Review Article

Chandra Sekhar Dash and S. R. S. Prabakaran*

Nano Resistive Memory (Re-RAM) Devices and their Applications

<https://doi.org/10.1515/rams-2019-0014>

Received Mar 28, 2018; accepted Oct 04, 2018

Abstract: Use of solid state ionic conductors the so-called Solid Electrolytes has brought new impetus to the field of solid state memories namely resistive random access memory (Re-RAM). In this review article, to begin we present the detailed understanding on the basics of solid electrolytes. Later, the same has been reviewed focusing on its application in novel solid state memory applications. Few examples of solid electrolytes are considered and their impact on the state-of-art research in this domain is discussed in detail. An in-depth analysis on the fundamentals of Resistive switching mechanism involved in various classes of Memristive devices viz., Electrochemical Metalization Memories (ECM) and Valence change Memories (VCM). A few important applications of Memristors such as Neuristor and artificial synapse in neuromorphic computing are reviewed as well. Finally, the most anticipated energy efficient battery-like cells as artificial synapse in brain-inspired computing is also covered.

Keywords: memristor; resistive switching; filamentary conduction; neuromorphic computing

1 Introduction

The key parameters that determine the performance of the memory element is reproducibility, endurance, density, cost, read time, write time, Read/Write Energy. Although loads of memory technologies are present in the market but they have almost reached their lithographic limit and they cannot be scaled beyond certain limit, moreover they

are power hungry and occupy more die area [1–4]. The silicon based memories have dominated the market but they suffer from shortcomings such as high power consumption, poor endurance and Read/Write access speed. For instance, the emerging non-volatile memory technologies that are explored recently are Magneto resistive Random access memories (MRAM) and Phase change random access memory (PCRAM) [5–7]. In MRAM resistive switching is caused by magnetic field while in PCRAM the joule heating plays a crucial role which thermodynamically transits the phase of the switching material such as GeSbTe(GST) from high resistance amorphous state to low resistance crystalline state and vice versa [5–8]. The only issues pertaining with the above class of memory technologies is that they cannot be scaled below certain nanometer *i.e.* the density attained with MRAM and PCRAM is almost equivalent to the existing flash today. Although many non-volatile memory technologies are explored, most importantly NVM's based on the change in resistance state of the Metal-Insulator-Metal (MIM) under the influence of an external electric field proposed by Hickmott *et al.* [9]. This class of memory is generally placed under the umbrella of Resistive Switching Random access Memories commonly termed as ReRAM. The term 'M' stands for metal which can be any good electron conductor and it serves as top and bottom electrode. Both the top and bottom electrode can be made up of similar metal layers or asymmetric metallic layers. *I* is an active layer having electron insulating characteristics yet it is the modest ion conducting material for instance, metal Oxides, selenides, tellurides, nitrides, iodides etc. Leon chua in the year 1971 coined the name "Memristor" which is the fourth missing electronic passive circuit element linking between charge (*q*) and magnetic flux [10–12]. The research in this area fade away with the advent of silicon integrated circuit technology and its rapid development [13]. About 37 Years later HP lab came out with the memristor device in the year 2008 [14, 15]. It is a Metal-Insulator-Metal (Pt/MO_x/Pt) [MO = Metal oxide] stacked structure that exhibits functional features as memory element constituted by ionic charge transport in solid state by controlled flux variations. The intrinsic bulk resistivity is altered due to the movement of the ions under

*Corresponding Author: S. R. S. Prabakaran: SRM Research Institute, Directorate of Research, SRM Institute of Science and Technology, Potheri, Kattankulathur, Kancheepuram District, pincode 603203, India Email: srsprabakaran1611@gmail.com; Tel.: +919080222078

Chandra Sekhar Dash: School of Electronics Engineering, Vellore Institute of Technology, Vandalur-Kellambakkam Road, Chennai-600127, India

the effect of an external electric field. Upon removal of the electric field the ion motion ceases and the migrated ions occupies the defect sites where it is migrated and this is supposed as memory tuned exclusively by the resistivity changes the so called non-volatile memory. The fingerprint of memristor is a hysteresis loop pinched at origin elucidates the word write and erase in a cyclic manner. This lies under the umbrella of ReRAM [12].

This fundamental passive element has been regarded recently as an element of surprise for electronic computation of different levels. The typical computing application for such class of device is resistive switching random access memories (ReRAM). The dynamic non linearity in current voltage characteristics encouraged researchers around the globe to develop alternate memory architecture. The existing digital computer is extremely capable to emulate the brain functionality of the biological creatures such as spider, mouse, and cat. The configurations of brain of biological creatures are completely unlike to the existing Von Neumann architecture [16]. The biological systems are more efficient because of complex connection between the neurons that aid in parallel processing. The synaptic weight between the post and pre neuron can be adjusted by controlling the ionic flow through them and it is widely accepted that adaptation of synaptic weight enables the biological system to learn. If the conductance of memristor is considered as synaptic weight it functions similarly to the nonlinear transmission characteristics of synapse mimicking the brain functionalities for developing artificial intelligence (AI) [16, 17]. Recently memristor is being used to fabricate neuristor which is considered to be the electrical equivalent of the biological neuron [18].

The only impediment that has restricted the memristor from being commercialized is the lack of extrapolative and robust understanding of the underlying switching mechanism [13]. During the last decade memristor have been fabricated utilizing a wide variety of materials and intuitive characterization techniques are used to investigate the switching mechanism involved in memristor. In this paper first basics of solid electrolytes is presented and its application in novel memory applications is studied in detail in the subsequent section. An in-depth analysis on fundamentals of Resistive switching mechanism involved in ReRAM devices is done with aid of advanced characterization and their impact on state of art of research in this domain is discussed in detail. A few important applications of Memristors such as Neuristor and artificial synapse in neuromorphic computing are reviewed as well. For the first time an attempt is made to compare the working of the artificial synapse and neuristor to the biological synapse and neuron respectively. Finally, the energy

efficient battery-like cells as artificial synapse in brain-inspired computing are also covered.

2 Why fast ion conductors?

In general ionic conductors are broadly categorized into two categories namely normal ion conductors and fast ion conductors. The family of materials that exhibit high electronic conduction and low ionic conductivity named normal ion conductors. Fast ion conductor exhibits high ionic conductivity and low electronic conduction. The application of external bias causes migration of randomly oriented ions in bulk material in the direction of electric flux thereby initiating ionic conduction. The ionic conduction in solids is closely related to its atomic structure as the presence of defects and imperfections aid in enhancing it. The ionic conductivity in normal ion conductors is temperature dependent as at an elevated temperature defects are generated thermally [19]. The process of activation involves two steps namely energy required for the formation of defects (h_f) and energy due to migration of ion (h_m). The total ionic conductivity in normal ion conductor is given by (1)

$$\sigma_i = \sigma_0 \exp\left(\frac{-h_f}{kT}\right) \exp\left(\frac{-h_m}{kT}\right) \quad (1)$$

Where

$$\sigma_0 = \frac{e^2 g_0 f \lambda^2 N x}{kT}$$

e = Charge of mobile ions

g_0 = Jump Frequency

N = charge carrier density

x = Fraction of Mobile charge carriers

T = absolute temperature

k = Boltzmann's Constant

h_f = Energy of defect formation

h_m = Energy of defect Migration

Schotky and Frenkel defects are predominantly found in this class of ionic conductors, where ionic conductivity is in the order of 10^{-14} to 10^{-12} scm^{-1} . While in fast ion conductors the population of carrier ion concentration is very high at room temperature as well as at higher temperature and even the enthalpy of formation (h_f) is zero. The total ionic conductivity in it is given by (2)

$$\sigma = \sigma_0 \exp\left(\frac{-h_f}{kT}\right) \quad (2)$$

Furthermore, fast ion conductors can be classified on the basis of presence of mobile charge carriers that take part in charge transport viz. anionic and cationic conductors. The mobile charge carriers in anionic conductors are mainly

Figure 1: (a) General 3-D Bilayer stack structure of Memristor, Initial electroforming and the typical subsequent quasi-static I-V cycles for the Ag/a-LSMO/Pt memristor cells with a Compliance current of 10mA shown on (b) linear scale and (c) semilogarithmic scale. Reprinted with permission from D. Liu, H. Cheng, X. Zhu, G. Wang and N. Wang // *ACS Appl. Mater. Interfaces* 5 (2013)11258, (C) 2013 American Chemical Society.

oxide and fluoride ions, whereas cationic conductors are predominantly Ag^+ , Cu^+ , Li^+ , Na^+ etc [19]. The proper understanding of kinetics of ionic conductors is extremely critical to identify suitable materials to develop efficient ReRAM. For instance, the use of fast ion conductors will not only enhance the Write/Read access time, but also lowers the overall power consumption. We will discuss about this in detail in subsequent sections. The basic 3D stack structure of memristor is shown in Figure 1. The memristor is basically a MIM cross layer structure in which a metal oxide or metal oxides layers is sandwiched between top and bottom perfect ion blocking electrode (Pt, Au, Pd etc.) [13, 14]. To achieve memristive effect a typical amount of ion vacancy is intentionally created within the host sub-lattice

of metal oxide. The resulting stack structure upon creation of vacancy is $\text{Pt}/\text{MO}_{x-y}/\text{MO}_x/\text{Pt}$, which comprises of low resistant, defect abundant (MO_{x-y}) layer, in series with high resistant defect free metal oxide. To achieve memristive effect a typical amount of ion deficiency is created within the host sub-lattice of metal oxide. For instance a rutile phase of titanium oxide (TiO_2) is partially created with oxygen deficiencies making it to be TiO_{2-y} . Indirectly a large number of defects and void sites are created within the sub-lattice metal oxides so that oxygen ions can hop freely from one position to another. The resulting structure after creation of vacancy is $\text{Pt}/\text{MO}_{x-y}/\text{MO}_x/\text{Pt}$, which comprises of a non-stoichiometric layer of metal oxide (low resistance state

Table 1: Definitions and Quantitative estimates for required performance metrics of ReRAM

	Desired	Best Reported
Endurance: It is the count of number of reliable write/Erase operation that can be performed on a memory cell before it turns unreliable.	Existing Flash exhibits between 10^3 to 10^7 write cycles. Better endurance performance is desired.	10^{12} cycles
Retention time: The ability of a memory cell to hold its data for long period of time at an extreme thermal stress of 85°C and under a minor electrical stress such as constant chain of read pulses.	10 years	10^{14} seconds
Switching Energy: The amount of energy required to switch the ReRAM device from LRS to HRS and vice versa.	< 1 pJ	1 pJ
Switching Speed: The time required by a ReRAM device to switch between LRS to HRS and vice versa under the effect of an external electrical bias.	< 10 ns	0.1 ns
Density: It is the measure of quantity of information bits that can be stored in a given volume of the computer storage medium.	$(20 \text{ nm})^{-2}$ & Multilayers	$(10 \text{ nm})^{-2}$ & 4 layers

***Write Voltage:** The potential applied to write into or erase the content of the memory cell. A ReRAM which exhibits bipolar switching, typically a positive/negative bias is required to write in to the memory cell (Write '1') and negative /positive potential is necessary to erase the content of the cell (Write '0'). Its amplitude lie in the order of few hundred mV to Volts.

***Read Voltage:** The potential required to fetch the content of the memory cell. In memristor basically the read voltage is much lower than the write voltage as it should not cause any significant change in the internal resistance state of the ReRAM. In general the polarity of the read and SET voltage is same.

MO_{x-y}) in series with a high resistance defect free metal oxide.

When a moderate potential is applied to the top metal electrode, an enormous E-Field is developed as thickness of the stack is in nano regime. This bias potential provides energy to break M-O bond in the buffer layer resulting in the hopping of oxygen ions from the buffer layer (MO_x) to the non-stoichiometric (MO_{x-y}). As a result of this vacancies are spread over a larger area of the metal oxide thus reducing the overall resistance of the device. This movement of oxygen vacancies results in a conduction modulation that makes device to transfer from high Resistance State (HRS) to low resistance State (LRS) causing the device to SET. Similarly, upon reversal of polarity of applied bias, it alters from low resistance State (LRS) to high resistance State (HRS) causing it to RESET. Thus, the movement of oxygen ions under the influence of external electric field help transform the transition of metal oxide from insulator to conduction phase and vice versa. The defect concentration (n_d) of the order of 10^{21} cm^{-3} makes the metal oxide to behave like a fast ion conductor [19–27]. Thus, it is construed that each of such carrier ions (q_i) possesses the memory content [18].

3 General switching mechanism of ReRAM

Prior to getting into the switching mechanism associated with resistive switching it is important to understand the performance metrics which are need to be achieved by the proposed ReRAM technology to replace the existing NAND flash and SRAM which are widely employed for memory storage applications. Table 1 describes the various memory parameters with their corresponding required desired result and the best reported results till date.

3.1 Electrochemical Metallization Memories (ECM)

The switching in ReRAM is mainly determined by the factors like electrical, ionic and thermal. It is basically of two kinds namely unipolar and bipolar. If the polarity of the SET and RESET voltage is identical then it is said to be unipolar switching otherwise bipolar switching. The process of transit of device from high resistance state to low

Figure 2: (a) Pinched hysteresis loop of Ag/a-LSMO/Pt memristor (b) Region 1 indicating the initiation of the growth of Ag filament from the bottom inert platinum electrode to the top non inert (Ag) electrode, (c) In region 2 device is in LRS as the conducting filament connects both top and bottom electrode, (d) region 3 corresponds to the beginning of process of RESET as conducting filament gradually starts obliterating (e) Device is in HRS as conducting filament completely obliterated. Reprinted with permission from D. Liu, H. Cheng, X. Zhu, G. Wang and N. Wang // *ACS Appl. Mater. Interfaces* 5 (2013)11258, (C) 2013 American Chemical Society.

resistance state is termed as SET and RESET when vice versa. The bipolar switching in ReRAM is mainly due to the movement of randomly oriented ions in the direction of electrical flux and electrochemical redox reactions at the electrode and switching material interface [2]. Although, there are ample reports on switching mechanism of memristor, but till date none of the mechanisms are elucidated, rather they are suggested on the basis of theoretical understanding or with aid of advanced physical and electrical characterization techniques [28]. Among all suggested mechanism for resistive switching filamentary conduction is widely accepted by researchers around the globe. In order to explain filamentary conduction here we consider three examples one from anion and two from cation conducting ReRAM. The general memristive structure using Ag as an active electrode can be in any of the following structures such as Ag/MSe_x/Pt, Ag/MS/Pt, Ag/MO/Pt [MO- Metal oxides, MS- Metal sulphides and MSe_x-Metal Selenides] where the switching layer is sandwiched between top non- blocking electrode and bottom blocking electrode. The best switching performance can be achieved by using fast ion conducting material as switching layer. The anodic dissolution occurs under the effect of an external electric field

as shown below (3)

This causes the Ag⁺ ions to hop across the ionic conductor towards the cathode and get reduced, which is an ion blocking electrode viz. Pt, Au and W.

Beside due to the effect of external field an electro-crystallization process takes place that causes the development of metal nanofilaments towards the active electrode (Ag). The top electrode being electrochemically active, an unceasing oxidation takes place on it and silver metal cations dissolve into the switching layer supporting in the process of growth of metal filaments. When the metal nanofilaments join the top and bottom electrode, the ReRAM turns ON, i.e. the device is in LRS. The device retains its resistance state until the polarity of the applied E-field is not inverted. The inversion of polarity of applied bias causes electrochemical annihilation of metal nanofilaments causing the transit of resistance state of the device from LRS to HRS. These kind of devices are sometimes called as ECM memories.

As illustrated in Figure 2 at point “1” of the hysteresis loop indicates the beginning of process of SET, there

Figure 3: The phenomenon of conducting filament dynamics in SiO_2 -based ReRAM. (a) TEM image of an as-fabricated SiO_2 planar ReRAM device fabricated on SiN_x membrane. Inset: schematic of SiO_2 planar ReRAM device. TEM image of the same device (b) after the forming process (c) after erasing. The arrows highlight several representative filaments. scale bar, 200 nm. (c) TEM image of the same device scale bar, 200 nm. Current versus time curve corresponding to (d) Forming process at 8V bias voltage (e) Erase process at -10 V bias voltage (f) schematic of the filament growth process showing the transport and reduction of Ag cations. (g) schematic of the dendrite structure formation. (h) TEM image of another device with larger electrode spacing after the forming process. scale bar, 200 nm. Inset: zoomed-in image of the filament (highlighted by the upper arrow) near the dielectric/inert electrode interface. scale bar, 20 nm. (i) TEM image of the same device as in (h) after erasing. The breaking of the filaments took place at the interface of inert electrode. Current versus time curve corresponding to (j) Forming process at 10 V bias voltage (K) Erase process at -10 V bias voltage. (Reprinted with permission from Y. Yang, P. Gao, S. Gaba, T. Chang, X. Pan and W. Lu// *Nat. Commun.* **3** (2012) 732 (C) 2012 Nature publishing group.

is the initiation of the process of growth of metal nanofilaments towards the top electrode. At point “2” a complete filament is formed joining the top and bottom electrode indicating that the device is in LRS. Upon reversal of applied bias at point “3” initiation of rupture of filament occurs and finally at “4” metal nanofilaments are completely obliterated.

Contrasting to above study Yang *et al.* studied the geometry of filaments in Ag/ SiO_2 /Pt stack structure, where they reported the observation of thinnest region of the filaments near the inert electrode/dielectric interface. As thinnest zone of the filament plays a critical role in controlling the dissolution and reformation of filament, thus it directly impacts the process of write/erase in the memory cell. Same kind of mechanism is also elucidated by Ag/ Al_2O_3 /Pt and Ag/a-Si/Pt structure [29, 30]. The typical shape of the filaments observed with aid of HRTEM is shown in Figure 3.

Xu *et al.* observed the direct formation and rupture of conducting pathway in superionic (Ag_2S) Ag/ Ag_2S /W

memory cell in inside HRTEM (High- Resolution- Transmission electron Microscope) comprising of STM unit inside it. Reproducible switching characteristics were observed in this class of device as shown Figure 4. By using in tandem spatially resolved energy-dispersive X-ray spectroscopy (EDS) and HRTEM lattice imaging the crystal structure of the device during the HRS and LRS is studied. In the off state the switching layer Ag_2S is in acanthite phase which is basically HRS, upon the effect of an external electric field its phase transits to high conducting argenteite Ag_2S phase. Hence, the conduction pathway grown out of the original surface of the electrolyte, comprises of mixture of Ag and the argenteite phase [31].

In 2007 Liang *et al.* for the first time observed resistive switching in thin film RbAg_4I_5 which is reported to be a room temperature super ion conductor [32]. It exhibited reversible switching characteristics in Ag/ RbAg_4I_5 /Pt ReRAM structure and further Valov *et al.* confirmed phenomenon of filamentary conduction, by demonstrating

Figure 4: Low-magnification TEM image of Ag₂S-based ReRAM. Low-magnification TEM image corresponding to (b) LRS of the device, due to the growth of a new nanocrystal (c) HRS, the newly grown crystal, Low magnification TEM image corresponding to the off-state. The grown crystal disappeared. Pinched hysteresis loop of Ag₂S-based ReRAM in (d) linear scale Inset: logarithmic scale. (Reprinted with permission from Z. Xu, Y. Bando, W. Wang, X. Bai and D. Golberg // *ACS Nano* 4 (2010) 2515 (C) 2013 American Chemical Society.

the electrochemical Ag phase formation on the surface of the RbAg₄I₅ [33].

Let us consider a basic Cu/MO/Pt structure, where {MO = metal oxide} switching layer. The lack of Cu ions in the host lattice of switching layer restricts it from exhibiting repeatable switching characteristics. The application of external bias causes the Cu ions to migrate through the amorphous metal oxide layer, thereby incorporating themselves into matrix of switching layer. This causes an irreversible nano morphological change in the ion conducting switching layer by forming low conducting incomplete filaments [34, 35]. This process is termed as electroforming which is extremely essential to enable the device to exhibit reproducible switching characteristics. Celano and Hubbard *et al.* investigated the restive switching in Cu/Al₂O₃/TiN based ReRAM, using atomic force microscopy based tomography which assists in spotting 3D conducting filaments. They observed the direction of growth of conducting filament from the active (Cu) to the inert (TiN) electrode which is completely contradictory to the previous studies. Under the effect of external bias copper atoms gets ionized and migrate into switching layer

causing an enhancement of oxygen vacancies within the Al₂O₃ sublattice. These vacant sites assist in migration of Cu ions through the oxygen sites of Al-O bonding in the amorphous matrix. Owing to the low mobility of cation (Cu⁺) in switching layer, they travel short distance and get reduced by capturing electrons that are unceasingly introduced into the Al₂O₃ layer due to the presence of external E-field. As a result Cu⁺ ions reduced to Cu and turn out to be an extension of top Cu electrode, and this process continues until it forms a contact with the bottom inert electrode. These assumptions explain the cause for growth of conducting filament from non-blocking (Cu) electrode to blocking electrode. In order to visualize the shape of the conducting filament at various resistance state of the ReRAM Conductive-Atomic force microscopy based tomography is used. The Figure 5 shows the image of conducting filament joining top and bottom electrode *i.e.* in LRS. The conducting diamond tip is utilized as a scalpel for controlled removal of material layers as shown in Figure 5.

The 2D image of the conducting filaments is recorded at each stage and joined together to produce 3D image (tomogram) of the conducting filament [34]. The same technique is employed to observe the shape of filaments when the device is in LRS and HRS. The complexity in understanding the switching mechanism of the device surges up when the device fabricated with same material exhibit dissimilar switching characteristics during the RESET operation as shown in Figure 6 [36]. For the same structure during RESET there is an abrupt and progressive decline in the level of current at V_{reset} (−0.5V) is observed, where both broken and non-broken filaments were spotted while carrying out C-AFM tomography. The abrupt decline in the level of current at V_{reset} is made fit to a direct conduction model explaining the rupture of conducting filament which is further confirmed by 3D tomogram confirming the presence of broken filament with a gap of 0.4nm whereas for the case of progressive decline in the current at V_{reset} , it follows a quantum point contact. The filament is not completely broken while low conducting filaments observed throughout the switching layer. Undeniably 3D tomogram exhibit the shape of the conducting filament but the material composition of the filament is still under debate. Hence, future scope lies with development of advanced characterization technique to determine the material composition of the conducting filaments.

3.2 Valence change Memories (VCM)

In order to explain resistive switching in anion conducting ReRAM, the resistive switching in Pt/ TiO₂/Pt based

Figure 5: (a) Planar 2D C-AFM, performed on Cu/Al₂O₃/TiN ReRAM crosspoint while it is in LRS, due to the shielding effect of top Cu electrode Conducting filaments (CF) were not observed. (b) Elucidates the C-AFM tomography procedure, where in order to collect several slices at different heights of the CF, a diamond tip is employed. (c) Over imposition of the collected 2D C-AFM slices, prior to the 3D interpolation. Note, the average space between each slice is ~0.5 nm. (d) The data set for the 3D interpolation is constituted by collection of 2D slices, and the CF is observed near the center of the active electrode upon removal of top electrode. The top-left and bottom right region exhibited highly conductive features corresponding to exposed region of the TiN BE, which is gradually exposed during the process of Al₂O₃ removal. (Reprinted with permission from U. Celano, L. Goux, A. Belmonte, K. Opsomer, A. Franquet, A. Schulze, C. Detavernier, O. Richard, H. Bender, M. Jurczak, and W. Vandervorst // *Nano Lett.* 14 (2014) 2401 (C) 2014 American Chemical Society.

Figure 6: (a) Two different RESET mechanism are observed in similar devices operated under identical conditions. In the red trace, during the process of transfer to HRS the current decreases progressively corresponding to a lower value (HRS). The blue trace exhibits a steep reduction of the current at -0.5 V leading the device to HRS. No difference in forming and SET voltage are observed and they are not shown. The final obtained resistive states are comparable for both devices. (b) Schematic of the one-transistor-one-resistor configuration. Details of the cross-point cell are shown with AFM topography (2 × 0.9 μm scan size) and cross-sectional TEM. Reprinted with permission from U. Celano, L. Goux, A. Belmonte, K. Opsomer, R. Degraeve, C. Detavernier, M. Jurczak, and W. Vandervorst // *J. Phys. Chem. Lett.* 6 (2015) 1919 (C) 2015 American Chemical Society.

memristor is considered. On application of external bias at anode positively charged oxygen vacancies migrate towards the cathode-oxide interface with an improved mobility due to the presence of vacancies and grain boundaries. These $\text{Ti}_4\text{O}_5^{+2}$ ion hop towards the host lattice and react

with oxygen ions forming high conducting Ti_2O_3 nanofilaments (HCNF). The process of formation of conducting filaments involves two steps viz. nucleation and growth, nucleation site is determined by the localization of E-field owing to thinning of switching layer or localization of current due to presence of defects in abundance. With the end of process of nucleation, filament growth occurs by ion migration and reduction on the surface of the conducting filament. The above process ends when conducting filament forms a galvanic contact with the top electrode. Subsequently, on reversal of the applied bias vacancies retracts back to the anode-oxide interface, resulting in thinning of conducting filament and finally initiation of depleted gap from the anode [27]. Furthermore Chen *et al.* reported the thermal effects on the filamentary conduction in Pt/ZnO/Pt ReRAM structure with aid of in situ TEM observations. The shapes of the filament at various stages of switching were observed. Finally with the help of electron energy loss spectroscopy (EELS) they observed, it is the zinc conducting filament joining the top and bottom electrode. The switching is predominantly due to the migration of oxygen ions under the effect of an external E-Field causing toggling between low resistance ZnO_{1-x} and high resistance ZnO. The Figure 7 depicts the shapes of the conducting filament, during various resistance states of the ReRAM [37].

Figure 7: In situ TEM images of Pt/ZnO/Pt ReRAM explains the phenomenon of unipolar resistive switching during the process of reset (a) Initiation of the process of recording; (b) intermediate state; (c) Ultimate state of the ruptured filament upon accomplishment of reset process. (d) The corresponding I-V curve in red; the blue line corresponds to the forming process as a comparison. (e) Occurrence of multiple conductive filament elucidating the switching is caused by formation and rupture of multiple filaments. (f) The selected area diffraction pattern of the conductive filament in Figure 7e, where the red marked circle points to Zn (101) diffraction spot. (g) The corresponding dark-field image obtained from the diffraction spot marked as a circle in the diffraction pattern f. (h) In a high-magnification TEM image Moiré fringes are observed at the disrupted region. (i) The conducting filaments were transformed back to ZnO_{1-x} along the $\langle 110 \rangle$ zone axis in the disrupted region. (j) The “zinc” conductive filament in the HRTEM image (j) The HRTEM of the “zinc” conductive filament along the $\langle 231 \rangle$ zone axis has been recognized. (k) Solid-sphere model of ZnO in a wurtzite structure along the $\langle 110 \rangle$ zone axis, where all the coordinate lines are the unit cell vectors. (l) Solid-sphere model of zinc in a HCP structure along the $\langle 231 \rangle$ zone axis. The 3-D schematic illustrations of (m) a ZnO unit cell and (n) a zinc unit cell, respectively, elucidating that the position of the zinc atoms remains unchanged as oxygen ions diffuse out. Reprinted with permission from J. Y. Chen, C.L. Hsin, C.W. Huang, C.H. Chiu, Y.T. Huang, S.J. Lin, W.W. Wu, L.J. Chen// *Nano Lett.* 13 (2013) 3671 (C) 2013 American Chemical Society).

Undeniably high speed Read/Write access, low power consumption is achievable in ECM memory cells, yet their compatibility with existing CMOS technology is questionable. As the write voltage is in the order of mV and is not enough to bias the existing CMOS transistors which are mainly employed as peripherals. In anion conducting ReRAM a reservoir of ions is highly essential just be-

neath the positive electrode, while in cationic conductors the role of reservoir is played by the active electrode [38]. For example the MIBM (Metal-Insulator-Base-Metal) structure $\text{Pt}/\text{Ta}_2\text{O}_{5-x}/\text{TaO}_{2-x}/\text{Pt}$, here the switching takes place by formation and dissolution of filaments in the insulating $\text{Ta}_2\text{O}_{5-x}$ layer. The filament comprises of positively charged oxygen vacancies (TaO_x conducting sub oxide

phase) which is conducting in nature. As the base layer (TaO_{2-x}) layer serves as a reservoir (abundance of TaO_x), under the application of negative bias the TaO_x ions move towards the top Pt electrode resulting in forming a filament across the $\text{Ta}_2\text{O}_{5-x}$ layer and dissolution takes place under the effect of an external positive bias. Thus the presence of vacancies ensures an improved endurance performance and enhanced stability in switching.

As discussed above filamentary conduction is dominant in ECM and VCM memories, an attempt is made here supporting the view of Goux *et al.*, to summarize the mechanism of growth of filaments by considering the cumulative effect of electrodes and nature of ion conducting insulating layer [39].

- a When the redox process is homogenous and ion mobility is high, the dissolved ions can reach the counter inert electrode causing the growth of conically shaped filament within a tip pointing to the active electrode from the bottom inert electrode. This phenomenon is widely observed in ECM cells.
- b When redox reaction rate is low and ion mobility is high, this leads to growth of branched filaments towards the active electrode from the counter electrode. Nucleation occurs near the counter electrode and reduction mainly at edges.
- c When both ion mobility and redox reaction rate is high, in this case ions gather within the solid electrolyte and when it attains the critical nucleation state, and bipolar electrode effect filament can proceed by cluster displacement from the active electrode towards the inert counter electrode.
- d The ion mobility is low but the electrode reaction rates are high. Nucleation can now occur inside the dielectric while large amounts of atoms can be deposited onto the cathode sides of the nuclei, leading to gap filling. After a connection between the nuclei and the active electrode is achieved, the process is repeated leading to an effective forward growth towards the inert electrode.

3.3 Carrier Transport in ReRAM

The phenomenon of ionic transport is identical in both anion and cation conducting ReRAM. Microscopic resistive switching in this class of device can be explained through solution of partial differential equations. The migration of oxygen ions and subsequent ordering of vacancies in the oxide layer under the effect of an external field is the cause for resistive switching, where presence of V_O (va-

cancies) assists in formation of low resistive channels for ionic transport. The migration of defects is defined by a flux and it consist of two components namely drift and diffusion. The process of migration of defects involves a series of jumps amid neighboring sites, considering a hopping distance 'a' and uniform energy barrier (E_a). The energy barrier is lowered by a factor of qaE due to the effect of external field (E) which accounts for enhancing the hopping rate and directional movement of ions which is extremely essential to achieve bipolar switching. The defect transport equation is given by (4)

$$\frac{dn_d}{dt} = \nabla \cdot (D\nabla n_d - vn_d + DS\nabla T) \quad (4)$$

Here, $D\nabla n_d$ is diffusion flux, vn_d is drift flux and $DS\nabla T$ is called as Soret diffusion flux which describes the tendency of vacancies to migrate towards hotter region in presence of thermal gradient. The ionic diffusivity (D) is defined by $D = \frac{1}{2} a^2 f \exp(-\frac{E_a}{kT})$ where a , f and E_a are hopping distance, escape-attempt frequency, activation energy for ion migration respectively. As size of device is in nano regime even a small applied bias may produce extremely high electric field and current density within device there by concluding the significant role of joule heating in the process of resistive switching. In addition to that the expression for ionic diffusivity (D) suggests that it is temperature dependent process following Arrhenius law. The Soret diffusion coefficient (S) is given by $S = \frac{-E_a}{kT^2}$ and velocity of migration of defects is given by $v = a f \exp(-\frac{E_a}{kT}) \cdot \sinh(\frac{qaE}{kT})$.

The current continuity equation for electronic conduction (5) is coupled with (4), given as

$$\nabla \cdot \sigma \nabla \varphi = 0 \quad (5)$$

To solve the above (5) the electrical conductivity (σ) of the oxide layer and the conducting filament is required and φ is the electrostatic potential related to the E-field (E) by the $\nabla \varphi = -E$. The conducting filament in case of ECM is assumed to be metallic, while in anion conducting device conducting filament is presumed to comprise of suboxide (oxygen deficient metal oxide with enhanced defects (n_d)) [40, 41]. The ion migration within the switching layer is thermally driven due to the dependency of electrical, thermal conductance on density of defects and it follows Arrhenius equation given by (6)

$$\sigma = \sigma_0 \exp\left(-\frac{E_a}{kT}\right) \quad (6)$$

In another study Larentis *et al.* observed rise in conductivity (σ_0), with increment of defects (n_d) thereby lowering

the overall resistance of the device causing a transit of resistance state from HRS to LRS. In this state the activation energy (E_a) is reported to be almost zero as conducting filament is joining top and bottom electrode. With decrease in defects (n_d) a semiconductor like conduction observed corresponding to conduction in low conducting broken filaments [42, 43].

In addition to (5), a steady state Fourier equation for joule heating is required to solve (4) i.e. (7)

$$-\nabla \cdot k_{th} \nabla T = \sigma |\nabla \phi(r, z)|^2 \quad (7)$$

where RHS denotes the local dissipated power density computed by the product of electric field by current density and LHS corresponds to the space variation of heat flow because of heat conduction. The thermal conductivity k_{th} is high for higher value of n_d , while low for lower value of n_d inferring to availability of free carriers thermal conduction [41–44].

4 Brief history of resistive switching

In 1960, Bruyere *et al.* for the first time observed bipolar resistive switching in NiO [45]. Although the conceptual thought was put forth by Leon Chua in 1971 [12], but practical device was developed by HP labs in the year 2008 by sandwiching a Titanium dioxide layer between top and bottom platinum electrode [14]. The serendipitous find of memristor by HP labs have invigorated researchers around the globe to investigate the possibility of resistive switching in other metal oxides [46]. However, prior to HP labs claim, the materials like Nb₂O₅, NiO, Pr_{0.7}Ca_{0.3}MnO₃, SrTiO_x, SrZrO₃, and VO₂ have exhibited filamentary resistive switching [47–50]. As it is mentioned in the previous section memristor belongs to the family of ReRAM, here few examples of cation and anion conducting ReRAM will be mentioned. To begin with cation conducting ReRAM, in 1976, Hirose *et al.* described the resistive switching in Ag /Ag-photodoped As₂S₃/Au Metal-Insulator – metal structure is due to the formation and rupture of silver dendrite [48]. In 1999, Koziciki *et al.* successfully observed resistive switching by employing GeSe as an ion conductor [49]. Kund *et al.* integrated Ag/GeSe_x/W based CBRAM with CMOS 90nm transistors and then fabricated a 1T-1M crossbar array of memory by placing all the 1T-1M cells at each cross point [50]. The Ag/a-LSMO/Pt analog exhibited pinched hysteresis at higher frequency like 500 Hz, 500 KHz, and 1.5 MHz. With increase in frequency the area bounded by pinched hysteresis loop

shranked. In order to operate memristor at higher frequency the device need to be electroformed below 10mA or at higher CC (Compliance Current) [28]. Gubicza *et al.* performed Read/Write operation at lower write/erase voltage and higher (GHz) frequency in Ag–Ag₂S–PtIr nanojunctions based ReRAM [51, 52]. Further Cheng *et al.* developed odd-symmetric Ag₂S/Ag/Ag₂S memristor that exhibited a pinched hysteresis loop with an odd symmetry which paved the way for development of odd-symmetric memristor in future [53]. Li *et al.*, Zhao *et al.* and Liu *et al.* reported filamentary switching in Ag/PEDOT:PSS/Ta, Ag/TiO_xN_y/Pt and Ag/ZrO₂/CuNC/Pt ReRAM [NC – Nanocrystal] respectively [54–56]. Devulder *et al.* performed a comparison study among Pt/Ag_{2-δ}Te/Al₂O₃/Si and Pt/Ag/Al₂O₃/Si based ReRAM, where both structures exhibited filamentary conduction. The incorporation of Ag_{2-δ}Te layer into the stack results in causing an improved RESET switching performance and an improvement in endurance and retention time is observed. This finding matches to their previous study on comparison of switching performance in TiN/Cu_{0.6}Te_{0.4}-C/Al₂O₃/Si and pure Cu_{0.6}Te_{0.4} as ion conducting material [57, 58].

4.1 Complementary Resistive Switching

In 2012, Lee *et al.* fabricated MIBM (Metal-Insulator-Base-Metal) bilayer structure consisting of Ta₂O_{5-x}/ TaO_{2-x} sandwiched between two ion blocking Pt electrodes as discussed in previous section [38]. Considering the device in HRS (MIBM), on application of bias at the top electrode causes a transit in the resistance state of the device to LRS i.e. it transits from MIBM to low resistant metal–metal (filament)–base–metal (MMBM) and back to MIBM on reversal of polarity of the applied bias. The thickness of the base plays a vital role in avoiding the device to turn into a MIM structure. For instance if the resistivity of the base layer (TaO_{2-x}) is very low, then it acts like metallic bottom contact while Ta₂O_{5-x} being an insulating ion conducting layer the devices acts as a MIM structure. If the resistance of the base layer is too high then there will be a higher voltage drop across resulting in electroforming through the whole TaO_{2-x} + Ta₂O_{5-x} layer, thus device acts as conventional MIM structure. The resistance of the insulating layer and base layer is of the order of 10⁷ to 10⁸ and 10³ to 10⁴ Ω respectively. A bilayer structure displayed a symmetric current profile in LRS, while an unsymmetrical current profile in HRS. The switching is as result of formation and rupture of conducting filament in Ta₂O_{5-x} switching layer [59]. 3D stacking is extensively used to reduce die area and place more memory cells within a small area. Usually memories

are designed in a crossbar array, where a single memory cell (ReRAM) is positioned at each crosspoint of bit and wordline. As all the cells in a row shares common horizontal and all the cells in a column shares the same vertical electrode, then there is a probability of undesired current flowing through the unselected cells, this unwanted current is called as the sneak path current or leakage current in memristor in ReRAM. In order arrest sneak path current a switching element such as diode, transistor in series with memory cell and complementary resistive switching. The technique of connecting two memory cells antiseriially to circumvent sneak path current is known as complementary resistive switching (CRS). The lack of symmetry in current profile during HRS of each MIBM cell CRS structure results in a region that circumvent the flow of current by creating schotky barrier between Pt electrode and Ta_2O_{5-x} ion conducting layer. This barrier arrests the flow of current within a potential window called threshold, there by completely arresting the sneak path current. In addition to that there are many reports on tantalum oxide based memristor and it is widely studied as it provides the highest reported endurance of 10^{12} cycles and low power consumption [60–62]. The complementary resistive switching in Nb_2O_{5-x}/NbO_y bilayer structure is reported where the top electrode Pt is replaced with W which led to the formation of oxygen barrier layer WO_x among the Nb_2O_{5-x} ion conducting layer and W top electrode. Furthermore the above described bilayer structures avoids the use of an extra transistor or diode, which drastically lowers the complexity involved in the process of fabrication and enhance the density [63, 64].

4.2 Effect of Doping on Resistive switching

The metal oxides like HfO_2 , ZrO_2 , Yb_2O_3 and tantalum oxide have been doped with metallic impurities like Gd, Al, La, Ti and Si in order to expedite the migration of oxygen vacancies under the effect of an E-field by altering the atomic structure to create preferential transport channels for vacancies thus allowing in tuning the resistive switching performance at atomic level by lowering the hopping distance and velocity of migration of oxygen vacancies [65–68]. Furthermore, Kim *et al.* doped the ion conducting (Ta_2O_{5-x}) with Si in $Pd/Ta_2O_{5-x}/TaO_{2-x}/Pd$ memristor and explained the effect of doping and ion transport phenomenon with the help of *ab initio* calculations. In their calculation they found that interatomic distance among Ta-O is greater than Si-O, subsequently all the oxygen atoms are gathered near the Si turning region beyond it into an oxygen deficient region as shown in Fig-

Figure 8: (a) Photographs of the amorphous Ta_2O_{5-x} and Si-doped Ta_2O_{5-x} structures attained in the *ab initio* simulation. The Ta, O, and Si atoms are colored in dark green, red, and blue, respectively. (b) The calculated Pair-correlation functions at room temperature of the amorphous Ta_2O_{5-x} and Si-doped Ta_2O_{5-x} . (c) Three oxygen atoms are randomly selected as displayed in Fig 8(a). Histograms representing the the OO distance from a selected oxygen atom to a neighbouring oxygen atom. (d) The atomic ratio of O and Ta adjacent to the selected oxygen atoms. Reprinted with permission from S. Kim, S.H. Choi, J. Lee and W. D. Lu// *ACS Nano* 8 (2014) 10262. (C) 2014 American Chemical Society).

ure 8. These defects facilitate the migration of oxygen vacancies by substitution across the region where oxygen atoms are gathered and interstitially in the region where defects are abundant [68]. Choi *et al.* reported ultrafast switching in Pt/SiO₂: Pt/Ta memristor by dispersion of Pt into SiO₂ forming a composite structure behaves as an ionic conductor which presented an extremely high endurance of 10^7 cycles and switching time lower than 100ps [69, 70]. Though a single layer exhibits resistive switching behavior, in order to enhance the speed of Write/Read access multilayer oxide are placed which acts as reservoir of oxygen vacancies. However, complexity linked with process of fabrication increases as the number of oxide layer increases [71–74]. Xu *et al.* observed uniform bipolar resistive switching in $Pt/Zn_{1-x}Cr_xO/Pt$ ReRAM structure. The effect of Cr doping exhibited an increased resistance ratio between HRS and LRS from 17 to 10^3 . Beside it eliminates the need of compliance current and initial electroforming process. Further to explain bipolar resistive switching behavior C-AFM technology is employed, where a conductive region is observed at high bias voltage while it disappeared upon reversal of polarity of the bias voltage clearly illustrating the LRS and HRS respec-

tively [75]. Xu *et al.* observed an improved switching performance in Pt/Co: ZnO/Pt ReRAM structure. This enhanced the stability in the process of switching and lowered the overall power consumption [76]. Zhang *et al.* studied the resistive switching in Ag/ZnS-Ag/CuAlO₂/Pt ReRAM. This device exhibited bipolar switching characteristics for lower compliance current (1-10mA) and unipolar switching for higher values of compliance current. The unipolar switching is due to formation and rupture of Cu-vacancies conducting filaments within the CuAlO₂ film [77], while bipolar is due to the formation and annihilation of Ag conducting filaments. Interestingly for the first time in the same device Cu and Ag ions are responsible for the process of resistive switching depending upon the value of compliance current [77]. Further Kuo *et al.* performed a comparison study of resistive switching involved in Au₇₀Ag₃₀/SiO₂/TiN, Au₃₀Ag₇₀/SiO₂/TiN and Ag/SiO₂/TiN ReRAM structures by doping the top active electrode. An improvement in switching time and lowering in SET voltage is observed when Au-Ag electrode is used as top electrode [78].

5 Electrochemical Impedance Spectroscopy in ReRAM

The properties of grain and grain boundaries play a pivotal role in determining the ionic conductivity of polycrystalline materials. Grain boundary is the region in a polycrystalline material isolating identical phase crystals. This region is abundant of defects, consequently facilitates ionic conduction. AC impedance spectroscopy is widely used in order to study the electrical property of polycrystalline material at its bulk and grain boundaries [79]. EIS can be used to study the intrinsic switching mechanism of memristor and to calculate ionic conductivity. When a pristine device is stimulated with an AC signal of magnitude 10mV scan rate varying from 1mHz to 1MHz, effects the existing ionic state and initiates the motion of oxygen vacancies. This makes the device capable to exhibit reproducible switching characteristics by causing a permanent nano morphological change from where it cannot recover. Alternatively, EIS can be used for electroforming the virgin device, in addition to that EIS can be used determine various resistance states of device like LRS, HRS, and the intrinsic switching mechanism can be studied by observing the variation of grain boundary resistance and bulk resistance with varying external electric field. To begin with Lee *et al.* for the first time studied EIS on Pt/TiO₂/Pt Memristor and studied the electrical conduction at HRS [80].

Qingjiang *et al.* performed EIS to explain the filamentary conduction in Pt/TiO_{2+x}/TiO₂/Pt ReRAM structure by perturbing the device with an AC signal of magnitude 10mV, scan rate varying from 10KHz to 10 MHz, at DC biasing point of 0 V. Impedance spectrum active cell is taken at HRS and LRS. During the process of toggling between HRS and LRS a conducting filament is formed and broken as shown in Figure 9(a) [81]. Mehonic *et al.* performed EIS in silicon rich silica based memristor to find the nature of conducting paths. In OFF state a single arc is observed which, conveyed that HRS is mainly controlled by the bulk properties of SiO_x switching layer, while in On state two different arcs are observed corresponding to destruction and formation of conducting pathways respectively [82].

Koza *et al.* reported repeatable unipolar resistive switching in Au/Mn₃O₄/AuPd based ReRAM and explained the SET and RESET operation with aid of electrochemical impedance spectroscopy [83]. The equivalent circuit used to define LRS contains an inductance (I_{wire} is the inductance due to connecting wire) in series with resistance ($R_{filament}$ corresponds to the resistance of filament joining top and bottom electrode) of 14.8 Ω . Upon transit of resistance state of the device from LRS to HRS a parallel combination of R and CPE (constant phase element usually used to model non perfect capacitances) and value R increased from 14.8 Ω to 30M Ω . The shape of the obtained impedance spectrum is identical to the impedance spectra of virgin device as shown in Figure 9(b). Greenlee *et al.* studied the analog resistive switching in LiNbO₂ based memristor and found that switching is due to the electric field induced migration and distribution of Li ions. Further they performed PDEIS in order to observe instances of meminductive and memcapacitance effect at certain frequency [84, 85].

6 Application of ReRAM in neuromorphic computing

6.1 Neuristor – An Electrical Equivalent of neuron

Neuromorphic engineering, also known as neuromorphic computing started as a concept developed by Carver Mead in the late 1980s, describing the use of very-large-scale integration (VLSI) systems containing electronic analogue circuits to mimic neurobiological architectures present in the nervous system especially the brain [86]. The mammalian brain is basically a neural network comprising of neurons and synapses which are considered as unit cell to

Figure 9: Impedance spectra of the Pt/TiO_{2+x}/TiO₂/Pt ReRAM structure (a) Device is in HRS as the conducting filament do not connect the top and bottom electrode. Impedance spectrum at (b) HRS (c) LRS. Impedance spectra of the Au/Mn₃O₄/AuPd ReRAM in (d) pristine state (black), high resistance state (HRS, blue), and (e) low resistance state (LRS, red). Points corresponds to experimental results and lines are fitted to generate the equivalent circuits, which are presented as insets. A constant phase element (CPE) is used to model the capacitor. (Reprinted with permission from J. A. Koza, I. P. Schroen, M. M. Willmering, and J. A. Switzer // *Chem. Mater.* **26** (2014) 4425 (C) 2014 American Chemical Society).

develop hardware based artificial neural networks (ANN) to emulate brain-like computing. The presence of complex neural networks in brain comprising of 10^{11} neurons communicating with 10^{15} synapses makes it capable of performing tasks like recognition of objects, abstract reasoning, and linguistic comprehension makes the human brain to outperform existing digital computers. The neuron models which are employed in ANNs are leaky integrate-and-fire (LIF) neuron, Hodgkin-Huxley neuron, and Izhikevich neuron models. There are reports on the hardware implementation of Hodgkin-Huxley neuron using memristor,

while leaky integrate-and-fire (LIF) neuron using memristor is successfully simulated [87–91].

The Hodgkin–Huxley proposed a model that defines how action potential is generated in biological axons, which is critical to analyze the computational ability of nervous system. Signal transduction in neurons is facilitated by sodium and potassium ion channels, which dynamically allow or obstruct the flow of polarizing currents, through which the cell membrane is charged or discharged. When the cell body is sufficiently polarized because of its dendritic inputs, a remarkable change in conductance of the system occurs with the application of voltage spike /ac-

Figure 10: Neuristor diagram and Mott memristor device characteristics. (a) Schematic of the lumped neuristor. The channels comprise of Mott memristors (M_1 and M_2) in parallel with capacitance (C_1 and C_2 , respectively) and are biased with opposite polarity d.c. voltage sources. (b) The bistable I-V curves of the Mott memristor obtained experimentally and Mott memristor model used for simulations, with the inset exhibiting the scanning electron micrograph Nb_2O_5 based Mott Memristor device included in (b). (Reprinted with permission from M-D Pickett, G. Medeiros-Ribeiro, R.S. Williams// *Nature Materials* 12 (2012)114 (C) 2012 Nature publishing group).

tion potential. The Neuristor which is an electronic equivalent of biological neuron proposed by Hewitt Crane in the year 1960, which generate a spike upon sufficient excitation [92]. The proposed prototype is equivalent to the size of shoe box as it is made up of large inductors. The original intent was to develop logic gates using it. Chua *et al.* proposed the revised memristive Hodgkin – Huxley model by modeling the sodium and potassium ion channels using memristor [93]. In the year 2013 Pickett and Williams came out with the prototype using NbO_2 Mott memristor, shown in Figure 10 [18, 94].

For proper understanding of working of neuristor an analogy between neuristor and biological neuron is discussed. Neurons are the basic building block of the central

Figure 11: A typical biological Neuron.

nervous system (CNS) that process information in the form of electrical signals (action potential) which are responsible for inter neuron communication. A typical biological neuron is shown in Figure 11.

It consists of two regions namely extracellular and intracellular, demarcated by lipid membrane. The cell body causes discrete distribution of Na^+ , K^+ , Cl^- and Ca^{2+} ions in the extracellular and intracellular region. The extracellular region comprises of Na^+ and Cl^- ions while intracellular region predominantly contains Ca^{2+} and K^+ ions [95, 96]. This uneven distribution is established by Na^+ - K^+ AT-Pase. The uneven distribution of ions results an electromotive force that is defined as Nernst potential across the membrane or concentration gradient. When the cell is at rest (in the absence of external bias) the membrane potential is around -70mV (close to equilibrium potential of K^+ ions) and this is commonly defined as Resting Membrane potential [95–97]. For the existence of potential difference across a lipid membrane, two conditions must be met (i) unequal distribution of ions across the lipid membrane. (ii) Presence of ion channels which is permeable to above mentioned ionic species.

At rest as more number of K^+ channels are open than Na^+ channels, therefore membrane permeability to K^+ ions is high. Hence, resting membrane potential is nearly equal to the equilibrium potential of K^+ . Pickett Neuristor comprises of two Mott memristor (M_1, M_2), three capacitors (C_1, C_2, C_{out}) and three resistors. Each memristor is fed with an external positive/Negative DC bias and in combination with shunt capacitor, acts as switchable dynamic conduction channel which can provide power to the core from the power lines [18]. This setup is identical to the potassium and sodium ions channel of Hodgkin–Huxley model and R_{L2} is the common load resistance which helps in stabilizing the circuit when it is inactive. It consists of an input resistance (R_{L1}) and while output consists of parallel RC

Figure 12: All-or-nothing response and state variable dynamics of the neuristor. (a), (b), Simulated super-threshold 0.3 V input pulse (a) and its corresponding spike output (b). The magnified spiking region (b, inset) highlights the time sequence of events for channels one and two. (c), (d), A sub-threshold 0.2 V input (c) to the same device yields an attenuated output (d). (e), (f), Phase portraits of the characteristic state variables u and q for channel 1 (e) and channel 2 (f) illustrate a stable trajectory for both channels during the spike activation period of (b). Points labelled α to ϵ on the phase portraits indicate the special points associated with switching events in each channel. (g), Trajectories around the quasi-static current–voltage curve illustrate the conductive state of the respective Mott memristor for each channel at each point of interest. (Reprinted with permission from M-D Pickett, G. Medeiros-Ribeiro, R.S. Williams// *Nature Materials* **12** (2012)114 (C) 2012 Nature publishing group).

stage which is mainly responsible for coupling signal between Neuristors. The nerve cell membrane comprises of ion channels namely ligand and voltage gated and mostly Na^+ and K^+ channels are liable for the process of generation of axon potential.

Under the effect of a depolarizing stimulus, voltage gated Na^+ channel opens and the membrane potential during this phase shoots up to the equilibrium potential of Na^+ (60mV) but does not reach as rise in conductance due Na^+ ions is transient *i.e.* Na^+ ions are fast to open and fast to close. This process is known as depolarization. In the absence of bias voltage the input and output node are fixed at $\pm V_{dc}$. Upon excitation at the input, capacitor (C_1) charges further and if the excitation is above a sharp threshold voltage memristor turns ON, resulting in transferring the device from HRS to LRS. This phenomenon relates to the process of opening of Hodgkin–Huxley ion channel. The coupling resistance R_{L2} must be chosen in such way that the depolarization caused by the capacitor (C_1) is sufficient enough to charge capacitor (C_2). During the process of charging of capacitor (C_2), the memristor (M_1) correlating to the closing of sodium ion channel. Upon completion next, the process of repolarization is initiated by opening

of voltage-gated K^+ channels, which are slow to open and close in comparison with Na^+ channels. This causes net movement of positive charge out of the cell due to K^+ efflux at this time helps complete the process of repolarization. As these channels are slow to close, further there will out-flow of K^+ ions resulting in decrease of cell membrane potential and this phenomenon is known as hyperpolarization followed by a coming back to resting membrane potential. When capacitor (C_2) is fully charged this will transfer the resistance state of the memristor (M_2) from HRS to LRS correlating to the opening of K^+ ion channels, which hyperpolarizes the core towards $+V_{dc}$. Finally, spike is produced over the output stage. The biomimetic properties of the Neuristor such as all or nothing spiking, refractory period, threshold is verified by providing both sub-threshold (0.2 V 10 μs) and super threshold voltage (0.3 V 10 μs). The Figure 12 illustrates the biomimetic properties such as threshold and signal gain. The sub-threshold pulse is attenuated while a signal gain is observed in case of super-threshold pulse and is compatible with traditional CMOS technologies. The intrinsic switching mechanism involved in Mott Memristor is yet to be addressed. Although metal to insulator transition is reported previously, still a group of new

Figure 13: (a) Schematic presentation of the concept of employing memristors as synapses between neurons. The inset exhibits the layered stack structure of the memristor and schematics of the two-terminal memristor device. (b) Schematic representation of CMOS neurons and memristor synapses in a crossbar configuration. (c) Analogous between Biological and Artificial synapse. (d) Drop in the level of ionic conductivity (σ_i) related to forgetting rate, analogous to memory decay. (Reprinted with permission from H. J. Sung, T. Chang, I. E. Ebong, B. B. Bhadviya, et al. // *Nano Lett.* **10** (2010) 1297 (C) 2014 American Chemical Society).

materials need to be predicted where metal to insulator transfer occurs at temperature around $\sim 200^\circ\text{C}$. This recent utilization of memristor based neuristor paved the way for transistor-free logic in thin film circuits and as these are compatible with existing CMOS technology, hence neuristor can be integrated with CMOS circuits to develop hybrid silicon-nanodevice architectures [18].

Recently, Pickett *et al.* have designed logic circuits using neuristor by adapting Wilamowski's scheme for neuristor logic [98–100]. Since neuristors are dynamic threshold spiking devices, the logic design is based on the existence, interpreted as logical '1', or absence, logical '0', of a spike at the input of a gate within a specific time window [96]. The four important properties of neuristor like threshold, pulse shaping during transmission, constant velocity of pulse transmission make it ideal candidate for its application in transmission lines [18]. The above sur-

vey suggests that all the blocks of the neural system can be implemented utilizing all passive elements thus it paves a roadmap for world without power hungry CMOS transistors. It does not claim to completely replace the existing CMOS technology; rather it would complement the existing technology.

6.2 Artificial Synapse

Memristor have been widely used for data storage and logical applications. The intrinsic non-linear ionic switching in this class of device has prompted researchers around the globe to utilize memristor to emulate various synaptic learning functions by correlating synaptic weight to the conductivity of memristor as shown in Figure 13 [16, 101, 102]. The synaptic learning rule Spike timing dependent

plasticity (STDP) have been successfully validated using memristor. In biological synapse, synaptic plasticity is attained through non-overlapping spikes and controlled by the activity of synapse [103]. The synaptic weight is determined by receptor level which is modulated by post synaptic Ca^{2+} ion concentration that acts as secondary state variable beside spikes. The incessant variation in the level Ca^{2+} concentration offers an internal timing mechanism to encode the activity information on the spikes. As the value of the Ca^{2+} concentration throughout the spike is determined by the cumulative effect from the current spike and remainder value from the previous activity [103]. This model have been predominantly employed in order to illustrate synaptic plasticity properties viz. LTP (long – term plasticity), STDP (Spike timing dependent plasticity) [103]. The Synaptic weight can be modulated by continuous spiking from post, pre synaptic neuron and by utilizing the non-volatile nature the memory device, the synaptic weight can be stored for a longer duration of time. This feature aid memristor to emulate the memory and learning capability of biological synapse. In order to enable learning in synapse, it is stimulated with pre and post synaptic spikes by following a specific order known as temporal order. An increase in conductance of memristor is observed when it is stimulated by a pre synaptic spike followed by a post synaptic spike termed as long-term potentiation, while fall in conductance observed upon reversal of the temporal order called as long-term depression. Large change in conductivity of the device is seen when it is stimulated with input spikes frequently, thus change in synaptic weight. An efficient synaptic learning can be achieved maintaining proper pulse width or amplitude such that overlapping of the spikes leads to proper programming pulse to encode the information on relative timing of spikes from pre- and postsynaptic neurons and to attain desirable conductance change [104].

Kim *et al.* noticed that above synaptic structures could not emulate synapse in a bio-realistic manner [104]. They considered memristor as dynamic device controlled by internal processes rather than mere programmable memory devices. In second order memristor there are two state variables which would control the total conductance of the memristor. A typical memristor is modeled using one state variable ‘w’ (size of the switching layer) which directly modulated by the external stimuli (8)

$$\frac{dw}{dt} = f(w, v, t) \quad (8)$$

The second order memristor is comprised of an additional state variable ‘T’, where two variables (w, T) jointly regulate the total conductance of memristor. By adapting second order memristor it is feasible to implement complex

biorealistic dynamic effects. The second order memristor can be mathematically stated as (9)

$$\frac{dw}{dt} = f(w, T, v, t) \quad (9)$$

The role of Ca^{2+} like internal dynamics is believed to be played by the second order variable ‘T’ by providing an internal timing mechanism and assists in activity – dependent modulation of the conductance state variable ‘w’. As mentioned in the previous section, filamentary conduction is dominant in most of the metal oxide based memristor. The resistive switching in this class of memristor is presumed to be due to migration of oxygen vacancies under the effect of an external bias. A low resistive channels or conducting filament is formed in the region comprising of more number of oxygen vacancies. The memristor conductance is determined by size of the filament which corresponds to the first order state variable (w). The drift and diffusion of oxygen vacancies under the effect of an external field and local temperature of the device causes formation of conducting filament. Under the effect of an external bias local temperature (T) of the device increases because of joule heating which play a vital role in the process of formation and annihilation of conducting filaments. Temperature (T) rises when the device is stimulated with voltage spikes and falls impulsively on the abstraction of stimulation. If the voltage pulse is applied prior to the completion of activity of the previous pulses then state variable ‘w’ may be affected by ‘T’ as T has not reached to steady-state value for previous pulses. Hence, relative timing between stimuli plays a pivotal role in determining the extent to which input voltage will get affected. Thus, T is not weight state variable but it plays a significant role in regulating synaptic weight [104].

There are basically two kinds of plasticity namely short term and long term plasticity (STP, LTP) on the basis memory retention characteristics; which corresponds to short term and long term memory behavior described in psychology. STP causes temporary potentiation while LTP causes permanent potentiation of neuronal connections. Repeated rehearsals are essential for converting STP to LTP which results in causing a physical change in the structure of neuron. This phenomenon is achieved in InGaZnO memristor reported by Wang *et al.* [105]. Previously Chang *et al.* in Pd/ WO_x /W based memristor reported the process of transfer of memories of importance from short term to long term memory. The existence of few oxygen vacancies results in rupture of conductive channels which causes the device to transit from LRS to HRS. This process is considered as loss of retention for LRS, [105–107] which bears striking resemblance to the memory loss in

Figure 14: (a) Pictorial representation of the phenomenon of Long- term potentiation and depression on the basis of formation and rupture of filament. The increase in change in weight causes rise in the size of the filament causing long term potentiation while vice versa upon decrease in change in weight (b) Learning process is illustrated where repeated stimulation causes transit from Short- Term memory (STM) to Long-Term Memory (LTM) causing a gradual increment in the size of filament.

Figure 15: (a) Schematic of ENODE device. (b) Schematic explaining the decoupling of the read and write operations. Non-volatile redox cell ensures a very high eV_b barrier between the two oxidation states of PEDOT '1' and '2' (corresponding to two conductance states of the postsynaptic electrode) during an open read operation and a very low barrier during a closed write operation. The open circuit potential (OCP), depicted in dashed lines, is dependent on the oxidation state of PEDOT and can be overcome by the bias. (Reprinted with permission from Y. Van de Burgt, E. Lubberman, E.J. Fuller et al.// *Nat. Mater.* 16(2017) 414 (C) 2017 Nature publishing group).

biological synapse, where this effect can be modeled by a stretched exponential function which is also known as Kohlrausch law. Mathematically, this can be stated as (10)

$$\varphi(t) = I_0 \exp\left[-\left(\frac{t}{\tau}\right)^\beta\right] \quad (10)$$

Where, $\varphi(t)$ = relaxation function, τ = characteristic relaxation time which is used to compute the forgetting rate, I_0 is the prefactor, and β is the stretch index ranging between 0 and 1. When $t < \tau$ the rate of decay will be high while oth-

erwise slower rate of decay [106]. Further Wang *et al.* proposed a mathematical model in order to define the process of relaxation of STP stated as (11).

$$M(t) = M_e + (M_o - M_e) \exp\left(-\frac{t}{\tau}\right) \quad (11)$$

$M(t)$, M_o are the measure of memory level at time t and $t=0$, while M_e corresponds to memory level at steady state after long time. The above expression can be used to deduce forgetting rate. With increase in the number stimulations, the relaxation time (τ) increased from several seconds to

tens of seconds, thereby lowering the forgetting rate which is analogous to human memory tendency *i.e.* a fast initial decay followed by an extended, slow decay. This phenomenon closely correlates to the STM to LTM transition in biological synapse [105–107]. As described in previous section filamentary conduction is predominantly responsible for switching in ReRAM, STP corresponds to the state prior to the formation of complete filament connecting the top and bottom electrode. The decay in conductance corresponds to the deformation of incomplete conducting filament. LTP corresponds to the LRS when a complete conducting filament is formed and persists for a longer time period.

When memristor is stimulated with large number of spikes to perform STM to LTM transition, on removal of bias a fall in synaptic weight is observed but interestingly its original conductance is attained with fewer number of external spike stimulation. This closely correlates to the learning function of biological synapse. The above mentioned phenomenon is clearly observed in Memristor. The biological process like pulse-paired facilitation (PPF) and post-tetanic potentiation (PTP) are positively tested by stimulating a chain of pulses and it is observed that with an increased rate of stimulation of pulse, there is an enhancement in retention time of memristor.

7 Electrochemical nonvolatile memories

Recently Moradpour *et al.* observed spectacular bipolar resistive switching in $\text{Au}/\text{Li}_x\text{CoO}_2/(\text{p}^{++})\text{silicon (Si)}$ nanobattery [108]. When a negative bias voltage applied to bottom Si electrode, Li^+ ions migrates towards the (p^{++}) silicon electrode where they are reduced to form Li_xSi complex thus generating an electromotive force (EMF). The SiO_2 interface layer grown thermally prior to the deposition of Li_xCoO_2 solid electrolyte layer serves as a solid electrolyte, which facilitates Li^+ ion diffusion and prevents the possibility of electrical short circuits between the top and bottom electrode. With the decrease of x from 0.95 to 0.75 in Li_xCoO_2 layer, there is a transition from high resistance insulating phase to a low resistance metal conducting phase and vice versa upon the reversal of polarity of the applied bias. The bipolar switching behavior is definitely not due to local filamentary conduction as in ECM and VCM, while it involves a bulk “homogeneous” process as conductivity is widely studied as battery cathode material. Further Mai *et al.* successfully realized synaptic learning rule STDP in the Li_xCoO_2 based nanobattery structure making it a

promising candidate for the field of neuromorphic computing [109].

Borrowing the principle of working of battery van de Burgt *et al.* fabricated a three terminal organic switch on a flexible polyethylene terephthalate (PET) substrate [110, 111]. The proposed device is extremely power efficient and it can be employed as an artificial synapse in neuromorphic computing.

Three terminal organic device is named as electrochemical neuromorphic organic device (ENODE). The working of ENODE is similar to a concentration battery. The device is fabricated on the PET substrate by sandwiching a proton conducting nafion layer between poly(3,4-ethylenedioxythiophene):polystyrene sulfonate (PEDOT:PSS) and PEDOT:PSS film partially reduced with polyethylenimine (PEI) which serves as presynaptic and postsynaptic electrode respectively. When the presynaptic electrode is applied with an presynaptic potential (V_{pre}), cations to flow from the presynaptic electrode to the post synaptic electrode causing protonation of the PEI, while electrons flow through the external circuit. This results in removal of holes from the PEDOT backbone in the postsynaptic electrode, thereby lowering its electronic conductivity while maintaining electroneutrality in the electrode. A reverse reaction is observed upon reversal of polarity of V_{pre} . The neutral form of the PEDOT:PSS/PEI electrode is stabilized by PEI, confirming the oxidation state of the postsynaptic electrode is maintained. In order to monitor the conductance states of the postsynaptic electrode a postsynaptic potential V_{post} is applied. This conductance (PEDOT:PSS/PEI channel) signifies the synaptic weight of the connection among two neurons, which is the required characteristics of an artificial synapse. The charge in the electrode is manipulated while performing Write operation. While performing ‘read’ operation the cell is disconnected thereby not altering the electronic charge of the electrodes by virtue of an ion conducting/electron blocking electrolyte. This enhances the retention capability of ENODE devices as during read operation the charge associated with the electrodes is unaltered [110, 111]. As the open circuit potential between presynaptic and postsynaptic electrode is low it allows extremely lower switching voltage and moreover they are nonvolatile. More studies are required to be performed in order to fabricate high density crossbar memory array utilizing ENODE devices.

8 Summary and outlook

Memristive devices are fabricated by employing a wide variety of solid electrolytic (fast ion conductors) materials over a decade or so owing to the renewed efforts imposed by the researchers and engineers around the globe, which threw much light into the state-of-art of non-volatile memory technologies. Recently different switching mechanisms have been suggested by various research groups for the same memory stack fabricated with identical materials. The lack of understanding of underlying switching mechanism has impeded its commercialization. Therefore, it is imperative that conductance behavior of such materials must be well understood so as to correlate the underlying switching mechanism when fabricated as memristive device. To expedite the process of memory access and lowering the power consumption, new materials need to be identified in order to have switching at very low voltage. As far as the bio-computation is concerned, these memory devices are widely being adopted to mimic the characteristics of biological synapse to further develop into neuristor. Extremely low switching energy and long retention time demonstrated by electrochemical neuromorphic organic device thanks to its organic nature which helps consider a significant step towards developing brain-inspired computing hardware. Further research in integration of ENODE devices in the form of massive crossbar arrays need to be investigated and steps needed to be taken in order to enhance device scalability. Moreover, it is required that circuit designers must go hand in hand to developing accurate SPICE models and search for new applications employing this device.

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