

Declaration

I hereby declare that the work presented in this thesis titled “*Flexible Resistive Memory Devices for Eco-friendly Electronics: Fabrication, Modeling, and Circuit Implementation*”, submitted to the Indian Institute of Technology Jodhpur in partial fulfilment of the requirements for the award of the degree of Doctor of Philosophy (Ph.D.), is a bonafide record of the research work carried out under the supervision of *Prof. Shree Prakash Tiwari* and *Dr. Harshit Agarwal*. The contents of this thesis, in full or in parts, have not been submitted to, and will not be submitted by me to, any other Institute or University in India or abroad for the award of any degree or diploma.



Anurag Dwivedi
MP19SIoT001

Certificate

This is to certify that the thesis titled “*Flexible Resistive Memory Devices for Eco-friendly Electronics: Fabrication, Modeling, and Circuit Implementation*”, submitted by Anurag Dwivedi (MP19SIoT001) to the Indian Institute of Technology Jodhpur for the award of the degree of Doctor of Philosophy, is a bonafide record of the research work done by him under our supervision. To the best of our knowledge, the contents of this report, in full or in parts, have not been submitted to any other Institute or University for the award of any degree or diploma.



Prof. Shree Prakash Tiwari



Dr. Harshit Agarwal

Abstract

The domain of flexible electronics has experienced an unprecedented rise in research and development activities, owing to its wide applications such as wearable devices, flexible displays, and sensors for biomedical purposes. This has motivated researchers to actively explore a suitable flexible memory device for storing the data generated or received by the flexible electronic circuit(s), to achieve monolithic integration i.e., fabrication of different flexible devices on the same substrate. Resistive random access memory (RRAM), a two terminal metal-insulator-metal structure device, with its various advantages such as ease of fabrication, low cost, high speed, ease of integration, and high scalability has emerged as a promising memory device for flexible electronic systems. Moreover, in view of ever increasing electronic waste, nature originated materials are being explored for the fabrication of different organic devices, and flexible electronics provide an added advantage of incorporating the organic materials in fabrication process, as most of these materials have properties such as solution processability and mechanical flexibility, along with non-toxicity, biocompatibility, and biodegradability which further instill eco-friendliness in devices.

In this work, initially, natural proteins gelatin and egg-albumen, were investigated separately as a switching layer of RRAM devices. The prepared solutions of gelatin and albumen were deposited on the Indium-doped tin oxide coated polyethylene terephthalate substrate, and silver was used as the top electrode. The fabricated flexible RRAM devices with gelatin switching layer, have exhibited excellent switching behavior with I_{on}/I_{off} ratio of greater than 10^5 and retention time of more than 10^4 seconds. Similarly, the albumen switching layer devices have also shown excellent resistive switching with high current on/off ratio of around 10^5 and memory retention time of 10^3 s without showing relevant degradation. The devices were then subjected to a mechanical bending of radius 7.5 mm, and it was observed that the device maintained the memory window of greater than 10^3 for more than 10^3 seconds. These results suggested that these organic proteins should further be explored for fabrication of flexible organic memory devices.

Furthermore, to enhance the multiple cycle switching (endurance) of the devices, these proteins were investigated in hybrid bilayer combination with an ultrathin (5nm) layer of HfO_2 as switching layer. Hybrid bilayer Ag/Gelatin/ HfO_2 /ITO devices have shown a very high memory window of greater than 10^5 and data retention of 10^4 s without any degradation in a pristine state. Moreover, after bending the devices at a 12 mm radius followed by 7 mm, it was observed that the devices have maintained the memory window of 10^5 without any degradation in data retention, indicating excellent electromechanical stability of the devices. Similarly, Ag/Albumen/ HfO_2 /ITO devices have demonstrated excellent switching characteristics with a current on/off ratio of greater than 10^4 , stable retention of both low resistance and high resistance states, reliable multiple cycle switching, and very low switching power (with set power as $0.5 \mu\text{W}$ and reset power as 3.1 mW). The devices have also shown excellent electro-mechanical stability, with bending radii of 7.5 mm, 5 mm, and 2.5 mm.

Additionally, to enable simulation based study of the fabricated device, a mathematical model of RRAM device has been studied and investigated. The model is then calibrated with the median of experimental results to extract the values of fitting parameters with less than 5% rms error. This ensures that the model can be utilized to simulate the switching characteristics of the fabricated device with greater accuracy. The model was further improved by introducing parameters for multiple layers of insulator, and multiple cycle variation parameters to make the model more robust. This improved RRAM model was then utilized to design a simple flexible hybrid electronic (FHE) circuit that is capable of generating 4 bit random numbers by utilizing intrinsic randomness of the device. The circuit is designed with 65nm technology node and the RRAM model

with cyclic variation is utilized as the source of entropy. To verify the randomness of the proposed FHE circuit, the generated outputs have been test with NIST SP 800-22 test suits, a widely accepted set of tests to verify randomness of a bitstream. The outputs of this circuit have passed all the applicable tests of NIST SP 800-22, indicating the presence of randomness. This not only represents taht the output bitstreams are random in nature but also reflects that the improved model is capable of taking care of cyclic variations to a larger extent.

Recently, Pectin was extracted from orange peel, and utilized as a switching layer. The fabricated flexible devices have demonstrated good resistive switching behavior with high current on/off ratio of 10^4 and retention time of 10^3 seconds. The fabricated device has then been investigated for synaptic behavior, probably for the first time, and it demonstrated depression characteristics with 10 ms input pulse, and the PPF relaxation time constants $\tau_1 = 0.3$ ms and $\tau_2 = 4.1$ ms are obtained. The results show a similar trend as that of a biological synapse, and thus it may be concluded that the fabricated device with pectin can be utilized for neuromorphic applications.

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Anurag Dwivedi
M.Tech - Ph.D. Student

*This thesis is dedicated to **my mother** for her limitless love, support, patience, and encouragement.*

Contents

Abstract	vii
Acknowledgements	x
Contents	xv
List of Figures	xvii
List of Tables	xxi
List of Symbols	xxii
Chapter 1: Introduction	1
1.1 Memory Devices and their Advancements	1
1.2 Classification of Memory Devices	2
1.2.1 Volatile Memory Devices	2
1.2.2 Non Volatile Memory Devices	2
1.3 Emerging Non-Volatile Memory Devices	4
1.3.1 Ferroelectric Random Access Memory	4
1.3.2 Phase Change Memory	5
1.3.3 Spin Transfer Torque Magnetic RAM	6
1.3.4 Resistive Random Access Memory	6
1.4 Sustainable Electronics for E-waste Management	8
1.5 Device Model and Simulation	9
1.6 Thesis Organization	9
Chapter 2: Resistive Random Access Memory Devices	11
2.1 Device Structure	11
2.2 Switching Characteristics and Modes	12
2.3 Resistive Switching Mechanisms	14
2.4 Flexible RRAM	16
2.5 Organic Flexible RRAM	17
Chapter 3: Experimental Techniques	19
3.1 Spin Coating	19
3.2 Thermal Deposition System	19
3.3 E-beam Deposition System	20
3.4 Atomic Layer Deposition System	20
3.5 Atomic Force Microscopy	22

3.6	2-D Surface Profilometer	22
3.7	Electrical Characterization	24
3.8	Model Parameter Extraction and its Utilization	25
Chapter 4:	Flexible Eco-friendly RRAM with Gelatin Switching Layer	27
4.1	Introduction	27
4.2	Devices with Pristine Layer	27
4.2.1	Experimental Details	27
4.2.2	Result and Discussion	28
4.3	Flexible Hybrid Bilayer Devices	30
4.3.1	Device Fabrication	30
4.3.2	Result and Discussion	30
4.4	Conclusion	37
Chapter 5:	Flexible Eco-friendly RRAM with Albumen Switching Layer	39
5.1	Introduction	39
5.2	Devices with Pristine Layer	39
5.2.1	Experimental Details	40
5.2.2	Result and Discussion	41
5.3	Flexible Hybrid Bilayer Devices	42
5.3.1	Experimental Details	44
5.3.2	Result and Discussion	46
5.4	Conclusion	50
Chapter 6:	RRAM Device Model Calibration	51
6.1	Introduction	51
6.2	Model Calibration with Eco-Friendly RRAM Devices	51
6.3	Induction of Cyclic Variability	53
6.4	Conclusion	55
Chapter 7:	Applications: RRAM-CMOS Circuits and Synaptic Devices	57
7.1	Introduction	57
7.2	Flexible Hybrid Random Number Generator Circuit	58
7.2.1	Source of Randomness	60
7.2.2	RRAM-CMOS Hybrid RNG Circuit	63
7.2.3	Validation of Randomness in Circuit Output	66
7.2.4	Conclusion	67
7.3	RRAM for Neuromorphic Applications	67
7.3.1	Experimental Details	68
7.3.2	Result and Discussion	69
7.3.3	Conclusion	72
Conclusion		73
List of Publications		75
References		79

List of Figures

Figure	Title	Page
1.2.1	Schematic of the DRAM cell with (a) '1' bit stored and (b) '0' bit stored. (c) Schematic of 6T SRAM cell.	3
1.2.2	Schematic of (a) 2 X 4 ROM cell, and (b) floating gate flash memory cell.	3
1.3.1	(a) Leakage current with equivalent oxide thickness. (b) Trend of threshold voltage variation with technology node. Image Copyright © 2010, IEEE.	4
1.3.2	Schematic of (a) FeRAM cell, and (b) P - V curve showing switching of polarization with applied voltage.	5
1.3.3	Schematic of (a) PCM cell, and (b) programming and reading of PCM cell by applying electrical pulses with change of temperature.	6
1.3.4	Schematic of (a) MTJ cell structure. STT-MRAM cell with (b) write '0', and (c) write '1' operation.	7
1.3.5	Schematic of (a) RRAM cell, and (b) I - V characteristic of RRAM cell by applying voltage on top electrode.	7
1.4.1	Illustrative executive summary of Global E-waste Monitor 2024. Image copyright © 2024 International Telecommunication Union and United Nations Institute for Training and Research, licensed under CC BY-NC-SA 3.0 IGO.	9
2.1.1	Schematic representation of different device structures, (a) M-I-M cell, (b) Crossbar array, and (c) planar structure.	12
2.2.1	Schematic representation of switching characteristics of a RRAM cell co-related with its current state.	13
2.2.2	Schematic representation of different modes of switching, (a) unipolar switching, (b) bipolar switching, and (c) threshold switching.	13
2.3.1	Schematic representation of switching process in metal oxide RRAM. Reprinted with permission from [Yu <i>et al.</i> , 2011b].	14
2.3.2	Schematic representation of the switching steps for SET (A-D) and RESET (E) operation of an ECM cell. Reprinted with permission from [Valov <i>et al.</i> , 2011a].	15
2.3.3	Observation of conductive filament in CBRAM. Reprinted with permission from [Yang <i>et al.</i> , 2012].	16
2.5.1	The bio-materials as switching layer for flexible ReRAM. Reprinted with permission from [Raeis-Hosseini and Lee, 2017].	18
3.1.1	(a) Digital image of spin coater machine. (b-e) Steps and working schematics of spin coating process to obtain a uniform thin film.	20
3.2.1	(a) Digital image of thermal deposition system. (b) Illustrative representation of the machine, its parts, and working.	21

3.3.1	(a) Digital image of the e-beam deposition system. (b) Schematic of the e-beam deposition process.	21
3.4.1	(a) Digital image of the Savannah S200 ALD system. (b) Schematic representation of the ALD process flow.	22
3.5.1	(a) Digital image of Park Systems XE-70 AFM machine. (b) Basic schematic of working principle of an AFM machine.	23
3.6.1	(a) Digital image of the Burkert DektakXT surface profilometer. (b) Schematic diagram showing important components and working of stylus profilometer.(c-e) Limitation on lateral resolution of the system as the width of valley reaches to stylus dimension.	23
3.7.1	(a) Digital image of the probe station. Schematic of output characteristics during (b) Short circuit test, (c) SET cycle, (d) RESET cycle, and (e) Retention test.	24
3.8.1	Process flow to achieve circuit simulation from device results.	25
4.2.1	(a) Schematic of the fabricated device, and (b) Switching characteristics with forming, reset and set curves.	28
4.2.2	(a) Retention Characteristics for 10^4 seconds, and (b) Reset voltage distribution and its Gaussian fit.	28
4.2.3	Double log I-V Characteristics for (a) SET and (b) RESET cycle.	29
4.2.4	Schematic demonstrating the switching mechanisms.	29
4.3.1	(a) Device Schematic, (b) AFM image, and (c) Digital image of the fabricated devices.	31
4.3.2	(a) I-V Characteristics, (b) Endurance, (c) Retention and (d) Multiple device switching characteristics, inset shows I_{on} and I_{off} of different devices in pristine state.	32
4.3.3	LogI-LogV of (a) set and (b) reset region. (c) Schematic of conduction mechanism. All are for pristine state device.	33
4.3.4	(a) I-V Characteristics at different bending radii, (b) I_{on}/I_{off} at different bending radii. Inset shows AFM image of bent device, (c) Endurance after 12 mm bending and (d) Endurance after 7 mm bending.	34
4.3.5	LogI-LogV of (a) set and (b) reset region. (c) Schematic of conduction mechanism. All graphs are for bent device.	36
4.3.6	Distribution of (a) set voltage (V_{set}) and (b) reset voltage (V_{reset}) at different bending radii.	37
5.2.1	(a) Schematic of the fabricated device and (b) Atomic force microscope image of the albumen film.	39
5.2.2	(a) I-V characteristic and (b) Retention of the device in pristine state. Distribution and Gaussian fitting of SET voltages (c) and RESET voltages (d) for multiple cycle operation.	40
5.2.3	(a) Switching characteristics and (b) Retention characteristics of the device after 7.5 mm bending. Distribution and Gaussian fitting of SET voltages (c) and RESET voltages (d) for multiple cycle operation after bending.	42
5.2.4	(a) Switching characteristics and (b) Retention characteristics of the device after 7.5 mm bending. Distribution and Gaussian fitting of SET voltages (c) and RESET voltages (d) for multiple cycle operation after bending.	43
5.3.1	(a) Device Schematic. Digital image of (b) an egg and the prepared solution of egg-albumen with DI water, (c) Fabricated device. (d) Atomic force microscope (AFM) image of the obtained film for hybrid bilayer device.	44

5.3.2	(a) I - V , and (b) Endurance Characteristic of Ag/Albumen/ITO device. (c) I - V , and (d) Endurance Characteristic of Ag/Albumen/HfO _x /ITO device. (e) Retention plot, and (f) V_{SET} and V_{RESET} distribution for Ag/Albumen/HfO _x /ITO device.	45
5.3.3	(a) I - V characteristics and (b) current on/off ratio vs time plot for 10 ³ seconds at different bending radii of 7.5 mm, 5 mm, and 2.5 mm.	47
5.3.4	V_{SET} and V_{RESET} distributions of (a) 7.5 mm and (b) 5 mm bent device for 100 cycles each.	48
5.3.5	Log(I)-vs-log(V) plot for set and reset region and slopes in respective regions for (a) Ag/Albumen/HfO _x /ITO, and (b) Ag/Albumen/HfO _x /ITO device.	49
5.3.6	Schematic representation of the device in (a) SET state where filament is formed by applying positive voltage at the top active electrode, (b) RESET state where the filament has been dissolved by reversing the applied voltage.	49
6.1.1	Comparative analysis of few widely accepted RRAM models.	52
6.2.1	Fitting of simulated characteristic with median of experimental result obtained from fabricated Ag/Gelatin/HfO _x /ITO device.	53
6.3.1	Simulated I - V characteristics with (a) initial gap variation, (b) activation energy variation, (c) both δ_0 and E_a variation of the device for 1000 cycles. (d) Statistical distribution of activation energy and initial gap.	54
7.1.1	Schematic of the main applications explored for solution-processed memristors. Reprinted with permission from [Pazos <i>et al.</i> , 2024].	57
7.2.1	(a) Schematic, and (b) digital image of the Ag/Gelatin/HfO ₂ /ITO device. Switching characteristics with applied (c) SET pulse with 2 V amplitude, and (d) RESET pulse with -2 V amplitude. (e) Distribution of SET and RESET switching time. (f) Schematic representation of a RRAM device and switching mechanism during SET and RESET cycle.	59
7.2.2	(a) I - V characteristic showing median and fitted simulated curve. 100 switching cycles with (b) δ_0 variation, (c) E_a variation, and (d) both δ_0 and E_a variation simultaneously.	62
7.2.3	(a) Schematic of flexible hybrid RNG circuit using flexible RRAM with XOR, AND, and 4-bit Counter block, and (b) layout of the circuit utilizing the 65 nm UMC PDK.	63
7.2.4	Waveform of (a) Input voltage V_{in} , (b) voltage obtained at BE of RRAM V_a , and (c) output of the XOR gate V_{out} for single cycle operation. (d) V_{in} , (e) V_a , and (f) V_{out} profile for 50 cycle operation.	64
7.2.5	Waveform of (a) V_{out} from XOR, (b) Q_0 , (c) Q_1 , (d) Q_2 , and (e) Q_3 from counter circuit for 50 cycles operation. Different colors of '0' and '1' represents states for different cycles.	65
7.3.1	Process of obtaining pectin from fresh orange peel, and device digital image showing the as fabricated flexible RRAM devices on ITO PET substrate with pectin switching layer and Ag top electrode.	69
7.3.2	(a) I - V characteristics showing SET and RESET cycles. (b) Retention characteristics at read voltage of 0.2 V, showing current ON/OFF ratio of more than 10 ⁴ . (c) Endurance characteristics showing reliable multi cycle switching. (d) Multiple device distribution shows a low standard deviation of 0.25 V with mean of 2.11 V.	70
7.3.3	Double log (I - V) characteristic of the device with slopes indicating different regions of operation. Inset shows schematic of switching mechanism.	71

7.3.4 (a) Depression characteristics of the device showing synaptic behaviour, and the fitted curve shows that at least 10 spikes are required for STM to LTM transition, inset shows the applied input voltage waveform. (b) PPF index showing relaxation time constants $\tau_1 = 0.3$ ms and $\tau_2 = 4.1$ ms.

72

List of Tables

1.3.1	Comparison of few emerging memory technologies	8
2.4.1	Summary and comparative analysis of bio-organic material based resistive switching devices.	17
4.3.1	Performance Comparison of Gelatin/HfO ₂ device with reported pristine and hybrid devices	38
5.3.1	Performance Comparison Table: Albumen/HfO _x with pristine Albumen devices	48
7.2.1	Value of Some Important Parameters of RNG Circuit	66
7.2.2	NIST SP800-22 Test Result	68

List of Symbols

Other symbols

η	Viscosity
ω	Angular velocity
ρ	Density of the solution
h	Thickness of the spin-coated film
h_0	Initial height constant of spin-coating
I_{cc}	Compliance current
I_{cell}	Total current flowing through the RRAM cell
I_{on}/I_{off}	Current on-off ratio
$R_{bending}$	Bending radius
t_{eo}	Effective oxide thickness
V_{cell}	Voltage applied across the electrodes of a RRAM cell
$V_{FORMING}$	Forming voltage
V_{RESET}	Reset voltage
V_{SET}	Set voltage
V_{out}	Output of RRAM
χ	Gaussian variation
γ	Local field enhancement factor
τ_1	Relaxation time constant for rapid phase
τ_2	Relaxation time constant for slow phase
τ_{RESET}	RESET time delay
τ_{SET}	SET time delay
A_0	Atomic spacing
E_a	Activation energy
g	Average tunneling gap distance
k	Boltzmann constant

k_{low-k}	Dielectric constant of low-k material
L	Length for PMOS
q	Elementary charge
R_{th}	Equivalent thermal resistance
T_0	Room temperature
T_{clk}	Time period of the clock
t_{lowk}	Thickness of low-k material
V_a	Input to the XOR gate comes from the BE of the RRAM
V_{clk}	Clock signal voltage
V_{in}	Voltage applied at the TE of the RRAM
W	Width/finger for PMOS

List of Abbreviations

DRAM	Dynamic Random Access Memory
ROM	Read-Only Memory
RAM	Random Access Memory
NVM	Non-Volatile Memory
PROM	Programmable ROM
EEPROM	Electrically Erasable Programmable ROM
HDD	Hard Disk Drive
CD	Compact Disk
DVD	Digital Versatile Disk
FeRAM	Ferroelectric Random Access Memory
PZT	Lead Zirconium Titanate
BTO	Barium Titanate
SBT	Strontium Bismuth Tantalate
TRFE	Tetrafluoroethylene
PCM	Phase Change Memory
GaN	Gallium Nitride
CMC	Compact Model Coalition
M-I-M	Metal-Insulator-Metal
RS	Resistive Switching
LRS	Low Resistance State
HRS	High Resistance State
IRS	Initial Resistance State
CF	Conductive Filament
OxRAM	Oxygen Vacancy RAM
CBRAM	Conductive Bridge RAM
VCM	Valance Change Memory
ECM	Electrochemical Metallization Memory
TMV	Tobacco Mosaic Virus
QCM	Quartz Crystal Microbalance
ALD	Atomic Layer Deposition
ALE	Atomic Layer Epitaxy
AFM	Atomic Force Microscopy
ECM	Electrochemical Metallization
ITO	Indium Tin Oxide
PET	Polyethylene Terephthalate
IPA	Isopropyl Alcohol
SCLC	Space Charge Limited Conduction
BE	Bottom Electrode
TE	Top Electrodes
IoT	Internet of Things
RNG	Random Number Generator
CMOS	Complimentary Metal Oxide Semiconductor
RNG	Random Telegraph Noise
NIST	National Institute of Standards and Technology
FHE	Flexible Hybrid Electronic
RMS	Root Mean Square