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Introduction

Memory is one of the essential parts of a human or machine. It is impossible to process data without storing it, so memory technology is always a necessary part of a computing machine. Conventional memory technologies such as HDD, USB Flash drive, SSD etc., which are being used as data storage devices over the past few decades, are failed to store the huge amount of data generated by the explosion of digital information and internet of things(IoT) [Gao et al., 2019; Lv et al., 2020]. With the miniaturization of electronic devices, silicon-based memory technology suffers from various theoretical and physical limits of downscaling [Lin et al., 2014; Schulz, 1999; Wang et al., 2020a]. With the advent of new nanotechnology, emerging memory technologies such as FERAM, MRAM, PCM and RRAM have been introduced recently, fulfilling the need for massive data storage and leading the future memory technology industries.

1.1 Semiconductor Memory Devices

Semiconductor memory devices can be classified into mainly volatile memory and nonvolatile memory. Volatile memory can be further classified into SRAM and DRAM, where data will be lost after switching off the device. Nonvolatile memory can be classified into conventional flash memory and emerging memory such as FERAM, MRAM, PCM, and RRAM. The data can be safely stored in a nonvolatile memory even after switching off the device. The SRAM, DRAM, and flash memory are the current memory technology, while FERAM, MRAM, PCM, and RRAM are the emerging memory technology to be used in the future. The different type of memory devices has been illustrated in Figure 1.1.

1.1.1 Current Memory Technologies

Current memory technology includes DRAM, SRAM, and flash memory. DRAM has a very simple structure consisting of one transistor and one capacitor, as shown in Figure 1.2a. The storage in DRAM depends on the amount of charge stored in the capacitor. In DRAM, the charged state is known as bit 1, while the discharged state is known as bit 0. The main advantage of DRAM is its high on-cheap density and hence low manufacturing cost. As the capacitor discharges over time, it is mandatory to refresh the device at some regular interval of time. It consumes high power, which is one of the disadvantages of DRAM. As it is a volatile memory, it can't be used as storage, but it can be used as a main memory or RAM to perform a logical operation. The SRAM consists of a total of six transistors, out of which four transistors are cross-coupled to store the data, and another two transistors are used to access and control the memory cell during read and write operation. The basic structure of SRAM is shown in Figure 1.2b. The SRAM has a very fast operation speed and the access time for read/write operations is less than 1 ns. It is used as a cache memory owing to its very fast access speed. As there is no capacitor involved, it does not have any leakage problem and needs not to be refreshed like DRAM. The main disadvantage of this technology is very low on-chip density and, therefore, high manufacturing costs. As it is also a volatile memory, it can't be used as main storage.

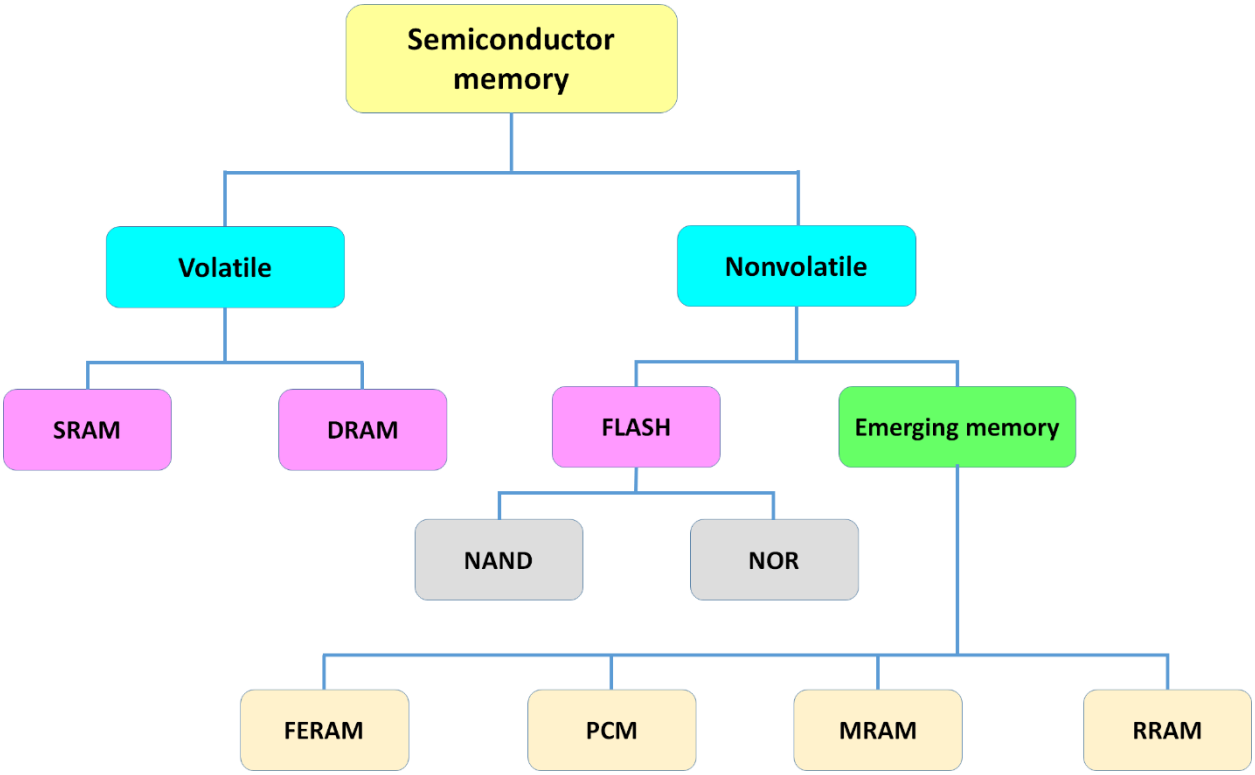


Figure 1.1: Classification of semiconductor memory technology

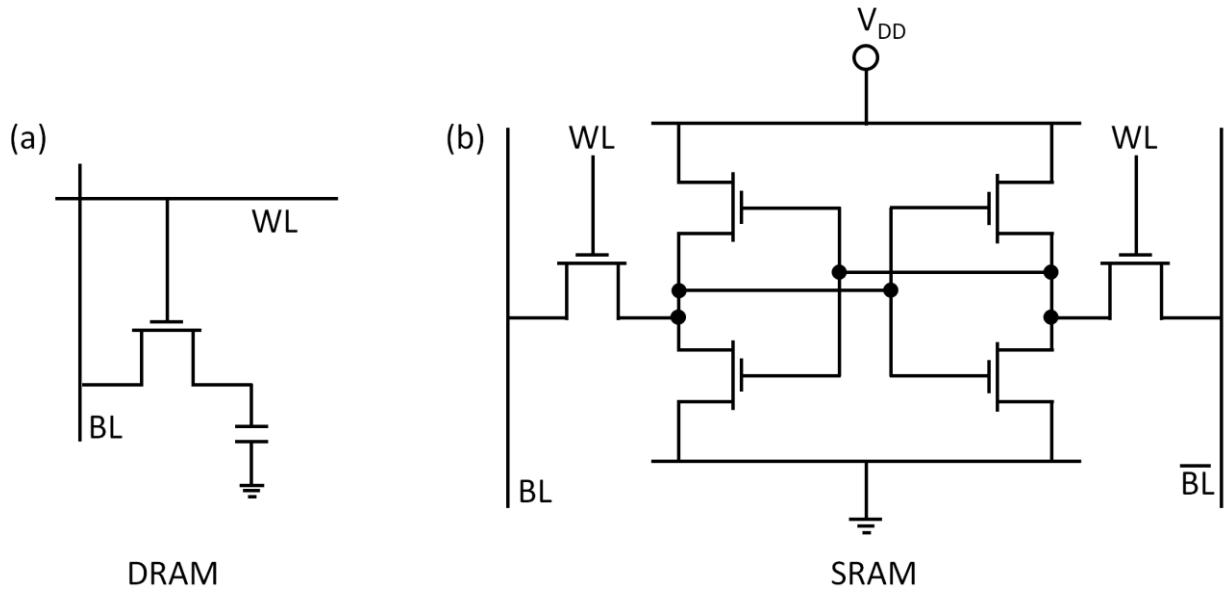


Figure 1.2: Basic structures of (a) DRAM and (b) SRAM

For the long-term and a large amount of data storage, nonvolatile memory is used because DRAM and SRAM can't retain the data when electrical power is off. The most commonly used NVM is flash memory. The flash memory has drawn much attention because of its high-density data storage and long retention time. The data is stored in flash memory by storing electrons in the control gate, which is separated from the conductive channel by a thin tunneling oxide layer. The basic structure of flash memory is shown in Figure 1.3a. When the top control gate is biased positively, the electrons from the channel tunnel through a thin tunneling oxide layer and are stored in the floating gate, as shown in Figure 1.3b. As floating gates are charged by electrons. The device is programmed and the corresponding bit value is considered bit 0. When the top control gate is grounded and the back gate is biased positively, the stored charges are released in

to the channel and the floating gate becomes empty or discharged, as shown in Figure 1.3c. The discharged state of the floating gate is erased state and the corresponding bit value is registered as bit 1. As the information is stored in terms of trapped electrons in the floating gate in flash memory, the data will not be lost even if power is switched off. This memory can be used as the main storage unit for big data storage. NAND-type flash memory is used in memory cards, USB flash drives and solid-state drives. The main disadvantage of flash memory is the leakage of electrons from the floating gate over time. Each programming or erasing operation slightly damages the thin tunneling oxide layer. As a result, charges start leaking out of the floating gate and the device can't be used after a few years. In flash memory, high voltage is required to erase, read and write operations; therefore, not suitable for low power consumption. The memory hierarchy of the current memory devices in terms of storage density, operational speed and cost per bit has been shown in Figure 1.4. As we go from SRAM to flash memory, the storage density increases but operation speed and manufacturing cost per bit decrease. That's why SRAM is used as cache memory and flash memory is used for long-term data storage.

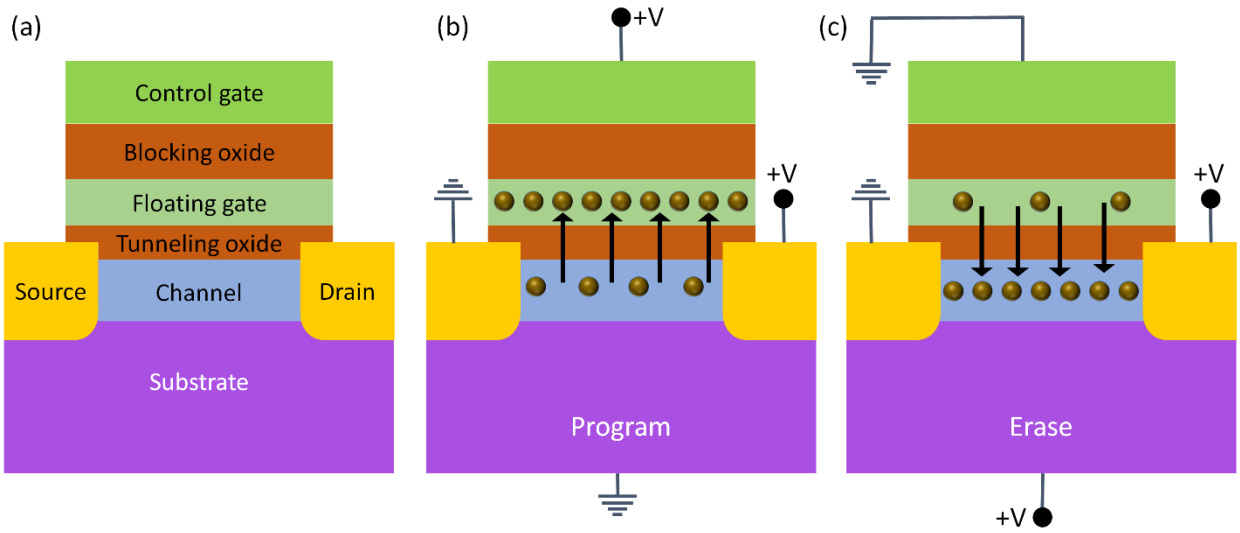


Figure 1.3: Basic structure and operation of a flash memory

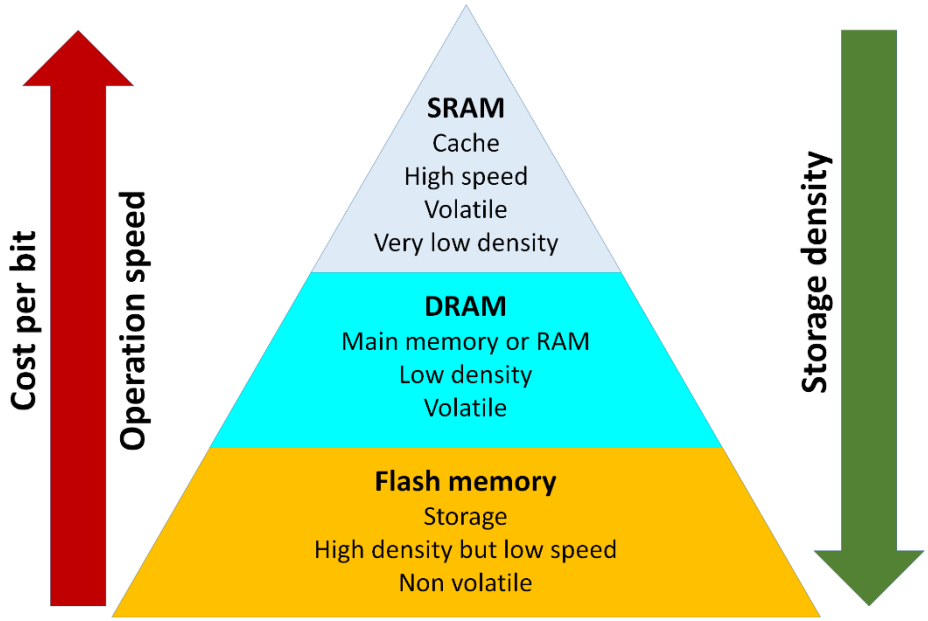


Figure 1.4: Current memory hierarchy in terms of storage density, operational speed and cost per bit

1.1.2 Emerging Memory Technologies

The current memory technologies suffer from several shortcomings, as discussed earlier. Though flash memory shows high retention, non-volatility, high on-chip density etc. but they are facing serious problems when downscaling to 45 nm computing node or beyond [Ielmini et al., 2005; Kim, 2005; Meena et al., 2014]. It is practically impossible to fabricate an oxide layer without any defect, and there will always be some defects. Because of these defects in the tunneling oxide layer, the stored electrons leak out of the floating gate by trap-assisted tunneling mechanism [Lu et al., 2009]. So there must be a minimum thickness of tunnel oxide to avoid leakage of stored charge. Therefore, there is a big question about the reliability of floating gate-based flash memory devices when scaled down to a 10 nm node or below [Ielmini et al., 2005; Meena et al., 2014]. There is an urgent need for alternate nonvolatile memory technologies with high on-chip density, long retention time, high endurance, low operating power, high operation speed and to be scaled below 10 nm node without losing data. Hence, lots of research works are going on emerging memory technologies capable of fulfilling the requirement of universal memory, such as low operating voltage below 1V, scalability below 10 nm, and long retention time greater than 10 years and high endurance greater than 10^{16} cycles. The emerging memory technologies include FERAM, PCM, MRAM and RRAM.

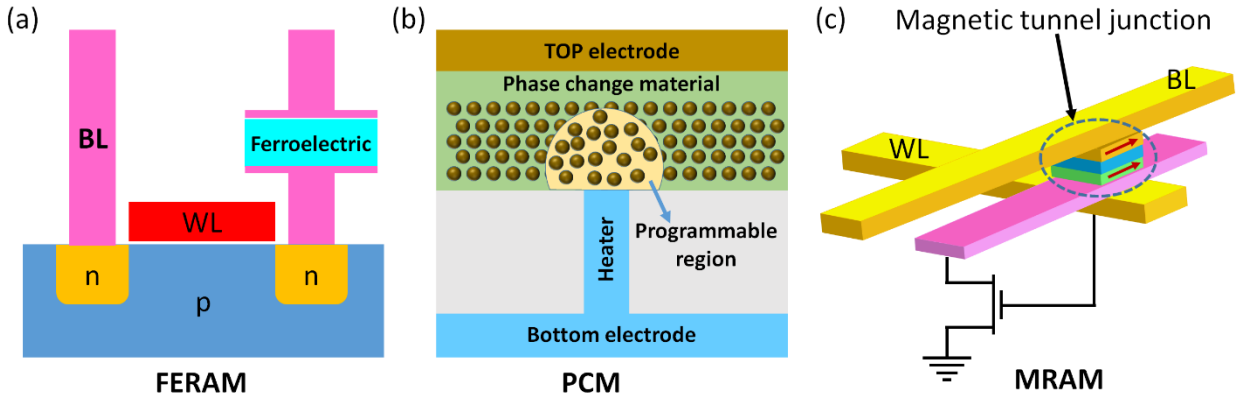


Figure 1.5: Basic structure of (a) FERAM, (b) PCM and (c) MRAM

The construction of FERAM is similar to DRAM, but a ferroelectric material such as $PbZrTiO_3$ is used instead of a dielectric layer in FERAM. The basic structure of FERAM is shown in Figure 1.5a. It is based on the polarization of ferroelectric materials. FERAM has a faster read access speed and lower power consumption than flash memory. Another emerging memory technology is PCM which is based on the toggle between the crystalline phase and amorphous phase of a phase change material by external voltage or heat as shown in Figure 1.5b. The amorphous phase is referred to bit 0, while crystalline phase is referred to bit 1 in PCM. With the application of a high voltage, the materials change from amorphous phase to crystalline phase and thus, write or SET operation is performed. In erase or RESET operation, the material is melted by heating and it turns into an amorphous phase again. Despite the high endurance cycle and long retention time, PCM's main disadvantage is the high operating voltage requirement. MRAM is another emerging memory which consists of magnetic tunnel junctions, as shown in Figure 1.5c. Depending upon the orientation of the magnetic moment, the information is stored in MRAM. If the magnetic moments are oriented in parallel direction, the information is considered as bit 0 and if the orientation is in the anti-parallel direction the information is considered as bit 1. Nonvolatile MRAM has high endurance cycles, long retention time, and high data operation speed, but the minimum cell size is greater than PCM and RRAM. RRAM is one of the most promising emerging memory technologies owing to its simple structure, excellent scalability below 10 nm, high operating speed, low power consumption and high endurance. The working principle of RRAM is based on modulating the resistance state of the device by an applied external voltage. It has a very simple structure of metal-insulator-metal (MIM), as shown in Figure 1.6a. The information is stored in terms of resistance, where the high resistance state (HRS) is 0 bit, and the low resistance state (LRS) is 1 bit. Because of its simple architecture and CMOS

compatibility, RRAM has a smaller minimum cell size as compared to MRAM, PCM and FERAM. RRAM can store the information as well as perform a logical operation; therefore, it can be used as a storage as well as main memory. The comparison of current memory technologies and emerging nonvolatile memory technologies in terms of minimum cell size, endurance cycle, retention time, and operating voltage has been listed in Table 1.1. It is seen that RRAM has the smallest cell size, highest operation speed, lowest operating voltage and high endurance. It can replace the von Neumann architecture where the computing units are physically separated from the storage unit, which means two separate devices are required to store data and perform a logical operation [Lv et al., 2020]. RRAM is capable of in-memory computing in which both storing data and logical operations can be performed in a single device. Also, recent studies revealed that RRAM could be used for neuromorphic computation where it can mimic the human brain operation. These excellent properties of RRAM make it the most promising candidate for universal memory to be used in future.

Table 1.1: Comparison of current memory and emerging memory technologies [Endoh et al., 2016; Wolf et al., 2010]

	Current memory			Emerging NVM			
	Volatile		NVM				
Type	DRAM	SRAM	Flash	FERAM	PCM	MRAM	RRAM
Minimum cell size	6 F^2	140 F^2	5 F^2	22 F^2	4 F^2	20 F^2	3 F^2
Write/erase time	10 ns / 10 ns	0.3 ns /0.3ns	1 ms /0.1ms	10 ns / 10 ns	10 ns / 50 ns	10 ns / 10 ns	5 ns / 5 ns
Endurance cycles	> 10^{16}	> 10^{16}	> 10^{14}	> 10^{14}	10^{18}	> 10^{16}	> 10^{12}
Retention time	NA	64 ms	10 years	10 years	10 years	10 years	10 years
Operating voltage	< 1.5V	< 1.5V	> 10V	< 1.5V	< 3V	< 1.5V	< 1V
Usage	Main memory	Cache	Storage	Storage	Storage	Storage and main memory	Storage and main memory

1.2 Resistive Random Access Memory (RRAM)

As discussed earlier, the problems faced by DRAM, SRAM and Flash memory can be overcome by RRAM. RRAM has several advantages such as simple device structure, excellent scalability below 10 nm, high stacking density, high operating speed, low power consumption, high endurance and capability of in-memory computing, which make RRAM one of the most promising future memory technologies. The basic structure of the RRAM device is a simple MIM structure. The active layer may be an insulator, semiconductor, or composite, is sandwiched between two metal electrodes. It can be in a vertical configuration (Figure 1.6a) or a lateral configuration (Figure 1.6b). RRAM works on the principle of change in electrical resistance with an applied external voltage. If the resistance is high, the state is called HRS or off state. If the

resistance is low, the state is called LRS or on state. When an external voltage is applied to the device, it switches from off to on state, which is called the SET or WRITE process of the device. If the device switches from on to off state, RESET or ERASE process occurs. The resistive switching (RS) can be categorized into two classes depending on the behavior of SET and RESET with the polarity of the external voltage. If both SET and RESET processes occur in the same polarity of the voltage, the resistive switching is called unipolar resistive switching (URS), as shown in Figure 1.7a. If the SET and RESET processes occur in opposite polarity of bias, it is called bipolar resistive switching (BRS), as shown in Figure 1.7b. Sometimes it is needed to apply a higher voltage than SET voltage initially to SET the device for the first time, which is called forming voltage and the process is known as electroforming. A compliance current is set to protect the device from permanent breakdown. There are some devices which may show only the SET process after crossing the threshold voltage and cannot be switched back to the off state. This type of resistive switching is known as write once-read many times memory (WORM).

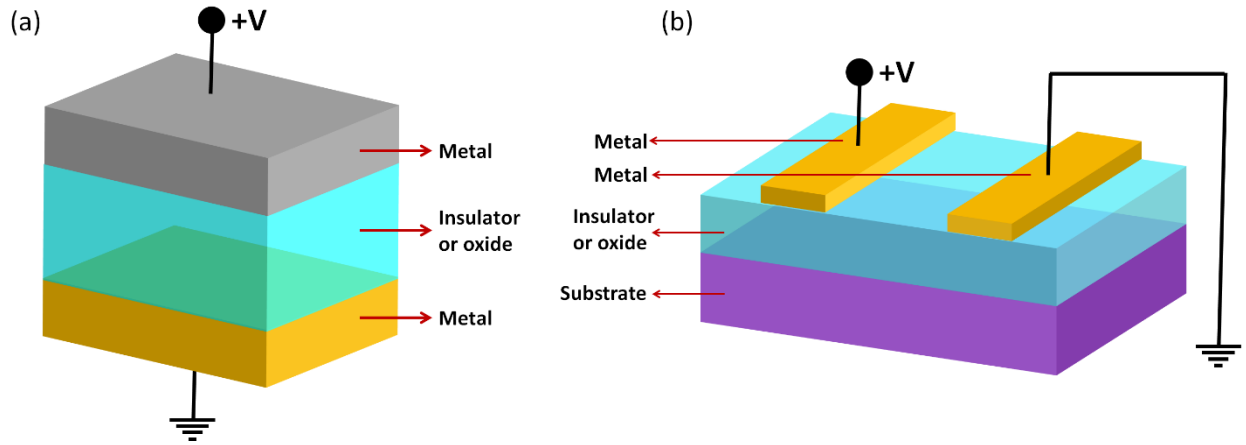


Figure 1.6: Structure of an RRAM device with (a) vertical configuration and (b) lateral configuration

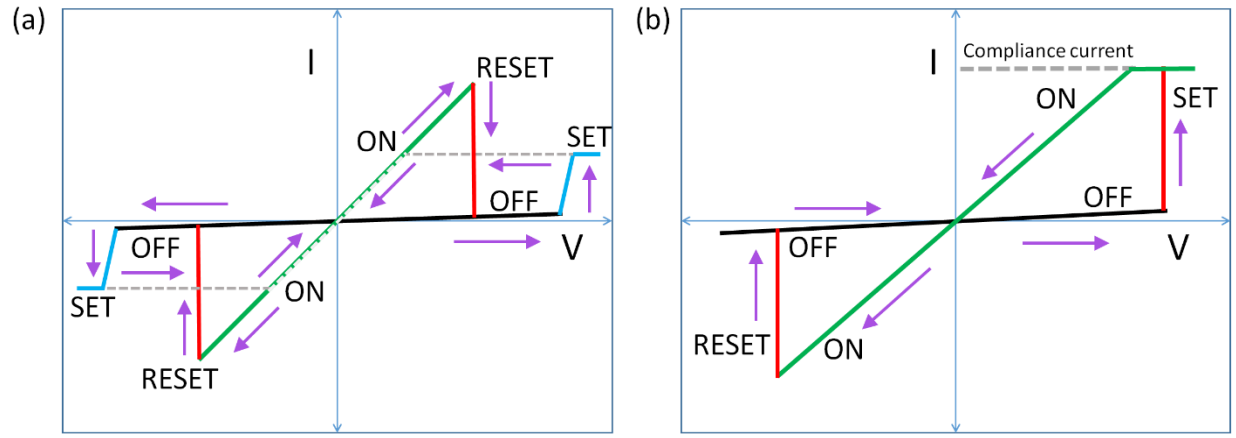


Figure 1.7: (a) Unipolar resistive switching and (b) bipolar resistive switching

1.2.1 Switching Mechanisms in RRAM

The RS mechanism can be classified into conductive filament (CF) formation and charge trapping. The conducting filament formation involves the formation and rupture of CF made by metal ions, oxygen or sulfur vacancies or defects. If one of the electrodes is chemically active metal (Ag, Cu etc.) and the other electrode is inert metal (Au, Pt etc.), the active metal ions can migrate through the active material. When an external positive voltage is applied to the active metal top electrode, the oxidation of chemically active metal occurs and metal cations are generated. These metal cations migrate towards the bottom inert electrode (cathode). These cations are reduced at the bottom electrodes and converted into metal atoms. As the voltage increases, more numbers of metal ions are reduced to metal atoms and make a conductive bridge of metal atoms, as shown

in Figures 1.8a and 1.8b. The device goes to the on state because of the formation of the CF by metal atoms. The application of a reverse bias rupture the CF and the device goes to the off state and the RESET process occurs, as shown in Figure 1.8c. If the active materials are made of oxides or sulfides, the oxygen/sulphur ions or vacancies take part in the filament formation. The oxygen/sulphur ions can migrate toward the anode and the oxygen/sulphur vacancies can migrate toward the cathode to form conductive filaments. Sometimes resistive switching occurs because of the formation and disruption of metal oxides between the interface of metal electrodes and oxides. When an external voltage is applied, the metal oxide forms because of the electrochemical reaction between the metal electrode and the active layer.

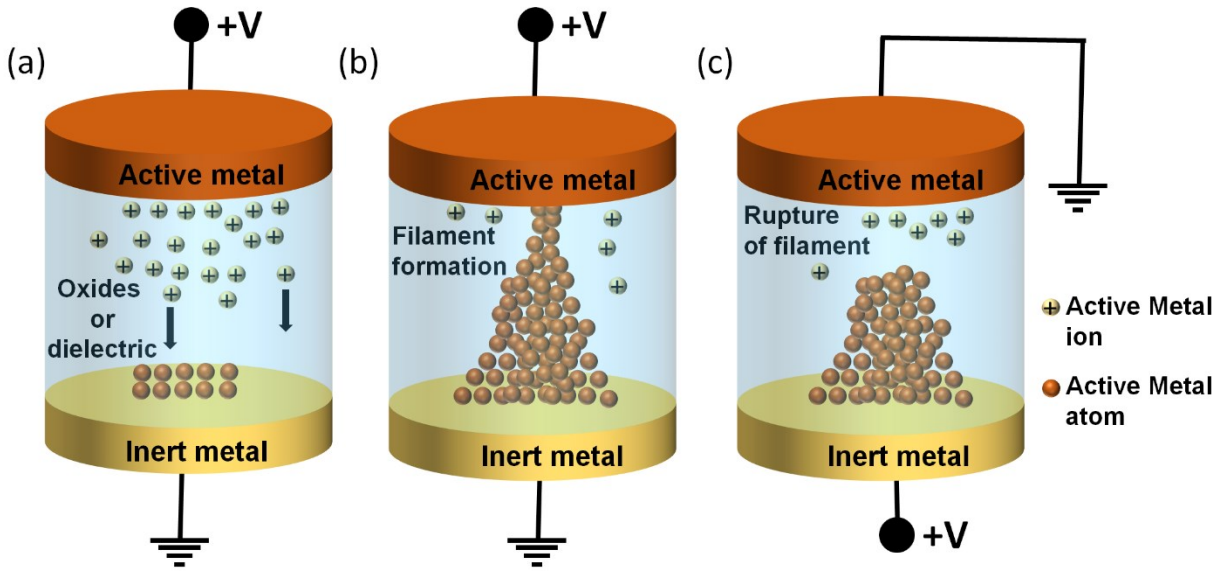


Figure 1.8: (a) Migration of active metal ions when the active metal electrode is positively biased. (b) Formation of the conductive filament by active metals when sufficient voltage to the active metal electrode is applied. This is the SET process where the current is high because of the formation of conductive filament. (c) Rupture of CF when a reverse bias is applied and RESET process occurs at this stage

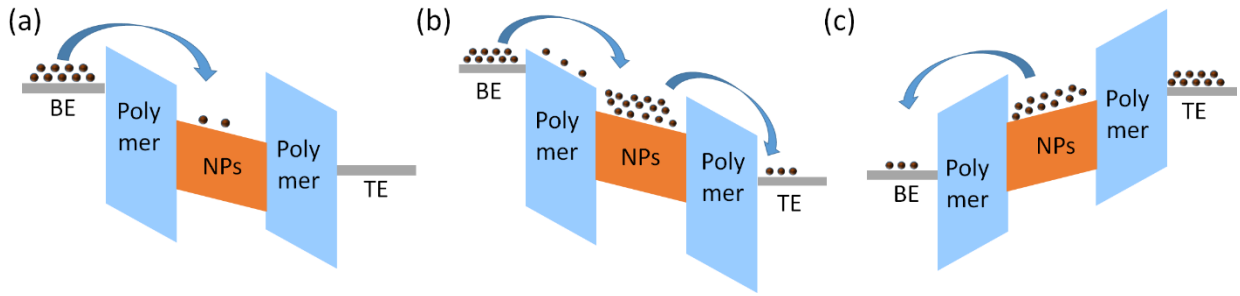


Figure 1.9: (a) Trapping of electrons in the active layer when the top electrode (TE) is positively biased. The active layer is a composite of nanoparticles and polymer. (b) When voltage is increased further, all the traps are almost occupied by the electrons and they can offer a conductive path across the active layer and the SET process occurs. (c) Application of an opposite polarity bias will extract the electrons from traps and the conductive path will be completely destroyed, which will give rise to the RESET process

The charge trapping in the active layer or in the interface of the active layer and electrode may give rise to RS. When the interface between the metal electrode and the active material is Schottky type, traps play an important role in RS. When an external voltage is applied to the device the injected hot electrons from metal electrodes are accumulated in the active layer or in the interface of the active layer and electrode, as shown in Figure 1.9a. With further increased voltage, traps are almost occupied by the electrons and they can generate a local internal field. The internal field is strong enough to make a conductive path across the film, which will switch the device to the on state as shown in Figure 1.9b. However, an opposite bias can extract the

electrons from the trapping center, as shown in Figure 1.9c and completely destroy the conductive path and thus, the device switches to the off state. The conduction mechanism can be analyzed by fitting the current-voltage data into different conduction models, as listed in Table 1.2.

Table 1.2: List of different conduction mechanism models where J is the current density, V is the applied voltage, $\hbar$ is the reduced Planck's constant, K_B is the Boltzmann constant, ε is the dielectric constant, $\emptyset$ is the barrier height, d is the barrier width, m^* is the effective mass of the carrier and q is the elementary charge

Conduction mechanism model	Characteristic equation	Current-voltage relation
Thermionic emission	$J \sim T^2 \exp\left(-\frac{\emptyset - q\sqrt{\frac{qV}{4\pi\varepsilon d}}}{K_B T}\right)$	$\ln(J) \sim V^{1/2}$
Space charge limited current (SCLC)	$J \sim \frac{V^2}{d^3}$	$J \sim V^2$
Poole–Frenkel emission	$J \sim \frac{V}{d} exp\left[-\frac{q\left(\emptyset - \sqrt{\frac{qV}{\pi\varepsilon d}}\right)}{K_B T}\right]$	$\ln\left(\frac{J}{V}\right) \sim V^{1/2}$
Fowler–Nordheim tunneling	$J \sim V^2 exp\left(-\frac{4d\emptyset^{3/2}\sqrt{2m^*}}{3q\hbar V}\right)$	$\ln\left(\frac{J}{V^2}\right) \sim \frac{1}{V}$
Direct tunneling	$J \sim V exp\left(-\frac{2d}{\hbar}\sqrt{2m^*\emptyset}\right)$	$J \sim V$
Hopping conduction	$J \sim V exp\left(-\frac{\emptyset}{K_B T}\right)$	$J \sim V$

1.2.2 Metal Oxides Based RRAM

Metal oxides have been widely used as active materials for RRAM devices for the last few decades. Transition metal oxides (TMO) such as ZrO_2, TaO_x, HfO_2 and TiO_2 have shown great potential in RRAM technology. HfO_2-based RRAM device with a thin Ti layer exhibited excellent memory behavior with a high value of I_{ON}/I_{OFF} (> 10^3), fast operation speed (~ 5 ns), high endurance cycle (~10^6) and long retention time (> 10^4 s) [Lee et al., 2008a]. ZrO_2-based RRAM device shows RS behavior with high I_{ON}/I_{OFF} (> 10^4), fast operation speed (~ 10 ns), high endurance cycle (~10^3) and long retention time (> 10^7 s) [Liu et al., 2009; Wang et al., 2010]. Also, TiO_2-based memory device shows high I_{ON}/I_{OFF} (> 10^2), high endurance cycle (> 10^6) and long retention time (> 10^6) [Park et al., 2011]. Besides, TMO other oxides such as $BiFeO_3$, ZnO, NiO, $SrTiO_3$ etc., exhibit resistive switching. Recent studies reveal that the oxides-based resistive switching device can be used in neuromorphic computing [Kim et al., 2016; Li et al., 2010b; Russo et al., 2009; Simanjuntak et al., 2016]. The oxides layer is generally deposited by solution process, atomic layer deposition (ALD) and sputtering techniques. The ALD and sputtering give a more uniform deposition as compared to the solution process and hence a high-performance RRAM device. The switching mechanisms in oxide-based RRAM devices are mainly based on the redox process, which includes metal atoms filament formation and filament formation due to the oxygen vacancies. The migration of oxygen vacancies can play an important role in the oxide-based RS device. The main problem in filamentary type mechanisms is a requirement of high voltage, which is not favorable for low-power RRAM [Jo et al., 2009]. Often a high voltage is

needed for the first time to initiate the filament formation in oxides which is called the electroforming process. Electroforming is one of the disadvantages of oxides-based RS devices. Furthermore, repeated formation and rupture of conducting filament induce Joule heating which reduces the storage capacity and degrades the performance of the RRAM device. Various efforts have been tried to form free resistive switching [Ku et al., 2018; Liu et al., 2009]. Though oxide-based RRAM show excellent memory behavior but the poor control over filament formation and external voltage have set the limitation. Also, the oxide thin film fabrication process using ALD is very costly, which increase the fabrication cost.

1.2.3 Organic Molecules and Polymers Based RRAM

Other promising active materials for resistive memory device are organic molecules which consist of organic compounds. In comparison to metal oxides, organic molecules have several advantages. The electronic properties of organic materials can be tuned by molecular design and changing the synthesis process. The fabrication of organic thin film can be processed by solution process hence can be favorable for low cost, flexible and lightweight electronics. The active layer of an organic memory device may be organic small molecules, organic polymers, graphene oxide and metal-organic frameworks. Organic small molecules have been widely used in organic RRAM devices in the past two decades. Most commonly used structure was metal/small molecules/metal-nanocluster/small molecules/metal. Commercially available organic materials such as AIDCN, Alq_3, NPB, pentacene etc., are well known for active layer [Bozano et al., 2005; Ma et al., 2003, 2002; Nau et al., 2015; Park et al., 2009; Tondelier et al., 2004]. In this type of device, the current remains low at low voltage because of the large barrier for injected electrons from metal electrodes to organic small molecules. When sufficient voltage is applied, the metal-nanoclusters become polarized and opposite charges are stored in the interface of the metal-nanocluster and organic small molecules. These stored charges can reduce the interfacial resistance and the device switches to the on state. Application of a reverse bias can restore the device to the initial off state. These organic small molecules-based RRAM devices can exhibit excellent resistive switching with high I_{ON}/I_{OFF} ($> 10^4$), fast operation speed (~10 ns), high endurance ($> 10^6$), and long retention time ($> 10^5$ s) and multilevel data storage. However, the deposition of metal-nanocluster in between small molecules is not an easy process and hence increases the complicacy of the device fabrication process. It is also noted that the RS behavior is insensitive to the type of metal-nanocluster in these types of devices, which limits the tenability of the resistive behavior. Those organic small molecules which have donor-acceptor groups are favorable for showing intrinsic resistive switching behavior. Donor groups such as triphenylamine (TPA), diethylamino, thiophene etc. are capable of donating electrons, whereas acceptor groups such as BIP, oxadiazole (OXD), sulfone, nitro group etc. have electron deficiency; hence capable of accepting electrons [Gu et al., 2015; Wang et al., 2014, 2015a, 2015b; Zhang et al., 2016c]. When an external electric voltage is applied, the transfer of electrons from the donor group to the acceptor group occurs, which results in the formation of a conductive channel in the small molecule's thin film. Thus, the device switches from the off to on state. Under the application of a reverse bias, the conductive channel may be permanent, giving rise to WORM behavior, or it may be destroyed, giving rise to reversible RS. The switching behavior is sensitive to the number of incorporated donor and acceptor groups in the small molecule. Although several organic small molecules have been designed for RS it is worth mentioning that most of the molecules exhibit intrinsic WORM-type switching behavior. In spite of showing multilevel switching, the scope of organic small molecules is limited because they are non-rewritable. Therefore, much attention is needed to design small molecules with intrinsic rewritable switching.

Polymers are more attractive in resistive switching devices as compared to small molecules because of their excellent intrinsic flexibility and easy solution processability. Polymers can be deposited by low-cost solution processes on flexible substrates. Various types of conjugated and non-conjugated polymers with the donor-acceptor group have been found to show RS behavior. By arranging the donor and acceptor groups in the polymer chain, their resistive behavior nature may be manipulated. Conjugated polymer Polyazomethine (PAM)

incorporated with TPA as donor and OXD as acceptor exhibits rewritable type resistive nonvolatile switching behavior [Pan et al., 2013]. The same polymer PAM incorporated with OXD as donor and 3,3′-dinitro-diphenylsulfone (NPS) as acceptor exhibits WORM-type switching behavior [Pan et al., 2013]. Designing a hyperbranched PAM incorporated with TPA group stable bipolar resistive switching was observed [Zhang et al., 2014]. Another type of approach to obtain resistive switching in the polymer is the formation of conducting filament by active metal ions such as Cu, Ag etc., penetrating through the small pinholes [Cho et al., 2011b; Gao et al., 2012, 2013; Krishnan et al., 2016]. Also, filaments can be formed by local thermal degradation of the polymer film [Lee et al., 2015; Pender et al., 1975; Segui et al., 1976]. Direct observation of CF formation under TEM has been observed in Cu/ pEGDMA/ITO/PET resistive switching devices [Lee et al., 2015]. Besides single metal ion filament, Al ions and oxygen vacancies based dual-channel filament can grow through the carbazole groups in Al/PVK/ITO RS device [Ling et al., 2017]. Polymers blending with small molecules can also exhibit RS behavior. Polymer-small molecule composites may give rise to better solution processability and mechanical flexibility with rewritable resistive switching properties. Most commonly polymers for blending with small molecules are PEDOT:PSS, poly(4-vinylpyridine), poly(4-vinylphenol), Polyvinylpyrrolidone, polymethyl methacrylate (PMMA) etc. Small molecule, DDQ blended with poly(4-vinylphenol) polymer exhibits excellent RS with high I_{ON}/I_{OFF} ratio when sandwiched between Al and ITO electrodes [Vyas et al., 2016]. The RS behavior is due to the filament formation by the metal ions through the pinholes on the surface as well as due to the conformational change of the organic small molecule DDQ upon the applied voltage. Semiconducting organic molecules such as organic dyes, polycyclic aromatic compounds, oxadiazole derivatives etc. can be blended with polymer to be used in resistive switching devices where donor-acceptor charge transfer plays an important role in RS [Bandyopadhyay et al., 2003; Liu et al., 2013; Sun et al., 2015; Yu et al., 2013]. Polymer blended with redox active molecules exhibit good RS behavior owing to the oxidation and reduction process in the molecules upon applied voltage [Kim et al., 2019; NS et al., 2020]. PMMA blended with P3BT showed excellent resistive switching with flexibility and reproducibility which indicates that polymer-polymer composites also can be used as an active material in RRAM device [Lai et al., 2013]. Though organic resistive memory devices are cost effective, easy to fabricate on any type of flexible substrate, but the organic molecules based device are less stable when exposed to ambient and various environment factors such as air, moisture etc. can degrade the device performance.

1.2.4 Quantum Dots and Nanoparticles Based RRAM

Quantum dots (QDs) or nanoparticles (NPs) embedded in the polymer matrix are one of the promising active materials in the RS device. QDs are semiconducting nanoparticles with a size less than Bohr excitonic radius. The size of the QDs is generally ranging from 2 to 10 nm. Because of the size in nm scale, they exhibit a quantum confinement effect and the energy levels are discrete in QDs, whereas energy levels are continuous in bulk. Therefore, the band gap of the QDs can be easily tuned by varying the size of the particles. As the size of the QDs increases, the band gap decreases and vice versa. The surface of the QDs is generally capped with capping ligands to protect the QDs from degradation in the ambient. For the fabrication of a resistive switching device, QDs or NPs are blended with polymer to prepare a matrix solution which is used as an active layer of the device. The QDs or NPs embedded in the polymer matrix act as charge trapping layers, whereas the polymers act as the charge blocking layer. This concept was initiated in 2004 by Ouyang et al. by mixing DDT capped Au NPs and 8HQ with polystyrene as an insulating polymer matrix [Ouyang et al., 2004]. The Au NPs and 8HQ in polystyrene matrix were used as an active layer sandwiched between two Al electrodes and the fabricated device exhibited good bipolar restive switching behavior with set and reset voltages of 2.8 V and -1.8 V, respectively and high I_{ON}/I_{OFF} of $> 10^3$. Inspired by this work, a lot of experiments using nanocomposites of QDs and NPs in the polymer matrix as active materials in resistive switching devices have been carried out. A variety of metal and semiconducting NPs and QDs as charge trapping centers, including Ag NPs [Kim et al., 2010; Onlaor et al., 2018], Cu_2O NPs [Jung et al., 2006], ZnO NPs [Onlaor et al., 2014; Son et al., 2009; Sun et al., 2018], TiO_2 NPs [Cho et al., 2009],

CdS QDs [Das et al., 2008], CdSe QDs [Kouklin et al., 2000] have been explored. Most commonly used polymers for matrix are PEDOT:PSS, poly(4-vinylpyridine), poly(4-vinylphenol), Polyvinylpyrrolidone, polymethyl methacrylate (PMMA), polystyrene, poly(vinyl alcohol) etc. When these QDs or NPs embedded in a polymer matrix are sandwiched between two electrodes, the injected charges with applied voltage are trapped in the QDs or NPs layers which act as trapping centers for electrons. As voltage increases, the trapping centers are almost filled by the electrons and the electrons may generate a local internal field. This internal field will induce a conducting path across the active layer and the device will switch to the on state. However, the application of a sufficient opposite bias will extract the electron from the trapping centers and destroy the conductive path which leads to RESET of the device. The switching mechanism of NPs-polymer nanocomposites based resistive device is shown in Figure 1.8. Using Ag NPs as trapping centers and PMMA as a polymer matrix bipolar restive switching with $I_{ON}/I_{OFF} > 10^3$ and endurance $> 10^4$ cycles was observed in Al/Ag NPs-PMMA/ITO device [Kim et al., 2010]. Several studies revealed that QDs such as Co_9Se_8 QDs [Zhang et al., 2016b], CdSe-ZnS Qds [Li et al., 2007; Ma et al., 2016; Son et al., 2008; Yagati et al., 2017], InP-ZnSe-ZnS QDs [Kim et al., 2018], $CuInS_2$-ZnS QDs [Wan Han et al., 2011], MoS_2 QDs [Wang et al., 2017], WS_2 QDs [An et al., 2020], black phosphorus QDs [Han et al., 2017], carbon QDs [Mihalache et al., 2014] and graphene QDs [Cosmin Obreja et al., 2014; Lin et al., 2015b] exhibited resistive switching when they were blended with polymers. The resistive switching in these QDs-polymer nanocomposites is ascribed to the charge trapping and detrapping in the QDs where polymers act as the charge blocking layer. Recently popular halide perovskite QDs also exhibit RS. The RS behavior in popular halide perovskite QDs such as $CsPbBr_3$ QDs can be ascribed to the formation and rupture of CF formed by electrochemical metallization of metal atoms with a combination of Br vacancies [Chen et al., 2019a; Wang et al., 2018]. In most of the QDs based RRAM devices, QDs are incorporated in the polymer matrix and the advanced resistive memory behavior of individual QDs without using any matrix is still under investigation.

1.3 Literature Review and Motivation of the Work

The studies on resistive switching based memory were initiated using various oxide materials in early 1960 [Hickmott, 1962][Gibbons et al., 1964][Nielsen et al., 1964][Hiatt et al., 1965]. In 1971, Leon Chua introduced resistive switching memory as a memristor which is a resistor capable of storing information [Chua, 1971]. With the conceptual similarity with resistors, inductors and capacitors, Leon Chua proposed the memristor as the fourth fundamental circuit component. The RS phenomenon was observed in several oxide materials such as hafnium oxide (HfO_x) [Chen et al., 2015; La Torre et al., 2016; Long et al., 2013; PhilipáWong, 2014; Su et al., 2018], titanium oxide (TiO_x) [Acharyya et al., 2014; Bousoulas et al., 2016; Huang et al., 2016a; Lu et al., 2016; Tsigkourakos et al., 2017; Yang et al., 2009a], tantalum oxide (TaO_x) [Chung et al., 2014; Maikap et al., 2014; Prakash et al., 2013, 2014, 2015], nickel oxide (NiO) [Lee et al., 2008b; Long et al., 2011; Ma et al., 2015; Nardi et al., 2010], zinc oxide (ZnO) [Chang et al., 2008; Han et al., 2011; Huang et al., 2016b; Simanjuntak et al., 2016], zinc titanate (Zn_2TiO_4) [Chen et al., 2018], manganese oxide (MnO_x) [Yang et al., 2009b; Zhang et al., 2009], magnesium oxide (MgO) [Chiu et al., 2012], aluminum oxide (Al_2O_x) [Banerjee et al., 2015; Lin et al., 2008; Wu et al., 2010], and zirconium dioxide (ZrO_2) [Li et al., 2010c; Lin et al., 2007; Sun et al., 2009; Wang et al., 2009; Wu et al., 2012]. The switching mechanism in oxides memristors is ascribed to the formation and rupture of CF by redox-based electrochemical metallization. Often a high voltage is needed for the first time to establish the conducting filament in oxides which is called the electroforming process. Electroforming is one of the disadvantages of oxides based RS devices. Furthermore, repeated formation and rupture of conducting filament induce Joule heating which reduces the storage capacity and degrades the performance of the RRAM device. Various effort have been tried for forming free resistive switching [Ku et al., 2018; Liu et al., 2009]. Though oxides based RRAM show excellent memory behavior but the poor control over filament formation and external voltage have set the limitation. Also, the oxides thin film fabrication process using ALD is very costly which increase the fabrication cost.

The organic small molecules and polymers are also being used for resistive switching materials because of their easy solution processibility, low fabrication cost, and compatibility in flexible and wearable electronics. Various organic small molecules such as AIDCN [Ma et al., 2003, 2002], Alq_3 [Bozano et al., 2005; Park et al., 2009], pentacene [Nau et al., 2015; Tondelier et al., 2004], DDQ [Vyas et al., 2016], 5-mercapto-1-methyl tetrazole (MMT) [Betal et al., 2022], metal Phthalocyanines [Das et al., 2021a; Koo et al., 2012] and polymers such as poly(ethylene glycol dimethacrylate) (pEGDMA) [Lee et al., 2015], PVK [Whitcher et al., 2016], PEDOT:PSS [van de Burgt et al., 2017], polyaniline (PANI) [Eskandari et al., 2020] etc. exhibited resistive switching phenomenon. In spite of the low cost and flexibility of the organic-based resistive memory device, their stability and operation are susceptible to various environmental factors such as air, light, moisture, and temperature. Also, organic materials often suffer from ageing which reduces the lifetime of organic memristors.

The QDs or NPs embedded in polymer matrices exhibit excellent RS. This concept was initiated by Ouyang et al. in 2004 using a mixture of DDT capped Au NPs and 8HQ with polystyrene as an insulating polymer matrix [Ouyang et al., 2004]. The Au NPs and 8HQ in polystyrene matrix were used to fabricate the Al\DDT-Au NPs-8HQ\Al device and the fabricated device exhibited good bipolar RS with set and reset voltages of 2.8 V and -1.8 V, respectively and high $I_{ON}/I_{OFF} > 10^3$. Inspired by this work, a lot of experiments using nanocomposites of QDs and NPs in the polymer matrix as active materials in resistive switching devices have been carried out. Using Ag NPs as trapping centers and PMMA as a polymer matrix, bipolar restive switching with $I_{ON}/I_{OFF} > 10^3$ and endurance > 10^4 cycles were observed in Al/Ag NPs-PMMA/ITO device [Kim et al., 2010]. Multilevel resistive switching was observed in Al/Ag NPs-PVK/ITO devices where Ag NPs were embedded in PVK matrix while no resistive switching was observed in pure PVK was used as an active material [Onlaor et al., 2018]. Au NPs incorporated with polyvinylpyrrolidone (PVPY) exhibited resistive switching and this device can be used as an artificial synapse for brain-inspired computing (Zhang et al., 2019). Self-assembled CdS QDs arrays by electrodeposition were designed by Kouklin et al. and the fabricated vertical and lateral devices both exhibited resistive switching [Kouklin et al., 2000]. Later, Mohanta et al. fabricated CdSe QDs based device where CdSe QDs were assembled using LBL technique [Mohanta et al., 2006; Sahu et al., 2007]. Different thicknesses of CdSe QDs layers were investigated and it was found that the device with higher layer thickness has higher I_{ON}/I_{OFF} though the I_{ON}/I_{OFF} was limited to 100. Also, QDs of different sizes were investigated and the resistive switching was ascribed to the quantum confinement effect which results in charge trapping in QDs [Das et al., 2007]. It is observed that the I_{ON}/I_{OFF} of pure QDs based device is low. Higher resistive switching performance can be achieved by using core-shell QD instead of using a single QD. To improve the electrical bistability and I_{ON}/I_{OFF} CdS-PbS core-shell QDs were used as an active layer in which charge confinement is controlled by energy levels of core and shell QDs [Ghosh et al., 2008]. A maximum I_{ON}/I_{OFF} of 10^5 was achieved in this CdS-PbS core-shell QDs based device in which PbS assists charge injection and CdS captured the injected charges because of the higher band gap of CdS. The same group demonstrated a CdS-Ag_2S core-shell QDs based device which exhibited an I_{ON}/I_{OFF} of 10^4 [Ghosh et al., 2008]. Other core-shell QDs such as CdSe/ZnS, and $CuInS_2$-ZnS QDs embedded in various polymer matrices exhibited resistive switching behavior [Li et al., 2007; Ma et al., 2016; Son et al., 2008; Wan Han et al., 2011; Yagati et al., 2017]. Further investigation revealed that embedding core-multishell QDs in the PMMA matrix can increase the I_{ON}/I_{OFF} of the resistive memory device [Kim et al., 2018]. In addition, CdSe-ZnS core-shell QDs were assembled on a virus mutant (CPMV-T184C) modified substrate to show resistive switching [Portney et al., 2008]. CPMV assist the QDs in being assembled on the substrate with better bioconjugation. The conduction mechanism in the off state is the injection of electrons from electrode to CPMV and Poole-Frenkel emission dominates in the on state in the CPMV-CdSe QDs based device. A PbSe QDs based lateral structured RRAM was reported by Yu et al., where the strong electron coupling between two adjacent QDs resulted in low resistance and the high resistance is ascribed to the Coulomb repulsion of the trapped charge [Otto et al., 2013]. Kannan et al. fabricated a memristive device with Al/CdSe QDs/Al/CdSe QDs/ITO

structure with a middle Al layer thickness of 10 nm and CdSe QDs with sizes 3 nm and 5 nm were used [Kannan et al., 2011c]. The fabricated device exhibited bipolar RS with I_{ON}/I_{OFF} of 10^4 and the bigger size QDs based device had larger I_{ON}/I_{OFF}. The device had a fast response time of 10 ns and 40 ns in the SET and RESET process, respectively. The thin middle Al layer was converted into Al_2O_3 under ambient, and the oxide introduced a barrier between QDs. This barrier acted as a charge blocking layer, and QDs acted as charge trapping centers. CdSe QDs spin-coated on indium oxide (In_2O_3) nanostructure-based device exhibited RS with an I_{ON}/I_{OFF} of $\sim 10^3$ and endurance cycles over 10^4 [Kannan et al., 2016b]. The RS mechanism of this device was ascribed to the trapping and detrapping of charges in QDs, while the In_2O_3 acted as the Coulomb blockade layer. The interface stability of QDs can play an important role in enhancing the performance of the resistive switching device, which can be improved by depositing an oxide layer on the QDs layer [Pourret et al., 2009]. ZnO QDs embedded in PMMA matrix-based device with Al and ITO electrodes exhibited bipolar RS with I_{ON}/I_{OFF} greater than 10^4 [Son et al., 2009, 2010]. Possible conduction mechanisms in the OFF state are thermionic emission and the SCLC process, while the FN tunnelling process dominates in the ON state in this ZnO QDs-PMMA based device. Cu doped PbS QDs embedded in polyvinyl alcohol (PVA) matrix exhibited unipolar resistive switching where two different concentrations of Cu were studied [Sarma et al., 2016]. It is observed that a larger concentration of Cu in active material enhanced the conductance and hence the I_{ON}/I_{OFF} of the memristive device.

The surface functional group in QDs can play a crucial role in QDs based memristors. Cao et al. performed a comparative study on the RS performance of pure BP QDs and functionalized BP QDs with PFCz-NH_2 [Cao et al., 2019]. The PFCz-NH_2 functionalized BP QDs based device exhibited a large I_{ON}/I_{OFF} of 10^7 with more than 600 endurance cycles. Therefore, the covalent functionalization of QDs surface with conjugated polymers can effectively enhance the device's performance and stability. Multilevel resistive states have been reported in GO QDs covalently functionalized with arylamine polyazomethine (TPAPAM) based device by the same group [Fan et al., 2017b]. Graphene QDs sandwiched between PMMA stacking exhibited resistive switching with three different resistance states over 10^4 s and the device was stable after 1000 endurance cycles [Ooi et al., 2016]. The resistive switching properties of carbon QDs and Poly (ethylene glycol) (PEG) hybrid film were investigated and after heating, the shallow trapping centers were removed which resulted in resistive switching at high temperature [Mihalache et al., 2014]. MoS_2 QDs embedded in the PMMA matrix sandwiched between two PMMA layers with Au and FTO electrodes exhibited resistive switching [Wang et al., 2017]. In this device, the conductance is quantized in SET and RESET processes. The quantization of conductance is ascribed to the trapping and release of electrons in QDs and the quantum tunnelling effect where MoS_2 QDs act as charge trapping centers and PMMA acts as the charge blocking layer. Kim et al. studied the RS behavior of ZnO-graphene QDs embedded in PS based one diode-one resistor device with an I_{ON}/I_{OFF} of 10^3 and retention time of 10^4 s [Ji et al., 2015]. In this device, the conduction mechanism in the OFF state is related to thermally activated electrons, while the SET process is due to the SCLC mechanism owing to charge trapping in ZnO-graphene QDs and charge transport through a conducting filament like path. Graphene QDs incorporated with P3HT was used as an active layer to investigate the nonlinear conductive behavior [Cosmin Obreja et al., 2014]. In this graphene QDs-P3HT based device higher concentration of graphene QDs showed a higher value of current than that of a lower concentration of graphene QDs, which implies that graphene QDs effectively enhance the conductance of the nanocomposites film. In another study, graphene QDs were embedded in polymethylsil-sesquioxane (PMSSQ) matrix to fabricate a memristive device [Lin et al., 2015b]. Incorporation of GO QDs into $Zr_{0.5}Hf_{0.5}O_2$ (ZHO) film significantly enhanced the stability of Ag/ZHO/GO QDs/ZHO/Pt device because the GO QDs assisted the formation of conducting filament made of Ag atoms [Yan et al., 2017]. Solution-processed BP QDs were blended with poly(4-vinylphenol) (PVPOH) to fabricate a bipolar resistive switching device [Zhang et al., 2015]. Han et al. investigated the RS performance of the memristive device with BP QDs sandwiched between two PMMA layers using Al electrodes on a flexible PET substrate [Han et al., 2017]. Multilevel RS with a high I_{ON}/I_{OFF} of 10^7 was achieved

in this BP QDs based flexible resistive memory device, while the I_{ON}/I_{OFF} was maintained for 10^4 s.

The hybrid heterojunction of 0D/2D materials also exhibits resistive switching. MoS_2 QDs were arranged on 2D hBN nanoflakes to fabricate an Ag/MoS_2 QDs-hBN/ITO type memristive device with SET and RESET voltages of +1.4 V and -1V, respectively [Rehman et al., 2018]. The resistive switching behavior of non-toxic and environment-friendly $CuInS_2$ QDs decorated in 2D GO layer on ITO substrate was investigated [Yun et al., 2014]. The retention time of the device was longer than 10^5 s. The $CuInS_2$ QDs acted as charge trapping centers and the GO layer worked as the charge blocking layer. In addition to, a hybrid of 0D QDs and 1D materials can be used for resistive switching. Core-shell CdSe-ZnSe QDs were assembled on multiwall carbon nanotubes, and this hybrid material exhibited bipolar RS [Li et al., 2009]. The decoration of CdSe-ZnSe QDs significantly reduced the switching voltage. The injected electrons from the electrode were transported along the nanotubes and trapped in the QDs layer. The captured electrons in QDs generated an internal electric field, leading the device to ON state. CeO_2 QDs were decorated on a ZnO nanorod array to enhance the reliability and stability of the memory device [Younis et al., 2013]. The random charge trapping in pure CeO_2 QDs based devices resulted in poor retention characteristics. The stability of the device was significantly enhanced when CeO_2 QDs were decorated in a ZnO nanorod array, which is ascribed to the well-arranged trapping sites on the ZnO nanorods surface. In another study, carbon QDs assembled on vertically aligned ZnO nanorods were used in memristor [Wang et al., 2016]. The hybrid structure of the carbon QDs/ZnO nanorods based device exhibited 100 times higher I_{ON}/I_{OFF} than the I_{ON}/I_{OFF} of the device without QDs.

In 2017, popular perovskite material $CH_3NH_3PbBr_3$ ($MAPbBr_3$) QDs were utilized in memristive devices with an Ag/PMMA/$MAPbBr_3$ QDs-PMMA/PMMA/ITO type device structure [Yang et al., 2017]. This device showed bipolar RS with an I_{ON}/I_{OFF} of 10^3. Later all-inorganic $CsPbBr_3$ QD was used to fabricate a photo-modulated memristive device where it was observed that the formation and destruction of CF formed by Br^- ion vacancies modulated by the external bias and optical illumination are responsible for resistive switching [Wang et al., 2018]. Though halide perovskite QDs based RRAM shows good resistive switching properties, these materials are very sensitive to various environmental conditions, especially water and oxygen in the ambient. Therefore, the poor stability in the ambient restricts the use of halide perovskite QDs in commercial RRAM devices.

From these previous studies reported in the literature, it is found that semiconducting QDs embedded in polymer matrices can be effectively used in the memristive device to achieve a high I_{ON}/I_{OFF} and high stability. Not only good stability and high I_{ON}/I_{OFF} but also low power consumption is also an important factor for energy-saving memristive devices. Though various QDs-based devices showing resistive switching were reported, fewer studies on low-power memristors have been carried out. Therefore, more studies need to be carried out on high-performance and low-power resistive memory devices. It is also noted that the use of less toxic and noncarcinogens materials is favorable for RRAM for safe usage. In this work, we have fabricated CdSe QDs embedded in poly (4-vinyl pyridine) (PVP) based memristive device with two different structures. The CdSe QDs-PVP nanocomposites based devices show excellent bipolar RS with a very high I_{ON}/I_{OFF}, long retention time, high endurance, and fast response time and they consume very low power in the order of ~μW. But CdSe is toxic and found to be carcinogenic. Therefore, in search of less toxic and noncarcinogens, we have fabricated MoS_2 QDs-PVP based resistive memory devices. The MoS_2 QDs-PVP based device also shows high I_{ON}/I_{OFF}, fast operation speed, and high endurance with less toxicity and low operating power. In addition to the effect of temperature on the RS behavior has been studied in MoS_2 QDs-PVP devices. It has been found that the MoS_2 QDs-PVP device can be operated in a hot environment also.

1.4 Objectives of the thesis

The objectives of the thesis work are as follows:

- Synthesis of colloidal CdSe QDs using the hot injection method
- Carrying out the structural characterizations such as XRD, XPS, HRTEM, FESEM, AFM etc. and optical characterizations such as absorption spectra, photoluminescence spectra, etc. of synthesized CdSe QDs
- Preparing nanocomposite by blending CdSe QDs solution with poly (4-vinyl pyridine)(PVP)
- Fabrication of Al/CdSe QDs-PVP/ITO/glass device and Al/ CdSe QDs-PVP/Al/glass device using spin coating technique
- Electrical characterizations of fabricated Al/CdSe QDs-PVP/ITO/glass and Al/ CdSe QDs-PVP/Al/glass devices
- Synthesis of colloidal MoS_2 QDs using the reduction of $(NH_4)_2MoS_4$ under N_2 environment at a high temperature
- Structural characterizations such as XRD, XPS, HRTEM, FESEM, AFM etc. and optical characterizations such as absorption spectra, photoluminescence spectra, etc. of synthesized MoS_2 QDs
- Fabrication of Al/MoS_2 QDs-PVP/ITO/glass device using spin coating
- Electrical characterizations of fabricated Al/MoS_2 QDs-PVP/ITO/glass device
- Investigating the effect of temperature on the RS performance of the Al/MoS_2 QDs-PVP/ITO/glass device

1.5 Thesis Organization

The entire thesis has been organized into six chapters which are as follows:

- **Chapter 1: Introduction**

  In chapter 1, the basic background of semiconducting memory technologies has been discussed briefly. This chapter states the limitations of current memory technologies and how these limitations can be eliminated in emerging memory technologies. The working principles of different memory technologies have also been discussed in this chapter. Based on the literature review, the aim of the works and the objective of the thesis have been stated in this chapter.

- **Chapter 2: Experimental Methods and Instrumentation**

  Chapter 2 includes the synthesis procedure of colloidal QDs, which includes the hot injection method and thermal reduction of $(NH_4)_2MS_4$ (M=Mo, W, etc.) under an inert atmosphere. The basic working principle of various characterization techniques has also been discussed in this chapter.

- **Chapter 3: Hot Injection-Based Synthesized Colloidal CdSe Quantum Dots Embedded in Poly(4-vinyl pyridine) (PVP) Matrix Form a Nanoscale Heterostructure for a High On–Off Ratio Memory-Switching Device**

  Chapter 3 describes the synthesis procedure of colloidal CdSe QDs and a resistive switching device fabrication using CdSe QDs embedded in a PVP matrix. The RS performance of the fabricated device has been discussed in this chapter. The incorporation of CdSe QDs in the PVP matrix forms a nanoscale heterostructure which constructs a potential well type of energy band diagram. The mechanism of resistive switching is also discussed in this chapter.

- **Chapter 4: CdSe Quantum Dot-Based Nanocomposites for Ultra-Low Power Memristors**

Chapter 4 describes the fabrication of a CdSe QDs-PVP nanocomposite based device for ultralow-power memristors. The Al\ CdSe QDs-PVP\Al device exhibited excellent RS behaviour with high I_{ON}/I_{OFF}, high endurance, long retention time, fast response time and ultralow-power consumption. The synthesis procedure of CdSe Qds, different characterization techniques and the origin of the switching mechanism are also discussed in this chapter.

- **Chapter 5: Colloidal MoS_2 Quantum Dots for High-performance Low Power Resistive Memory Devices with Excellent Temperature Stability**

  Chapter 5 describes the synthesis procedure of a less toxic and non-carcinogen material MoS_2 QDs and the use of them in a high-performance, low-powered resistive switching device. The device fabrication technique, different materials characterizations and the resistive switching performance have been discussed in this chapter. In addition to, the effect of temperature on the RS performance of the device has also been explored in this chapter.

- **Chapter 6: Conclusions**

  Chapter 6 summarises the whole work done, starting from the CdSe QDs based resistive switching performance to less toxic and non-carcinogen MoS_2 QDs based resistive switching for low-power resistive memory devices. This chapter concludes the results. Also, a brief discussion about future work on the non-toxic materials-based resistive switching has been included in this chapter.