

© Copyright by Ramasahayam Mithun Kumar 2014
All Rights Reserved

Enhancement of EPIR Switching Characteristics of PCMO RRAM Using Oxygen Deficient Al₂O_x Diffusion Barrier

A Thesis

Presented to

the Faculty of the Department of Electrical and Computer Engineering

University of Houston

In Partial Fulfillment

of the Requirements for the Degree

Master of Science

in Electrical Engineering

by

Ramasahayam Mithun Kumar

May 2014

Enhancement of EPIR Switching Characteristics of PCMO RRAM Using Oxygen Deficient Al₂O_x Diffusion Barrier

Ramasahayam Mithun Kumar

Approved:

Chair of the Committee
Dr. Alex Ignatiev, Professor,
Physics, Chemistry and
Electrical and Computer Engineering

Committee Members:

Dr. Rabi Ebrahim, Senior Research
Scientist, Physics

Dr. Wanda Zagazdon-Wosik,
Associate Professor, Electrical and
Computer Engineering

Dr. Stanko R. Brankovic, Associate
Professor, Electrical and Computer
Engineering

Dr. Suresh Khator, Associate Dean,
Cullen College of Engineering

ACKNOWLEDGEMENTS

I would like to dedicate this work to my beloved family for their constant encouragement, support, and unconditional love. I am deeply indebted to them.

I am grateful to my advisor, Dr. Alex Ignatiev, for giving me an opportunity to pursue Master's thesis under his esteemed guidance. I would like to thank him for providing me the opportunity to be a part of the Center for Advanced materials.

I would like to thank my supervisor, Dr. Rabi Ebrahim, without whom this work would not be possible. I would like to extend my deepest gratitude to him for his invaluable training, suggestions, support and efforts in making this thesis possible.

My special thanks to Dr. Stanko Brankovic and Dr. Wanda Wosik for accepting the invitation to serve on my thesis committee.

I would like to extend special gratitude to Dr. Ali Zomorrodian for helping me in carrying out XRD analysis and giving valuable suggestions to improve my research activity. I am thankful to Yessica Contreas and all other members of Center for Advanced Materials.

**Enhancement of EPIR Switching Characteristics of
PCMO RRAM Using Oxygen Deficient Al_2O_x Diffusion
Barrier**

An Abstract

Of a Thesis

Presented to

the faculty of the Department of Electrical and Computer Engineering

University of Houston

In Partial Fulfillment

of the Requirements for the Degree

Master of Science

in Electrical Engineering

by

Ramasahayam Mithun Kumar

May 2014

Abstract

Resistive random access memory has gained lots of interest in the last decade as a promising replacement for non-volatile memory. Device retention stability and electric pulse induced resistance switching (EPIR) ratio (percent of change in resistance between the low and high resistance states) are very important characteristics of any resistive memory devices.

$\text{Pr}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ (PCMO) is one of the most promising materials which exhibit EPIR switching, however it suffers some short comings as low retention stability and low EPIR ratio. This work investigated the effect of oxygen ion/vacancy buffer layer of Al_2O_x in metal/buffer layer/PCMO/Metal heterostructure prepared by RF sputtering in Ar only and Ar: O_2 atmosphere. The diffusion barrier of the same is integrated into $\text{Pr}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ (PCMO) to study the resistance switching and retention properties of this heterostructure. The internal Al_2O_x barrier is placed between the “bulk” PCMO region of the sample and a top PCMO active interface region.

The Al_2O_x layer is believed to reduce/prevent change in the ion/vacancy concentration in the interface region after a certain concentration is set by the application of a short electric pulse, and also enhances the EPIR switching ratio. The switching performance of the buffer layer heterostructure has indicated that the buffer layer combined with top 10nm is active region in resistance switching. This work also addressed a model for the enhancement of the switching.

TABLE OF CONTENTS

ACKNOWLEDGMENTS.....	iv
ABSTRACT.....	vi
TABLE OF CONTENTS.....	vii
LIST OF FIGURES.....	x
LIST OF TABLES.....	xiv
Chapter 1: Introduction.....	1
1.1 Non-volatile memory technologies.....	1
1.2 Current technologies.....	2
1.3 Emerging technologies.....	3
1.4 Resistive Random Access Memory (RRAM).....	4
1.4.1 Types of resistance switching in RRAM.....	5
1.4.2 Materials exhibiting EPIR switching.....	6
1.5 RRAM as potential non-volatile memory.....	7
1.6 EPIR switching mechanisms observed in RRAM.....	10
1.6.1 Filamentary model.....	10
1.6.2 Oxygen vacancy model.....	11
1.7 Outline of the thesis	11
Chapter 2: $\text{Pr}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ (PCMO) as a Potential Material in Redox RRAM.....	15
2.1 Composition of PCMO.....	15
2.2 Physical structure of PCMO.....	16
2.3 Electronic structure of PCMO.....	17
2.4 Magnetic properties of PCMO.....	18

2.5	Electric conduction in PCMO.....	19
2.6	Electric pulse induced resistance switching in PCMO.....	21
2.7	Oxygen vacancy migration in PCMO.....	23
Chapter 3: Experimental Procedures and Thin Film Characterization Techniques		
3.1	Film growth techniques.....	26
3.1.1	Radio Frequency magnetron sputtering.....	26
3.2	Characterization Techniques.....	29
3.2.1	Scanning Electron Microscope (SEM) characterization.....	29
3.2.2	X-Ray Diffraction (XRD) analysis.....	31
Chapter 4: Experimental Procedure.....		
4.1	Deposition process of Al ₂ O _x and PCMO thin films.....	34
4.2	Electrical hysteresis and EPIR switching measurement system.....	36
4.2.1	Procedure of sample testing.....	37
4.3	I-V measurement system.....	38
Chapter 5: Results and Discussion.....		
5.1	Film thickness and surface analysis of fabricated samples.....	39
5.2	Crystalline structure analysis of fabricated samples.....	40
5.3	EPIR switching in M/PCMO/M stack	41
5.4	Investigation of Resistance Switching of PCMO RRAM with Al ₂ O _x buffer layer.....	44
5.4.1	EPIR Switching in 2.5nmAl ₂ O _x /420nmPCMO Samples.....	44
5.4.1.1	Regular Switching in 2.5nmAl ₂ O _x /420nmPCMO.....	45
5.4.1.2	Reverse switching in 2.5nmAl ₂ O _x /420nmPCMO.....	49

5.4.2 Effect of Al ₂ O _x thickness in switching and Retention Al ₂ O _x /PCMO/Pt.....	53
5.4.2.1 Regular switching observed in 5nm, 7.5nm and 10nmAl ₂ O _x /PCMO.....	53
5.4.2.2 Reverse switching observed in 5nm, 7.5nm and 10nm Al ₂ O _x /PCMO and its retention.....	60
5.5 Investigation of Resistance Switching in PCMO/Al ₂ O _x /PCMO/Pt.....	70
5.5.1 Regular Switching in 50nmPCMO/2.5nmAl ₂ O _x /PCMO sample.....	70
5.5.2 Effect of Al ₂ O _x thickness in switching & Retention of PCMO/Al ₂ O _x /PCMO/Pt.....	74
Chapter 6: Summary and Conclusions.....	83
REFERENCES.....	85

LIST OF FIGURES

Figure 1.1: Classification of current and emerging memories

Figure 1.2: Two terminal RRAM device

Figure 1.3: I-V characteristics of a) uni-polar switching b) bi-polar switching

Figure 1.4: a) Regular Switching in CuO_x b) Reverse switching in CuO_x

Figure 2.1: Viable materials in ABO_3 structure

Figure 2.2: Cubic perovskite unit cell. Blue spheres depict the A cations where yellow spheres depict the B cations, and red spheres depict oxygen anions forming an octahedral.

Figure 2.3: Lattice structures of PrMnO_3 and CaMnO_3

Figure 2.4: Energy level diagram for Mn in PCMO

Figure 2.5: Phase diagram showing transition temperature vs concentration

Figure 2.6: Double exchange process

Figure 2.7: Switching in PCMO under 18v and 100ns pulse

Figure 2.8: EPIR ratio loss in PCMO/Pt thin film samples for large numbers of pulses at room temperature and zero magnetic field 51v pulse for 108ns

Figure 2.9: Ion mobility in PCMO for a motion enthalpy of 1ev as a function of temperature and applied electric field

Figure 3.1: Components of an RF sputter system

Figure 3.2: JEOL JSM-5410 Scanning Electron Microscope

Figure 3.3: Bragg's diffraction

Figure 4.1: a) W/PCMO/Pt/TiN/ SiO_2 /Si

b) W/ Al_2O_x /PCMO/Pt/TiN/ SiO_2 /Si

c) W/PCMO/ Al_2O_x /PCMO/Pt/TiN/ SiO_2 /Si

Figure 4.2: RF magnetron sputtering chambers

Figure.4.3: RF sputtering plasma during PCMO deposition

Figure.4.4: Overview of custom made EPIR measurement system

Figure.4.5: I-V measurement system

Figure 5.1: SEM cross-section of $\text{Al}_2\text{O}_3/\text{Si}$

Figure 5.2: a) 400nmPCMO/Pt

b) 10nm Al_2O_3 /400nmPCMO/Pt

c) 50nmPCMO/ 10nm Al_2O_3 /400nmPCMO/Pt

Figure 5.3: XRD analysis of different stack structures

Figure 5.4: Position of vacancies in PCMO during switching

Figure 5.5: a) EPIR switching in PCMO/Pt

b) Retention in PCMO for 24hrs

Figure 5.6: a) Switching in 2.5nm Al_2O_3 /420nmPCMO

b) Retention of HRS and LRS for 24hours in 2.5nm Al_2O_3 / PCMO

c) Hysteresis in 2.5nm Al_2O_3 /420nmPCMO

d) Hysteresis in I-V measurement of 2.5nm Al_2O_3 /420nmPCMO

Figure 5.7: Position of oxygen ions and vacancies during regular switching

Figure 5.8: a) Switching in 2.5nm Al_2O_3 /420nmPCMO

b) HRS and LRS retention for 24hours

c) Hysteresis in 2.5nm Al_2O_3 /420nmPCMO

d) Hysteresis in I-V measurement of 2.5nm Al_2O_3 /420nmPCMO

Figure 5.9: Position of oxygen ions and vacancies during reverse switching

Figure 5.10: a) Regular switching in 5nm Al_2O_3 / PCMO/Pt

- b)** Retention of HRS and LRS in 5nm Al₂O_x/ 420nm PCMO/Pt
- c)** Hysteresis in 5nmAl₂O_x/420nmPCMO
- d)** Hysteresis in I-V measurement of 5nmAl₂O_x/420nmPCMO

Figure 5.11: a) Regular switching in 7.5nmAl₂O_x/ PCMO/Pt

- b)** Retention of HRS and LRS in 7.5nm Al₂O_x/ 420nm PCMO/Pt
- c)** Hysteresis in 7.5nmAl₂O_x/420nmPCMO
- d)** Hysteresis in I-V measurement of 7.5nmAl₂O_x/420nmPCMO

Figure 5.12: a) Regular switching in 10nmAl₂O_x/ PCMO/Pt

- b)** Retention of HRS and LRS in 10nm Al₂O_x/ 420nm PCMO/Pt
- c)** Hysteresis in 7.5nmAl₂O_x/420nmPCMO
- d)** Hysteresis in I-V measurement of 7.5nmAl₂O_x/420nmPCMO

Figure 5.13: a) Reverse switching in 5nmAl₂O_x/ PCMO/Pt

- b)** Retention of HRS and LRS in 5nm Al₂O_x/ 420nm PCMO/Pt
- c)** Hysteresis in 5nmAl₂O_x/420nmPCMO
- d)** Hysteresis in I-V measurement of 5nmAl₂O_x/420nmPCMO

Figure 5.14: a) Reverse switching in 7.5nmAl₂O_x/ PCMO/Pt

- b)** Retention of HRS and LRS in 7.5nm Al₂O_x/ 420nm PCMO/Pt
- c)** Hysteresis in 7.5nmAl₂O_x/420nmPCMO
- d)** Hysteresis in I-V measurement of 7.5nmAl₂O_x/420nmPCMO

Figure 5.15: a) Reverse switching in 10nmAl₂O_x/ PCMO/Pt

- b)** Retention of HRS and LRS in 10nm Al₂O_x/ 420nm PCMO/Pt
- c)** Hysteresis in 10nmAl₂O_x/420nmPCMO
- d)** Hysteresis in I-V measurement of 10nmAl₂O_x/420nmPCMO

Figure 5.18: a) Regular switching in 50nmPCMO/2.5nm Al₂O_x/ PCMO sandwich heterostructure

b) Retention for 24hours in 50nmPCMO/ 2.5nmAl₂O_x/ PCMO

c) Hysteresis in 50nmPCMO/2.5nmAl₂O_x / PCMO sandwich heterostructure

d) I-V characteristics 50nmPCMO/ 2.5nmAl₂O_x/ PCMO

Figure 5.19: Position of oxygen ions and vacancies during regular switching in sandwich structure

Figure 5.20: a) Regular switching in 50nmPCMO/5nmAl₂O_x/420nmPCMO/Pt

b) Retention in 50nmPCMO/5nmAl₂O_x/ PCMO/Pt

c) Hysteresis in 50nmPCMO/5nmAl₂O_x/PCMO/Pt

d) I-V characteristics of 50nmPCMO/5nmAl₂O_x/PCMO/Pt

Figure 5.20: a) Regular switching in 50nmPCMO/7.5nmAl₂O_x/ PCMO/Pt

b) Retention of HRS and LRS in 7.5nm 50nmPCMO/Al₂O_x/ 420nm PCMO/Pt

c) Hysteresis in 50nmPCMO/7.5nmAl₂O_x/PCMO/Pt

d) I-V characteristics of 50nmPCMO/7.5nmAl₂O_x/PCMO/Pt

Figure 5.21: a) Regular switching in 50nmPCMO/10nmAl₂O_x/PCMO/Pt

b) Retention of HRS and LRS in 10nm 50nmPCMO/Al₂O_x/ 420nm PCMO/Pt

c) Hysteresis in 50nmPCMO/10nmAl₂O_x/PCMO/Pt

d) I-V characteristics of 50nmPCMO/10nmAl₂O_x/PCMO/Pt

LIST OF TABLES

Table1: Various oxides in consideration to Resistive switching

Table2: Switching ratio and Retention loss in 2.5nmAl₂O_x/420nmPCMO/Pt

Table3: Effect of Al₂O_x thickness on EPIR ratio, retention stability in

Al₂O_x/420nmPCMO/Pt

Table4: Switching ratio and Retention loss in Al₂O_x/420nmPCMO and

50nmPCMO/Al₂O_x/420nmPCMO for different thickness of Al₂O_x

Chapter 1 General Introduction

The ultimate solution for memory storage- A nonvolatile random access memory that retains data without external power and can be read from or programmed like static or dynamic RAM and still achieve high-speed, high density and low-power consumption at an acceptable cost. It is not yet available however researchers achieved great developments in this regard by the name of flash memory, SRAM, DRAM for various applications. Considering the scaling down requirements of devices, research has been going on to improvise the memory devices with goals in mind like i) replace CMOS with highly scalable, high performance, low power information processing technology ii) develop a memory technology capable of scaling either volatile and/or nonvolatile memory technology beyond 14nm generation [1].

1.1 Non-volatile memory technologies

The future evolution of computer technology rests on embedded high density and fast responding non-volatile memory devices in computer systems. Over the past 20 years, numerous memory technologies have been brought to market with varying degree of commercial success in memory usage for different applications. EPROM, EEPROM, SRAM, DRAM, NAND flash and NOR flash are some of the different kinds of memories. Memories can be classified into two types volatile and non-volatile; Volatile memory will not retain data when power is turned off, conversely non-volatile memory will retain data once power is turned off. The two dominating memory technologies in the industry today are DRAM (volatile) and NAND flash (non-volatile). Figure1.1 summarizes the emerging and current technologies which are in mass production.

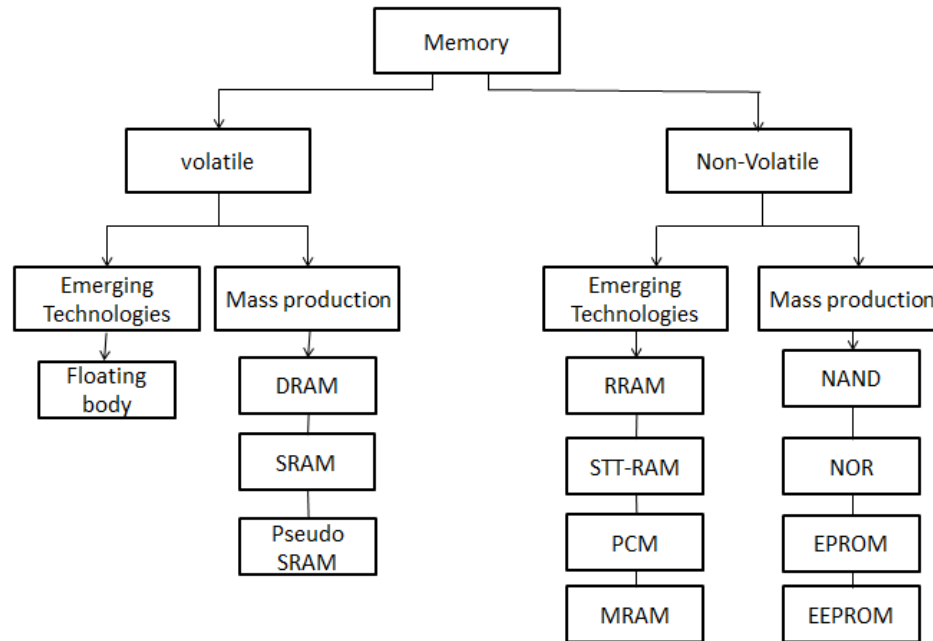


Figure 1.1 Classification of current and emerging memories [2]

The different kinds of memory storage technologies charted above have different operating mechanism which is discussed below.

1.2 Current technologies

Dynamic random-access memory (DRAM) is a volatile random-access memory that consists of a transistor, capacitor and refresh circuitry within an integrated circuit to store each bit. Based on the charge of capacitor being 1 or 0 two states are defined. Due to the leakage of charge in capacitors, the information will fade away without the capacitor charge being refreshed periodically [3].

Static random-access memory (SRAM) is a volatile random access memory. It is different from DRAM where constant refreshment of data was required, here the data is stored within the latch created by organization of inverters. It is complicated even in the terms of fabrication for single bit compared to DRAM. SRAM exhibits data

remanence, but it is still volatile in the conventional sense because the data is eventually lost when the power is turned off [3].

NAND Flash is a non-volatile metal-oxide semiconductor (MOS) memory in which the cells are arranged in series with the adjacent cell sharing the source and drain similar to the way NMOS are placed in building a cmos NAND gate. The common source and drain for an adjacent cell tremendously reduces the metal contact needed hence the die size [3].

1.3 Emerging technologies

PCM: Phase Change Memory is a non-volatile random access memory. It works based on the unique behavior of materials where heat produced by electric current across the sandwich structure switches this material between two states. The structure consists of switching material between two electrodes. The different states have different electrical resistance which can be used to store data. PCM is expected to have better scalability than other emerging technologies [1].

MRAM: The operating mechanism of MRAM is based on the phenomenon called Tunnel-Magneto resistance (TMR). The memory cell of MRAM product is composed of one MOS transistor and a device called MTJ (Magnetic Tunnel Junction). An MTJ has a stack structure composing of a thin tunnel insulator such as MgO sandwiched between two magnetic films with electrodes on both outer-side of the magnetic films. One of the magnetic layers is called the fixed layer or pinned layer in which magnetization is hard to be rotated. If the direction of magnetization in two magnetic films is parallel, a MTJ becomes low resistance. If they are anti-parallel the MTJ becomes high resistance. Writing is performed by introducing current to two adjacent wires for rotating the

magnetization direction of the free layer using the magnetic field produced by the current. The most outstanding feature of MRAM is its operating speed [1].

1.4 RRAM

RRAM (Resistive Random Access Memory): RRAM is a vertical two terminal device as shown in figure.1.2 where the active medium resistance can be modulated by applying short time (few hundred ns) electric pulse EPIR (Electric Pulse Induced Resistance Switching).

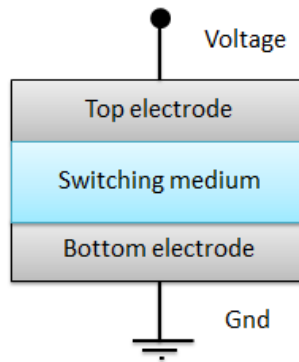


Figure 1.2 Two terminal RRAM device [4]

All Redox RAM technologies consist of an insulating dielectric sandwiched between two metal electrodes, to form a Metal-Insulator-Metal (MIM) structure. After fabrication, the first operation that is performed in these devices is a “forming” process where a voltage or current (based on material) is applied to form low resistance channels. Once a low resistance channel is formed, a “RESET” operation is performed and the “channel” returns to a higher resistance state. The device can then be driven into high conductance “SET” state by application of a field [5]. There can be competing electrochemical and thermochemical mechanisms that are involved in the resistive switching of these devices. These mechanisms can take part individually or together to

different levels depending on the electrode metallurgy and the oxides used which are tabulated in section 1.4.2.

1.4.1 Types of Resistance Switching Observed in RRAM

The materials listed in table 1 exhibit two types of resistance switching. In order to understand the switching modes they have been classified based on the electrical polarity required to switch the states.

a) **Unipolar switching:** In this type of resistive switching the device resistance is independent of the polarity of applied voltage pulse. During the SET process the current is limited by current compliance in the circuit and the device is switched to off state RESET at higher current and lower voltage value than the SET voltage as shown in figure. 1.3a [5].

b) **Bipolar switching:** In this type of switching successive positive and negative pulses are required to trigger the change in device resistance between the two resistance states low resistance state (SET state) and high resistance state (RESET state) as shown in figure. 1.3b.

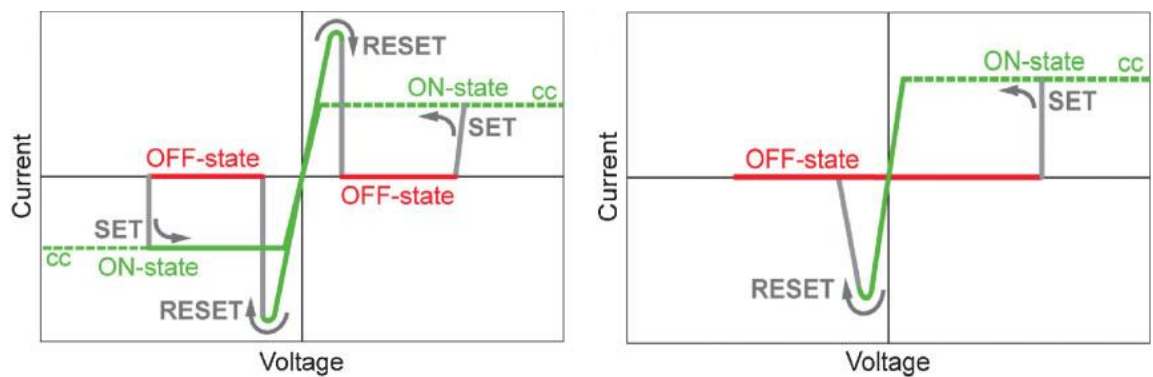


Figure 1.3 I-V characteristics of a) uni-polar switching b) bi-polar switching[5]

In case of bipolar switching the device could switch in:

Regular polarity Switching: when the positive voltage pulse will induce low resistance state and negative voltage pulse will induce high resistance state to the device it is known as regular switching as shown in figure 1.4a[6]

Or

Reverse polarity Switching: when the positive voltage pulse will induce high resistance state and negative voltage pulse will induce low resistance state to the device it is known as reverse switching as shown in figure 1.4b[6]

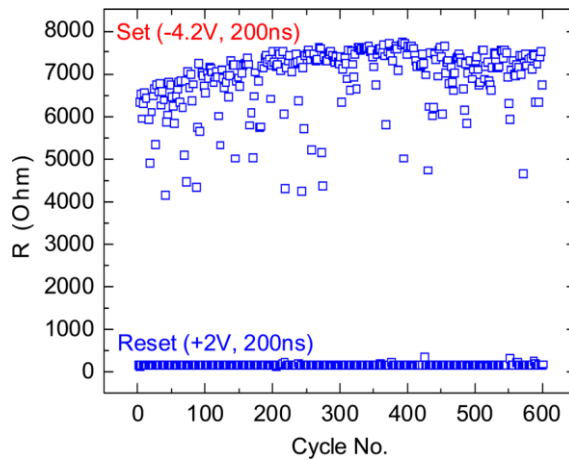


Figure 1.4a Regular Switching in CuO_x[6]

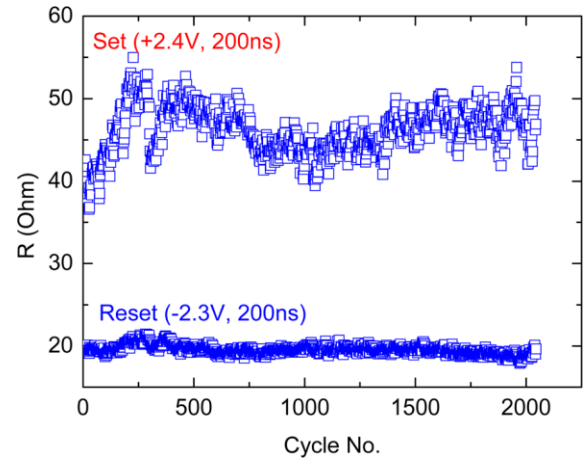


Figure 1.4b Reverse switching in CuO_x[6]

1.4.2 Materials Exhibiting EPIR Switching

Electric Pulse Induced Resistance switching phenomenon have been reported in various binary and heterostructure oxides, metal sulfides, perovskites, others. Some of the binary and complex oxide structure RRAM materials are listed in Table 1

Table.1 Various oxides in consideration to Resistive switching [7]

Binary metals oxides	TiO ₂ , NiO, Cu _x O, ZrO ₂ , MnO ₂ , HfO ₂ , WO ₃ , Ta ₂ O ₅ , VO ₂ , Fe ₃ O
Perovskite	PCMO (Pr _{0.7} Ca _{0.3} MnO ₃), LCMO (La _{1-x} Ca _x Mn ₃), BSCFO (Ba _{0.5} Sr _{0.5} Co _{0.8} Fe _{0.2} O _{3-δ}), YBCO(YBa ₂ Cu ₃ O _{7-x}), (Ba _x Sr)TiO ₃ (Cr, Nb-doped), SrZrO ₃ (Cr, V-doped) (La, Sr)MnO ₃ Sr _{1-x} La _x TiO ₃ , La _{1-x} Sr _x FeO ₃ , La _{1-x} Sr _x CoO ₃ , SrFeO _{2.7} , LaCoO ₃
K2NiF4	La _{2-x} Sr _x NiO ₄ , La ₂ CuO _{4+δ}
Others	Ge _x Se _{1-x} (Ag, Cu, Te-doped), Ag ₂ S, Cu ₂ S, CdS, ZnS, CeO ₂ , SiO ₂ , Carbon (sp ² -sp ³ transition)

1.5 RRAM as Potential Non-volatile Memory

RRAM memories are in research phase with potential to replace the current flash NAND memory. Figure 1.5 illustrates the requirements of RRAM outcomes in order to compete with the present non-volatile flash memory. Currently FRAM, MRAM, and PCM are in commercial production, but when compared to DRAM & NAND flash memories, they remain limited to niche applications. There is a view that MRAM, STT-RAM, and RRAM are the most promising emerging technologies. Any new technology must be able to meet current and some of future requirements, if not all of the following traits in order to drive industry adoption for mass production. a) Scalability of the technology b) speed of the device c) power consumption should be better than existing memories, endurance, densities superior to existing technologies and finally cost.

Requirements of RRAM

... to compete with Flash

Endurance:	$> 10^7$ cycles (Flash $10^3 \dots 10^7$)
Resistance ratio:	$R_{OFF} / R_{ON} > 10$
READ current:	I_{ON} approx. 1 μA (due to periphery circuit) approx. $10^4 A/cm^2$ (for 100nm x 100nm cells)
Scalability:	$F < 22$ nm and/or 3-D stacking
Write voltage:	approx. 1 ... 5 V (Flash > 5 V)
Read voltage:	0.1 ... 0.5 V
Write speed:	< 100 ns (Flash $> 10 \mu s$)
Retention:	> 10 yrs

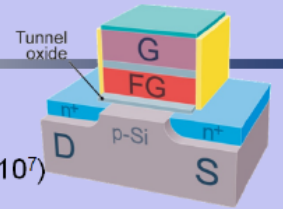


Figure.1.3 Requirements of RRAM to compete with Flash memory [8]

If the emerging technology can only manage 1 or 2 of these attributes, then, at best, it is likely to be designated to niche applications. Major challenge is, “what will be the next non-volatile memory to replace NAND flash?” At present nothing is concrete, but due to the limitations of NAND flash (endurance, reliability, speed) when compared to DRAM, researchers are inclined to believe a new non-volatile memory technology will evolve; but perhaps not replacing the current mainstream memories for at least the next 5 to 7 years. However the ultimate nonvolatile data memory (NVM) should display characteristics such as high density and low cost, fast read and write access, low energy operation, and high performance with respect to endurance (number of write cycles) and retention. Today, Si-based Flash memory devices represent the most prominent NVM because of their high density and low fabrication costs due to commercialization of manufacturing process in a profitable way. However, Flash memory also has drawbacks like low endurance, low write speed, and high operating voltages for the write operations. In addition, further scaling, i.e., increasing the density of Flash in accordance to moore

devices is expected to run into physical limits in the near future. Ferroelectric random access memory (FeRAM) and magneto resistive random access memory (MRAM) cover niche markets for special applications. One reason among several others is that FeRAM as well as conventional MRAM exhibit technological and inherent problems in the scalability, i.e., in competing with the current trend of improvements in density of Flash. To overcome the problems of current NVM concepts, a variety of alternative memory concepts is explored. Most prominently, NVMs based on electrically switchable resistance have attracted considerable attention [5], often summarized under the umbrella term resistance (switching) random access memory, short RRAM. In RRAM redox reactions and nano-ionic transport processes play the key role.

The requirements of RRAM as a replacement for flash have been set based on the device properties of: writing the state, reading the state, the resistance ratio between the two states, the endurance (switching stability), and the retention of the state. There are three criteria used to define potential of RRAM. They are EPIR ratio, stability and retention. EPIR ratio is the ratio between the high and low resistance states defined as $\frac{HRS-LRS}{LRS}$. Stability is defined as continuation of the switch between the same HRS level and LRS level or maintaining the EPIR ratio for an extended number of cycles. The device needs to be stable for at least 10^6 + cycles. Retention is the maintenance of high or low resistance state after the switching pulse has been removed from the sample. Loss of retention is calculated as a percentage loss per 24hours from the difference between the initial and final i.e. after 24 hours resistance states. For writing the resistance state the voltage is limited between a few hundred mV and V. The length of the pulse should be in the order of 100ns in order to make it compatible with DRAM or less than 10ns to

replace SRAM. The read voltage must be significantly less than write voltage in order to not disturb the resistance state. However the read voltage should be greater than $1/10^{\text{th}}$ the write voltage and the current during read should be greater than $1\mu\text{A}$ in order to be quickly detected by sense amplifiers. The overall read time should be less than the write time. The resistance ratio, defined as $R_{\text{OFF}}/R_{\text{ON}}$ needs to be greater than 10 for the sensing circuitry to be small and efficient. The endurance of the switch (also known as fatigue or switch stability) must be at least as good as flash which is 10^3 - 10^7 cycles. Finally the retention of the states must be greater than 10 years at 85°C and under continuous read type pulsing [5].

1.6 Suggested EPIR Switching Mechanisms in RRAM

ReRAM comprises of wide variety of MIM (Metal-Insulator-Metal) structures and materials as mentioned above in table 1 connected by the fact that they share reduction/oxidation (redox) electrochemistry as an important component of their physical mechanism for changing resistance state from low to high and vice versa [9][10]. These redox reactions can take place in the bulk I-layer forming a filamentary conducting path as in Cu_xO binary oxide. Or they can take place at the I-layer/metal contact interfaces in the MIM structure as in Pt / TiO_x / Pt stacking structure [11][12].

1.6.1 Filamentary Model

Electric pulse induced resistance change has been observed in some binary oxides such as Cu_xO_y . The study of Rabi et al. showed strong evidence for a metallic bulk filament formation under application of an initial forming electric pulse. This filament formation occurs by structural breakdown of the low oxygen comprising Cu_4O_3 to Cu^+ ion and corresponding Cu oxide formation. The metal filament formed between top and

bottom electrodes causes low resistance state (ON state). Upon reversing the polarity of voltage dissolution of the filament takes place resulting in high resistance state (OFF state) A model for the switching mechanisms based on Cu^+ ion motion in the interface region between the metallic filament and the top electrode is developed. Binary transition metal oxides typically show unipolar switching [6]. But bipolar switching was observed in Cu_xO_y . Resistive switching has been reported in copper oxide with both regular and reversed polarity switching [7]

1.6.2 Oxygen Vacancy Model

The electric field control of the distribution of the oxygen vacancies has been demonstrated in a similar MIM structure, such as a Pt / TiO_x / Pt stacking structure [15]. The charged oxygen vacancy was regarded as a mobile dopant in the oxide material and the electrical control of the vacancies used as the analog resistance change necessary to define the ON state and OFF state; this is one of the important aspect for constructing emerging research architecture.

Perovskite RRAM devices with M/Insulator/PCMO/Metal heterostructures have been studied before with the insulator grown between active CMR perovskite and top metal electrode. Oxygen ion/vacancy motion may play a role in the EPIR effect, a positive pulse moves oxygen ions toward the metal/PCMO interface and reduce the resistance there, and a negative pulse moves the ions away and increases the resistance there. The insulating buffer layers used were oxygen ion conductors and low temperature magnetic field measurements indicated that PCMO is the principal material driving the switching properties of the device. Hence the improvement of switching properties demonstrated indicate a mechanism where oxygen ions or vacancies are playing a role. [16]

1.7 Outline of This Thesis:

The properties of a material can be enhanced or modulated in a desired way by characterization of the material and understanding its properties. One method used to do this has been the introduction of additional layers into the device structure. Materials such as YSZ[17][18][19] and Sm-CeO₂[4] have been used as tunnel barriers between the PCMO layer and an electrode with the barrier height modified by oxygen content provided by the PCMO, while Z.W. Xing et al. [20] used a thin (nm) PbZrTiO₃ (PZT) ferroelectric layer between the top electrode and the PCMO. The PZT layer enhanced the resistance switching characteristics of the PCMO through modification of the depletion region thickness due to PZT ferroelectric polarization. Other experiments have focused on enhancing resistance switching by using a highly reactive metal such as Ti or Al deposited on the PCMO [21][22]. In this case enhancement arises due to the oxidation/reduction reaction that occurs in the reactive metal at the metal/PCMO interface upon application of a pulse. The PCMO here acts as a source or sink for oxygen ions. With the exception of the work on ferroelectric layers, none of the works on buffer layer integration with the PCMO material involved an enhancement of the EPIR switching effect of the PCMO layer.

It has been observed that for a metal/PCMO/metal device under applied electric field through voltage pulses in the device, motion of oxygen ions/vacancies and their pile-up at the top PCMO-electrode interface region is responsible for the EPIR switching effect. The changing concentration of vacancies within this interface region affects the resistivity of PCMO and results in resistance change. This change in concentration, however, results in a chemical potential difference which under certain conditions can

become a driving force in reducing the concentration gradient between the interface region and the bulk, leading to change in resistance state of the device as a function of time and yielding poor retention. This retention challenge has been seen in PCMO devices and requires a solution.

This short coming in PCMO encouraged us to do more research trying to improve its fatigue and retention stabilities. Based on the oxygen vacancy model for switching in PCMO there is a way of enhancing the EPIR characteristics by integration of oxygen ion conductor which may control the flow of oxygen vacancy migration under the action of electric field during the two resistance states and also may retain the oxygen vacancy concentrations in the absence of the applied voltage pulse for longer time (enhance the retention stability). In this study, Al_2O_x buffer layer of various (~ 2.5 nm to 10nm) thicknesses have been used as oxygen anti-diffusion layer. The EPIR characteristics of metal/ Al_2O_x /PCMO/metal and metal/PCMO/ Al_2O_x /PCMO/metal heterostructures have been investigated in order to improve the EPIR switching ratio and retention properties that define the performance of RRAM device.

Chapter 2. $\text{Pr}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ as a Potential RRAM Material

In 2000 Ignatiev et al. discovered an electric-pulse-induced reversible resistance change in perovskite oxide $\text{Pr}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ (PCMO)[23]. This change is found to occur at room temperature with zero magnetic field and as potential application in the field of Random Access Memory. Since the discovery many studies have been done looking at the switching, hysteretic, I-V curve, and spatial behavior of this effect. Several models have been proposed to explain the behavior seen in the oxide. Some of these models include bulk effects governed by a current-induced polaron order-disorder transition, charge carrier trapping and detrapping effect of a schottky barrier at the metal/oxide interface, formation/rupture of metallic filaments, and defects created/modified in the crystal by the application of an electric field. None of these models fully explain behavior of PCMO seen in studies. The model proposed by Nian et al.[24] which incorporates the movement of oxygen vacancies into and out of the interface region upon the application of an electric field, goes far to explain the behavior seen in PCMO during switching and improve the switching characteristics of PCMO especially with respect to switching ratio, endurance and retention.

PCMO is a type of composite metal oxide. These are commonly known as perovskites because of their structure and composition. Reversible and non-volatile resistance changes in the PCMO film are desirable using either with bipolar or unipolar pulsed bias. Therefore, an understanding the relationship between memory characteristics and PCMO thin film material structure that defines this change was necessary. PCMO also exhibits colossal magnetoresistive (CMR) properties. These are also strongly

affected by the crystal structure of thin film. A brief understanding of PCMO structure is necessary. PCMO has perovskite cubic structure

2.1 Composition of Perovskites

The general stoichiometry of ABX_3 is defined as perovskite structure, where “A” and “B” are cations and “X” is an anion. The “A” and “B” cations can have a variety of charges and in the original Perovskite mineral ($CaTiO_3$) A cation is divalent and B cation is tetravalent. In PCMO, the case where A cation is composition of rare-earth and alkali metal and B cations adopt a trivalent state were considered [26]. Other large number of perovskite compositions can also be possible from combinations of cations on the lattice site. The ions occupying the A and B lattice sites are detailed in figure.2.2.

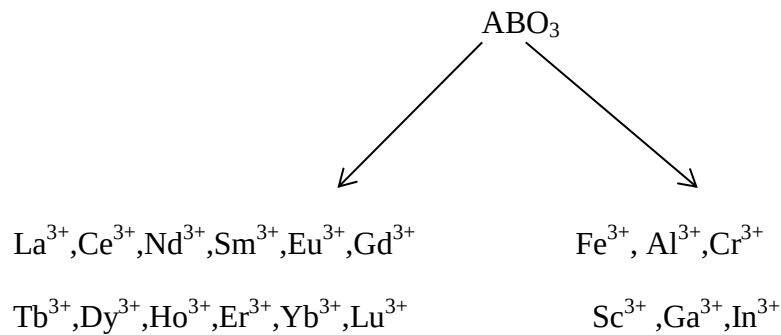


Figure 2.1 Viable materials in ABO_3 structure

The structure of an ideal cubic perovskite is shown in figure 2.2, where the A cations are shown at the corners of the cube, B cation in the center and oxygen ions in the face centered positions. The cubic perovskites have space group of $Pm\bar{3}m$ (221)[25].

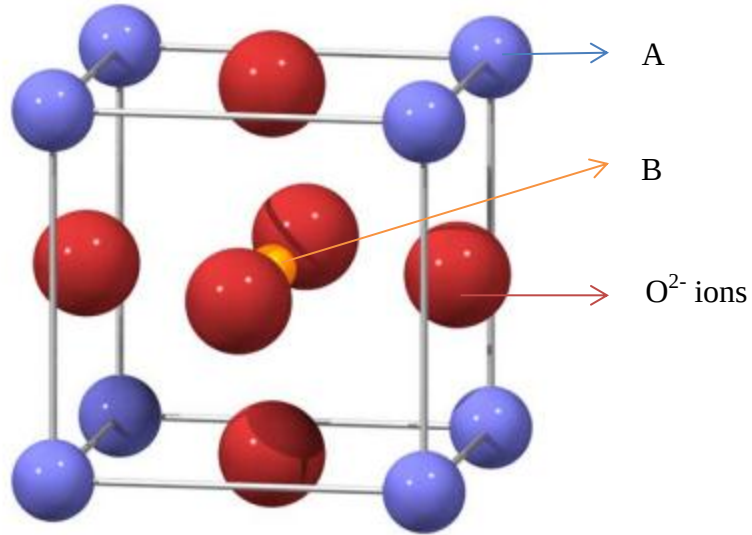


Figure 2.2 Cubic perovskite unit cell. Blue spheres depict the A cations where yellow spheres depict the B cations, and red spheres depict oxygen anions forming an octahedral [26].

2.2 Physical Structure of PCMO:

$\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$ is an electrically alterable resistive material whose memory resistance characteristics are related to the PCMO lattice structure. The unit cell of $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$ consist of two subunits units: PrMnO_3 and CaMnO_3 . The ideal lattice of each unit has the same perovskite cubic structure, as shown in the figure 2.3.

In the case of the $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$ composition, the sub units PrMnO_3 and CaMnO_3 have an orthorhombic structure belonging to the same space group Pb nm , but the distortion of the PrMnO_3 is almost negligible so that its structure can be considered as quasicubic. The change of the lattice constants when the composition parameter x changes from $x=0$ to $x=1$ are however not linear and exhibits some anomalies. Similar kind of anomalies, though different in detail were known to exist in other rare earth manganese perovskites [27].

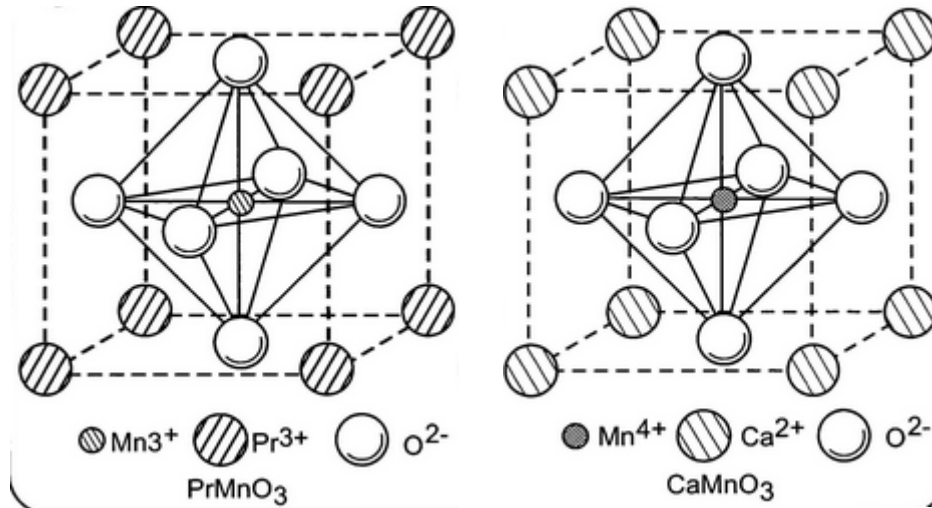


Figure 2.3 Lattice structures of PrMnO_3 and CaMnO_3 [27]

PrMnO_3 units have Pr^{3+} and Mn^{3+} ions. The deviations of $\text{Mn—O}_\text{I—Mn}$ and $\text{Mn—O}_\text{II—Mn}$ angles from 180° (which is the angle in ideal cubic perovskites) manifest the buckling and are the cause of the lattice distortion (especially the elongation of the b axis) in orthorhombic perovskites. The increase of the b parameter is reportedly enhanced in PrMnO_3 and other samples with high Mn^{3+} content due to the e_g orbital ordering shown in Figure 2.4.

2.3 Electronic Structure of PCMO [28]

In PCMO, the electronic structure is $\text{Pr}_{0.7}^{3+}\text{Ca}_{0.3}^{2+}\text{Mn}_{0.3}^{4+}\text{O}_3^{2-}$. The energy states of the Mn ion are the contributing factor in PCMO behavior. The isolated Mn ion has five-fold degeneracy in the orbital states that are available to the electrons in the 3d state with $l=2$. When placed in the crystal, the degeneracy is somewhat lifted by the cubic crystal field. The degeneracy is further lifted when the five orbital states split into 3 t_{2g} orbitals and 2 e_g orbitals $E_g \sim 1.5\text{eV}$. The energy levels for the Mn^{3+} and Mn^{4+} are: Mn^{3+} : $3d^4$ $t_{2g}^3 e_g^1$ $s=2$, Mn^{4+} : $3d^3$ t_{2g}^3 $s=3/2$. If the crystal symmetry is lower than cubic the e_g and t_{2g} degeneracies are lifted due to Jahn-Teller distortion of oxygen octahedral (axial

elongation). This is seen primarily in the Mn^{3+} ion due to the single electron in the e_g state.

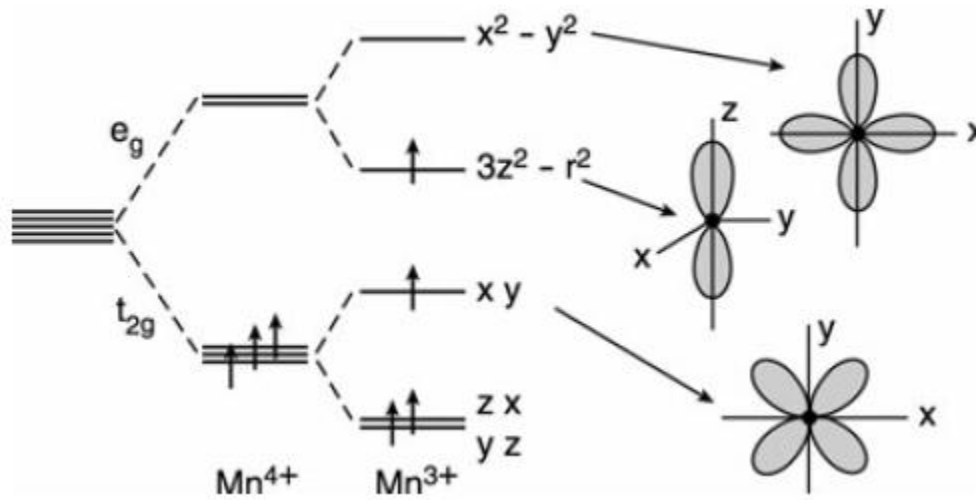


Figure 2.4 Energy level diagram for Mn in PCMO [28]

2.4 Magnetic Properties of PCMO[28]

For all the experiments conducted in this PCMO is in paramagnetic insulating phase. PCMO is paramagnetic insulating phase across all its composition at room temperature. The general phase structure for PCMO of various compositions and at various temperatures is as follows. For $0.3 < x < 0.5$ there are several phases available dependent upon temperature. The temperature for transition from paramagnetic insulating (PI) to charge ordered insulations (COI) is fairly high ($T \sim 240\text{K}$) for $x = 0.3-0.5$. In figure 2.5 the full phase picture for PCMO is shown for compositions $0 < x < 0.5$ and a wide range of temperatures. Further, both PrMnO_3 and CaMnO_3 are anti ferromagnetically ordered and insulating at low temperatures. With x in between the values of $0 < x < 0.4$ a spontaneous ferromagnetic moment appears that has been ascribed to the strong double exchange interactions $\text{Mn}^{3+} - \text{O}^{2-} - \text{Mn}^{4+}$, which results in a material transformation from (Mott) insulator to metallic conductor.

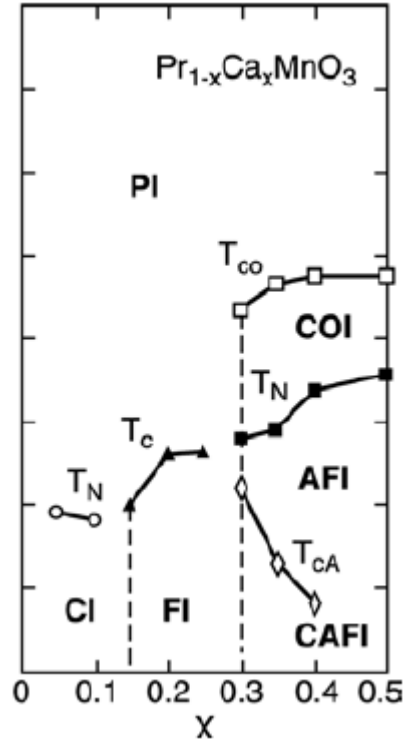


Figure 2.5 Phase diagram showing transition temperature vs concentration [28].

2.5 Electric Conduction Mechanism in PCMO

The method of conduction in PCMO contributes strongly to the non-volatile resistive switching behavior. The conduction in PCMO is mostly electronic and is believed to occur along the $\text{Mn}^{3+}\text{-O- Mn}^{4+}$ chain. It is controlled by the overlap between the d orbitals in Mn and the p-orbitals in O. In $\text{Mn}^{3+}\text{-O- Mn}^{4+}$ the Mn exchange their valence by a simultaneous move of the electron in the e_g level of the Mn^{3+} to the p-orbital of O and the electron in the p-orbital of the O to the e_g mechanism. The probability of the exchange is given by: $t_0 \cos(\theta/2)$; where θ = angle between the spins. Figure 2.6 graphically shows the double exchange mechanism.

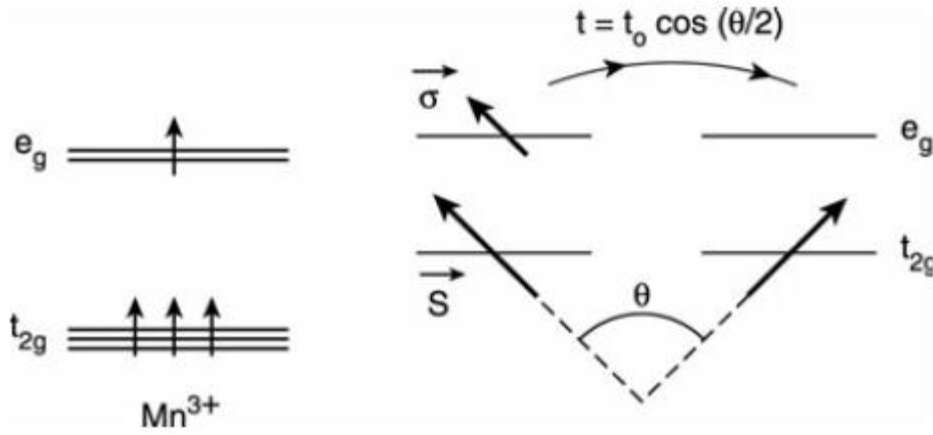


Figure 2.6 Double exchange process [28]

The double exchange mechanism is the basic conduction mechanism in PCMO. The carriers for conduction vary depending on the Ca concentration. For $x < 0.5$ the conduction band is half full and the charge carriers are holes. For $x > 0.5$ DE links decrease and the charge carrier motion is hindered. When this is the case exchange occurs between Mn^{4+} -O- Mn^{4+} . This gives rise to anti-ferromagnetic phase. For hole charge carriers there is a field associated with them due to the distortion caused when an electron is in the e_g level. In this instance the hole charge carrier is referred to as the hole polaron.

As with any conductor or semiconductor material, the resistivity has temperature dependence. At higher temperatures, above 240K, where our experiments were conducted at, and with strong double exchange, PCMO is a paramagnetic semiconductor or insulator. The paramagnetic insulating phase shows strong temperature dependence. In order to explain the temperature behavior in the paramagnetic insulating phase there are three models that are typically used to fit the data. The results from each of these models are virtually indistinguishable from each other for small temperature ranges. The three models are: thermal activation, hopping of adiabatic polarons, and Mott variable-range-hopping VRH. The thermal activation is due to the pseudogap at the Fermi level ($\sim 0.1\text{eV}$)

in the paramagnetic phase, $\rho = \rho_0 \exp(E_0/k_B T)$. where ρ is resistivity, E_0 is activation energy, k_B is Boltzmann constant, T is absolute temperature. The model using hopping of adiabatic polarons is based on the jahn-teller polaron, which is described as a lattice distortions induced by moving charge carrier, $\rho \sim T \exp(E_0/k_B T)$. Finally, Mott variable-Range-Hopping VRH is due to charge carriers localized by magnetic disorder, $\rho = \rho_0 \exp[(T_0/T)^{1/4}]$ [28]. The conduction mechanism in PCMO has important implications for a model to describe the EPIR behavior.

2.6 Electric Pulse Induced Resistance Switching in PCMO

Electric pulse induced resistance switching was observed in PCMO by Liu et al. at University of Houston in 2000 [23]. Resistance of PCMO thin film can be modulated between two states by changing the polarity of short electric pulse (ns) applied across the top and bottom electrodes of the device. The negative pulse will set the device into high resistance state (HRS) and the positive pulse will set the device to low resistance state (LRS) as shown in figure. 2.7. This change in resistance is non-volatile i.e, PCMO retained the resistance on removal of the electric pulse. Hence it can be used as non-volatile memory. The resistance switching by applied electric pulse is termed as “Electric Pulse Induced Resistance.” The Electric Pulse Induced Resistance (EPIR) switching ratio is defined as the ratio between the difference of high and low resistance states to the low resistance state $(\frac{HRS-LRS}{LRS})$ where HRS is high resistance state and LRS is low resistance state. Retention of these states is defined as the amount of time the device retains these individual states in the absence of electric pulse.

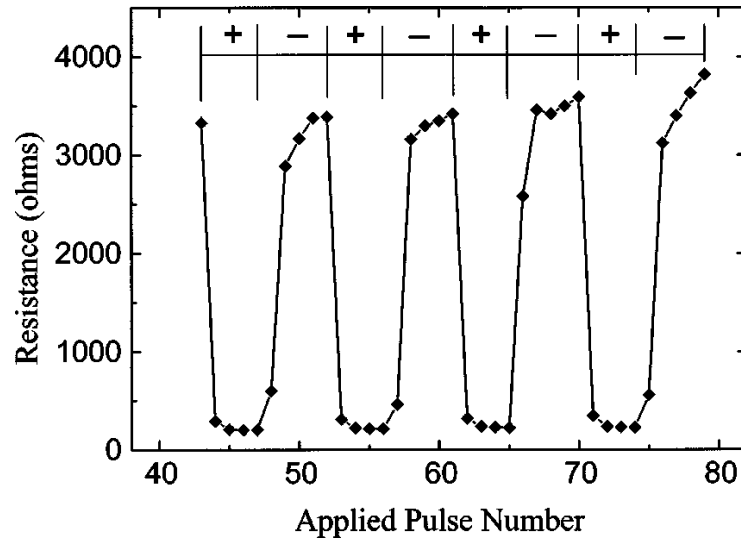


Figure. 2.7 Switching in PCMO under 18v and 100ns pulse [23]

PCMO based RRAM devices suffers from loss in EPIR ratio as the applied number of pulses increases as shown in Figure. 2.8 for about 12000 pulses 51v of height and 108ns width [23]. It can be seen that the EPIR ratio reaches an approximate saturation value after 5000 pulses. This can be termed as fatigue loss. It occurs due to the sample straining under continuous pulsing of voltage.

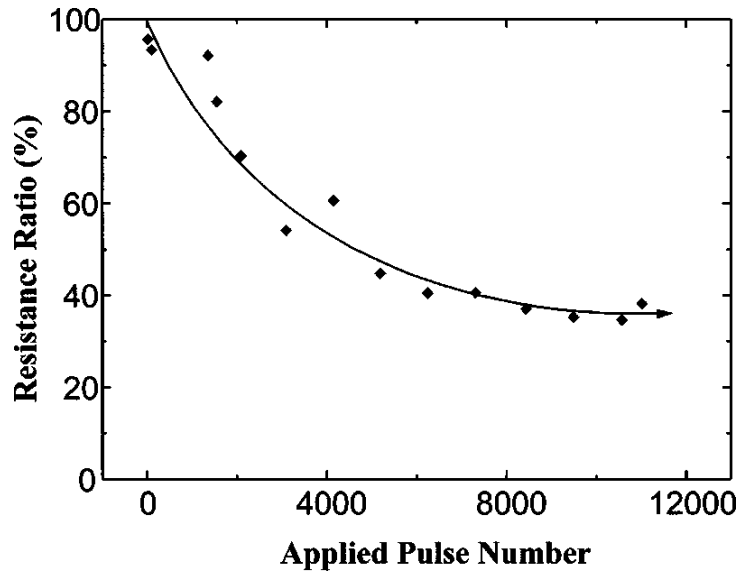


Figure 2.8 EPIR ratio loss in PCMO/Pt thin film samples for large numbers of pulses at room temperature and zero magnetic field 51v pulse for 108ns[24].

2.7 Oxygen Ion Motion in PCMO

For the oxygen vacancy model to be true the oxygen atoms in the PCMO should ionize and move in the direction determined by the field. High electric fields are produced by the applied short electric pulse which increases the mobility of oxygen ions exponentially. The distance the oxygen ions travel to make significant change in resistance value is in the order of nanometers. Ions can move by ion jump processes into oxygen vacancies or oxygen interstitials, oxygen ion transport can be thermally activated with a motion enthalpy of 0.5eV to 1.5eV[29]. at 700°C and above, oxygen mobility is sufficiently high to enable ionic conductivity. The ion mobility follows Arrhenius law:

$$D(T) = D_0 \exp\left(-\frac{E_A}{k_B T}\right). \quad (1)$$

E_A is migration enthalpy, D_0 is temperature independent pre-factor and k_B and T are Boltzmann coefficient and temperature, respectively. Ion (or vacancy) motion under electric fields is described by particle mobility which can be calculated from diffusion coefficient utilizing Nernst-Einstein's relation given by

$$\mu(T) = \frac{e_0 |z|}{k_B T} D(T). \quad (2)$$

In the above eqn. z is charge number of the ion and e_0 is the elementary charge. For (O^{2-}) $z = -2$. At low temperatures the mobility of ions is very less and at room temperature oxygen ions are generally considered immobile. We need to observe the distance travelled by oxygen ions and the effect of electric field on the mobility ions at atomic scale. Ion transport at this scale is explained by jump attempts over the potential barrier E_A , the drift velocity v_D of ion under an electric field E is given by

$$v_D \approx \frac{|z|e_0 v d^2 E}{k_B T} \exp\left(-\frac{E_A}{k_B T}\right). \quad (3)$$

for small electric fields drift velocity has linear dependence on Electric field.

$$v_D \approx v_d \exp\left(-\frac{E_A}{k_B T}\right) \exp\left(\frac{|z|e_0 d E}{2k_B T}\right) \quad (4)$$

Under high electric fields drift velocity has exponential dependence on E. At room temperature and small electric field the kinetic energy of an ion is too low for successful jump. Under large electric fields the potential barrier is lowered significantly contributing to successful jump events. Hence ion mobility and therefore, drift velocity increase exponentially under high electric fields.

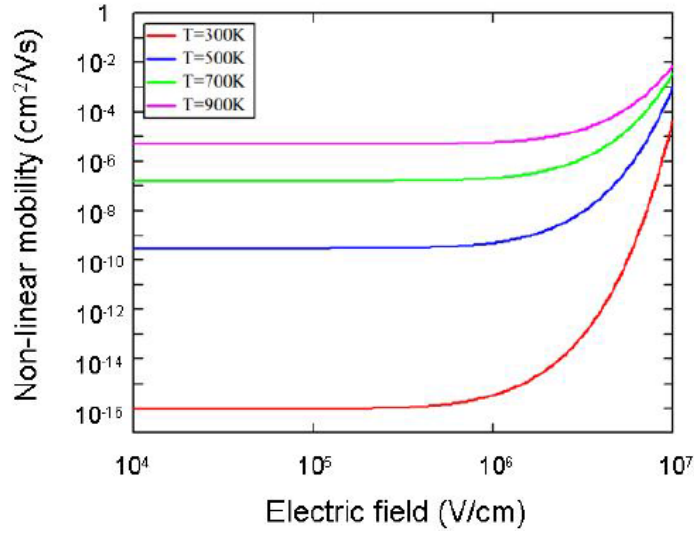


Figure 2.9 Ion mobility in PCMO for a motion enthalpy of 1ev as a function of temperature and applied electric field [29].

From figure 2.9 we can understand that the mobility at room temperature is comparable to mobility at 900k at higher electric fields of 10MV/cm. Electric field of this order can be generated using the applied set and reset voltage around 4-6V. In present work rough calculation have been done to estimate the thickness of active region taking part in defining the resistance switching based on the amplitude and width of short electric pulse. Assuming the active region will be 7.5nm thick as we have achieved better switching and

retention properties with this thickness of buffer layer. The electric field generated by application of an electric pulse with amplitude of 5v across this distance is

$$E = \frac{V \text{ volt}}{x \text{ cm}} = \frac{5}{7.5 \times 10^{-7}} = 0.8 \text{ v/cm}.$$

The oxygen ions have to travel this distance of x cm under the applied electric field during the time of 400ns i.e., pulse width of short electric pulse. We know that

$$E * \text{mobility} * \text{time} = \text{Distance travelled},$$

$$0.8 \text{ v/cm} * \mu \text{ cm}^2/\text{vs} * 400\text{ns} = 7.5 \text{ nm},$$

$$\mu = 9 * 10^{-7} \text{ cm}^2/\text{vs}.$$

The mobility of ions we calculated to achieve the distance of 7.5nm is $9 * 10^{-7} \text{ cm}^2/\text{vs}$. This is around the same amount of mobility achieved due to application of E-Field of 0.8 v/cm across the assumed length of depletion region which is obtained from ion mobility in PCMO as a function of temperature and applied electric field [29]. The circular region indicated depicts the region where there is tradeoff between E-field and mobility that compensate each other based on the length of depletion region up on which it is acting. So the assumed model considering the mobility of oxygen ions under the electric field produced by applied electric pulse is viable.

Chapter 3. Experimental Procedures and Thin Film

Characterization Techniques

PCMO RRAM samples used for conducting the experiments in this dissertation were fabricated mostly using RF sputtering on Pt/TiN/SiO₂/Si substrates provided by sharp Co. Three different stacks M/PCMO/M, Al₂O_x/PCMO/M and PCMO/Al₂O_x/PCMO/M samples were under studied. The samples were analyzed for their structure through physical analysis and characterization techniques. These techniques consists of scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDXS) and X-ray diffraction (XRD). The techniques used were EPIR switching measurements, voltage and resistance hysteresis loops, dynamic current measurements. The electrical characterization techniques will be described in this chapter as a general overview of each type of measurement.

3.1 Film Growth Techniques

3.1.1 Radio Frequency Magnetron Sputtering

Sputter deposition is a physical vapor deposition process for depositing thin films by sputtering, sputtering means ejecting material from a target and depositing it on a substrate by bombardment of energetic ions in partially ionized plasma. The target consists of source material. Substrates are placed inside a vacuum chamber and are pumped down to a ultra-high vacuum known as base pressure. Sputtering starts at working pressure of argon gas when a negative charge is applied to the target material produces energetic plasma or glow discharge. Positively charged gas ions are generated in the plasma region are attracted to the negatively biased target plate at a very high speed and strike the target to eject atoms of target material. This collision creates a momentum

transfer and ejects atomic size particles from the target. The bombardment also results in generation of ejected secondary electrons which are attracted toward the gas ions and help to maintain the plasma [30]. These ejected particles from plasma are deposited as a thin film onto the surface of the substrates.

Sputtering can be done either in DC or RF power. DC sputtering is used with conducting materials. If the target material is a non-conducting then positive charge will build up on the material and it will inhibit sputtering. RF sputtering can be used in case of conducting and non-conducting materials. RF magnetron sputtering is developed to do depositions at low working pressures. Magnets used keep electrons in magnetic field lines hence, the percentage of electrons that take part in ionization of events and thereby the probability of electrons striking the argon atoms increase further improving ionization efficiency significantly.

In our case we used ATX-600 Advanced Energy RF sputtering system. One limitation to the deposition of thin films by any of the DC sputtering techniques just covered is the requirement that the material to be sputtered be electrically conductive. This restriction is not true for radio frequency AC sputtering. In this process an AC power supply is used to apply a voltage that varies sinusoidally with time to a set of electrodes in a vacuum chamber. The target made of the desired material which is to be sputter deposited is attached to cathode. If the target material to be RF sputtered is an electrical conductor, an electrical insulator will be introduced between target and the electrode. When negative potential is applied to target, it is bombarded by positive ions and the positive charge keeps on building on the target until it repels further positive bombardment by electrons and is thus neutralized. Substrates needed to be coated may

be placed on the other electrode, or mounted elsewhere in the vessel as shown in figure.

3.1.

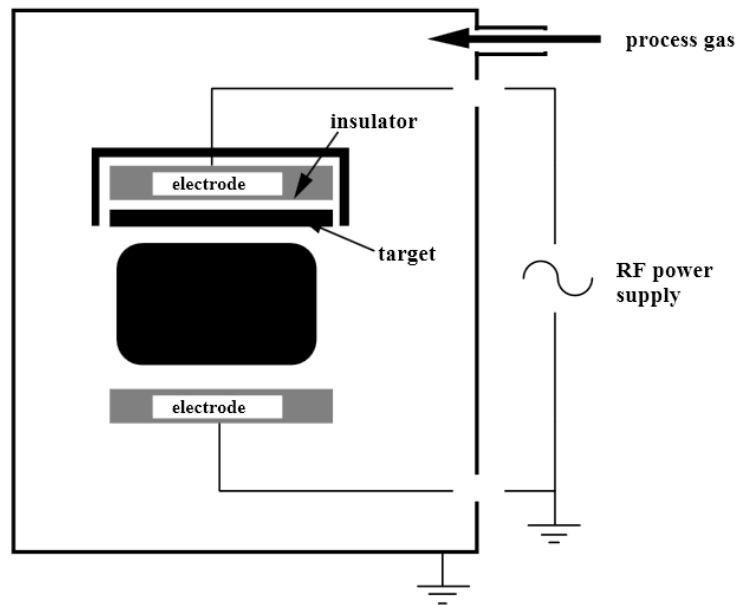


Figure 3.1 Components of an RF sputter system [29]

Materials which can be deposited by RF sputtering include metal oxides (SiO_2 , Al_2O_3 , ZnO , TiO_2 , etc.),[31] mixed oxides (Indium-tin oxide, which forms a transparent, electrically conductive film used to defrost wind shields), plastics, and glass. The composition of the deposited thin film is very close to that of the cathode. As with DC sputtering, special power supplies are required for RF sputtering see figure 3.1. The radio frequency AC power supply operates at a frequency of 13.56 kHz; many of these supplies output power is in the range of 0.5 to 10 kW.

RF sputtering process

- i) Frequencies less than about 50 kHz
- ions and electrons in plasma are mobile
- switching of the anode and cathode occurs
- notably DC sputtering of both surfaces

- ii) Frequencies above about 50 kHz
- ions (heavy) can no longer follow the switching
- electrons will neutralize positive charge build up on the cathode

Advantages:

- Easier for plasma regeneration under these conditions
- Can operate at lower Ar pressures (1-15 mTorr)
- fewer gas collisions => more line of sight deposition

3.2 Characterization Techniques

We have employed some characterization techniques in order to confirm the structure and composition of the fabricated stacks. A scanning electron microscope was used for imaging the cross-section of the samples and X-ray diffraction analysis was used for confirming the crystal structure of layers deposited. These techniques were discussed in detail below.

3.2.1 Scanning Electron Microscope (SEM) Characterization [32]

Electron microscope uses a beam of electrons to form an image. The outside view of an SEM is shown in figure 3.2 Inside the SEM we have an electron gun which induces beam of electrons down to our specimen inside the vacuum chamber to focus the beam onto specimen a series of electromagnets are used we cannot use regular glass lens like in optical microscope because electrons cannot go through glass but the electrons have charge that means they can be influenced by magnetic field so the condenser lens in the shape of ring focus the beam of electrons. These beams of electrons are produced by thermionic emission gun which consists of sharp electrodes close to each other when 15-30kv is passing through them.

We have anode right below each condenser lens which attracts the electrons downwards as there is hole right in the middle of anode the electrons moving towards go right through it. Also the stage on which the sample is mounted also has positive charge that also keeps electrons moving in that direction. When the electron beam hits the specimen there are two types of electrons are produced one of them is secondary electrons. Secondary electrons come from atoms that have absorbed the energy of electron beam. There is +300v charge beside the specimen to pick up these electrons this is called faraday cage which is connected to detector, as the electrons are absorbed into it the detector and then the detector uses the information from those electrons to create an image of the specimen.

The second type of electrons are backscattered electrons, these electrons actually do not come from the atom. Backscatter electrons reflect off the surface and deeper from within the specimen. Backscatter electrons which get trapped deep inside the specimen also give off x-ray. Here the secondary electrons give us the information about the surface of the specimen. The electron beam makes the picture pixel by pixel left to right and top to bottom hitting the surface electrons from that part of specimen.

In present work SEM model JEOL JSM-5410 was used to do the analysis. We have obtained the SEM images using secondary electron emission with this apparatus. The secondary electron emission rate of some oxides is around the same value which makes it difficult to identify individual layers however, thickness can be measured accurately.



Figure 3.2 JEOL JSM-5410 Scanning Electron Microscope

3.2.2 X-ray Diffraction (XRD) Analysis

The impact of electromagnetic radiation on periodic structures with different geometrical variations on the length scale of wavelength of radiation causes diffraction of incident wave. The interatomic distances in crystals and molecules range from 0.4-0.15nm which is the wavelength of X-rays in electromagnetic spectrum with photon energies between 3 and 8keV [33]. Hence we observe either constructive or destructive interference when crystalline and molecular structures are exposed to x-rays.

3.2.2.1 The Basic Phenomenon

The incoming X-rays and matter can interact in three different ways. Firstly, photoionization in which the incoming radiation transfers the energy and momentum to electron in bound atomic state and liberates it from the atom this is an inelastic scattering process. Secondly, Compton scattering in which the incoming radiation transfers energy and momentum to electron without ejecting it from the parent atom it is also inelastic

process. Thirdly, X-rays can be scattered elastically by electrons which is called Thomson scattering in this process electron oscillates like a hertz dipole at the frequency of incoming beam and becomes source of dipole radiation. The wavelength (λ) of X-rays is conserved in this process. The Thompson component in this elastic collision is used to make structural investigations by X-ray diffraction.

3.2.2.2 Structural Characterization of Thin Film by X-ray Diffraction:

By conservation of energy and momentum Braggs were able to analyze structure of crystals. X-rays were diffracted of various crystal planes as shown in Figure 3.3. The x-rays will then be collected in an ionization chamber and the level of ionization was measured as a function of incident angle of X-rays it is evident that each material produces its own intensity level and it is repeatable any number of times and every individual matter will have its own pattern.

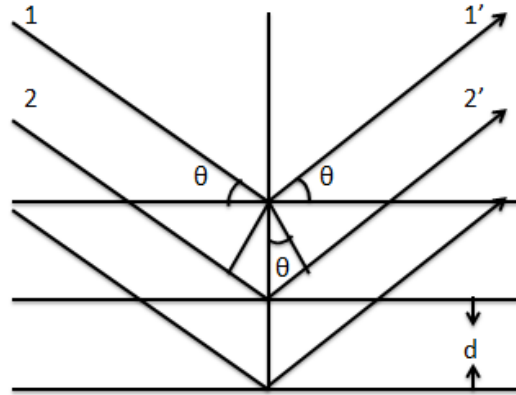


Figure 3.3 Bragg's diffraction

For a cubic structure with a being length of unit cell and where h,k,l represent the miller indices we have

$$\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2}. \quad (5)$$

When two parallel incident rays 1 and 2 are incident on the surface with a contact angle θ the reflected beam has maximum intensity if the waves 1' and 2' will be in phase. The difference in path length between 1 to 1' and 2 to 2' must be integral multiple of λ . This can be expressed with Bragg's law as

$$2d\sin\theta = n\lambda \quad . \quad (6)$$

Therefore the possible 2θ values where we can have reflections are determined by the unit cell dimensions. Nevertheless, the intensities of the reflections are determined by the distribution of the electrons in the unit cell. The highest electron density is found around atoms. Therefore, the intensities depend on the type of atoms we have and where in the unit cell they are located. Planes passing through areas with high electron density will reflect strongly and planes with low electron density will reflect weak intensities creating unique pattern of intensity with respect to angle 2θ . In this project the X-ray diffraction (XRD) measurements were carried out using a Siemens D- 5000 spectrometer. The scans were done in the standard θ - 2θ configuration, employing the Cu K_α radiation of wavelength 1.54Å with a scan step of 0.02°. The indexing of the major peaks and structure identification were done using reference X-ray diffraction cards.

Chapter.4 Experimental Procedure

The understudied RRAM stacks as shown in Figure. 4.1a, 4.1b were grown on Pt/TiN/SiO₂/Si substrates using RF magnetron sputtering, where two custom made RF sputtering chambers shown in figure. 4.2 have been used to grow PCMO and Al₂O_x separately. Where W/PCMO, W/Al₂O_x/PCMO, W/PCMO/Al₂O_x/PCMO have been deposited on Pt/TiN/SiO₂/Si substrate made by sharp Tech.

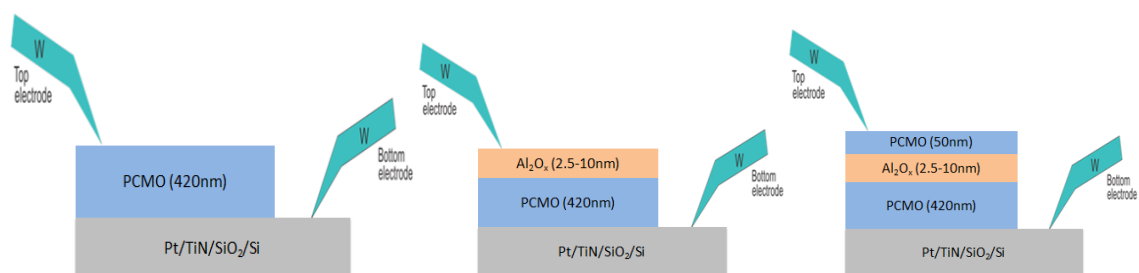


Figure 4.1a
W/PCMO/Pt/TiN/SiO₂/Si

Figure 4.1b
W/Al₂O_x/PCMO/Pt/TiN/SiO₂/Si

Figure 4.1c
W/PCMO/Al₂O_x/PCMO/Pt/TiN/SiO₂/Si

4.1 Deposition Process of PCMO and Al₂O_x Thin Films

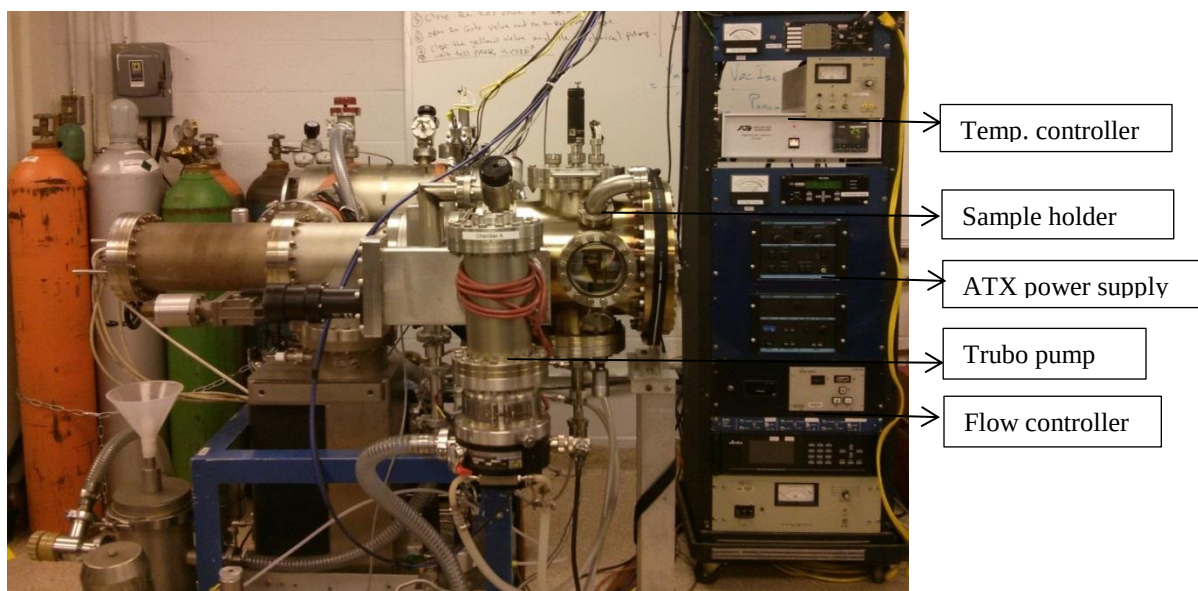


Figure.4.2 RF magnetron sputtering chambers

In both stacks shown in figure 4.1a, 4.1b, the bulk PCMO layer is grown in chamber one on a Pt/TiN/SiO₂/Si substrate by using a 2 inch PCMO (Pr_{0.7}Ca_{0.3}MnO₃) target made from grounded fine powder which is pressed into ¼ inch thick disc and then sintered in a furnace at a temperature of 1300°C. The substrates were degreased by sonication in acetone then methanol, DI water and then dried by blowing nitrogen gas. The substrate was placed into a custom made vacuum chamber as shown in Figure 4.3 on a controlled temperature hot stage facing down with 2inch separation form the target. The chamber was evacuated in two stages: first by mechanical pump then by turbo pump. The base pressure of the chamber was 2x10⁻⁷ torr. The substrate was then heated to 500°C in vacuum. The camber pressure was set to be 60mTorr by letting pure Ar into the chamber which was controlled by an MKS multi gas flow controller 647C (5cc/min). The radio frequency AC power supply (ATX-600) operated at a frequency of 13.56 kHz. The depositions were done using a 30W RF power level for 2hours at a deposition rate of 3.6nm/min in order to grow PCMO on the substrate. Similarly Al₂O_x is grown by transferring the sample into another chamber now the substrate is heated to 500°C, pressure is maintained at 60mtorr by letting in Ar and O₂ with flow rate of 1.5cc/min and 0.3cc/min respectively. Deposition is done at 40w RF power for different times to achieve desired thickness at a deposition rate of 2.5nm/min.

The RF plasma is shown in Figure.4.3. The sample holder is right above the RF target. The sample holder is heated to desired substrate temperature by using lamp heated with the help of a temperature controller.

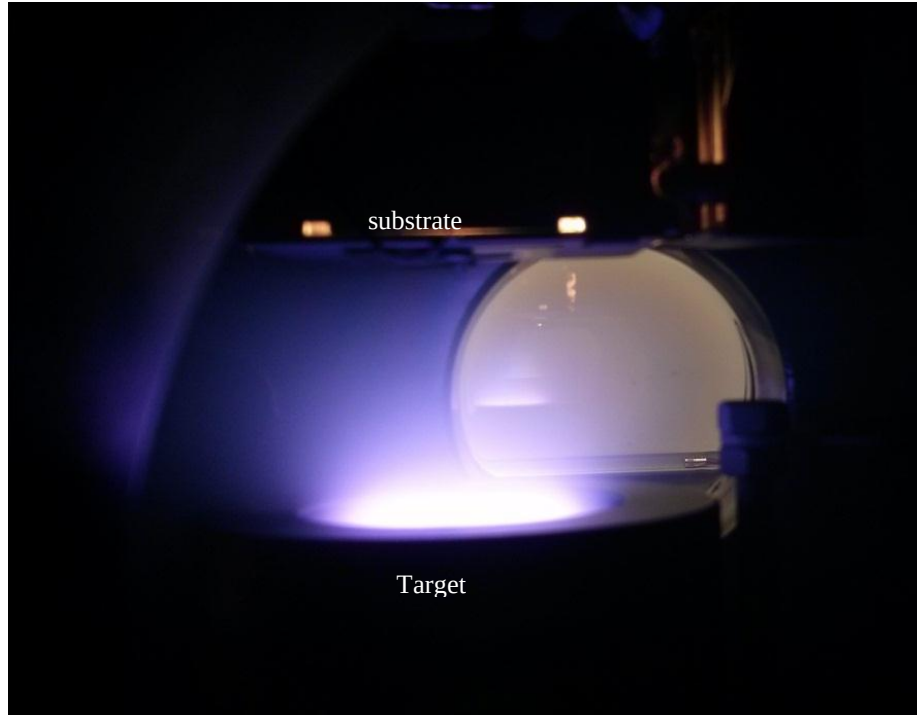


Figure.4.3 RF sputtering plasma during PCMO deposition

4.2 Electrical Hysteresis and EPIR Switching Measurements Setup

The stacks were characterized for EPIR endurance and retention properties using a computerized setup shown in Figure. 4.4 with the aid of custom made Lab View computer programs. Two-probe measurements were done using tungsten tips. The experimental setup consists of the following instruments:

- 1 - Agilent 8114A, 100V/2A Pulse Generator
- 2- Keithley programmable 7001 Switch System
- 3- Keithley programmable 230Voltage Source
- 4- Keithley programmable 6517A Electrometer
- 5- Tektronix TDS 520 Oscilloscope
- 6- Keithley 2341 Trigger controller

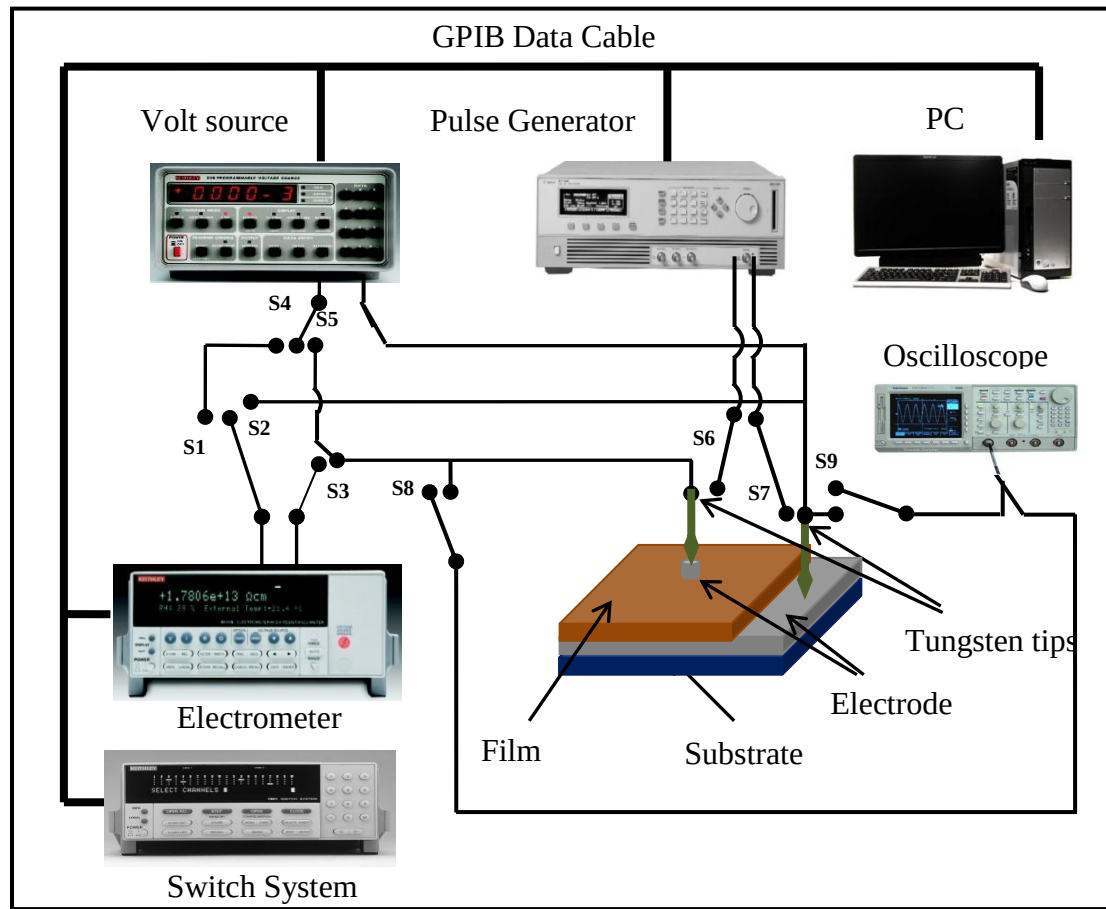


Figure.4.4 Overview of custom made EPIR measurement system [34]

4.2.1 Procedure of Sample Testing:

Once the sample is placed between the electrodes on the test bench, we use a LabView program to perform the desired function. The pulse generator gives voltage pulses of desired amplitude and pulse width. The trigger controller is used to control the number of pulses making sure that only the given numbers of pulses are sent to the sample. The oscilloscope is used to read the voltage across the sample after the voltage pulse is sent. The multiplexer is used to control the order of various signals oscilloscope (the switch system connects switches S6, S7, S8, and S9 only during the pulsing cycle).

After the voltage pulse is sent, a separate DC voltage source is used to generate the test voltage (usually 100mv or 200mv). The electrometer is used to measure the current flowing and thus allows for calculation of the resistance of the sample (the switch system connected switches S1, S3, and S4 only to measure the circuit current, then it connected switches S2, S3, and S5 only to measure the applied voltage).

4.3. I-V Measurement Setup:

A two probe I-V measurement was done using a computerized I-V setup as shown in figure. 4.5 The I-V characteristics of the sample is tested by applying DC voltage sweep between desired range say $-V$ to $+V$ with certain step $[0v \rightarrow -Vv \rightarrow 0v \rightarrow Vv \rightarrow 0v]$ during which the current is measured at each individual step. The representation of the setup can be seen in figure.4.5 it consists of a Keithley 236 source measurement unit automated with computer using GPIB interface.

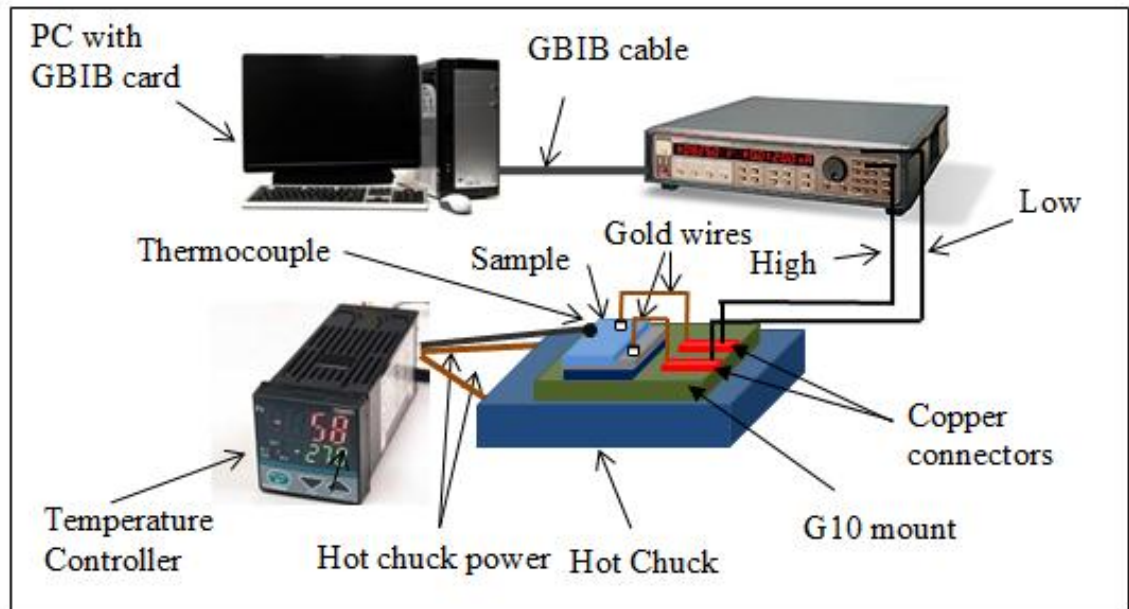


Figure.4.5 I-V measurement system [34]

Chapter 5 Results and Analysis

5.1 Film Thickness and Surface Analysis

To find the thickness of Al_2O_x film, we have deposited Al_2O_x under similar conditions for 1hour and examined the cross-section of sample under a SEM and measured the thickness of Al_2O_x at different points over the sample and calculated the average length to be 120~130nm. The cross-section can be seen in Figure. 5.1

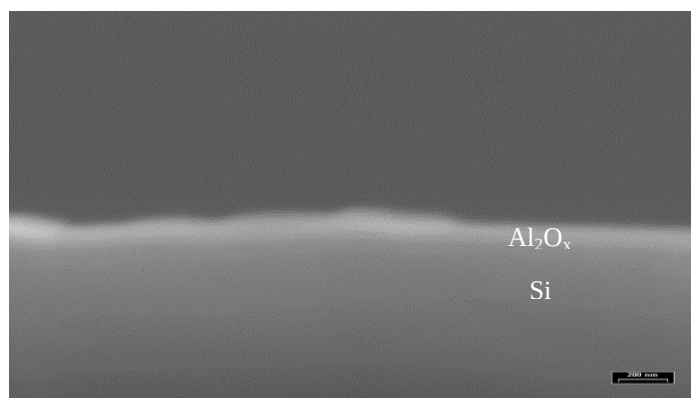


Figure. 5.1 SEM cross-section of $\text{Al}_2\text{O}_x/\text{Si}$

In the same way the cross-sections of three stacks under study were observed in order to find the thickness and confirm the different layers in the stacks. The images of PCMO/Pt, $\text{Al}_2\text{O}_x/\text{Pt}$ and PCMO/ $\text{Al}_2\text{O}_x/\text{Pt}$ are shown in figure 5.2a,b,c respectively. The following images are taken at 75,000X magnification with the scale of 200nm. The thickness of PCMO in figure 5.2a is approximately 420nm and the thickness of Al_2O_x , PCMO in figure 5.2b is approximately 10nm and 420nm. Whereas the thickness of top PCMO in figure 5.2c is about 50nm and the next two layers are 10nm of Al_2O_x and 420nm of PCMO.

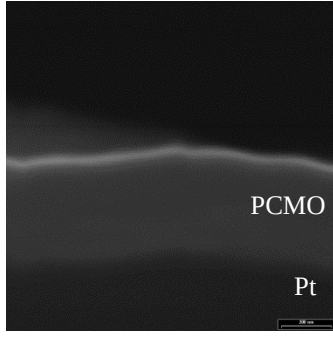


Figure 5.2 a)
400nmPCMO/Pt

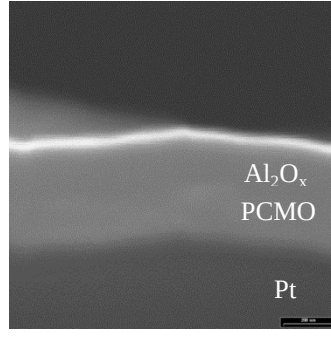


Figure 5.2 b)
10nmAl₂O_x/400nmPCMO/
Pt

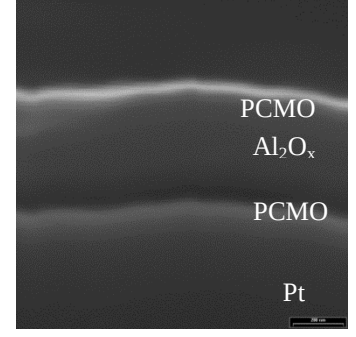


Figure 5.2 c) 50nmPCMO/
10nmAl₂O_x/400nmPCMO/
Pt

5.2 XRD analysis of PCMO/Pt, Al₂O_x/PCMO/Pt and PCMO/Al₂O_x/PCMO/Pt

The XRD analysis of the stacks PCMO/Al₂O_x/PCMO/Pt, Al₂O_x/PCMO/Pt, PCMO/Pt yielded the following pattern confirming the crystal structure of PCMO (200) which is predominant in switching characteristics of PCMO [35]. In PCMO/Pt the major peak in PCMO/Pt is at $\theta = 32.55$ which indicates PCMO (200) as shown in Figure. 5.3 which is diminished in case of Al₂O_x/PCMO/Pt due to presence of Al₂O_x on the top of PCMO. We can see PCMO (200) peak with reduced intensity in the PCMO/Al₂O_x/PCMO/Pt heterostructure indicating presence of PCMO at the top. The crystal structure of Al₂O_x is not evident due to its small thickness. The PCMO (202/040) peaks appears at $\theta = 44.6$ and 46.4 whose intensity can be noticed reduced in case of Al₂O_x on the top and increased in case of PCMO on the top for PCMO/Al₂O_x/PCMO/Pt heterostructure as shown in Figure. 5.3.

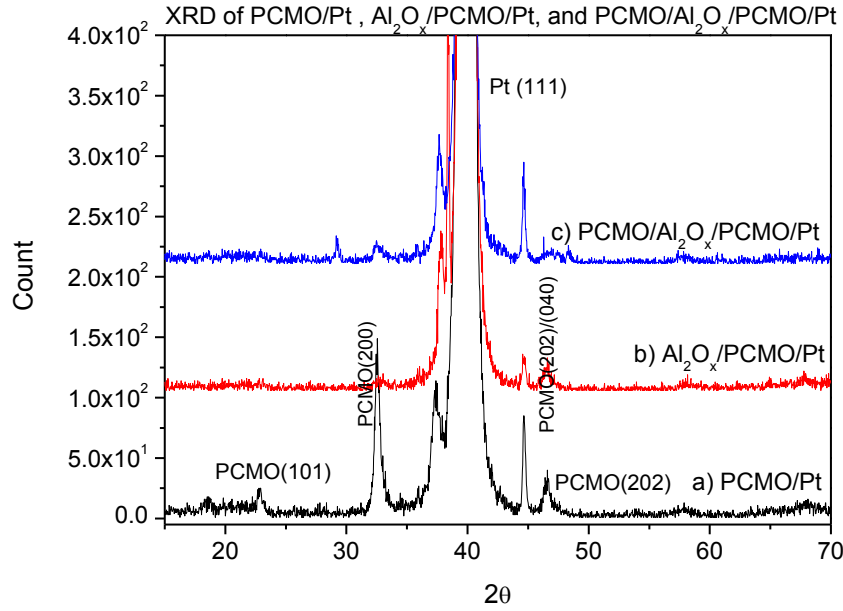


Figure 5.3 XRD analysis of different stack structures

5.3 EPIR Switching Behavior in PCMO RRAM

Only regular polarity switching was observed in PCMO as reported earlier [17]. Several mechanisms have been suggested for EPIR switching in PCMO. Also the phenomenon of switching in metal/PCMO/metal structure was explained by the movement of oxygen ions into metal/PCMO interface region where it is always oxygen deficient (occurs at the top PCMO interface during the RF sputtering growth). Filling the vacancies present at the top interface region causes low resistance state (LRS) under positive electric pulse and depleting the top interface of PCMO from oxygen ions and leaving the vacancies by driving oxygen ions into bulk PCMO with the influence of negative electric pulse will cause the high resistance state (HRS). The positive pulse direction is defined as from the top electrode to the bottom electrode. Here the bulk PCMO is considered as the source of oxygen ions as shown in figure 5.4

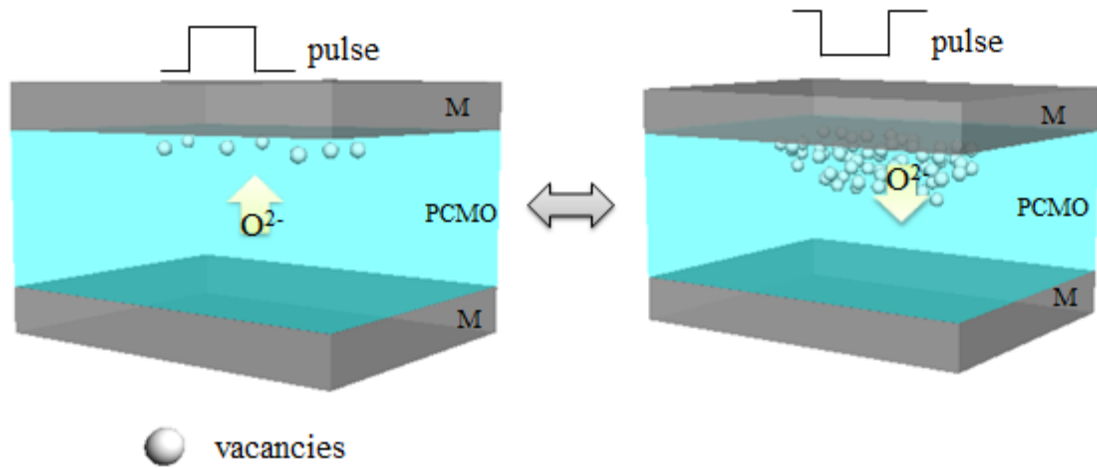


Figure 5.4 Position of vacancies in PCMO during switching

The performance of any RRAM device is characterized by electric-pulse-induced-resistance (EPIR) ratio which is defined as the ratio between the high resistance state (HRS) and low resistance state (LRS): $(HRS-LRS)/LRS$; and the stability of the resistance state which is a combination of low fatigue and high endurance of resistance state after the switching pulse has been removed from the sample. In the present work W/PCMO/Pt exhibited only regular polarity switching under 4v of positive electric pulse and 5v of negative electric pulse of 400ns width and a test voltage of 0.2v during endurance and retention measurements. we see undesired behavior in terms of high fatigue loss (150%) and unstable retention (20% change in HRS and 50% change in LRS) over a period of 24hours i.e., 50000 cycles of testing as shown in figure 5.5a, 5.5b This retention instability is believed due to the back migration of O^{2-} ions and vacancies with time.

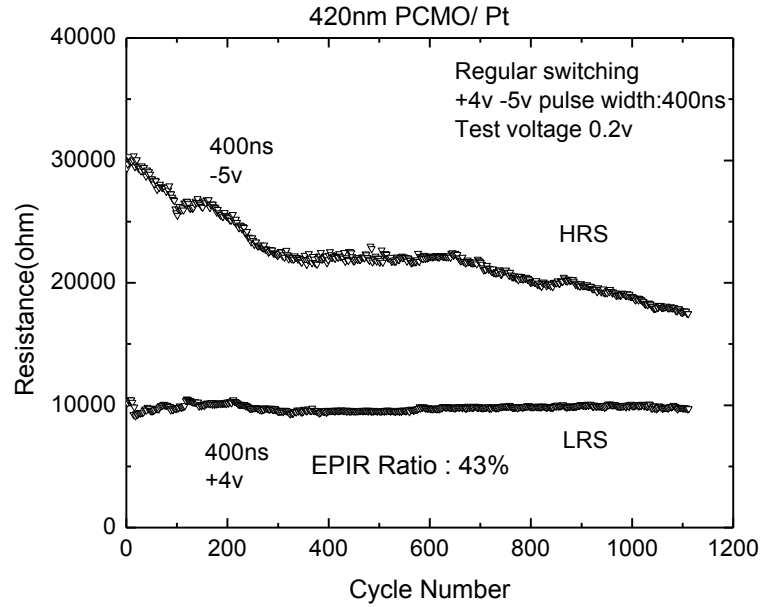


Figure 5.5a EPIR switching in PCMO/Pt

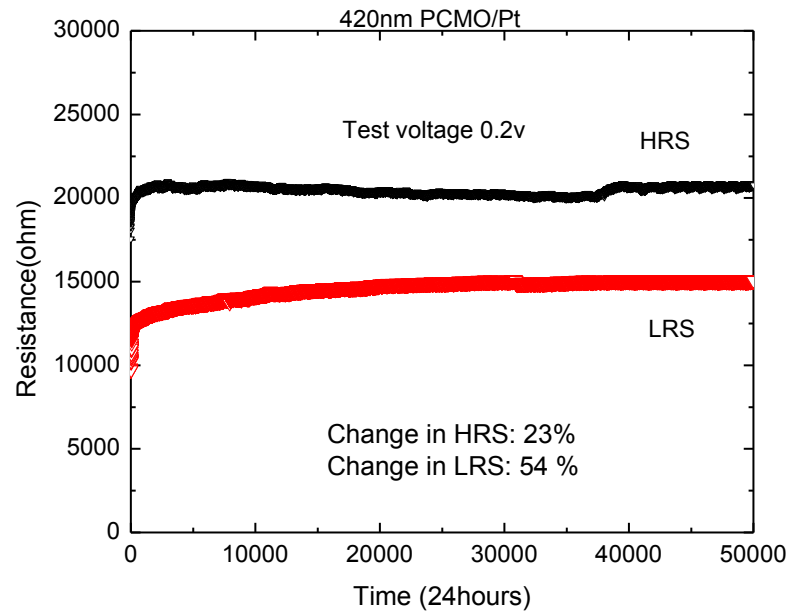


Figure 5.5b Retention in PCMO for 24hrs

We believe that including a Al_2O_x buffer layer may slow down the relaxation effect of O^{2-} ions and vacancies which may lead to not only enhancement in the retention behavior but also the EPIR switching ratio. We have observed a change in the switching mechanisms with the inclusion of the buffer layer upon applying varied electric pulses, a reverse polarity switching mechanism in the bipolar switching is observed with small

applied voltage as compared to the voltage required for regular PCMO switching. With higher amplitude electric pulse, the PCMO is driven to a switching mechanism with improved retention properties and previously observed regular switching of figure 5.5a.

5.4 Investigation of Resistance Switching of PCMO RRAM with Al₂O_x buffer layer

Oxygen deficient Al₂O_x buffer layer with different thickness have been used in two positions of the stack (Al₂O_x/PCMO, and PCMO/Al₂O_x/PCMO). In all samples switching endurance measurements have been carried out with test voltage of 200mv by applying + and – voltages of 400ns pulse width. Hysteresis measurements have also been investigated using -4v to 4v 400ns voltage ramping with a step of 0.1v. Finally I-V measurements are performed using source measure unit with a DC voltage sweep from -2.5v to 2.5v and compliance current of 20mA.

In order to switch the samples we start with +3v, -3v peak voltage, 400ns pulse width and a test voltage of 200mv was used to measure the resistance after pulsing. EPIR switching Endurance is measured for 1000 cycles, then the sample is set to High resistance state (HRS) and retention of HRS is measured for 50,000 cycles (approximately 24 hours) after HRS retention the sample is again switched for 500 cycles and set to Low resistance state (LRS) and similarly retention of LRS is measured.

5.4.1 EPIR Switching in 2.5nmAl₂O_x/420nmPCMO Samples

2.5nmAl₂O_x/420nmPCMO heterostructure with aluminum oxide grown on top of PCMO using RF sputtering technique under process conditions of 60mtorr pressure with Ar:O₂ ratio of 1:5 at 500°C for 1 minute is tested, The sample exhibited both regular and reverse polarity EPIR switching by applying 400nsec pulsing. Switching endurance,

retention, Hysteresis and I-V measurements have been taken performed on the above sample in order to determine the effect of buffer layer by comparing it with PCMO/Pt sample.

5.4.1.1 Regular Switching in 2.5nmAl₂O_x/420nmPCMO

When applied electric pulse amplitude during negative cycle is higher than positive cycle we observe regular polarity switching [-ve pulse gives HRS and +ve pulse gives LRS]. Details on this regular polarity switching appeared in this sample were endurance, retention, hysteresis and I-V characteristics are shown in Figure 5.6a,b,c,d respectively. The switching stability for 1000 cycles of switching is shown in Fig. 5.6a, retention of the individual states over a period of 24hours is shown in Figure 5.6b. The EPIR ratio (ΔR) was 78% and constant over the period, with nearly negligible fatigue loss and from figure 5.6b the loss in high resistance state was 6% and the change in low resistance state was 12% which is improvement as compared to normal PCMO. The improvement without fatigue loss and decrease in retention loss is due to Al₂O_x buffer layer which inhibits the diffusion of oxygen ions trying to settle back causing a drop in retention.

As we apply short electric pulse with short increase in voltage, the negative pulse takes the sample to high resistance state and it continues to stay there until enough positive pulse is applied again to switch the sample to low resistance state as shown in Figure 5.6c depicting the hysteresis measurements of the sample. The short tail observed in the hysteresis is believed due to oversaturation of resistance i.e. when the applied voltage pulse is removed the resistance drops short before the next voltage pulse. This relaxation of sample is the cause of instability in retention during the initial stage when

the applied voltage pulse is removed. During regular switching the resistance of sample drops at high positive pulse and requires lesser voltage to produce same amount of current whereas at higher negative pulse the resistance of sample increases requiring higher voltage to produce same amount of current as shown in Figure 5.6d.

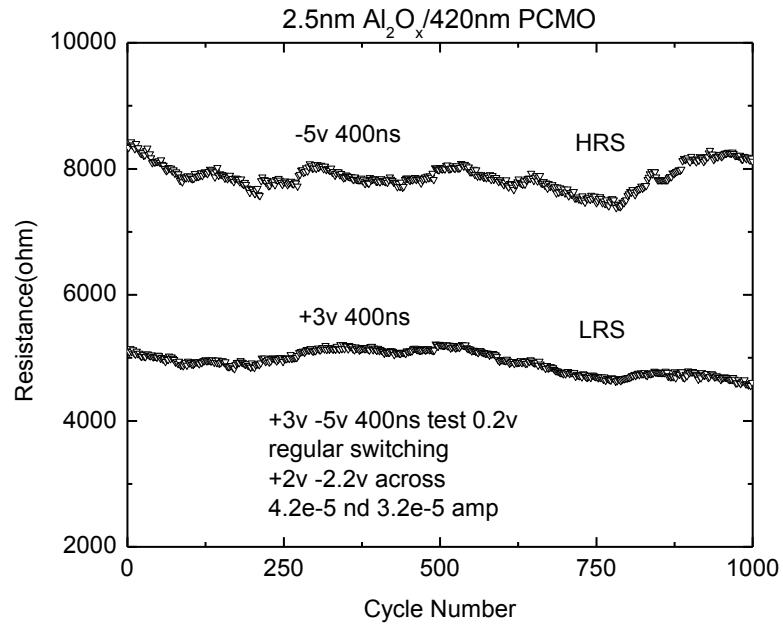


Figure 5.6a Switching in 2.5nmAl₂O_x/420nmPCMO

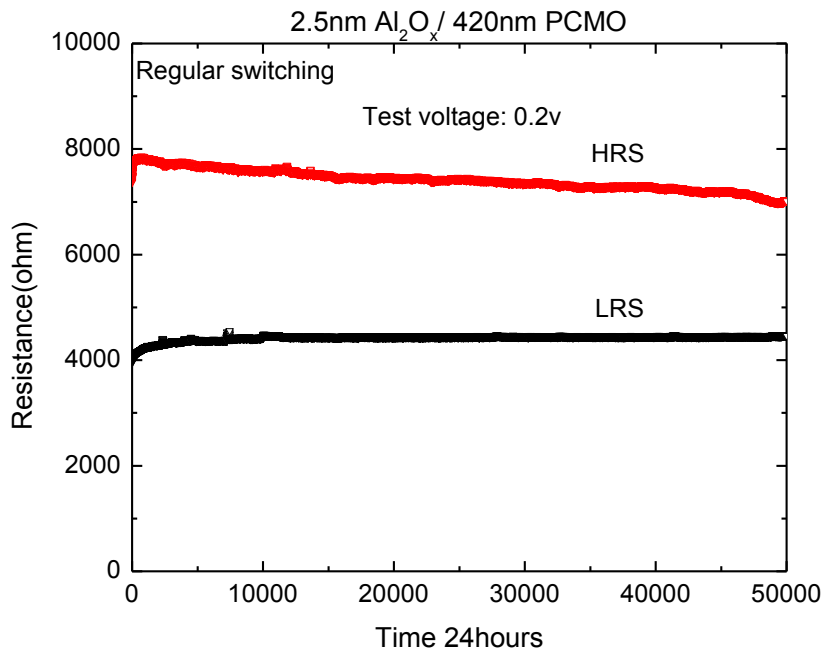


Figure 5.6b Retention of HRS and LRS for 24hours in 2.5nmAl₂O_x/ PCMO

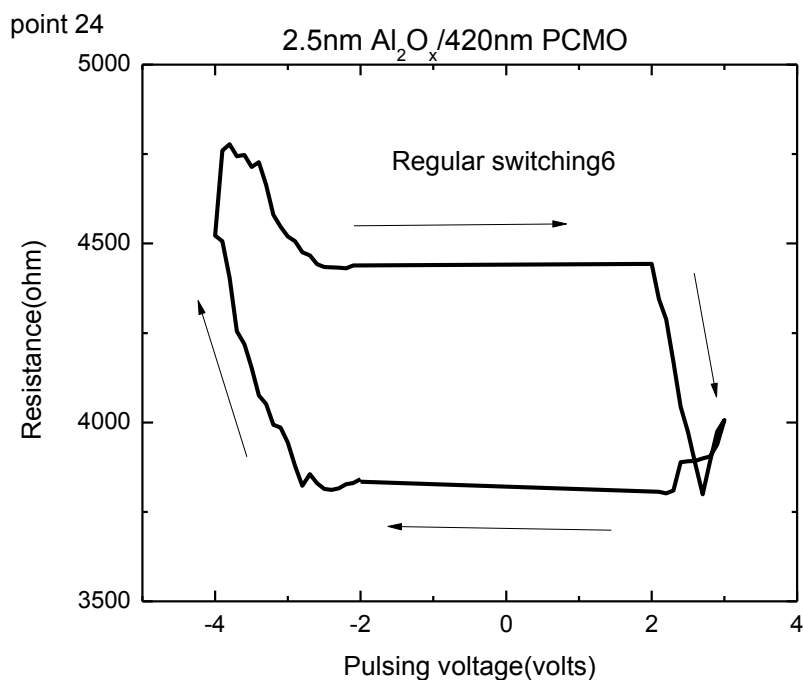


Figure 5.6c Hysteresis in 2.5nmAl₂O_x/420nmPCMO

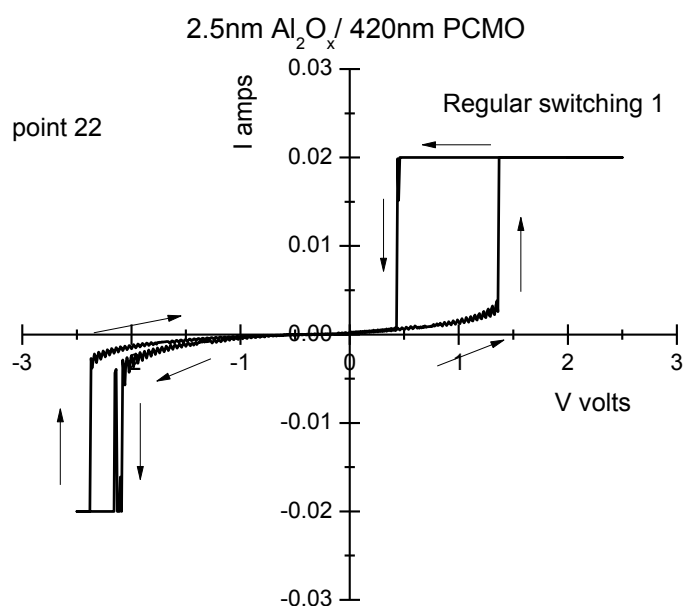


Figure 5.6d Hysteresis in I-V measurement of 2.5nmAl₂O_x/420nmPCMO

From the data illustrated in Figure 5.6a,b,c,d regular polarity switching mechanism can be explained by a model illustrated in schematic shown in Figure 5.7. The bulk PCMO can be considered as a source of oxygen ions the concentration of

oxygen decreases as we approach the interface of $\text{Al}_2\text{O}_x/\text{PCMO}$. On the first instance of pulse the resistance of sample is high due to presence of vacancies at the interface, when positive voltage pulse is applied the oxygen ions are drawn towards the interface from bulk PCMO at the bottom which acts as source, filling the vacancies at interface and resulting in Low Resistance State (LRS). Once the switching began we believe that under the high negative pulse due to movement of oxygen ions into the bulk PCMO from the top interface of $\text{Al}_2\text{O}_x/\text{PCMO}$ drives the device to a high resistance state (HRS). While upon applying the positive voltage pulse the vacancies are filled back in with oxygen ions causing a low resistance state (LRS) as resulting in regular polarity switching in $\text{Al}_2\text{O}_x/\text{PCMO}/\text{Pt}$. The amount of electric field $1\text{e}^7\text{V}/\text{cm}$ is generated by electric pulse is enough to drive the oxygen ions in opposite direction of electric field. The amplitude of pulse voltage is not enough to change vacancy concentration in Al_2O_x . Al_2O_x only acts as diffusion barrier in this mechanism.

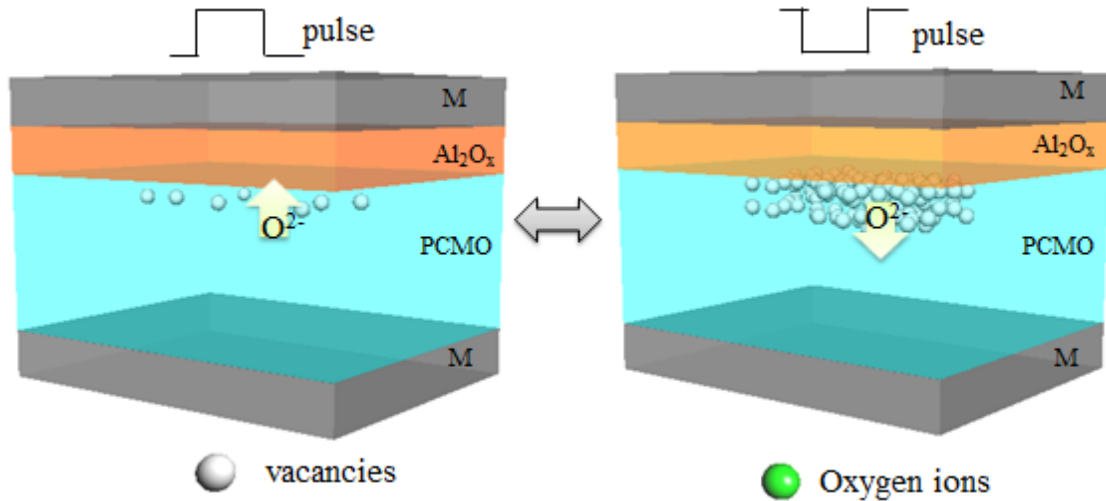


Figure 5.7 Position of oxygen ions and vacancies during regular switching

5.4.1.2 Reverse switching in 2.5nmAl₂O_x/420nmPCMO:

Reverse switching has been observed in 2.5nmAl₂O_x/420nmPCMO heterostructure with applied electric pulse amplitude during positive cycle is higher than negative cycle driving the oxygen ions in between Al₂O_x and PCMO rather than interface and bulk of PCMO. After we have reached 1000 cycles of switching the sample was tested for retention for HRS (High resistance state) first followed by LRS (Low resistance state) for 24hours each respectively. The switching and retention results for the above sample can be seen in Figure 5.8a, 5.8b.

The EPIR ratio (ΔR) was 53% constant over the period with nearly negligible fatigue loss. The loss in the high resistance state is 3% and the change in low resistance state is 4% which is also an improvement as compared to normal PCMO. The improved retention properties are because of migration of oxygen ions between Al₂O_x/PCMO where Al₂O_x inhibits the movement of ions in the absence of applied electric voltage pulse.

When we apply short electric pulse with short increase in voltage, the negative pulse takes the sample to low resistance state and it continues to stay there until enough positive pulse is applied again to switch the sample to high resistance state as shown in Figure 5.8c. During reverse switching the resistance of sample increases at high positive pulse and requires higher voltage to produce same amount of current whereas at higher negative pulse the resistance of sample decreases requiring lower voltage to produce same amount of current therefore we see different path for the I-V characteristics compared to regular polarity switching as shown in Figure 5.8d.

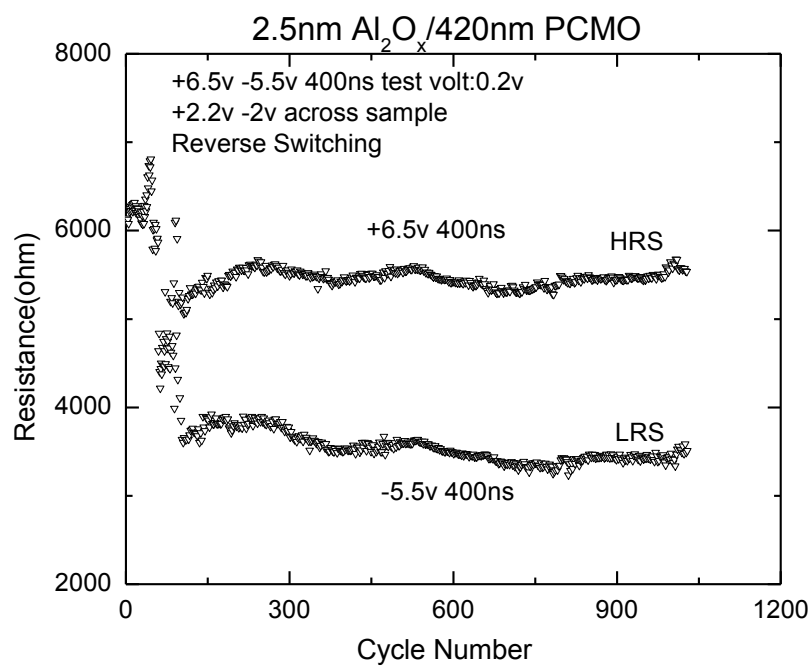


Figure 5.8a Switching in 2.5nmAl₂O₃/420nmPCMO

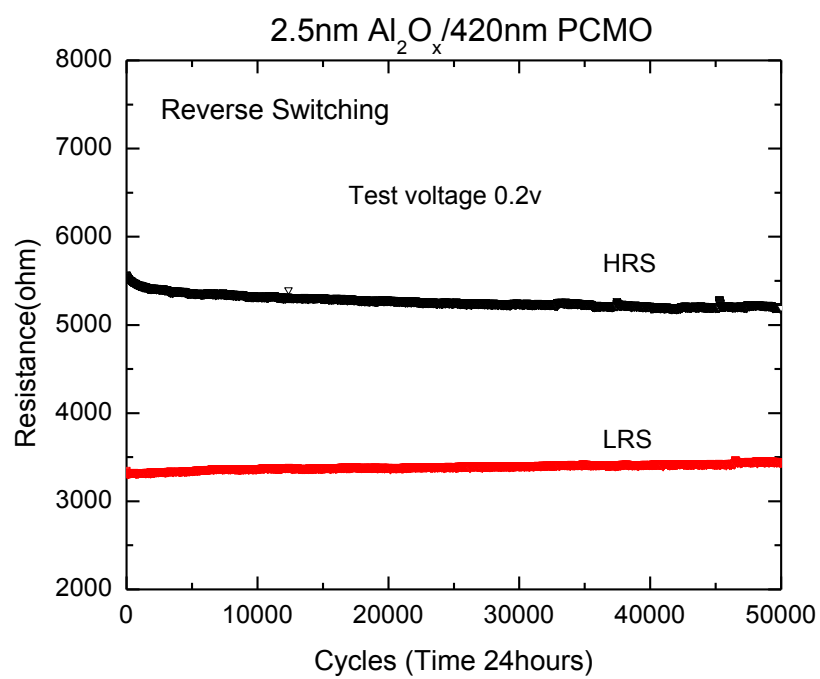


Figure 5.8b HRS and LRS retention for 24hours

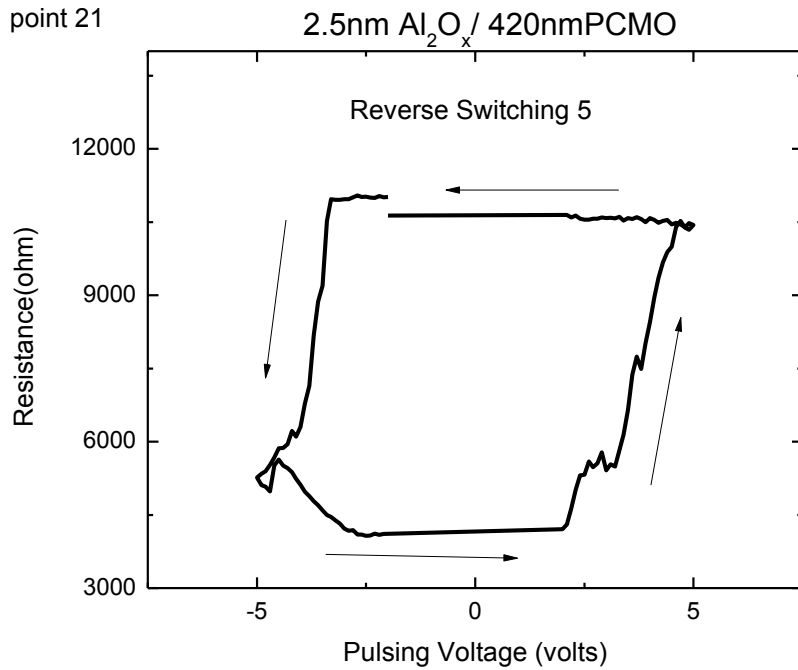


Figure 5.8c Hysteresis in 2.5nmAl₂O_x/420nmPCMO

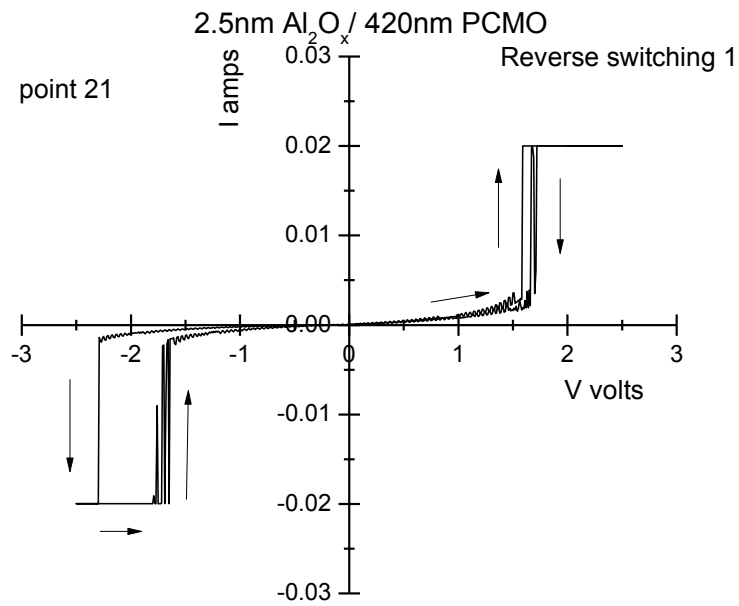


Figure 5.8d Hysteresis in I-V measurement of 2.5nmAl₂O_x/420nmPCMO

From the data illustrated in Figure 5.8a,b,c,d. Reverse polarity switching in Al₂O_x/PCMO can be explained by a model in schematic Figure 5.9.Reverse polarity

switching is due to the movement of oxygen ions into the oxygen deficient Al_2O_x leaving vacancies behind causing high resistance state (HRS) under negative voltage pulse, and filling of these vacancies back with oxygen ions from the Al_2O_x under positive pulse which causes the low resistance state (LRS). Because of initial High Resistance State (HRS) due to positive electric pulse there is larger potential drop across Al_2O_x . During consecutive negative electric pulse large E-Field is concentrated across this region leading to large field driven vacancy motion. Hence we require a higher positive voltage pulse to fill the vacancies back. The vacancies present in Al_2O_x also contribute to low resistance as the resistance of Al_2O_x increases with stoichiometry and decreases with non-stoichiometry.

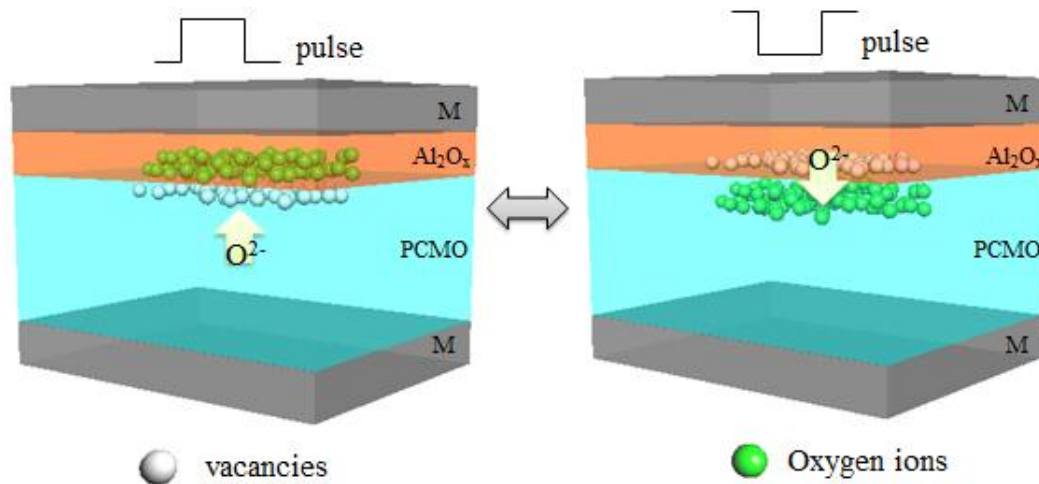


Figure 5.9 Position of oxygen ions and vacancies during reverse switching

The EPIR ratios, retention of high and low resistance states for $2.5\text{nmAl}_2\text{O}_x/420\text{nmPCMO}/\text{Pt}$ have been compared with PCMO/Pt in Table 1. The improvement in the retention in case of the $\text{Al}_2\text{O}_x/\text{PCMO}$ sample's regular switching is due to the Al_2O_x top layer preventing the structural relaxation of the top PCMO interface region. Whereas, the highly improved retention properties are seen for the case of reverse

switching. In this structure, switching is due to movement of ions in and out of the Al_2O_x layer, which doesn't conduct ions unless there is an electric field.

Table 2. Switching ratio and Retention loss in $2.5\text{nmAl}_2\text{O}_x/420\text{nmPCMO/Pt}$

	420nm PCMO	2.5nm Al_2O_x / 420nm PCMO	
	Regular	Regular	Reverse
High Resistance State (HRS)	17,000 Ω	8,200 Ω	5,522 Ω
Low Resistance State (LRS)	11,000 Ω	4,600 Ω	3,596 Ω
EPIR ratio (ΔR)	43%	78%	53%
% change in HRS 24h	23%	-6%	-3%
% change in LRS 24h	54%	12%	4%

5.4.2 Effect of Al_2O_x thickness in switching and Retention $\text{Al}_2\text{O}_x/\text{PCMO/Pt}$

The thickness of the diffusion barrier was varied and then switching properties of the resulting stacks have been studied in order to see the effect of thickness of buffer layer on the EPIR ratio, retention and to observe the dominance of type of switching regular or reverse in each case.

5.4.2.1 Regular switching observed in 5nm, 7.5nm and 10nm $\text{Al}_2\text{O}_x/\text{PCMO}$

The stacks with 5nm, 7.5nm, 10nm $\text{Al}_2\text{O}_x/\text{PCMO}$ can be switched in regular polarity by applying higher amplitude of electric pulse during negative cycle compared to

the positive cycle used for switching the sample. In case of 5nmAl₂O_x buffer layer in 5nm Al₂O_x/420nm PCMO heterostructure switching endurance, retention, hysteresis and I-V characteristics have been studied and plotted as shown in Figure 5.10a,b,c,d.

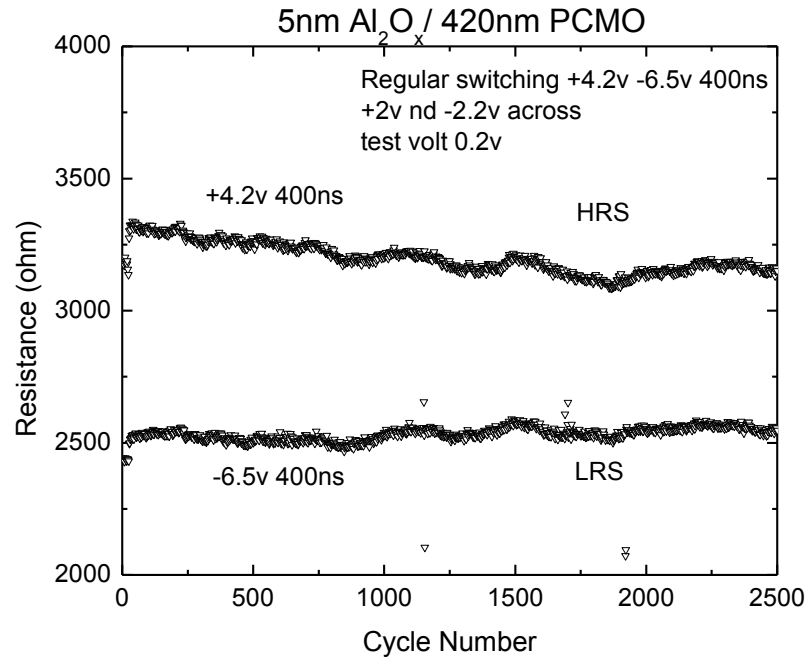


Figure 5.10a Regular switching in 5nm Al₂O_x/ PCMO/Pt

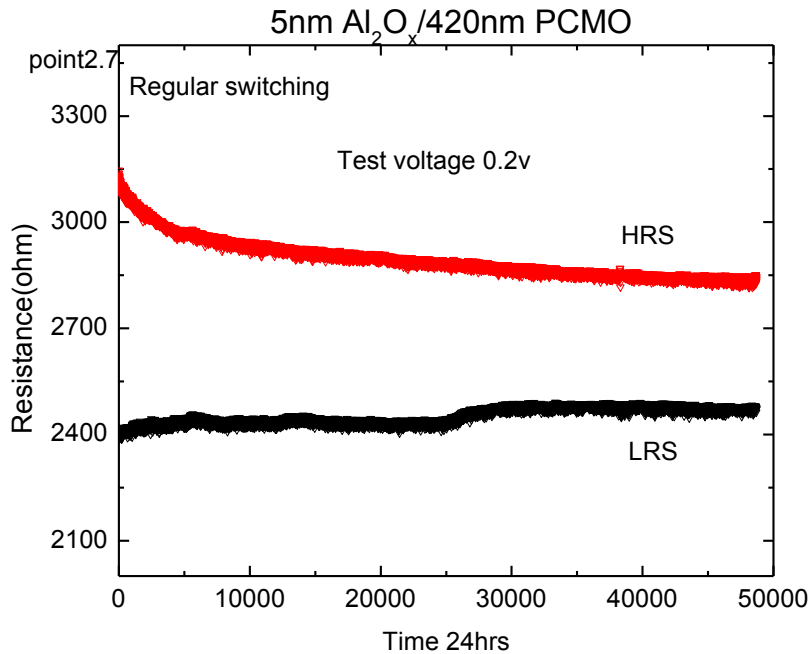


Figure 5.10b Retention of HRS and LRS in 5nm Al₂O_x/ 420nm PCMO/Pt

The EPIR ratio (ΔR) was 21% constant over the period with nearly negligible fatigue loss. The loss in the high resistance state is 10% and the change in low resistance state is 2%. Hysteresis measurements follow the regular switching trend. The loop at bottom right corner in Figure 5.10c and extension at top left corner indicate the over saturation in resistance explaining the retention loss in this structure.

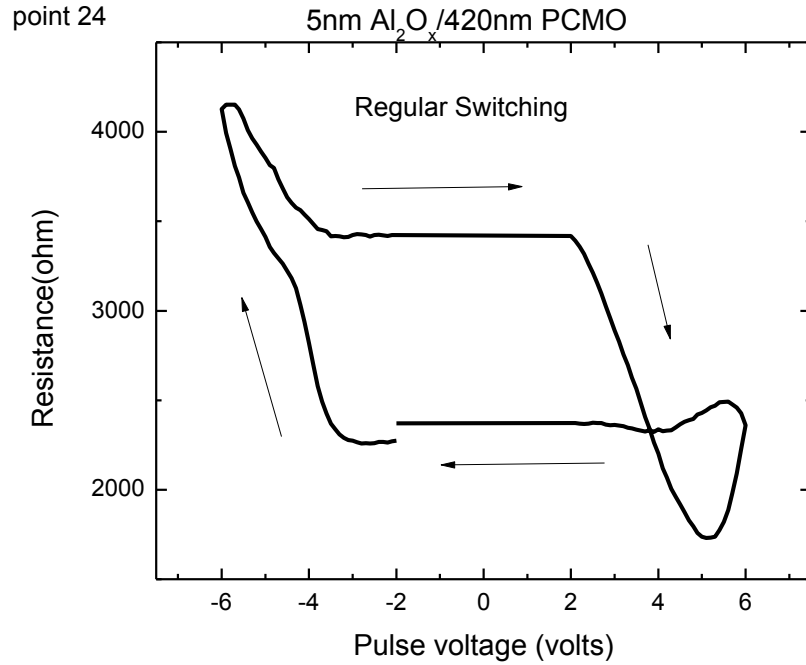


Figure 5.10c Hysteresis in 5nmAl₂O_x/420nmPCMO

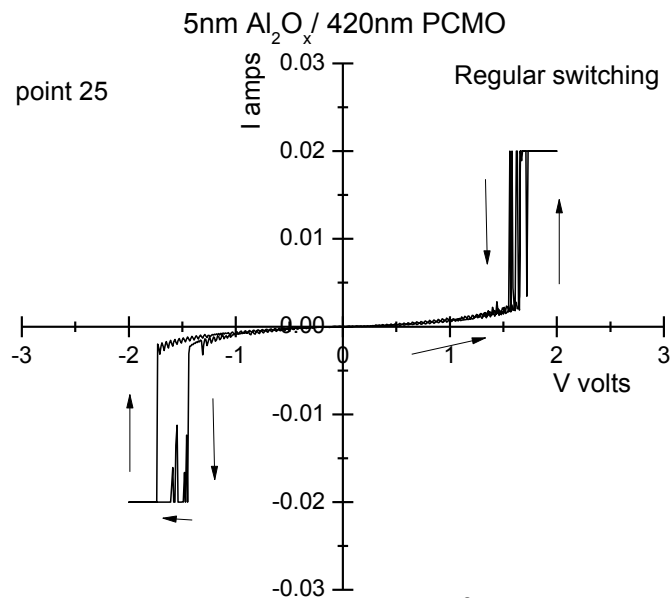


Figure 5.10d Hysteresis in I-V measurement of 5nmAl₂O_x/420nmPCMO

In case of 7.5nmAl₂O_x buffer layer in 7.5nm Al₂O_x/420nm PCMO heterostructure switching endurance, retention, hysteresis and I-V characteristics have been studied and plotted as shown in Figure 5.11a,b,c,d The EPIR ratio (ΔR) was 94% constant over the period after increasing during initial switching and settling at constant value with negligible fatigue loss. The loss in the high resistance state is 11% and the change in low resistance state is 10%. The loop in hysteresis in Figure 5.11c has reduced here indicating less relaxation in structure as it has very high EPIR ratio. Hence we have improved retention stability.

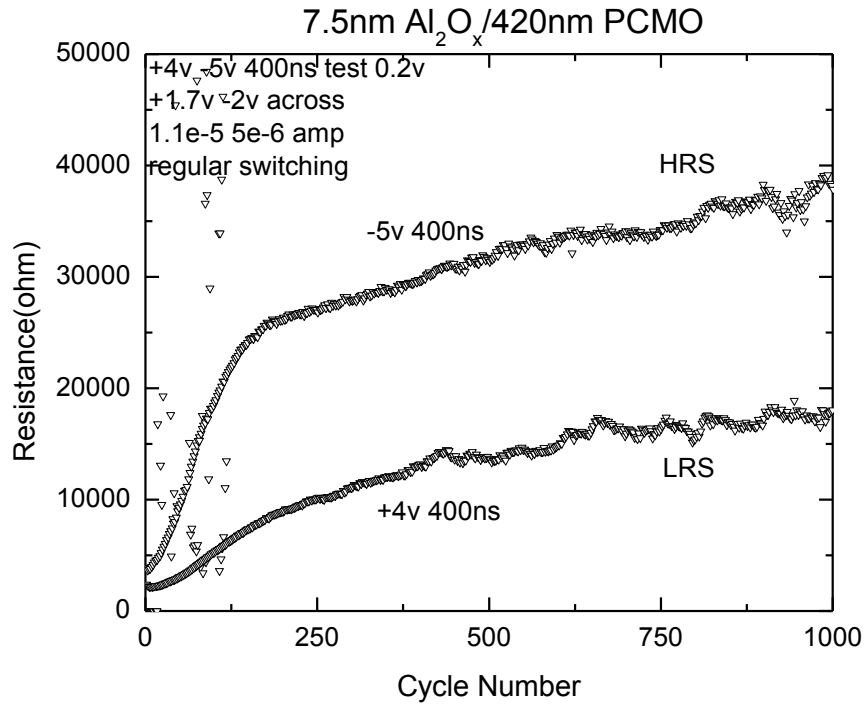


Figure 5.11a Regular switching in 7.5nmAl₂O_x/ PCMO/Pt

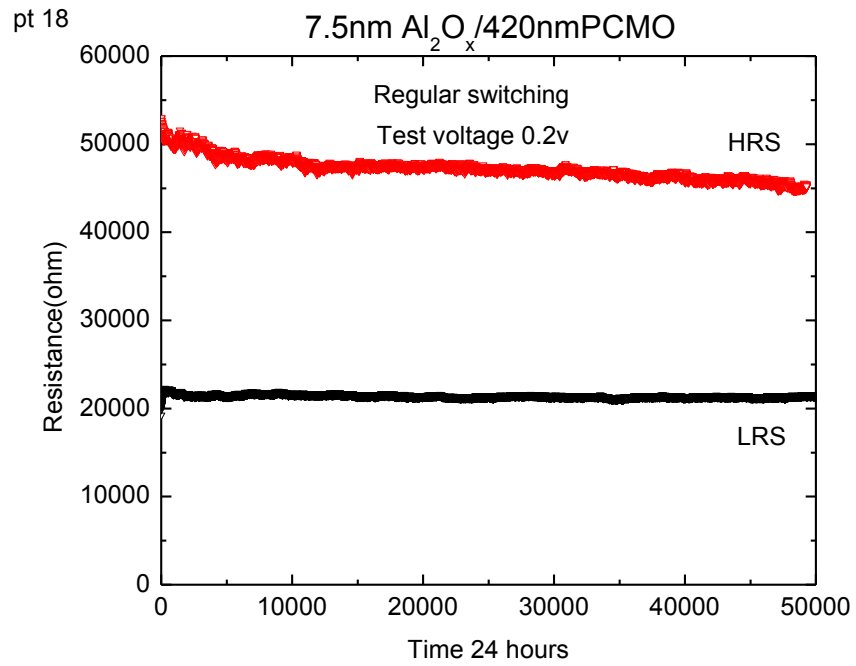


Figure 5.11b Retention of HRS and LRS in 7.5nm Al_2O_x / 420nm PCMO/Pt

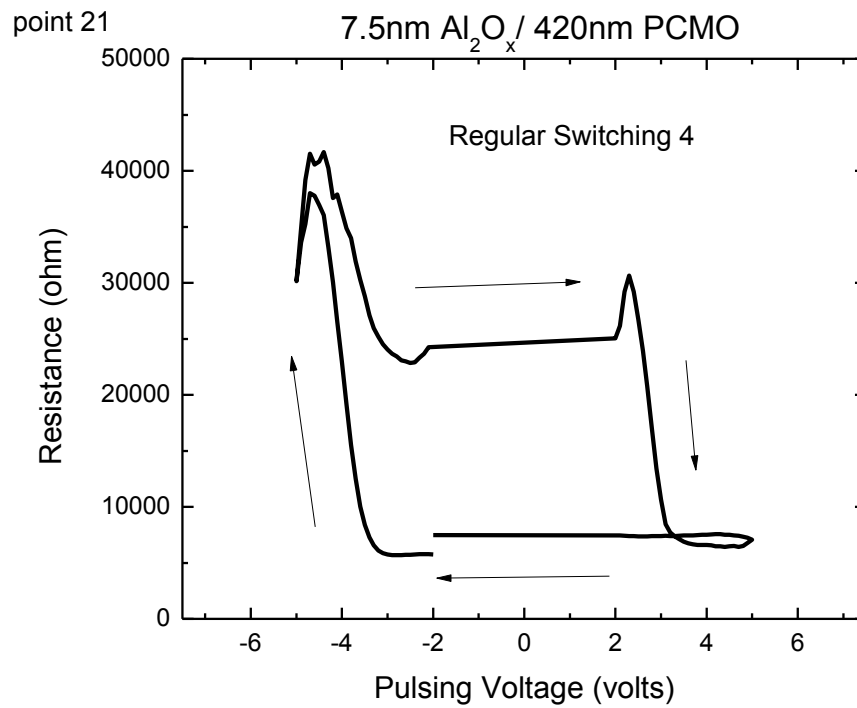


Figure 5.11c Hysteresis in 7.5nm Al_2O_x /420nmPCMO

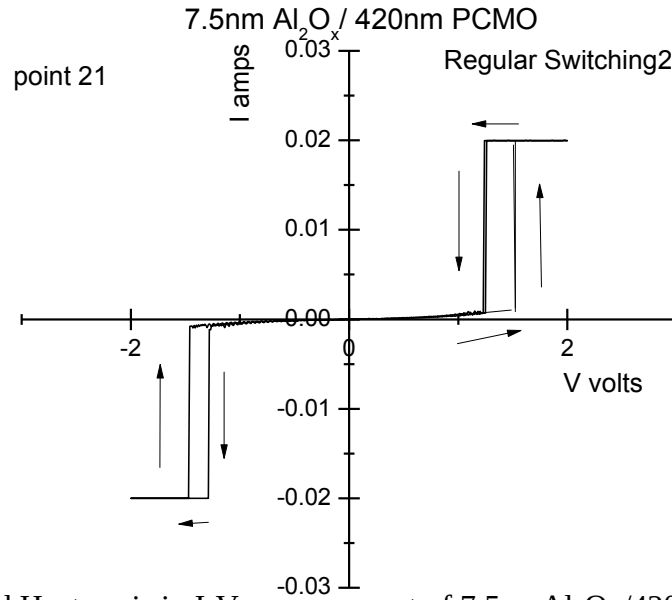


Figure 5.11d Hysteresis in I-V measurement of 7.5nmAl₂O_x/420nmPCMO

In case of 10nmAl₂O_x buffer layer in 10nm Al₂O_x/420nm PCMO heterostructure switching endurance, retention, hysteresis and I-V characteristics have been studied and plotted as shown in Figure 5.12a,b,c,d. The EPIR ratio (ΔR) was 20% constant over the period and it is decreasing with time. The change in the high resistance state is 16% and the change in low resistance state is 6%. The HRS is very unstable as indicated in hysteresis Figure 5.12c.

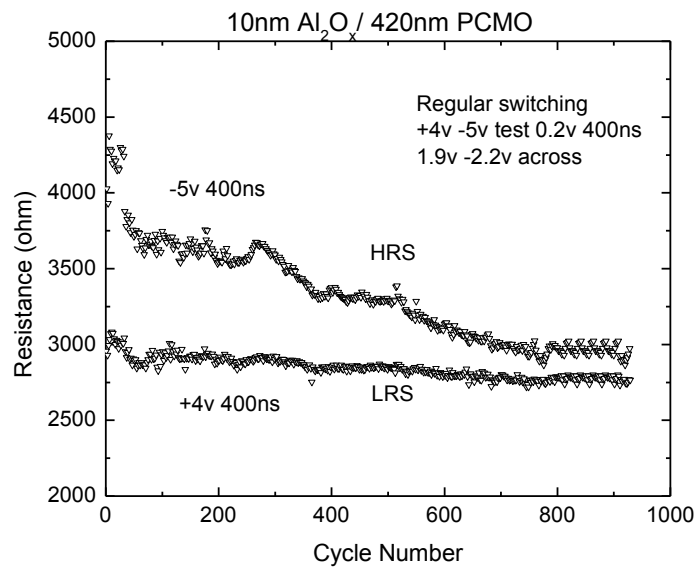


Figure 5.12a Regular switching in 10nmAl₂O_x/ PCMO/Pt

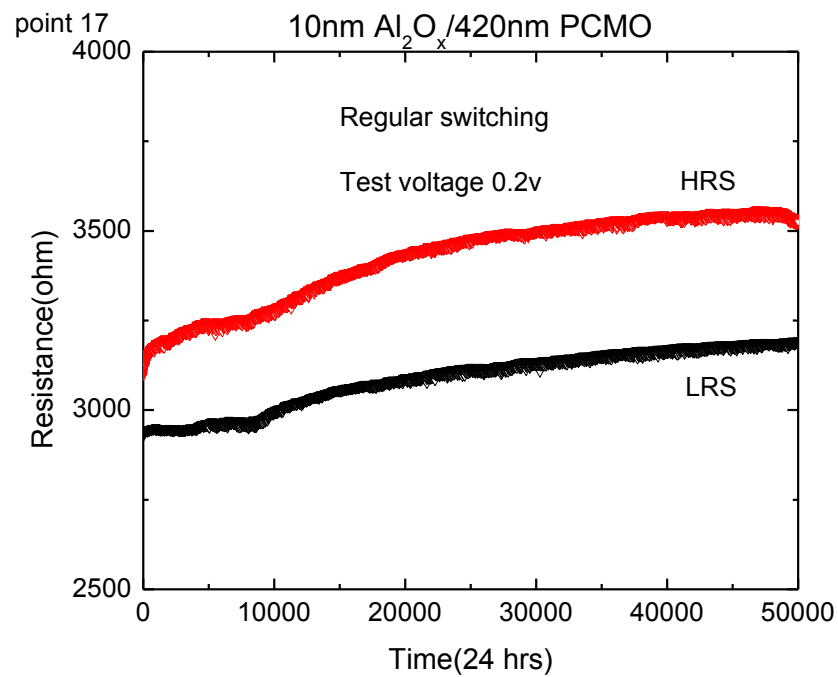


Figure 5.12b Retention of HRS and LRS in 10nm Al₂O_x/ 420nm PCMO/Pt

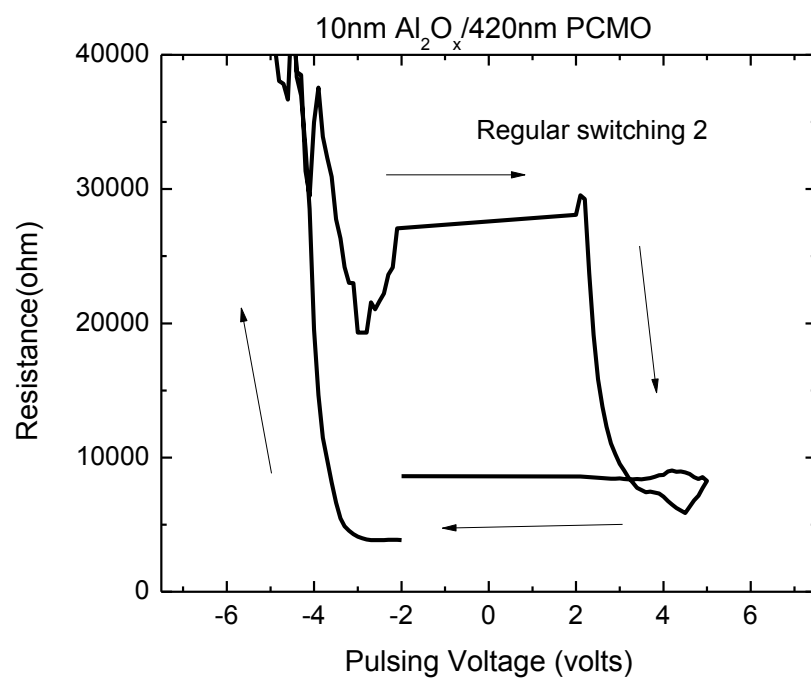


Figure 5.12c Hysteresis in 7.5nmAl₂O_x/420nmPCMO

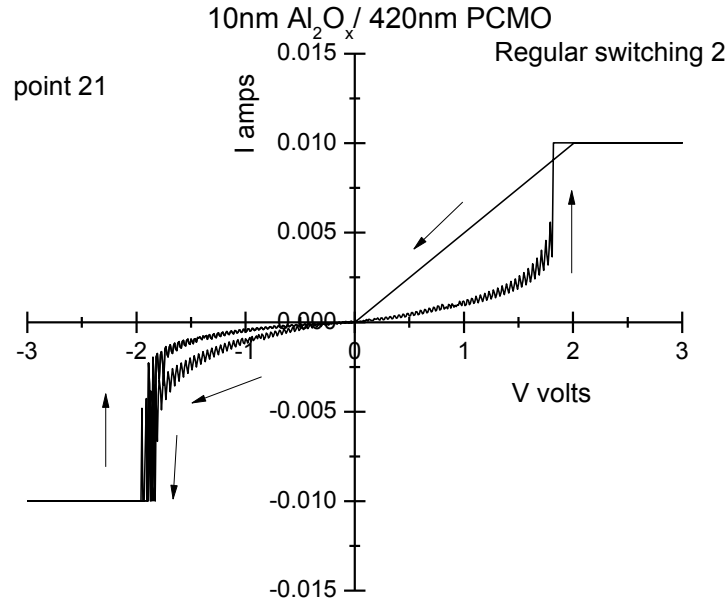


Figure 5.12d Hysteresis in I-V measurement of 7.5nmAl₂O_x/420nmPCMO

5.4.2.2 Reverse switching observed in 5nm, 7.5nm and 10nm Al₂O_x/PCMO and its retention

The stacks with 5nm, 7.5nm, 10nm Al₂O_x/PCMO can be switched in reverse polarity by applying slightly higher amplitude of electric pulse during positive cycle compared to the negative cycle used for switching the sample. The EPIR switching, retention, hysteresis and I-V characteristics of 5nmAl₂O_x/PCMO/Pt were shown in figure 5.13a,b,c,d respectively. The EPIR ratio (ΔR) was 33% constant over the period and it has little fatigue loss. The change in the high resistance state is 3% and the change in low resistance state is 29%. The HRS is very stable as indicated in hysteresis Figure 5.13c.

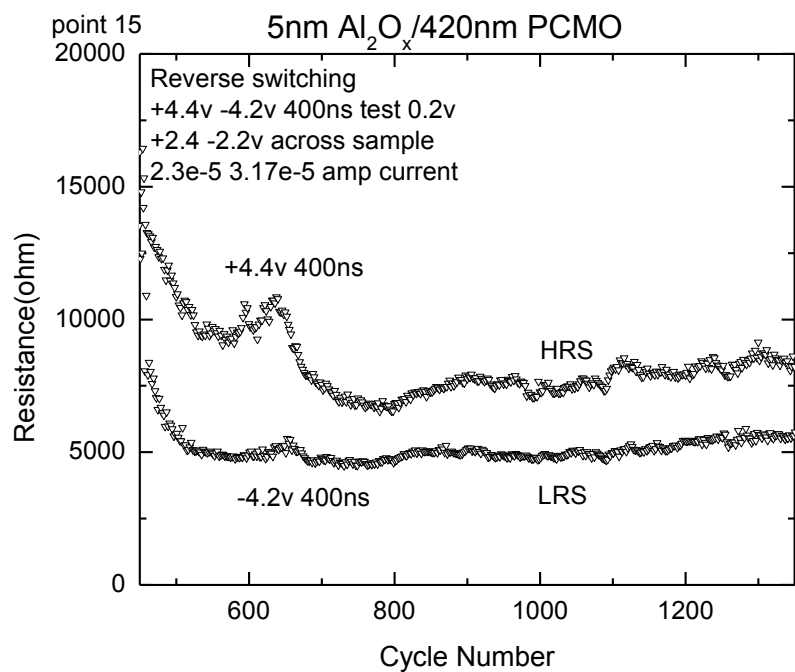


Figure5.13a Reverse switching in 5nmAl₂O_x/ PCMO/Pt

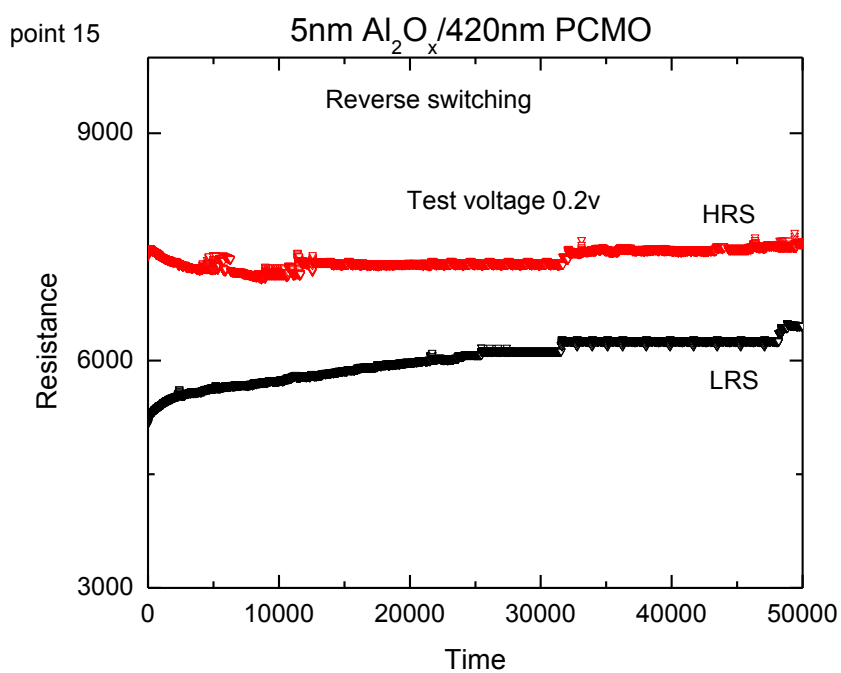


Figure. 5.13b Retention of HRS and LRS in 5nm Al₂O_x/ 420nm PCMO/Pt

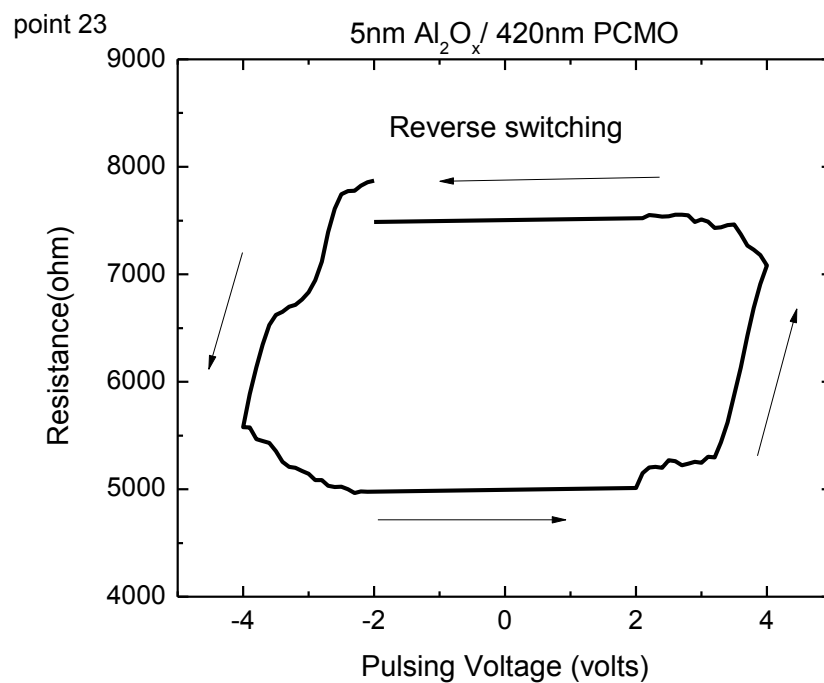


Figure 5.13c Hysteresis in 5nm Al_2O_x /420nmPCMO

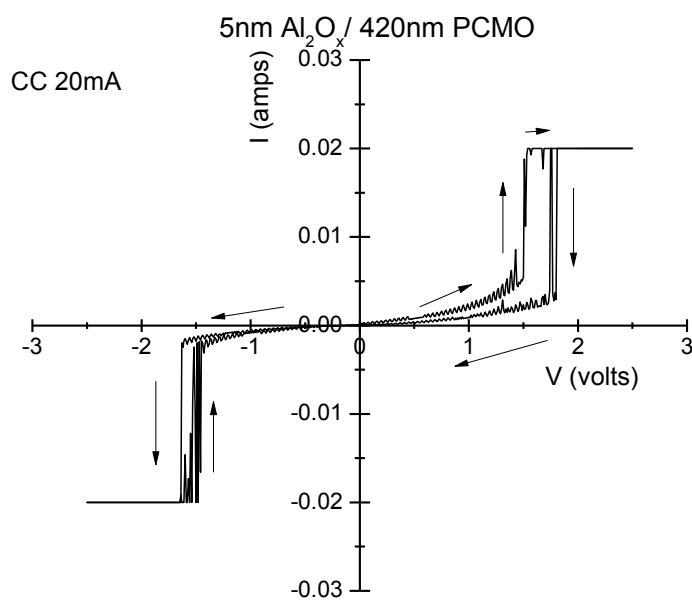


Figure 5.13d Hysteresis in I-V measurement of 5nm Al_2O_x /420nmPCMO

In case of 7.5nmAl₂O_x buffer layer in 7.5nmAl₂O_x/420nm PCMO heterostructure switching endurance, retention, hysteresis and I-V characteristics have been studied and plotted as shown in Figure 5.14a,b,c,d The EPIR ratio (ΔR) was 77% constant over the period and it has little fatigue loss. The change in the high resistance state is 4% and the change in low resistance state is 4%. The HRS and LRS were very stable as indicated in hysteresis Figure 5.14c.

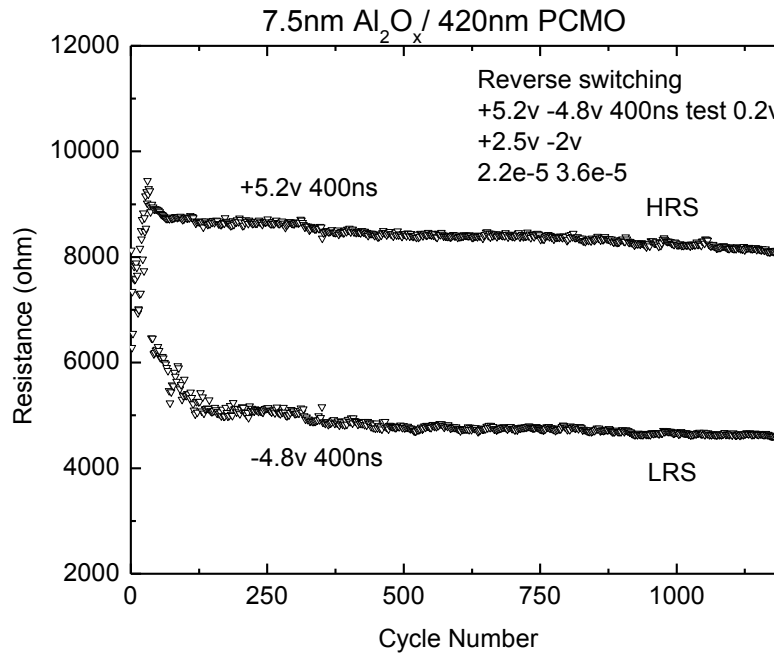


Figure 5.14a Reverse switching in 7.5nmAl₂O_x/ PCMO/Pt

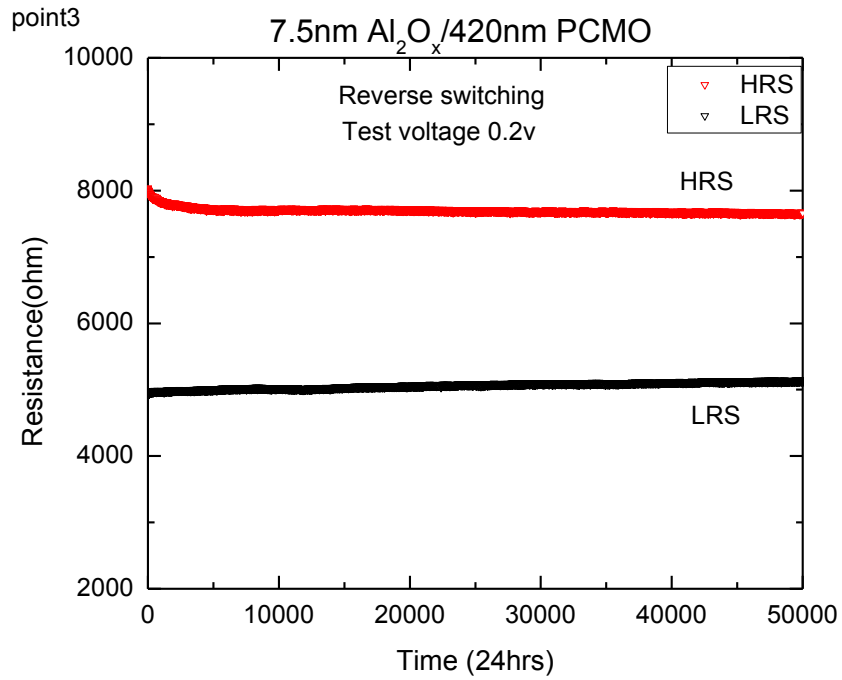


Figure 5.14b Retention of HRS and LRS in 7.5nm Al₂O_x/ 420nm PCMO/Pt

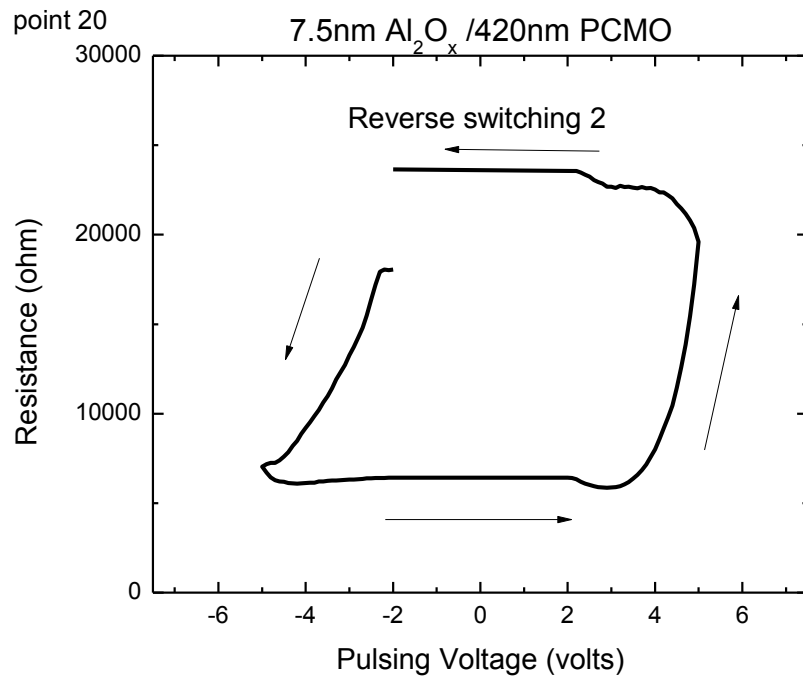


Figure 5.14c Hysteresis in 7.5nmAl₂O_x/420nmPCMO

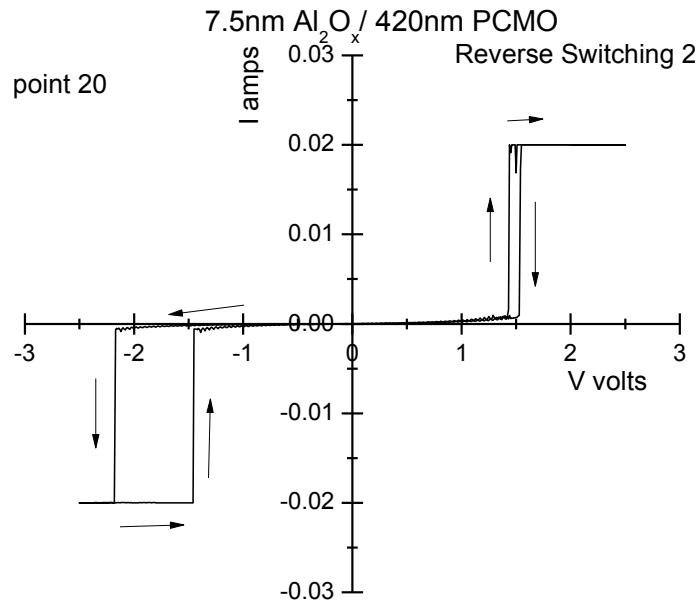


Figure 5.14d Hysteresis in I-V measurement of 7.5nmAl₂O_x/420nmPCMO

In case of 10nmAl₂O_x buffer layer in 10nm Al₂O_x/420nm PCMO heterostructure switching endurance, retention, hysteresis and I-V characteristics have been studied and plotted as shown in Fig. 5.15a,b,c,d. The EPIR ratio (ΔR) was 36% constant over the period and it has no fatigue loss. The change in the high resistance state is 4.6% and the change in low resistance state is 23%. The high resistance state (HRS) is stable and low resistance state (LRS) were very unstable as indicated in retention Figure 5.12b which is followed up by the hysteresis measurements.

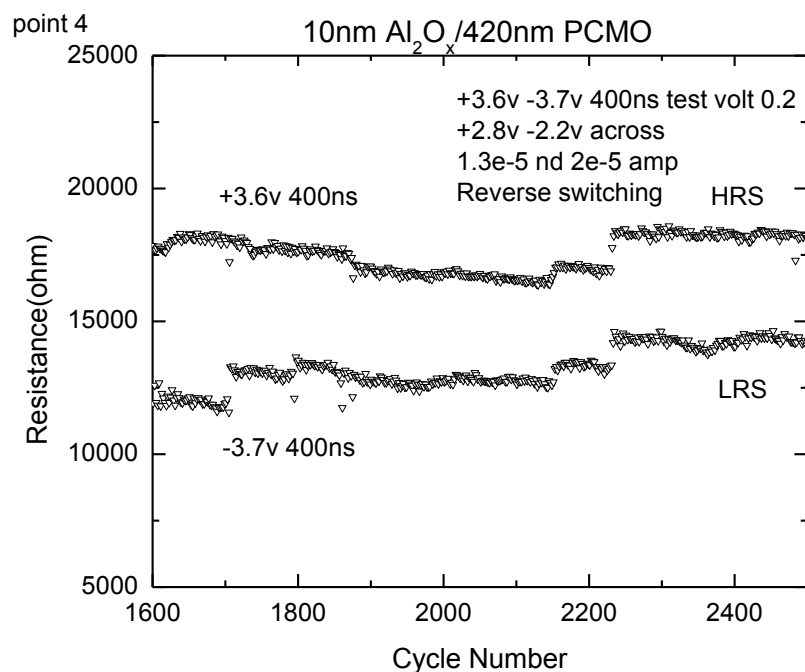


Figure 5.15a Reverse switching in 10nmAl₂O_x/ PCMO/Pt

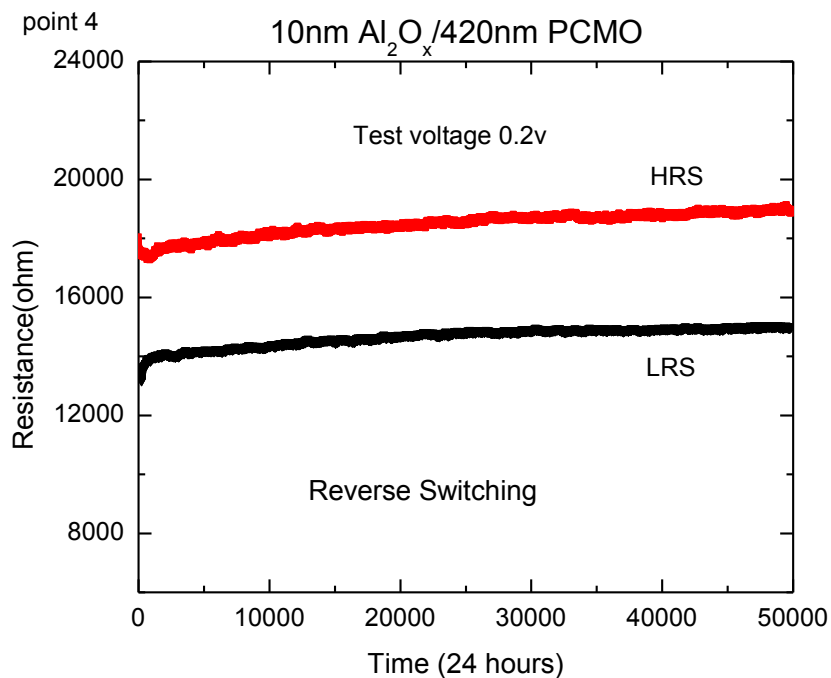


Figure. 5.15b Retention of HRS and LRS in 10nm Al₂O_x/ 420nm PCMO/Pt

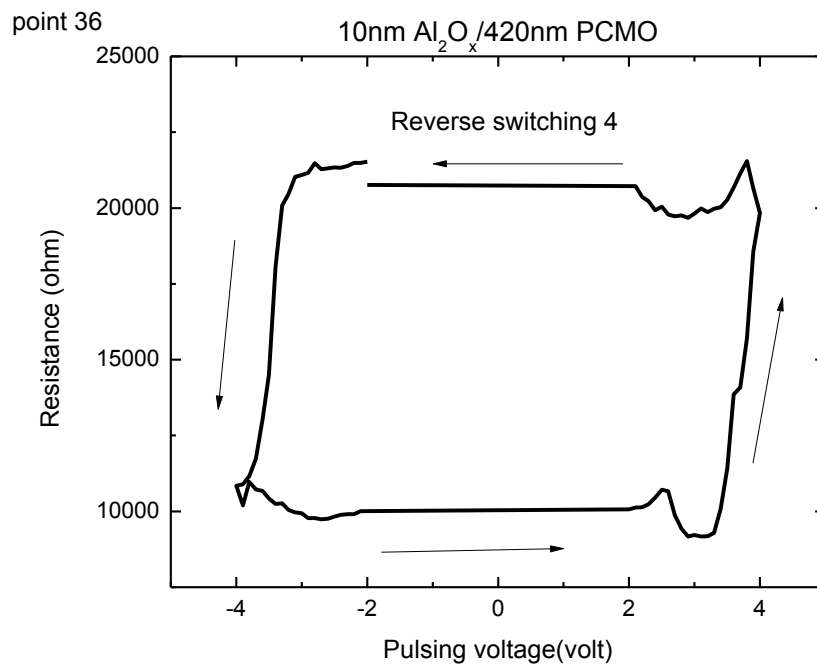


Figure 5.15c Hysteresis in 10nmAl₂O_x/420nmPCMO

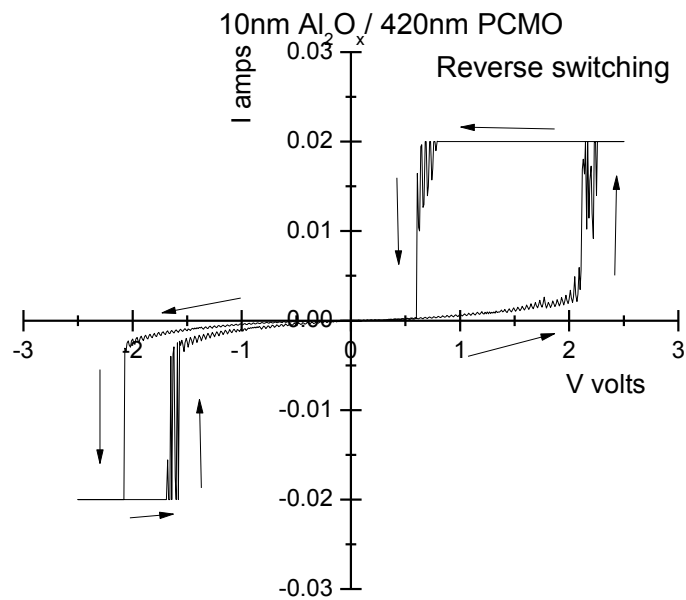


Figure 5.15d Hysteresis in I-V measurement of 10nmAl₂O_x/420nmPCMO

In case of regular switching the amount of positive pulse needed for switching is less compared to negative pulse and the positive voltage across the sample reduces as the thickness increases, this can be explained by the model. The higher negative voltage pulse is needed to push the oxygen ions back to source at the bottom whereas a comparatively smaller positive voltage pulse will attract the ions back to interface.

We can see that the applied positive pulse voltage is higher than the negative pulse voltage required for stable switching of the sample and the voltage measured across the sample after pulsing also indicates that slightly higher positive voltage is applied to induce reverse switching in the above samples. As the thickness of the buffer layer increases the amount of voltage applied for stable switching is increasing relative to previous thickness. The higher positive voltage pulse is required to move the oxygen ions across the interface into Al_2O_x creating vacancies at interface and thus inducing high resistance state (HRS). Lower negative voltage is sufficient to move the ions back to fill the vacancies at top part of PCMO to induce low resistance state (LRS). The different voltages needed for stable switching have been summarized in Table 2 in order to give a clear view of applied voltage pulses for different thickness of Al_2O_x in $\text{M}/\text{Al}_2\text{O}_x/\text{PCMO}/\text{M}$ heterostructure.

Table 3. Effect of Al₂O_x thickness on EPIR ratio, retention stability in Al₂O_x/ 420nm PCMO/Pt

	2.5nmAl ₂ O _x / 420nm PCMO/Pt		5nmAl ₂ O _x / 420nm PCMO/Pt		7.5nmAl ₂ O _x / 420nm PCMO/Pt		10nmAl ₂ O _x / 420nm PCMO/Pt	
	Regular	Reverse	Regular	Reverse	Regular	Reverse	Regular	Reverse
HRS	8,200Ω	5,522Ω	3,088Ω	7,103Ω	40,000Ω	8060Ω	3,500Ω	17,777Ω
LRS	4,600Ω	3,596Ω	2,540Ω	5,321Ω	19,000Ω	4549Ω	2,900Ω	13,000Ω
Positive pulse	+3v	+6v	+4.2v	+4.4v	+4v	+5.8v	+4v	+3.6v
	2v	2.2v	2v	+2.4v	+1.7v	+2.5v	+1.8v	+2.8v
	across	across	across	across	across	across	across	across
Negative Pulse	-5v	-5.5v	-6.5v	-4.2v	-5v	-4.8v	-5v	-3.6v
	-2.2v	-2v	-2.2v	-2.2v	-2v	-2v	-2.1v	-2.2v
	across	across	across	across	across	across	across	across
Delta R	78%	53%	21%	33%	94%	77%	20%	36%
%HRS 24h	-6%	-3%	-10%	3%	11%	-4%	16%	4.6%
%LRS 24h	12%	4%	2%	29%	10%	4%	6%	23%

5.5 Investigation of Resistance Switching in PCMO/ Al_2O_x /PCMO/Pt

5.5.1 Regular Switching in 50nmPCMO/2.5nm Al_2O_x /PCMO samples

For the heterostructure with a 1min Al_2O_x deposition in between a 20min top PCMO deposition and a 2hr bulk PCMO deposition, only regular switching is obtained for various pulsing voltages applied as shown in Figure 5.18a. The high resistance state (HRS) retention test was done for 24hrs setting the HRS during the switching study. The sample was then switched again and set into the low resistance state (LRS) and was tested in this state for 24 hours. Due to continuous testing the sample was measured continuously for 50,000 times each in HRS and LRS test.

The EPIR ratio (ΔR) was 32% with fatigue loss (30%) and the loss in high resistance state is 9% and the change in low resistance state is 4% improved compared to normal PCMO. The retention is improved due to the buffer layer inhibiting the backward migration of oxygen ions in the absence of electric voltage pulse. The fatigue loss still exists as the active switching medium is only PCMO. The EPIR ratio (ΔR) is constant at 32% although it is low as compared to the other structures; it is higher than PCMO alone for which the EPIR ratio (ΔR) keeps degrading until a low of 20% before it is steady.

In the case of PCMO/ Al_2O_x /PCMO sample there is reduction in switching ratio due to the diffusion Al_2O_x barrier reducing the number of ions moving under the field. However there is enhancement in the retention property due to the Al_2O_x acting as the diffusion barrier for the oxygen ions which try to settle back without the electric field.

As we apply short electric pulse with short increase in voltage, the negative pulse takes the sample to high resistance state and it continues to stay there until enough positive pulse is applied again to switch the sample to low resistance state as shown in

figure 5.18c depicting the hysteresis measurements of the sample. The short tail observed in the hysteresis is believed due to oversaturation of resistance. i.e, when the applied voltage pulse is removed the resistance drops short before the next voltage pulse. This relaxation of sample is the cause of instability in retention during the initial stage when the applied voltage pulse is removed. During regular switching the resistance of sample drops at high positive pulse and requires lesser voltage to produce same amount of current whereas at higher negative pulse the resistance of sample increases requiring higher voltage to produce same amount of current as shown in figure 5.18d.

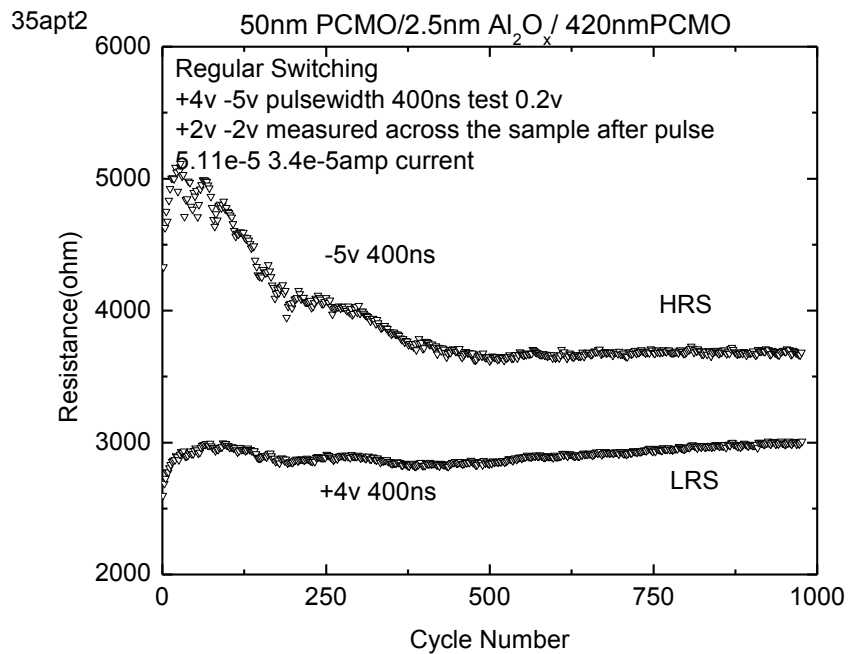


Figure5.18a Regular switching in 50nmPCMO/2.5nm Al₂O_x/ PCMO sandwich heterostructure

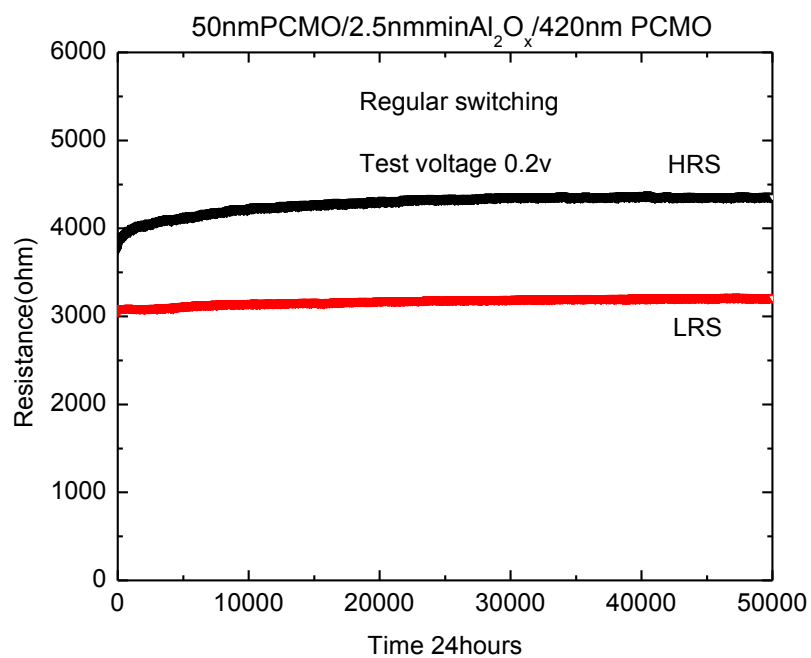


Figure 5.18b Retention for 24hours in 50nmPCMO/ 2.5nmAl₂O_x/ PCMO

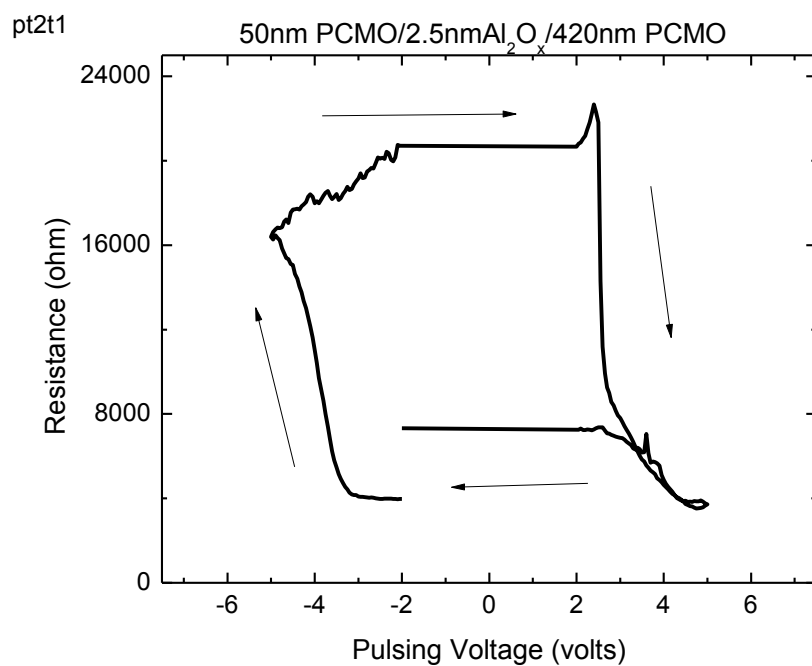


Figure5.18c Hysteresis in 50nmPCMO/2.5nmAl₂O_x / PCMO sandwich heterostructure

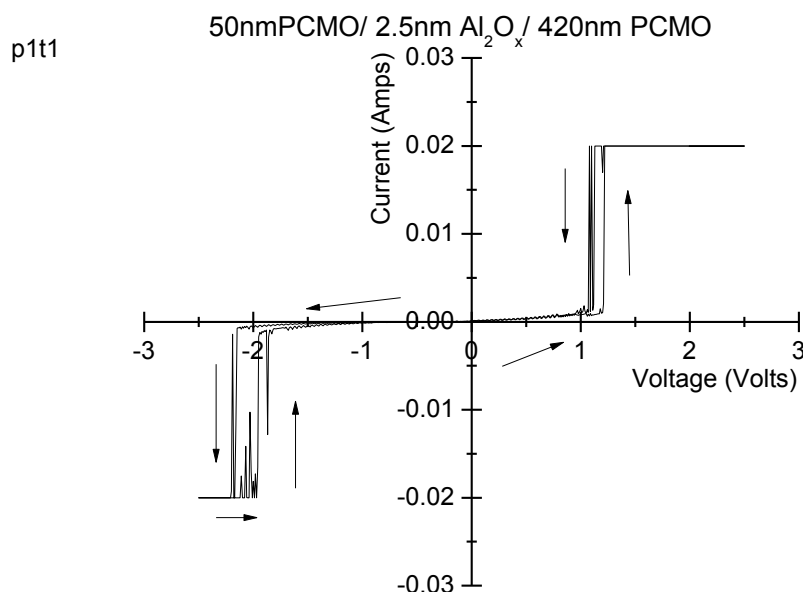


Figure 5.18d I-V characteristics 50nmPCMO/ 2.5nmAl₂O_x/ PCMO

Form the data illustrated in Figures 5.18a,b,c,d. for 50nmPCMO/2.5nmAl₂O_x/PCMO sample, we observed only regular polarity switching mechanism. The bulk PCMO can be considered as source of oxygen ions the concentration of oxygen decreases as we approach interface of Al₂O_x/PCMO. The mechanism of regular polarity switching can be explained by schematic model in Figure 5.19, suggesting the movement of oxygen ions from the top active PCMO and the bottom bulk PCMO layer through the Al₂O_x buffer layer in the presence of electric field. The oxygen ions move into the top PCMO layer filling the vacancies of the oxygen deficient top PCMO thus causing the low resistance state (LRS). A negative voltage pulse drives the oxygen ions back into bulk PCMO and leads to a high resistance state (HRS) as shown in figure 5.19. Here Al₂O_x layer acts only as diffusion barrier and doesn't contribute to resistance because it is non-stoichiometric and of low resistance.

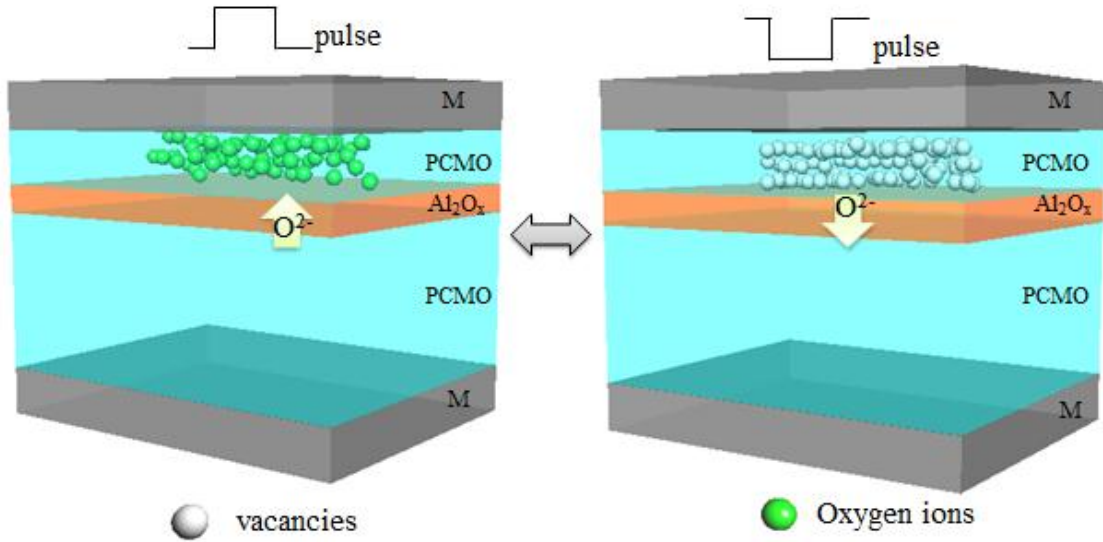


Figure. 5.19 Position of oxygen ions and vacancies during regular switching in sandwich structure

5.5.2 Effect of Al_2O_x thickness in switching & Retention of PCMO/ Al_2O_x /PCMO/Pt

Only regular switching is observed in PCMO/ Al_2O_x /PCMO/Pt sandwich structure due to migration ions from bottom bulk PCMO to top PCMO through the Al_2O_x barrier. Various pulse voltages were tried for switching all the trials showed regular switching for various thickness of diffusion barrier of 5nm, 7.5nm, 10nm.

In case of 5nm Al_2O_x buffer layer in 50nmPCMO/5nm Al_2O_x /420nm PCMO heterostructure switching endurance, retention, hysteresis and I-V characteristics have been studied and plotted as shown in Figure. 5.20a,b,c,d The EPIR ratio (ΔR) was 36% constant over the period and it has no fatigue loss. The change in the high resistance state is 13% and the change in low resistance state is 31%. The HRS is stable and LRS were very unstable as indicated in retention Figure 5.20b which is followed up by the hysteresis measurements.

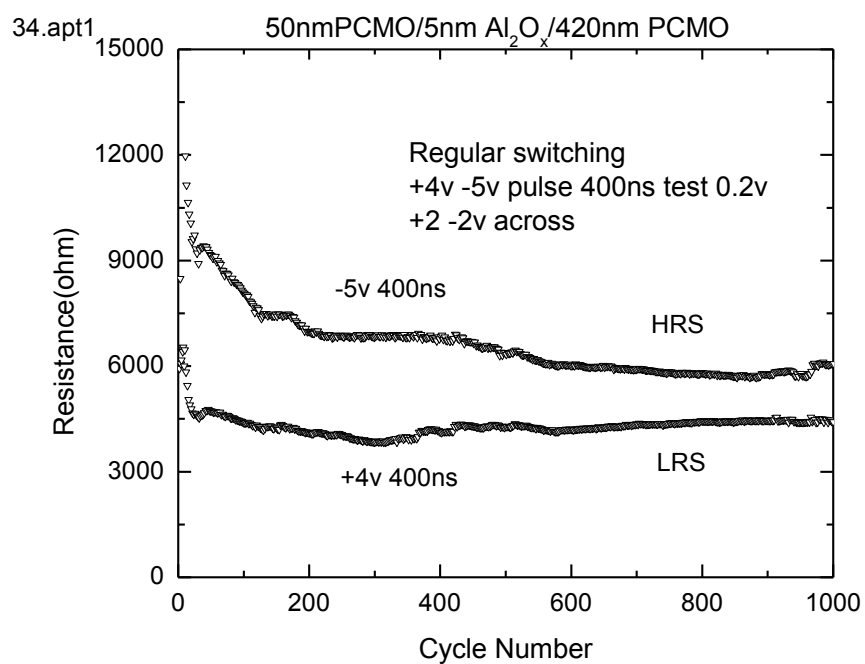


Figure5.20a Regular switching in 50nmPCMO/5nmAl₂O₃/420nmPCMO/Pt

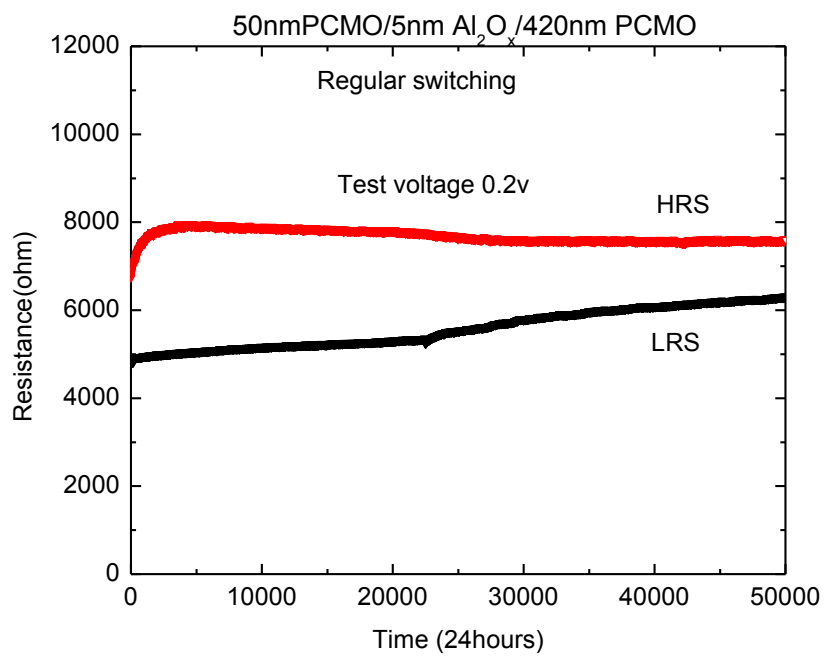


Figure 5.20b Retention in 50nmPCMO/5nmAl₂O₃/ PCMO/Pt

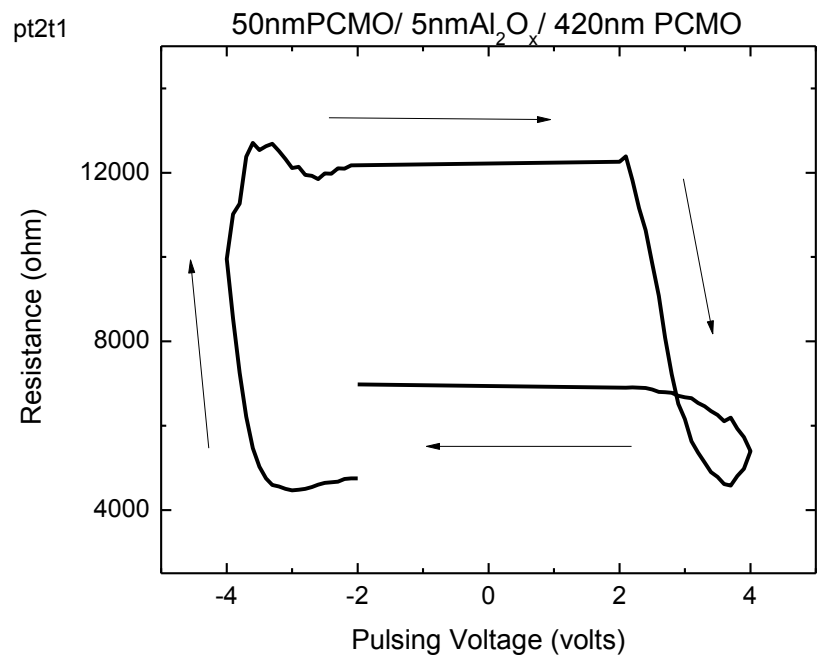


Figure5.20c Hysteresis in 50nmPCMO/5nmAl₂O_x/PCMO/Pt

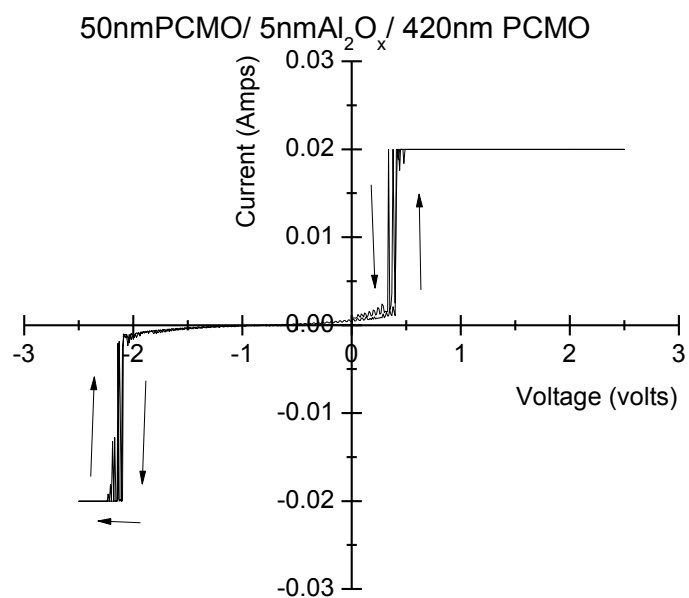


Figure 5.20d I-V characteristics of 50nmPCMO/5nmAl₂O_x/PCMO/Pt

In case of 7.5nmAl₂O_x buffer layer in 50nmPCMO/7.5nm Al₂O_x/420nm PCMO heterostructure switching endurance, retention, hysteresis and I-V characteristics have been studied and plotted as shown in Figure. 5.21a,b,c,d. The EPIR ratio (ΔR) was 90% constant over the period and it has no fatigue loss. The change in the high resistance state is 10% and the change in low resistance state is 10%. The HRS is stable and LRS were very stable as indicated in retention Figure 5.20b which is followed up by the hysteresis measurements in Figure 5.20c we can see there is no oversaturation of resistance and tail is absent at the right corner.

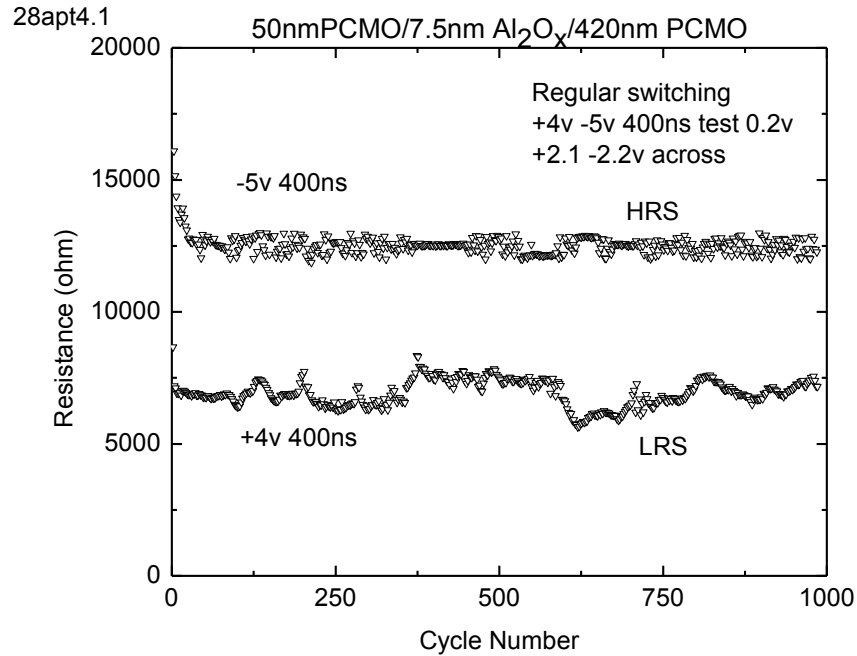


Figure 5.20b Regular switching in 50nmPCMO/7.5nmAl₂O_x/ PCMO/Pt

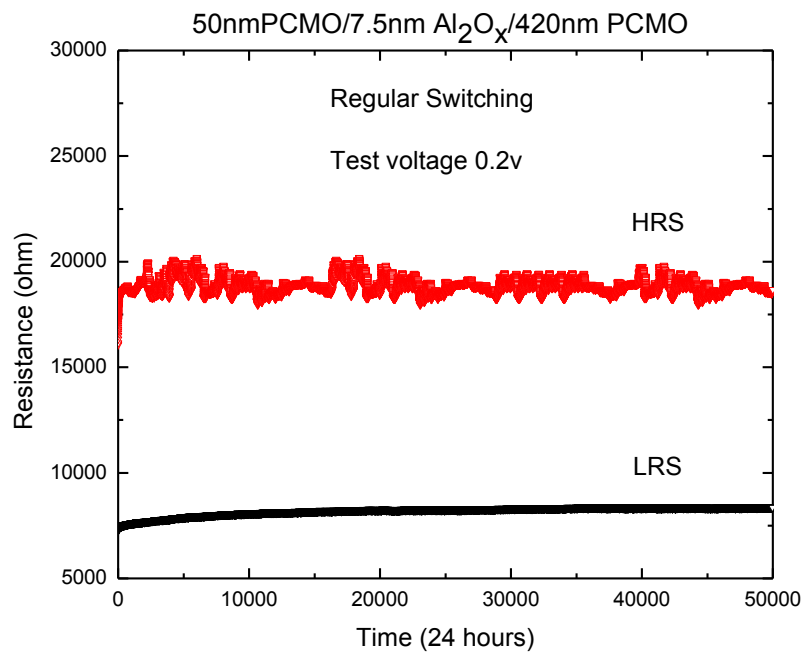


Figure 5.21b Retention of HRS and LRS in 7.5nm 50nmPCMO/Al₂O_x/ 420nm PCMO/Pt

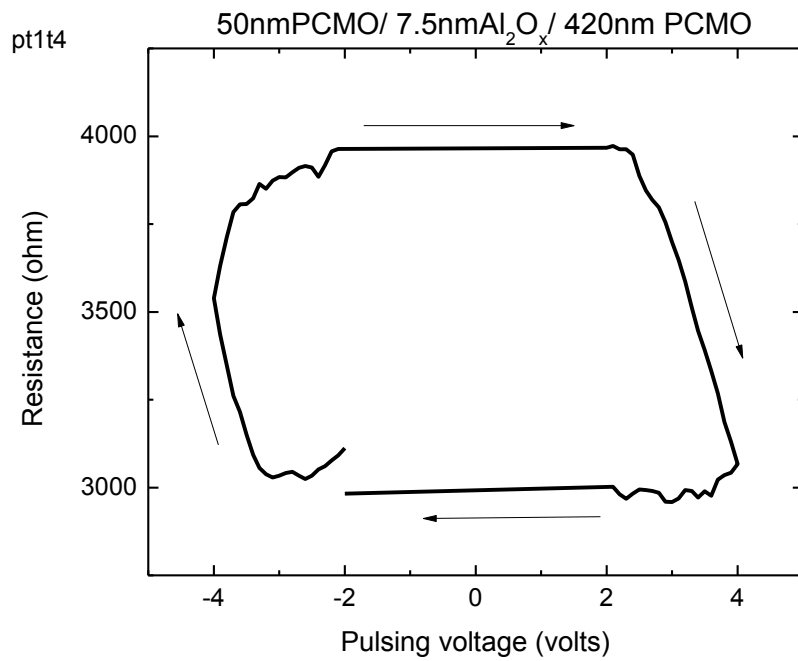


Figure 5.20c Hysteresis in 50nmPCMO/7.5nmAl₂O_x/PCMO/Pt

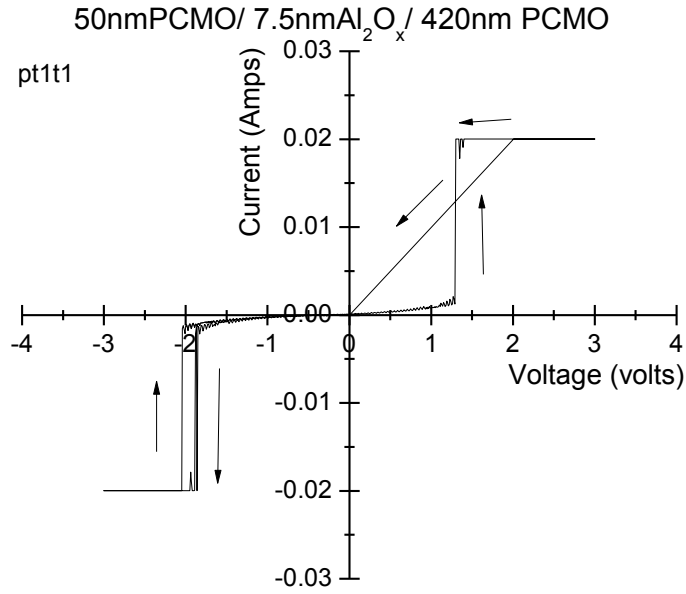


Figure 5.20d I-V characteristics of 50nmPCMO/7.5nmAl₂O_x/PCMO/Pt

In case of 10nmAl₂O_x buffer layer in 50nmPCMO/Al₂O_x/420nm PCMO heterostructure switching endurance, retention, hysteresis and I-V characteristics have been studied and plotted as shown in Figure 5.21a,b,c,d. The EPIR ratio (ΔR) was 28% constant over the period and it has no fatigue loss. The change in the high resistance state is 11% and the change in low resistance state is 10%. The epi ration is small this can be due to increase in thickness of diffusion barrier resulting in reduction of ion migration through the barrier under electric field.

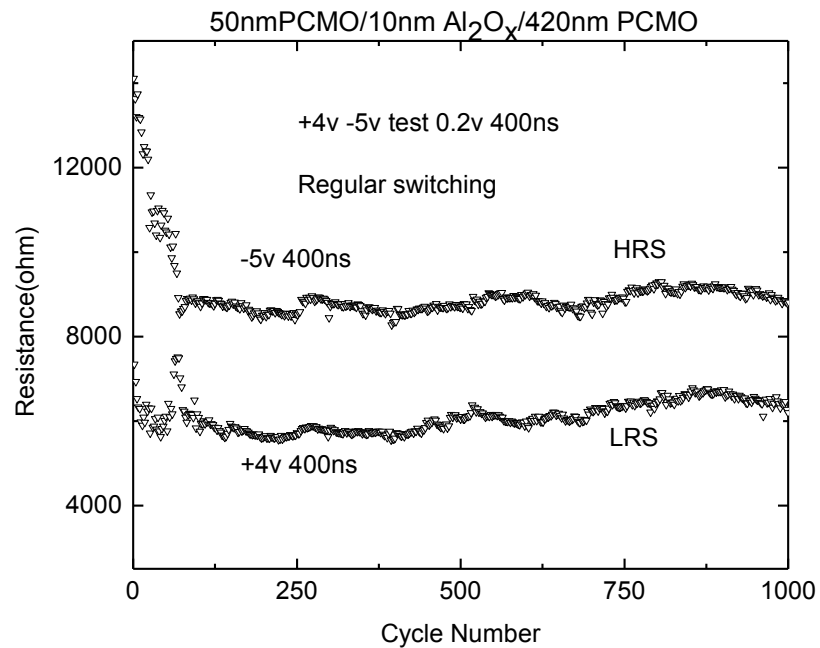


Figure 5.21a Regular switching in 50nmPCMO/10nmAl₂O_x/PCMO/Pt

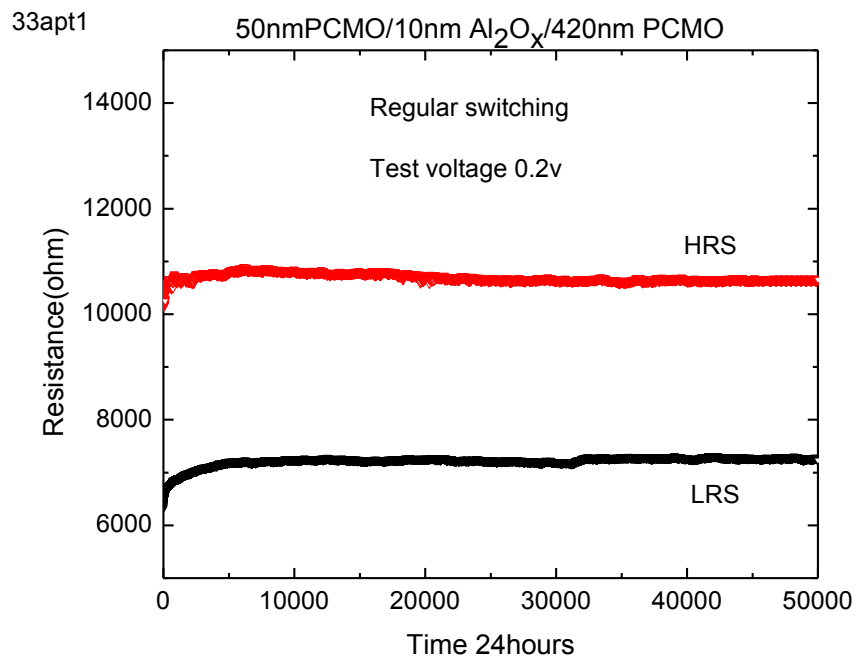


Figure 5.21b Retention of HRS and LRS in 10nm 50nmPCMO/Al₂O_x/ 420nm PCMO/Pt

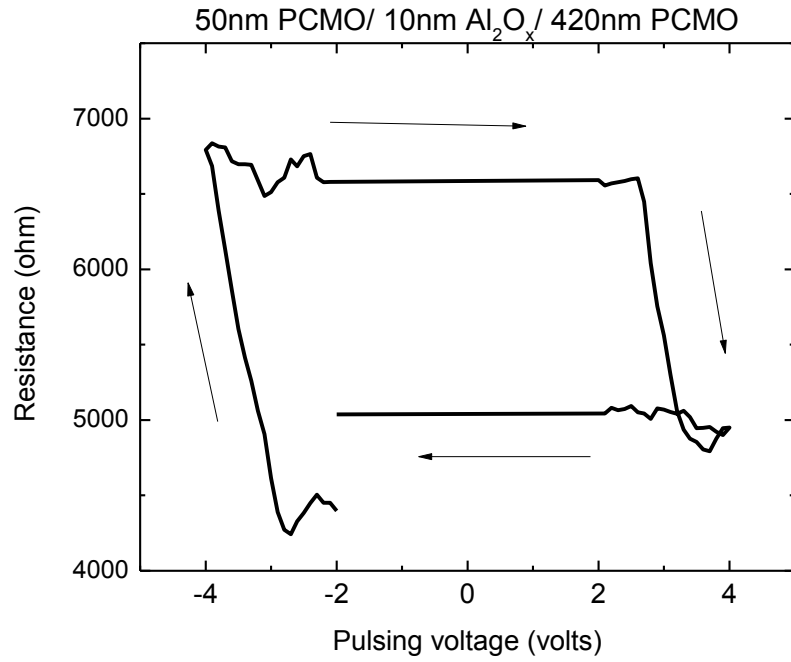


Figure 5.20c Hysteresis in 50nmPCMO/10nmAl₂O_x/PCMO/Pt

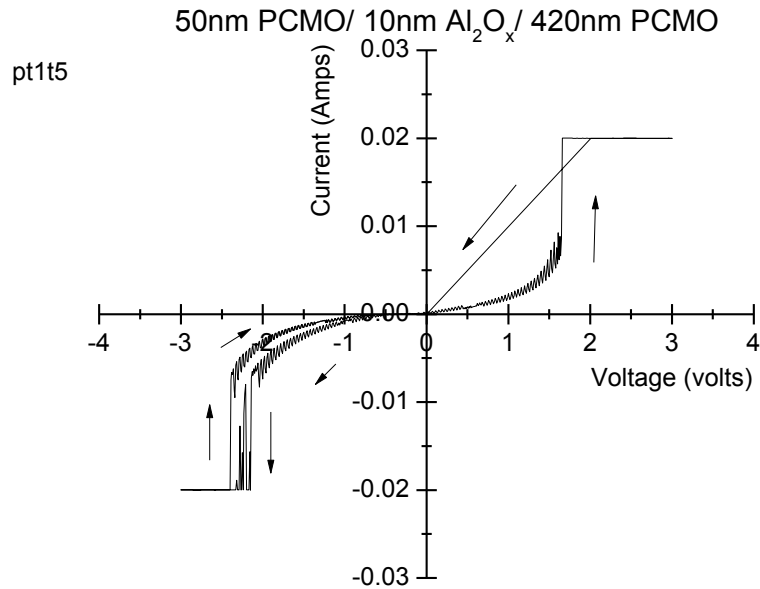


Figure 5.20d I-V characteristics of 50nmPCMO/10nmAl₂O_x/PCMO/Pt

The EPIR switching ratio and the change in the retention of both the high and low resistance states have been calculated and tabulated for various thickness of buffer layer in order to compare the effect of buffer layer in Table-3. It is seen that with the inclusion of the diffusion barrier there is improvement in EPIR ratio and retention properties of the low resistance state by a huge margin.

Table4. Switching ratio and Retention loss in Al₂O_x/420nmPCMO and 50nmPCMO/Al₂O_x/420nmPCMO for different thickness of Al₂O_x

50nmPCMO on top for sandwich structure		$\Delta R(\frac{HRS-LRS}{LRS})\%$	%loss in HRS $(\frac{final-initial}{initial})$	%loss in LRS $(\frac{final-initial}{initial})$
2.5nmAl ₂ O _x / 420nm PCMO	Regular	78%	-6%	12%
	Reverse	53%	-3%	4%
	Sandwich	48%	-5%	9%
5nmAl ₂ O _x / 420nm PCMO	Regular	21%	-10%	2%
	Reverse	33%	3%	29%
	Sandwich	36%	13%	31%
7.5nmAl ₂ O _x / 420nm PCMO	Regular	94%	11%	10%
	Reverse	77%	-4%	4%
	Sandwich	90%	10%	10%
10nmAl ₂ O _x / 420nm PCMO	Regular	20%	16%	6%
	Reverse	36%	4.6%	23%
	Sandwich	28%	10%	11%

Chapter 6. Summary and Conclusions

From the results it is understood that the $\text{Al}_2\text{O}_x/\text{PCMO}$ buffer layer samples are exhibiting both regular and reversed polarity switching with EPIR ratio increased to 78% and 53% respectively in case of 2.5nm $\text{Al}_2\text{O}_x/\text{PCMO}$ compared to 42% in PCMO alone. Further negligible fatigue loss is observed, and the retention properties have been improved to only 6%, 3% change in High resistance state, 12%, 4% change in Low resistance state switching compared to 23%, 54% change in regular switching for PCMO samples for regular and low reverse polarity switching. Whereas, the PCMO/ $\text{Al}_2\text{O}_x/\text{PCMO}$ heterostructure samples have shown reduced fatigue loss of 30% with EPIR ratio of 32% and 9% for high resistance state and low resistance state respectively, and a 4% change in retention which is highly improved as compared to PCMO alone.

With the change in thickness of buffer layer we have observed evident improvements in case EPIR ratio and retention. From the various thickness studied 7.5nm $\text{Al}_2\text{O}_x/\text{PCMO}$ has very high switching ratio of 94% in regular switching, 77% in reverse switching, 90% in sandwich structure with 10%, 4% change in retention in regular, reverse switching while 10%in HRS, 10% in LRS in case of sandwich structure. Hysteresis and I-V 5tmeasurements of the samples confirm both regular and reverse switching modes are acting in the EPIR switching of the heterostructures depending on voltage of applied electric pulse.

Though the EPIR ratio in case of regular switching in 7.5nm $\text{Al}_2\text{O}_x/\text{PCMO}/\text{Pt}$ is high it is not advisable for application as it is difficult to control the mode of switching. We can conclude that 50nmPCMO/7.5nm $\text{Al}_2\text{O}_x/\text{PCMO}/\text{Pt}$ is the best configuration for switching and retention properties in this type of heterostructures as it exhibits only one

way switching. A physical model was developed with oxygen ions and vacancies as the mobile species driving the resistance switching mechanism under the influence of the electric field produced by short electric pulse in $\text{Al}_2\text{O}_3/\text{PCMO}/\text{Pt}$ and $50\text{nmPCMO}/\text{Al}_2\text{O}_3/\text{PCMO}/\text{Pt}$ heterostructures. Improved retention properties have been observed due to integration of Al_2O_3 buffer layers into metal/PCMO/metal structure.

References:

1. Nonvolatile Semiconductor Memory technology, William D Brown Joe. E. Brewer. 1997.
2. International Technology Roadmap for Semiconductors 2011 Edition Emerging Research Devices, s.l. : ITRS, 2011. www.itrs.net.
3. Sharma, Ashok K. Advanced Semiconductor Memories: Architectures, designs and applications. New Jersey : IEEE Press, 2003.
4. X. Chen, N. Wu, and A. Ignatiev, "Perovskite RRAM devices with metal/insulator/PCMO/metal heterostructures," in Proc. Non-Volatile Memory Technol.Symp., Nov. 2005, pp. 125–128.
5. R. Waser, R. Dittman, G. Staikov and K. Szot. 2009, Advanced Materials, Vol.21, pp. 2632-2663.
6. K. Fujiwara, T. Nemoto, M. J. Rozenberg, Y. Nakamura, and H. Takaga, Jpn. J. Appl. Phys., 47, pp. 6266 (2008).
7. Rabi Ebrahim, Naijuan Wu, and Alex Ignatiev. 2, 2012 J Appl. Phys., vol.111, 034509
8. Yoshio, N. (2011). "Challenges and opportunities for future non-volatile memory technology." Current Applied Physics 11(2, Supplement): el01-el03.
9. The International Technology Roadmap for Semiconductors, s.l. : ITRS, 2010. Update Edition, www.itrs.net.
10. (11)V. V. Zhirnov, R. K. Cavin, S. Menzel, E. Linn, S. Schmelzer, D. Brauhaus, C. Schindler, and R. Waser. "Memory Devices: Energy–Space–Time Tradeoffs." *Proceedings of the IEEE*, vol. 98, pp. 2185-2200, 2010.

11. (13) H. Akinaga and H. Shima. “ Resistive Random Access Memory (ReRAM) Based on Metal Oxides.” *Proceedings of the IEEE*, vol. 98, pp. 2237-2251, 2010.
12. (14) J. J. Yang, M. D. Pickett, X. Li, D.A.A. Ohlberg, D. R. Stewart, R. S. Williams. “Memristive switching mechanism for metal / oxide / metal nanodevices.” *Nature Nanotech.*, Vol. 3, pp. 429-433, 2008.
13. (15) N. Zhong, H. Shima, and H. Akinaga. “Rectifying characteristic of Pt / TiOx / Pt controlled by electronegativity.” *Appl. Phys. Lett.*, vol. 96, pp. 042107, 2010.
14. N. Zhong, H. Shima, and H. Akinaga. “Rectifying characteristic of Pt / TiOx / Pt controlled by electronegativity.” *Appl. Phys. Lett.*, vol. 96, pp. 042107, 2010.
15. (17)R. Waser, R. Dittmann, G. Staikov, K. Szor. “Redox-based resistive switching memories – nanoionic mechanisms, prospects, and challenges.“ *Adv. Mater.*, vol. 21, pp. 2632–2663, 2009.
16. (18)D.-H. Kwon, K. M. Kim, J. H. Jang, J. M. Jeon, M. H. Lee, G. H. Kim, X.-S. Li, G.-S. Park, B. Lee, S. Han, M. Kim, and C. S. Hwang. “Atomic structure of conducting nanofilaments in TiO₂ resistive switching memory.” *Nature Nanotechnology*, vol. 5, 148-153, 2010.
17. R. Meyer, L. Schloss, J. Brewer, R. Lambertson, W. Kinney, J. Sanchez and D. Rinerson. 2008, IEEE 978-1-4244-5/08.
18. X. Chen, N.J. Wu , A. Ignatiev, Q. Chen, and Y. Zhang. 2006, Japanese J Appl Phys., Vol. 45, p. 1602.
19. X. Liu, K.P. Biju, S. Park, I. Kim, M. Siddik, S. Sadaf, H. Hwang. 2011, Current Applied Physics, pp. 1-4.
20. Z. Xing, N. Wu and A. Ignatiev. 5, 2007, ECS Trans., Vol. 11, p. 47.

21. S.-L. Li, Z L Liao, J Li, J.L. Gang and D.N. Zheng. 2009, J. Phys. D: Appl. Phys, Vol. 42, p. 045411.
22. D.-J Seon, M. Hassan, H. Choi, J. Lee, J. Yoan, J.-B. Park, W. Lee, M.-S. Oh and H. Hwang. 9, 2009, IEEE Electron Device Letters, Vol. 30, p. 919.
23. S.Q. Liu, N.J. Wu and A. Ignatiev. 19, 2000, Appl. Phys. Lett., Vol. 76, p. 2479.
24. Y.B. Nian, J. Strozier, N.J. Wu, X. Chen and A. Ignatiev. 2007, Phys. Rev. Lett., Vol. 98, p. 146403.
25. C. J. Howard, B. J. Kennedy, and B. C. Chakoumakos. Neutron powder diffraction study of rhombohedral rare-earth aluminates and the rhombohedral to cubic phase transition. Journal of Physics-Condensed Matter, 12(4):349–365, 2000.
26. Mark R. Levy (2005) Crystal Structure and Defect Property Predictions in Ceramic Materials. A dissertation submitted to the University of London for the degree of Doctor of Philosophy and the Diploma of Imperial College
27. Li, Tingkai (Vancouver, WA, US), Zhuang, Wei-wei (Vancouver, WA, US), Evans, David R. (Beaverton, OR, US), Hsu, Sheng Teng (Camas, WA, US) PCMO thin film with resistance random access memory (RRAM) characteristics, 7060586, 2006.
28. A-M Haghiri-Gosnet, and J-P Renard. 2003, J. Phys. D: Appl. Phys., Vol. 36, pp. R127-R150.
29. R. Meyer, L. Schloss, J. Brewer, R. Lambertson, W. Kinney, J. Sanchez and D. Rinerson. 2008, IEEE 978-1-4244-5/08.

30. Chapman, B. (1980). "Glow Discharge Processes, Sputtering and Plasma Etching." Wiley-Inter science publishes.
31. Kelly, P. (1999). "Control of the structure and properties of aluminum oxide coatings deposited by pulsed magnetron sputtering." J. Vac. Sci. Technol. A 17(3): 945-953.
32. Batten, C. F. (2000). "Auto-focusing and astigmatism correction in the scanning electron microscope." A thesis submitted to the faculty of electrical engineering, University of Cambridge.
33. Thinfilm analysis by X-ray scattering M.Birkholz Copyright © 2006 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim ISBN: 3-527-31052-5
34. Rabi Abd El-Hady Ebrahim (2011) "Detailed Study on Filamentary Bipolar EPIR Switching In Copper Oxide and Amorphous Silicon RRAM". A Dissertation Presented to the Faculty of the Department of Physics University of Houston.
35. Yuji Nishi, Toshimasa Suzuki, Hiroshi Koyama, Masayuki Fujimoto, Local epitaxial growth of $\delta\text{Pr}_{0.7}\text{Ca}_{0.3}\text{PMnO}_3$ thin films on (1 1 1)-oriented polycrystalline Pt electrodes doi:10.1016/j.jcrysgro.2006.10.252.