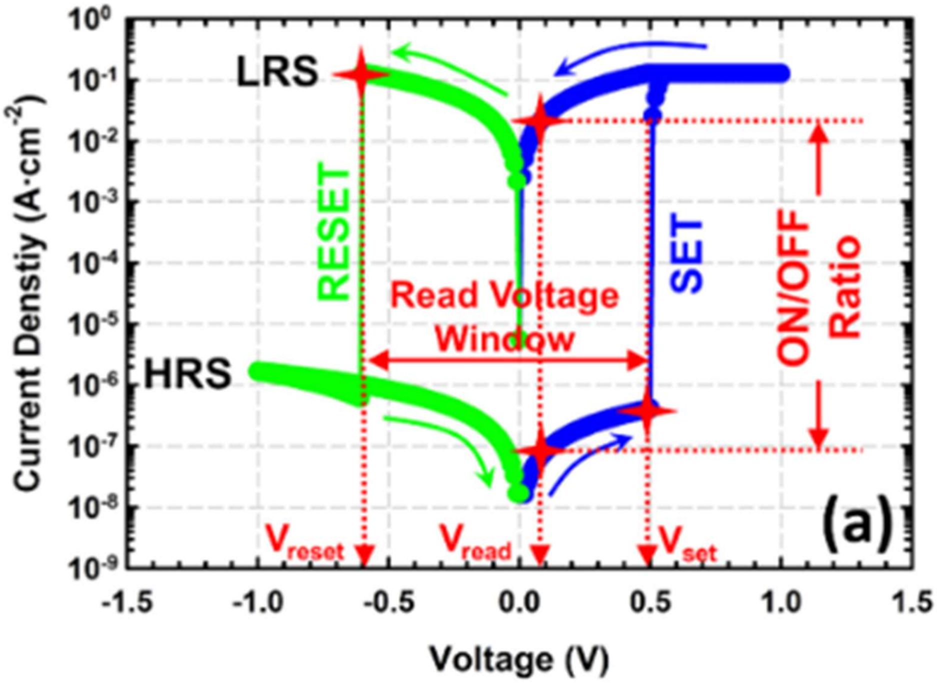

Figure 2.5: A typical current density and voltage plot of resistive switching RAM which shows the high and low resistive states, labeled as HRS and LRS respectively. The graph also presented the Vset, Vreset, Vread, read voltage window and the ON/OFF ratio (Cheong et. al., 2021).

2.4 THE MATERIALS OF INSULATING FILM IN RRAM DEVICES

The materials used for NVM including ferroelectrics dielectrics, metal oxides, ferromagnetic metals, chalcogenides and carbon materials (A. Chen, 2016). While it is reported that the materials used for RRAM needs to be able to switch between two or more resistance states to achieve the resistive switching process.(Meena et al., 2014) There are many companies investing in metal oxides nanolayers switched by voltage pulse. Researchers think that electric fields applied onto the device will produce a conducting filament through the insulating oxide layer, created the so-called "filament model" (Akinaga & Shima, 2012; Meena et al., 2014). The reviews about resistance switching had started since 1970 (Akinaga & Shima, 2012). The resistance switching phenomena have been observed in many types of oxide materials and an excellent resistance switching had been reported in binary metal oxides, and a practical development had been done on the usage of so-called high-k oxides, such as HfO_x (Akinaga & Shima, 2012).

2.4.1 Bio-Organic Materials for Resistive Switching RRAM

However, a "green" electronic device, by using bio-organic materials started to gain attention in the electronics world for resistive switching applications due to one of the major global issues in this era, which is the increasing of electronic wastes in the Earth. There is an urge to replace the engineering materials currently using to bio-organic materials that originate from plants, viruses, non-living, living or once-living things to produce a biocompatible and environmentally friendly electronics (Cheong et al., 2021)(Sun et al., 2016). Table 2.1 is the list of bio-organic materials reported as active thin film for resistive switching RRAM. There are several categories of bio-organic material such as polypeptides, polysaccharides, plant extract and virus (Cheong et al., 2021). The molecular structures of bio-organic materials mainly contain 3 elements which are the carbon (C), hydrogen (H), and oxygen (O), while some also contains nitrogen (N), and some trace elements such as iron (Fe), zinc (Zn), copper (Cu), manganese (Mn), etc. Due to the difference of elements contain in the molecular structure of the bio-organic materials, different materials will have different resistive switching effect (Sun et al., 2020).

One of the advantages of bio-organic materials as the thin film of RRAM is they can demonstrate their resistive switching characteristics even without going through their forming stage while still having a reasonable figure of merit which is required for non-volatile memory application (Cheong et al., 2021). These bio-organic materials are also expected to be able to naturally degrade within a specific time without causing environmental degradation (Sun et al., 2020). However, it is still reported that, by comparing the RRAM devices fabricated with bio-organic materials and inorganic materials, inorganic materials are better in terms of the switching behaviour, energy consumption and retention time (Shen et al., 2020).

Table 2.1: List of bio-organic materials used for the thin film of RRAM devices.

Category	Bio-Organic Material	Electrodes		Mode of Switching	ON/OFF ratio (10^n)	Year	Reference
		Top	Bottom				
Polypeptide	Ferritin (silk protein/ Fe NP)	Ag	Pt	Bipolar	2	2011	(Ko et al., 2011)
	Ferritin (E. coli protein/ Fe ion)	Au	Au	Bipolar	1	2014	(Meng et al., 2014)
	Silk fibroin	Al	ITO	Bipolar	1	2012	(Hota et al., 2012)
	Fibroin: Au NP	Al	ITO	Bipolar	4	2013	(Gogurla et al., 2013)
	Fibroin	Ag	Au	Bipolar	7	2013	(Mukherjee et al., 2013)
	Fibroin	Ag	Au	Bipolar	7	2015	(H. Wang et al., 2015)
	Fibroin	Ag	Au	Bipolar	5	2016	(Sun et al., 2016)

Silk Fibroin	Mg	Mg	Bipolar	2	2016	(H. Wang, Zhu, Ma, et al., 2016)
Silk Fibroin	Ag	Au	Bipolar	1	2016	(H. Wang, Zhu, Wang, et al., 2016)
Silk-worm Hemolymph Protein	Al	ITO	Bipolar	3	2017	(L. Wang & Wen, 2017)
Silkworm Haemolymph	Al	ITO	Bipolar	5	2021	(L. Wang et al., 2021)
Silk Fibroin	Au	Pt	Bipolar	1	2017	(Yong et al., 2017)
Silk (Bombyx Mori Body Fluid)	Al	ITO	Bipolar	4	2019	(L. Wang & Wen, 2019)
Enzyme	Ag	Pt	Bipolar	2	2012	(Baek et al., 2012)
Sericin	Ag	Au	Bipolar	6	2013	(H. Wang et al., 2013)
Gelatin	Mg	W	Bipolar/ Unipolar	2	2014	(Chang & Wang, 2014)
Gelatin: Al ion	ITO	ITO	Bipolar	4	2015	(Chang & Wang, 2015)

Gelatin	Al	ITO	Bipolar	4	2016	(Ge et al., 2018)
Gelatin: Ag ion	Al	ITO	Bipolar	5	2018	(Chang et al., 2018)
Gelatin: Co ion	Al	ITO	Bipolar	7	2018	(C. J. Lee et al., 2017)
Gelatin: Fe ion	Al	Al	Bipolar	5	2019	(Chang et al., 2019)
DNA or DNA: Ag ion	Au	Au	Bipolar	1	2015	(Hung et al., 2015)
DNA: Cetyltrimethylammonium: Ag NP	Au	Au	Bipolar	1	2015	(Hung et al., 2015)
Al NP-DNA-CuO NP	Au	Au	Bipolar	1	2015	(Sun et al., 2015)
DNA (salmon): CTMA	Ag, Cu, Al	ITO	Bipolar	3	2018	(Jeng et al., 2018)
DNA (salmon): Cu ion	Pt	ITO	Bipolar	3	2019	(Abbas et al., 2019)
DNA	PEDOT:PSS	PEDOT:P	Bipolar	4	2020	(Lam et al., 2020)

			SS				
	Albumen	Al	ITO	Bipolar	3	2015	(Y. C. Chen et al., 2015)
	Albumen	Mg	W	Bipolar	3	2016	(He et al., 2016)
	Albumen: PVP-Au NP	Al	Pt	Bipolar	3	2018	(S. J. Kim et al., 2018)
	Azurin	Al	ITO	Bipolar	1	2017	(Moudgil et al., 2017)
	Melanin	Ag	Stainless Steel	Bipolar	1	2018	(Gurme et al., 2018)
	Eumelanin	Ag	SS	Bipolar	3	2016	(Gurme et al., 2018)
	Collagen	Ag	ITO	Bipolar	-	2019	(di Mauro et al., 2016)
	Keratin	Ag	ITO	Bipolar	3	2019	(Zeng et al., 2019)
Polysaccharide	Cellulose Nanofiber Paper: Ag NP	Ag	Pt	Bipolar	6	2014	(Nagashima et al., 2014)
	Nanocellulose	Ag	ITO	Bipolar	7	2016	(Celano et al., 2016)
	Cellulose Fiber	Ag	Al	Bipolar	1	2018	(Rananavare et al., 2018)
	Nitrocellulose	Au/Al	P-Si	Bipolar	2	2020	(J. H. Lee et al., 2020)

Bio-cellulose	Al	Ag	Bipolar	4	2021	(Hosseini & Lee, 2015)
Chitosan: Ag ion	Mg	Mg	Bipolar	2	2015	(Huang et al., 2021)
Chitosan	-	-	Bipolar	2	2018	(Cifarelli et al., 2018)
Chitosan	Ag, Al	FTO	Bipolar	-	2019	(Tran et al., 2019)
Chitosan	Ti	Pt	Bipolar	1	2021	(Min & Cho, 2021)
Starch/starch + Chitosan	Au	ITO	Bipolar	3	2016	(Raeis-Hosseini & Lee, 2016)
Chitosan- GO	Al	FTO	Bipolar	2	2021	(do Ho et al., 2021)
Lignin	Au	ITO	Bipolar	3	2017	(Y. Park & Lee, 2017)
Pectin	Ag	FTO	Bipolar	3	2017	(Sun et al., 2017)
Pectin	Ag	ITO	Bipolar	2	2019	(J. Xu et al., 2019)
Pectin	Ag	ITO	Bipolar	4	2020	(Arshad et al., 2021)
Aloe Polysaccharide	Al, Ag, Mg, Cu, Au	ITO	Bipolar	6	2018	(Lim & Cheong, 2018)
Aloe Polysaccharide	Al, Ag, Mg, Cu	Ti	Bipolar/ Unipolar	-	2019	(Lim et al., 2019)

Banana Peel	Ag	FTO	Bipolar	1	2018	(Zheng, Sun, Mao, et al., 2018)
Orange Peel	Ag	ITO	Bipolar	3	2018	(X. Wang et al., 2018)
Citrus	Al	ITO	Bipolar	5	2021	(Lin et al., 2021)
Dead Leaves	Ag	Ti	Bipolar	1	2018	(Sun et al., 2018)
Pristine Leaves	W	W	Bipolar	-	2021	(Adhikari et al., 2021)
Glucose	Al	Si	Bipolar	3	2018	(S. P. Park et al., 2018)
κ-Carrageenan: CM	Ag	Pt	Bipolar	3	2018	(M. K. Kim & Lee, 2018)
Mushroom Extract	Ag	Al, Cu, Ag, Ti	Bipolar	1	2018	(Zheng, Sun, Chen, et al., 2018)
Lotus Leaves	Ag	ITO	Bipolar	1	2019	(Qi et al., 2019)
Lotus Roots	Ag	Cu	Bipolar	1	2020	(T. Li et al., 2020)
Sweet Potato Peels	Ag	FTO	Bipolar	-	2020	(Zhu et al., 2020)
Honey	Cu	Cu_xO	Bipolar	7	2020	(Sivkov et al., 2020)
Honey	Ag	ITO	Bipolar	-	2022	(Sueoka et al., 2022)

	Lophatherum Gracile Brongn.: Ag	Ag	FTO	Bipolar	1	2020	(Y. Xu et al., 2020)
	Polymannose	Ag	ITO	Bipolar	5	2021	(Tayeb et al., 2021)
	Fructose	Al, Ag		Bipolar	5 - 6	2021	(Y. Xing et al., 2021)
Plant-Extract	Aloe Vera	Al	ITO	Bipolar	3	2015	(Lim & Cheong, 2015)
	Garlic	Ag	FTO	Bipolar	1	2019	(Mao et al., 2019)
Virus	Tobacco Mosaic Virus: Pt NP	Al	Al	Bipolar	3	2006	(Tseng et al., 2006)

2.4.2 Pectin in Resistive Switching

Pectin is structurally and functionally the most complex polysaccharide that originates from the cell walls of fiber plants. In its chemical structure, it consists of mainly esterified D-galacturonic acid which resides in an α-(1, 4) chain. The acid groups in the structure are also mostly esterified with methoxy ($R-O-CH_3$) groups. Sometimes, there are acetyl groups present on the free hydroxy groups too, or rhamnose groups present on the main chain which can disrupt the chain helix formation. The variability of the pectin structure makes it to be the most complex polysaccharides in plant cell walls (Medina & Dzalto, 2017).

As shown in Table 2.1 above, there are few researches had been done by Sun et al, Xu et al, and Arshad et al regarding the reliability of pectin as resistive thin film. Pectin was first introduced as the insulating layer of the Ag/Pectin/FTO RRAM device by Sun et al. in the year of 2017, it was revealed that the Ag/Pectin/FTO device has a high-performance resistive switching memory behaviour with large resistance memory window. Furthermore, pectin as the insulating film makes the device has highly stable resistive switching effects and exhibit minimal degradation, it is mentioned that pectin has a promising application for NVM applications (Sun et al., 2017).

Xu et al. (2019) has also introduced the uses of natural pectin from natural orange peel to fabricate Ag/pectin/ITO device. It exhibits excellent resistive switching characteristics such as low operating voltages, fast switching speed, long retention time and multilevel resistive switching behaviours. Furthermore, it can last for 10000 bending cycles