

To Be or Not to Be – Review of Electrical Bistability Mechanisms in Polymer Memory Devices

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Organic memory devices are a rapidly evolving field with much improvement in device performance, fabrication, and application. But the reports have been disparate in terms of the material behavior and the switching mechanisms in the devices. And, despite the advantages, the lack of agreement in regards to the switching behavior of the memory devices is the biggest challenge that the field must overcome to mature as a commercial competitor. This lack of consensus has been the motivation of this work wherein various works are compiled together to understand influencing factors in the memory devices. Different works are compared together to discover some clues about the nature of the switching occurring in the devices, along with some missing links that would require further investigation. The charge storage mechanism is critically analyzed alongside the various resistive switching mechanisms such as filamentary conduction, redox-based switching, metal oxide switching, and other proposed mechanisms. The factors that affect the switching process are also analyzed including the effect of nanoparticles, the effect of the choice of polymer, or even the effect of electrodes on the switching behavior and the performance parameters of the memory device.

development of organic devices and the public demands for slimmer devices and flexible, wearable technology.^[4,5]

Organic memory devices (OMDs) are a rapidly evolving field with much improvement in device performance, fabrication, and application. Much work has been done in this field with reports about new material properties^[6–8] or device structure^[9–13] or even novel fabrication techniques^[13–17] being reported. But the reports have been disparate and hugely diverse and, there is no consensus of the observed electrical behavior; this review article is thus intended to present an overview of the development of the field and the different mechanisms that explain the switching behavior of various systems and contradictions among the reported work. Various works have been compiled together in the context of the materials and the device mechanisms to understanding the factors that seem to influence the device operation. Different

1. Introduction

In the recent past, there has been a steady and gradual improvements in the area of organic and polymer electronics. With an increasing demand for cheaper electronic devices for certain applications (for example, disposable electronics, environmentally friendly materials, or green electronics), organic electronics seems to be seated in a favorable spot to satisfy these requirements. The contribution of organic electronics is evident in the everyday life with organic light emitting diodes (LEDs), wearable technologies, and organic solar cells.^[1–3] One such area that is undergoing a rapid evolution is the area of the electronic memory device. The growth in this area is mostly motivated by the simple fabrication process involved in the

works have been compared together to discover some clues about the nature of the switching occurring in the devices, along with some missing links that would require further investigations. Many open questions seem to arise too, for example, how can one material exhibit charge storage switching behavior when measured by one study and have a conductive filament (CF) switching when investigated by other research group? This question has been discussed in detail in Section 5 by considering the example of a Tris(8-hydroxyquinoline)aluminium(III), commonly known as Alq₃. But this material is not an exception; various materials have been reported to exhibit a spectrum of switching mechanism, which has been one of the reasons for the confusion that persists to surround the memory devices even to this day.

There has been many reports that have published the resistive switching mechanisms like conductive filament (CF) mechanisms, metal oxide switching, carbon-based switching, and redox-based switching.^[9,13,17–22] Therefore these mechanisms have been mentioned only superficially; the focus, however, has been in the charge storage mechanisms wherein careful inspection of various studies has demonstrated a variety of meaning that charge storage mechanism seem to carry. These nuances, or differences in the meaning, have been pointed out and the consequent consequence has been identified wherever possible. Each of these has been portrayed as being various “models” within the same umbrella of charge storage mechanism. This has been done to clarify the term “charge storage” in the context of when and how it is used.

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2. Scope and Motivation

A general overview of the large number of publications that have been reported in the area of OMDs will reveal the complexities, or rather simplicity as reported, on the subject. A number of research groups have reported bistable non-volatile memory devices but the results differ with varying materials and device structure.^[23] The problem is further compounded by the reports of varying bistable switching even in the same system and material. This points to the fact that the physics behind the switching of systems and the corresponding material properties is not completely understood.^[20] The role of individual components of the devices, the interplay of different components with each other, the effect of the system taken as a whole, etc., need addressing. There is also a lack of complete understanding about the mechanism of the switching and electrical bistability in the nanocomposite memory devices that needs to be brought to the attention of material engineers and theoretical physicists and chemists alike to encourage greater cooperation and involvement. Challenges such as reaching a consensus on the multiple prevalent and often contrasting proposed mechanisms of device switching and non-volatile operation, need to be achieved before this field can begin to mature into a commercial industry.^[24]

Such muddled and murky explanations invoke the need for a review article that brings together numerous works to identify the questions that need addressing, recognize any relationships that may exist, and acknowledge the gaps of knowledge that needs reckoning in the future works. The collation of results from diverse reports is therefore attempted in this review article, so as to present different perspective on the subject and contested opinions of interpretation of data results in order to achieve a big-picture-view of the system and encourage further research- all this in the limited scope of its ability. A number of review articles have been published in the past;^[9–20,24–44] but this article is intended to address a specific class of devices, namely, the memory devices with admixtures of macromolecules and/or nanoparticles (NPs) embedded in polymer matrices. These devices have largely remained unaddressed by a lot of review articles, and those that do mention these devices have done it only partially or superficially.

Further to the discussion of the switching mechanisms and the device structure, much attention needs to be paid on the materials used and the switching behavior that has been observed. This can be clearly seen from **Table 1**, which outlines the device behavior that has been reported using the same material- Alq₃. This should clearly demonstrate the need for a systematic investigation of the memory device that's been fabricated, so as to acquire ability to extract useful information from the studies. Table 1 however, is incomplete at this point, lacking in some information to put things in better context; will be focused in depth in the following section.

The evolution and the development of the field will be traced along with the various reported switching mechanisms. The device behaviors will be explored to address the various switching mechanisms like charge-storage mechanism, redox-based switching, resistive switching due to conductive filament formation, and metallic filamentary growth. The device structure will be analyzed to find any dependent factors that affect the switching behavior of the devices. But a confession is due in regards to the extent of the survey of reported works not

Table 1. The table indicates the devices that have been fabricated using Tris(8-hydroxyquinoline) aluminium (III) (known as Alq₃); Despite the use of same material, and in cases, similar device structure, the switching mechanisms have been reported to be quite diverse; There has been a lack of consensus about the mechanisms which begs the question, as to what are the factors that affect the switching in devices.

Device structure	Switching mechanism	Reference
Al/Alq ₃ /Al/Alq ₃ / Al,Cr,Cu,ITO,Au,Ni	Simmon-Verderber-like switching	[45]
Al/Alq ₃ /Ag,Cr,Mg,Cu/Alq ₃ /Al	Simmon-Verderber-like switching	[45]
Al/Alq ₃ /Ni/Alq ₃ /Al	Space- Charge- Limited Current (SCLC), Thermionic-field-emission	[46]
Al/ α -NPD/Alq ₃ /Ni/ Alq ₃ / α -NPD/Al	SCLC	[47]
ITO/Alq ₃ /Ag	CF formation	[48]
Al/Alq ₃ /Al/Alq ₃ /ITO	Fowler Nordheim tunneling (ON state) Poole-Frenkel (OFF state)	[49,50]
Al/Alq ₃ /MoO ₃ /Alq ₃ /ITO	Thermionic emission (OFF state) Ohmic conduction (ON state)	[51]
Al/Alq ₃ /Al/Alq ₃ /Al	Thermionic emission (ON state)	[52]
Al/ZnS/Al/Alq ₃ /Al	Ohmic conduction (OFF state)	
Al/Alq ₃ /Al	CF formation	[53]
Al/Alq ₃ /n-Si	Schottky-type conduction	[54]

being exhaustive- this is not intentional; it is simply because of the sheer volume of data that have been published.

3. Overview

The scope and objectives of this review article have been presented in the following sections. The main objective is to trace the development of the OMDs, particularly the admixtures and the nanocomposite devices. Section 4 will introduce basic terms and switching patterns which have been used consistently throughout the latter portions in the article. This will be followed by the historical evolution of the field and its development by tracing the various publications and works in a general chronological fashion. The next section (Section 6) will examine different reports and the results obtained from them to interpret the role that each component in the device, plays in the switching behavior, like the role of the nanoparticles, the role of polymers, etc. Many publications that have been very specific in their investigations, have therefore, been introduced here while having been excluded from Section 5. Many subsections are presented to include the parameter that has been observed to influence the component in the main focus. For example, while the role of nanoparticles in the switching of the devices has been presented in Section 6.1., it has also been reported that the role of the nanoparticles might vary depending on the capping molecule, or depending on whether the device has been exposed to electroforming procedure. These factors that have been reported to determine how the nanoparticles behave and interact in the switching process; was found integral to be included. These have been added in the further subsections (Section 6.1.1., 6.1.2...) for clarity of understanding.

Sections 7 and 8, focus mainly on the different switching mechanisms that have proposed and reported for various

materials and device structures. The charge storage mechanism has been presented in great detail in Section 7; attempts are made to present the differences within the different models that exist under the broad umbrella of charge storage mechanisms and how they differ from each other. There has been a lot of confusion in this area and hence various works have been looking carefully, sketching to the best of the ability, the nuances of the charge storage mechanisms. Section 8, is on the other hand a broad survey of the other mechanisms that have been reported. Many switching behaviors have been observed for various materials and device structures over the years. A detailed report of all these mechanisms has not been the focus, since many prior articles already exist to address this.^[9,13,20,24,30,32,34] Moreover, most of these mechanisms include inorganic systems and is, therefore, beyond the scope of this article.

The latter parts include future scope (Section 9) and conclusion (Section 10) where some future directions of developments have been suggested. The gap in the knowledge based, on the published works, has been pointed out in hopes of motivating further involvement toward the development of the field.

4. Nanotrap Memory

4.1. Introduction

The term “nanotrap” was first used by Bozano et al.^[55] in 2005, when it was first suggested that the switching phenomenon could be attributed to the charge trapping occurring in the metal nanoparticles (NPs). The study of a switching phenomenon since then, has evolved through decades of reports and investigation and has, in effect, evolved in entirely separate areas of study within itself. There are works that report switching on different materials: Semiconducting, ferroelectric, dielectric, binary metal oxides, etc., but these will not be focused here.^[13,20,30]

The nanoparticles embedded OMDs store bits in the form of reversibly switching levels of electrical conductivities. The device has a simple architecture in which the nanoparticle-dispersed medium is sandwiched between two metal electrodes. The nanoparticle dispersed layer is usually referred to as the active layer; wherein the matrix in which the nanoparticles are embedded could be either insulating or semiconducting in nature (see **Figure 1**). The high switching speed and low switching voltages also make it a perfect candidate for the emerging non-volatile memory device applications in high speed applications and low power applications.

The following portions has been devoted to the clarification of terminologies and device behavior patterns that have been extensively and consistently been used in all the following sections. Most of the recurring behavioral patterns (like current-voltage behavior) have been described, although there may be other patterns that have been overlooked here. In such cases, explanations have been offered in the latter sections.

4.2. Types of Curves

These devices have the ability to achieve bistability, meaning that it can switch between two different values of electrical conduction

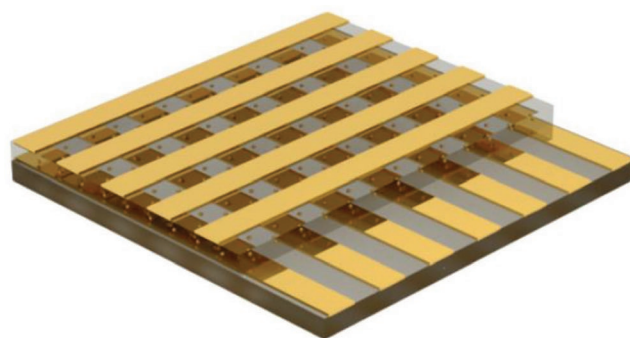


Figure 1. The figure depicts a general structure of a trilayer device. The top layer and the bottom layer consist of electrodes and the middle layer is sandwiched between them. The middle layer is an admixture of metal nanoparticles and polymer layer. Reproduced with permission.^[56] Copyright 2012, Elsevier.

states when an external electrical stimulus (known as the write signal), is applied; and it can retain the state even after the electrical stimulus is removed. But sometimes, the devices don't revert its state once having changed; such devices are known as write-once-read-many times (WORM) devices. Depending on the composition of the device, the materials used to fabricate it and the nature of switching involved; the current-voltage (*IV*) behavior might vary. These *IV* curves have been referred differently by several publications, but throughout this article, these curves will be addressed in the manner as Prime and Paul.^[36,57] Judging from the diaspora of results that have been reported, the *IV* curves can be broadly classified into three kinds of curves:

4.2.1. S-Curve

The S-curve is the first kind of current-voltage (*IV*) curve, where a pristine device first begins in a low conduction state (OFF state). The S-curve is characterized by a threshold voltage at which the device undergoes an abrupt transition from the initial low electrical conduction (OFF state) to a high conduction (ON state). Any voltage sweep beyond this threshold voltage results in the ON state, where the current may either saturate or it may increase at a very slow rate.

The S-curve may differ in its direction or the sequence of read, write or erase operation. For example, refer two distinct behavior shown in **Figure 2**. The symmetry of the *IV* curve in S-curve depends on the device structure and operation. Once the high conduction state is achieved, reduction in the voltage results in the device, following a high conduction path. Some devices are able to retain this state until an erase signal is applied to it. These are known as the non-volatile devices.

4.2.2. N-Curve

The N-curve is similar to the S-curve except that there are two threshold voltages in the N-curve. The devices exhibiting the N-curve begins with a low current level in the pristine state until the first threshold voltage is exceeded, after which it switches from the OFF state to the ON state (shown in **Figure 3**). If

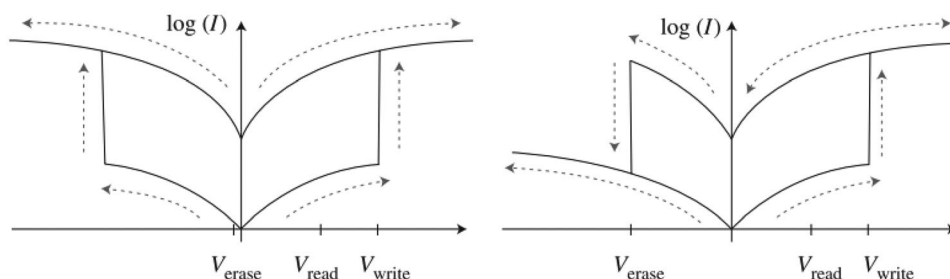


Figure 2. The S-curve in the left side shows a switching behavior where the write operation is determined by the threshold voltage required to achieve the OFF-state-to-ON-state transition. The read operation is done using a smaller voltage below the write voltage value. The erase operation is achieved with a tiny voltage applied in the opposite polarity, following which the device reverts back to the original OFF-state. The device behavior on the right side shows similar behavior except, both the erase operation and the write voltage have a minimum threshold voltage exceeding which leads to the respective device switching. Reproduced with permission.^[36] Copyright 2009, Royal Society.

the voltage is decreased before reaching the second transition voltage or the second threshold voltage, then the device will continue to remain in the ON state. But if the voltage increment is sustained even beyond the second threshold voltage, then the curve transitions into a region of decreasing current. This is called the negative differential region (NDR), where the slope of the current–voltage (IV) curve is negative.^[58–60] The device would be switched from ON state to the OFF state if the voltage sweep is permitted to exceed beyond the NDR. In such devices, therefore, both the switching, OFF state to ON state and vice versa can be achieved from the same voltage polarity. These devices do not require an opposite polarity voltage to reset the device, or to achieve the ON state to OFF state transition.

4.2.3. O-Curve

The O-curve is characterized by a smooth increment of current with an increase in voltage. Unlike the former (N-curve and S-curve), the O-curve, doesn't have a "knee" voltage or a threshold voltage where the current jumps suddenly by a few

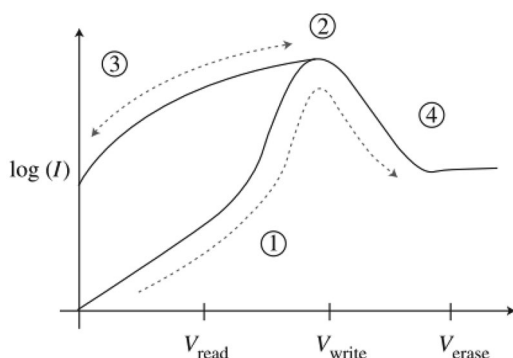


Figure 3. A typical N-curve with various regions. Region 1 is the low conduction state in which a pristine device first begins; it leads to region 2, which is when the device switches from the low conduction state to a high conduction state. Region 2, marks the first threshold voltage- if the voltage is decreased from this point, it remains in the high conduction state (region 3), but if the device is exerted beyond region 2, the device undergoes an erase operation and enters region 4. After reaching region 4, the device then retains the low conduction state (region 1). Reproduced with permission.^[36] Copyright 2009, Royal Society.

orders to a high conduction state. But it must be noted that once the voltage sweep is reversed after an increase, the device follows a different path indicating a change in the conduction of the device. The hysteresis assists in distinguishing one state from the other and the direction of the hysteresis curve could differ too. The conduction change is gradual, and the difference between the high and low conduction states may not be as big as the two former curves (refer Figure 4).

4.3. Unipolar and Bipolar Switching

The differences lie not just in the curves, but also on how the "write" and "erase" operations are performed in a memory device. The "write" operation is usually performed when a device switches from low current state to high current state, while the reverse switching is known as the "erase" operation. Depending on the type of device structure or operation, the write and erase function might occur differently. Whenever the write and erase operations occur at the same polarity of voltages, the switching is known as a unipolar switching. On the other hand, for opposite polarities of voltage required for write and erase, such a device is known as a bipolar switching device.^[13,20]

5. History: Materials and Mechanisms

The history of the bistable switching devices is much older than the coining of the term "nanotrans" itself. The early works in

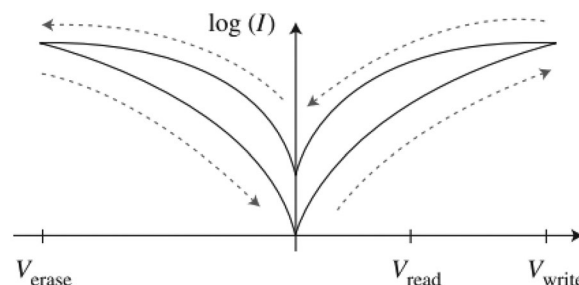


Figure 4. A typical O-curve, with no abrupt current transitions. Reproduced with permission.^[36] Copyright 2009, Royal Society.

1960s by Hickmott^[61,62] demonstrated that thin films could be “conditioned” to electrically switched.^[62] The “conditioning” process was referred to as electroforming. Hickmott observed and studied this electrically switching with metal oxides like aluminium oxide (Al_2O_3), Ta_2O_5 , ZrO_2 , TiO_2 , and SiO_x .^[62] Although the switching operations were not too effective, this demonstrated the potential of the switching properties. Soon, many other materials were found to exhibit the same switching behavior and the field began evolving.^[63,64] Organic materials too, were observed to exhibit such behavior.^[65,66]

In 2002, Ma et al.^[67] reported bistable switching in a three-layer (3L) device, where aluminium (Al) interlayer was embedded between two layers of semiconducting polymer called 2-amino-4, 5-imidazoledicarbonitrile (AIDCN) and aluminium electrode. The switching from OFF state and ON state was observed to undergo a six-order increase in current but the conduction mechanism was reported to be unclear.

Despite the uncertainties regarding the conduction mechanism, it was concluded that the switching was not due to filamentary conduction since the magnitude of ON state current was scalable, and depended on the device area. Ma et al.^[68] repeated the measurements by using different metal interlayers like gold (Au), copper (Cu), and aluminium (Al) were used as interlayer, due to the varying degree of reactivity and to observe if any effect the metals had in the switching process. All the devices were found to switch, except for the ones that had no metal interlayer; proving, thus that the metal interlayer was integral to the switching process. The presence of conducting filaments was again refuted based on the temperature, dependent ON state current and the device area dependence of the current. It was observed that the ON state current of the device reduced with the reduction in temperature; thereby demonstrating a temperature-based conduction process to be responsible. The exact mechanism of the switching, however, was not reported until it was found that the capacitance plot showed the evidence of charge storage in the interlayer.^[69] The conduction mechanism proposed thereafter was that the metal interlayer acted like a charge trap which led to the doping of the organic layer on the either side of the interlayer and enhancing the conduction of the device to the ON state.

Bozano et al.^[45] investigated the same device structure later with tris(8-hydroxyquinolino)aluminium (Alq_3) being used as an organic layer and aluminium interlayer was used to investigate the bistable switching. As can be seen in **Figure 5**, different metals were used and several configurations were tested to analyze the dependent parameters that affected the switching behavior. The switching of the device was consequently concluded to be independent of the metal being used within the polymer matrix and the dispersion technique used.^[55]

The conduction mechanism proposed by Bozano et al.^[45] was similar to the Simmons and Verderber (SV) model,^[70] in which the nanoparticles acted like “nanotraps.”^[55] However, a major difference from Ma et al.^[68] result, despite having replicated the same structure and the same material too, was that their device exhibited an N-curve instead of the S-curve, that was seen in the former case. Bozano et al.^[55] pointed out this difference in device behavior, even while observing the same system, to be a problem faced due to the fabrication of the device by different research groups. The NDR was proposed to be the result of

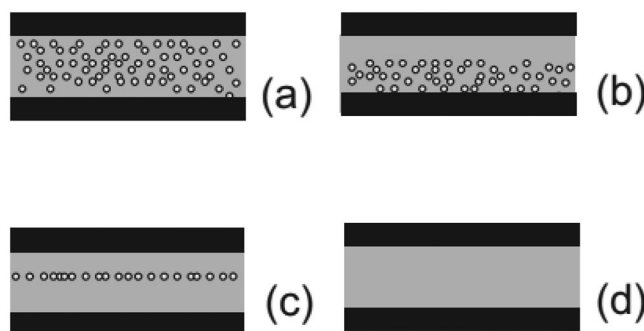


Figure 5. Cross section of Bozano et al.^[55] devices. Various device structures were tried- device (a) was a suspended nanoparticle matrix in polymer, fabricated as a 1L-device. Device (b) was a 2L-device configuration where a layer of suspended nanoparticles was laid on the bottom electrode, over which a polymer layer was evaporated. Device (c) was similar to the 3L-device that were investigated by Ma et al.^[67] and device (d) was the reference device, that was used to compare the polymer-only behavior, against the rest of the device behaviors. The image is reproduced with permission.^[55] Copyright 2005, John Wiley and Sons.

the charge trapping by the NPs and the space-charge inhibiting due to the electrostatic repulsion. The conduction of the device was found to demonstrate insufficient evidence for a temperature-dependence, which led to the conclusion that the conduction was happening due to direct-tunneling. This was quite distinct to Ma et al.’s^[68] result where the ON-state current was found to be temperature-dependent. The presence of aluminium oxide (Al_2O_3) was found, but it was largely overlooked in the discussion of the conduction mechanism, except that it was considered essential for the isolation of the nanoparticles from one another; thereby ensuring the trapped charges do not escape.^[67,69,71] The filamentary conduction mechanism was dismissed by Bozano et al.,^[55] first because no electroforming was necessary in their device and second because they found no switching in the absence of embedded NPs. They finally concluded that the NPs assisted in two ways: First, they induced impurity levels in the barrier insulator layer thereby assisting in the conduction of the device,^[55,70,72] and second, acted like an electrostatic barrier to avoid leakage current.^[55,73]

He et al.^[74] in 2005, reported that the switching speed of the device was measured to be less than or around 10ns, and proposed that Bozano et al.’s^[45] “charge-injection-travel-and-trapped picture”^[55] could not lead to such low switching speeds. It was also reported that the Al was forming metalorganic complex at the top electrode (metal)-organic interface due to the vacuum evaporation of hot metal over the organic layer. The switching was therefore proposed to be happening only at the bottom electrode, as the metalorganic complex formation led to the introduction an impurity level that assisted the electron injection into the metal interlayer without much of energy. However, the question of why such a metalorganic interface couldn’t be present in the interlayer-organic interface was left unattended when hot metal was interacting with organic materials at the lower interface of the interlayer too. Despite that, the results from this study brought into picture how the fabrication process and the material used could affect the final behavior of the device.

Tondelier et al.^[75] examined the three-layer (3L) and one-layer (1L) devices and investigated the switching behavior with

pentacene as the organic active layer. The 3L devices had the nanoparticle interlayer and the 1L device had no interlayer. The bistable switching was observed in both the 3L and 1L devices. It was therefore concluded, that the interlayer was not necessary for the switching and that the switching was due to the metal electrodes forming metallic filaments in the organic semiconductor matrix due to diffusion but no evidence of filaments formation was provided. Moreover, it was observed that the OFF-state current had a temperature-dependent behavior, while the ON-state current was “metallic” and temperature-independent. This concredited the filamentary conduction in the ON state, while the OFF-state was attributed to be due to Poole-Frenkel (PF) mechanism. It is however known today that pentacene has charge-trapping ability when used on its own.^[25,32] The switching in the 1L device and the conduction behavior can be due to the large charge-trap densities that are observed in pentacene itself, therefore leaving scope for investigation.

The feasibility of using readymade NPs was demonstrated by Paul et al. in 2003^[76] when a monolayer of gold nanoparticles was laid using Langmuir-Blodgett (LB) technique. This technique was used to fabricate a metal-insulator-semiconductor device embedded with Au-NPs in the gate layer. Measurements were done comparing the capacitance measurement of devices with and without the nanoparticle layer. A distinguishable hysteresis in capacitance was observed in the devices with nanoparticles which was attributed to be the result of electron trapping occurring in the nanoparticles in the gate. Ouyang et al.^[77] demonstrating the use of ligand-stabilized nanoparticles to fabricate metal-insulator-metal (MIM) devices, around the same time as this study.

The work done by Ouyang et al.^[77] can be considered significant in many aspects. Ouyang et al.^[77] used a solution-based-technique as opposed to Ma et al.^[68] who used thermal evaporation for depositing the nanoparticle layer and metal interlayer, respectively. The use of ligand stabilized gold nanoparticles ensured the isolation of the particles and therefore demonstrated an alternative to ensure isolation, apart from the deliberate oxidation of metals (like aluminium) that the previous works relied on.^[43,68,74,78] The second important difference lies in the choice of organic material that was used to disperse the nanoparticles in. The use of polystyrene (PS) ensured an inert polymer environment; but more importantly, it was more an insulator compared to materials like AICDN and Alq₃ which were semiconductors. These differences, however, did not affect the output, which showed an ON/OFF ratio of several orders and exhibited an S-curve. The switching behavior was therefore attributed to the charge transfer that took place between two species of materials that were used in the polymer matrix- gold NPs stabilized with 1-dodecanethiol (DT) and 8-hydroxyquinoline (8HQ).^[77] The 8-HQ molecules are known to be electron donors^[79] and the Au-DT nanoparticle was used as an electron acceptor. Hence the change in the conductance was attributed to the transfer of electrons from 8-HQ to Au-DT NPs in the presence of an externally applied electric field. Many other works followed this later, and confirmed the switching mechanisms further.^[80–83] There were although, some anomalies, like devices where the Au-NPs were capped with 2-naphthalenethiol (2NT),^[84] the results showed the device to be a WORM device.

The first all-OMD was reported by Kanwal, Paul, and Chowalla.^[85] Reported first in Material Research Society (MRS) Fall Meeting-2004, this device utilized fullerene (C-60) molecule instead of metal nanoparticles in poly(4-vinylphenol) (PVP) to fabricate an MIM device and demonstrated distinguishable bistability. The reference device Al/PVP/Al was compared with the device containing C-60 molecule (Al/PVP+C-60/Al) and analyzed to find clear evidence of a bistable behavior in the device containing C-60 molecule. The device operation was found to be promising, with the read time being ≈ 30 ns (the read time was believed to be as low as a few femtoseconds, being constrained only by the limitation of the measuring instrument), energy required for reading a bit being about 0.01 pJ and writing a bit being around 0.1 pJ. This demonstrated the capability of the OMD to fare equally with the commercial flash technology at such initial levels of development.^[86] These devices were further investigated by Paul, Kanwal and Chhowla in 2006,^[86] in which the nanoscale analysis of the devices was conducted using a conducting atomic force microscope (c-AFM). Although the ON/OFF ratio was very less, the current densities were considerably higher, since the scanning area and the AFM tip area were very small (≈ 100 nm²); demonstrating that the C-60 molecules were capable of holding electrons. These results were further strengthened by Raman analysis of the device. The A_{1g} mode of fullerene, which appeared at 1469 cm⁻¹, was observed to shift down by 9 cm⁻¹ when the device switched to the high conductance ON state. But after applying the erase voltage, the peak returned to the original wavenumber, indicating the OFF state of the device. This shifting and restoring of the peak was attributed to the change in the symmetrical stretching vibration of the C = C bond.^[88] The red shift observed in the Raman peak was indicative of electron trapping that occurred in the C-60 molecule when an external write voltage was applied and the electron escaping the C-60 molecule when an erase signal was applied.

The results published by Paul et al.^[85–87,89] were however quite distinct from the other works, in which the current-voltage (IV) behavior exhibits an O-curve. The ON/OFF ratio too, was reported to be lesser; there was no abrupt increase in current levels. However, the charge retention studies demonstrated sustained charge separation states. The well-studied donor-acceptor system of Au nanoparticles and 8-HQ molecules too,^[77,90] when investigated by Prime and Paul,^[89] the IV behavior showed an O-curve. The difference in the conduction values of the devices was proposed to be due to the separation of the charges, due to the donor-acceptor system, forming an internal electric field due to the polarization of charges.^[87] More information regarding the details has been presented in Section 7.1.4. (charge trapping and internal field mechanism); the differences in the results, however, demonstrate that the two states in this case are a function of the amount of charges that can be successfully trapped by the acceptor system (metal nanoparticles, C-60 molecules, etc.). The write voltage (+5 V) successfully creates this charge separation, while the erase signal leads to the reversal of the polarization. This charge separation and the orientation of it, was reported to the cause of the distinction of states.

The feasibility of using nanoparticles as memory devices was confirmed by Leong et al. too.^[91] Prime and Paul^[92] further

demonstrated the role of the nanoparticle by investigating the charging process using electrostatic force microscopy (EFM). These measurements were closely associated with the AFM measurements conducted by Ouyang et al.^[77] In these measurements the AFM images were taken after an electrical potential was applied across the electrodes of a device.

Prime and Paul^[92] aimed the experiment to confirm that there wasn't any contribution from the polymer in the trapping process. Hence a planar gap cell structure was fabricated to study the exclusive contribution of the nanoparticle in the charging process. As seen in **Figure 6**, after applying a write and erase of +10 V and −10 V respectively, and using the EFM tips to “read” the nanoparticle potential at 3 V; it was observed that there were charges being trapped into the nanoparticles through tunneling. It was also observed that the nanoparticle was able to retain the charges, although not for very long. But this could be due to the non-uniformity associated with the planar structure. This was a confirmation of the Ouyang et al.^[77] results and was again an evidence of the charge trapping to be contributing to the switching of the devices.

Several other devices were fabricated by the group over the course of the years which helped substantiate the internal field model to explain the switching behavior.^[23,57,79,93–95] There have been reports that claim the ON/OFF ratio to be nine orders, however less effort has been paid to investigate if

other parameters might be playing into the switching process. Paul and Salaoru,^[23] investigated a simple device structure consisting of polyvinyl acetate (PVAc) layer between two aluminium electrodes. The device consisted of no nanoparticles and the IV behavior was found to be exactly as expected- no hysteresis was observed. However, when the same device structure was tested with a layer of aluminium oxide on the bottom electrode, bistable switching was observed with an ON/OFF ratio of about 3 orders being measured. Similar results were found by many other works, where the switching was observed to occur even in the absence of the nanoparticle layer and demonstrating that that the switching is not being contributed from the embedded nanoparticle-type devices or from other electron-acceptor type molecules. In 2019, Nau et al.,^[96] investigated the interlayer device structure and analyzed the switching behavior from the unipolar switching behavior, essentially re-investigating the Bozano et al.^[45,55] studies. The switching was found to occur even in the absence of the interlayer.

The switching behavior demonstrated using selenium (Se) nanoparticles by Alotaibi et al. in 2017, once again pointed to the internal field mechanism to be responsible for the switching behavior.^[97] The nanoparticles were embedded in diamond-like-carbon matrix, which were fabricated at low temperatures (≈ 50 °C) using plasma enhanced chemical vapor deposition (PECVD), demonstrating the potential for deposition on flexible substrates. It was found that the Se nanoparticles were able to hold the charge and exhibit bistability, wherein the IV behavior exhibited an O-curve. The IV behavior was used to demonstrate the internal-field model, wherein a pristine device starts in the high conductance state. This is a crucial distinction separates the behavior of these devices from numerous others that claim the charge storage mechanism to be the cause of the switching behavior but show the device beginning from a low conduction state. This has been a core dilemma in the Bozano picture,^[43,53] as raised by Scott,^[27] that despite all other evidence, this problem remained unclear as to why their devices switched in the low conduction state in their pristine form. This device behavior and in-depth discussion of the internal-field model will be done in Section 7.1.4., and therefore will not be attended except in brief. The trapping of electrons inside the NPs accompanies the charge-building that develop an internal electric field inside the device (see **Figure 7**). This internal field develops a kind of screening effect wherein the total applied field gets either reduced or added up (depending on the bias that one applies next).^[98]

Alotaibi et al.^[97] demonstrated how the accumulation of charges could be achieved by the trapping of electrons to fabricate memory devices. This behavior was replicated by Saranti et al., but using silicon nanowires in 2016^[99] and subsequently further work.^[100] The internal field was developed in this case, not by using nanoparticles as traps, but the large surface defects densities on the nanowire surfaces. The high surface to volume ratio in the nanowires facilitated the charge trapping on the nanowires, at the sites of dangling bonds.^[101]

Saranti et al. in 2016,^[99] also demonstrated a voltage sweep scaling behavior in the devices, where the hysteresis of the IV curve depended on the voltage sweep window. The higher the applied voltage sweep, the greater the hysteresis became. The devices fabricated by Saranti et al.^[99,100] demonstrated multiple capacitance states that existed one within the other, thereby

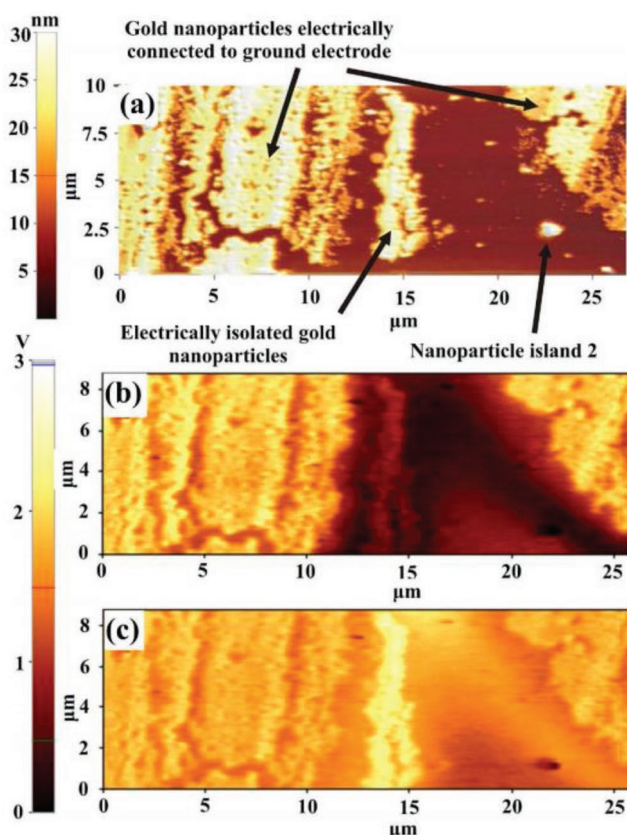


Figure 6. Image showing the atomic force microscope/microscopy tomography image of an isolated nanoparticle a) before and b) after applying a +10 V bias, and the image c) after applying −10 V. Reproduced with permission.^[92] Copyright 2010, AIP Publishing.

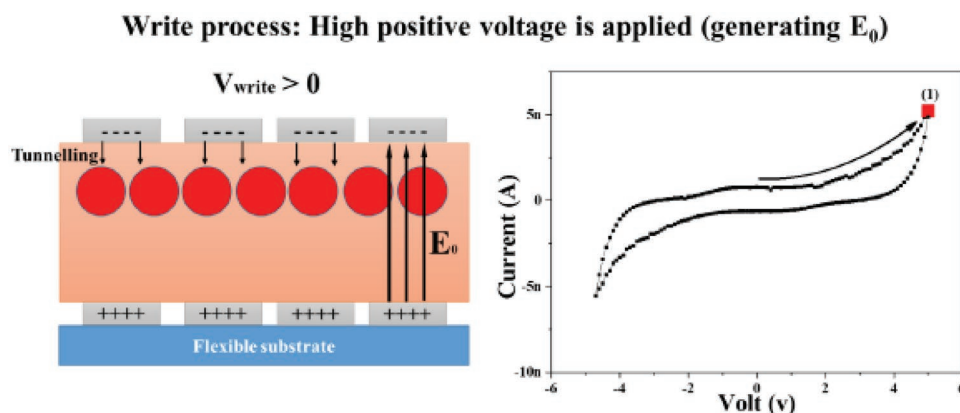


Figure 7. The explanation of the bistability demonstrated through the internal field mechanism. Reproduced with permission.^[97] Copyright 2017, Elsevier.

opening the prospect of multi-bit storage capability (refer **Figure 8**). The difference between the high conductance state and the low conductance state were found to be dependent on the window of voltage sweep, which in turn was dependent on the amount of charges trapped. Similar behavior with multiple conduction states was also observed by Salaoru et al.,^[93] too (refer **Figure 9**). Like other previously published works,^[78] these intermediate states can be used for multi-bit applications, the various states depending on the different write voltages.

Such voltage scalability goes to demonstrate how the applied voltage leads to the charge storage and how this charge trapping exhibits a voltage offsetting on the applied voltage. But the performance of a memory device is not merely based on the ON/OFF ratio, switching speed or the energy required to write, read or erase. The retention of the device is also a crucial parameter. The ability of the device to retain the charge (in this case charge storage) will determine how long can the device continue without losing the stored information. The retention

of the device was investigated by Suresh et al. in 2014,^[102] when the charge storage was investigated for gold superclusters. It was found that the superclusters were able to store the charges for more than 10^5 s. The results demonstrated a linear decay of capacitance, so that about 77% of the capacitance was retained after 10^5 s. When the results were extrapolated for more than 10 years, it was found that the device would be able to retain more than 50% of the device capacitance without losing it (refer **Figure 10**). This study demonstrated the ability of OMDs to be able to outperform some of the commercial devices.

Zhang et al.^[98] investigated the effect of high current electroforming procedure on the devices in 2019, when it was found that the heat produced due to Joule's heating led to the agglomeration of the nanoparticle, where the size of the particles increased by four times their initial size. This demonstrated how high current levels could impact the affect the device in various ways and must therefore be regulated to maintain the initial size distribution of the metal nanoparticles.

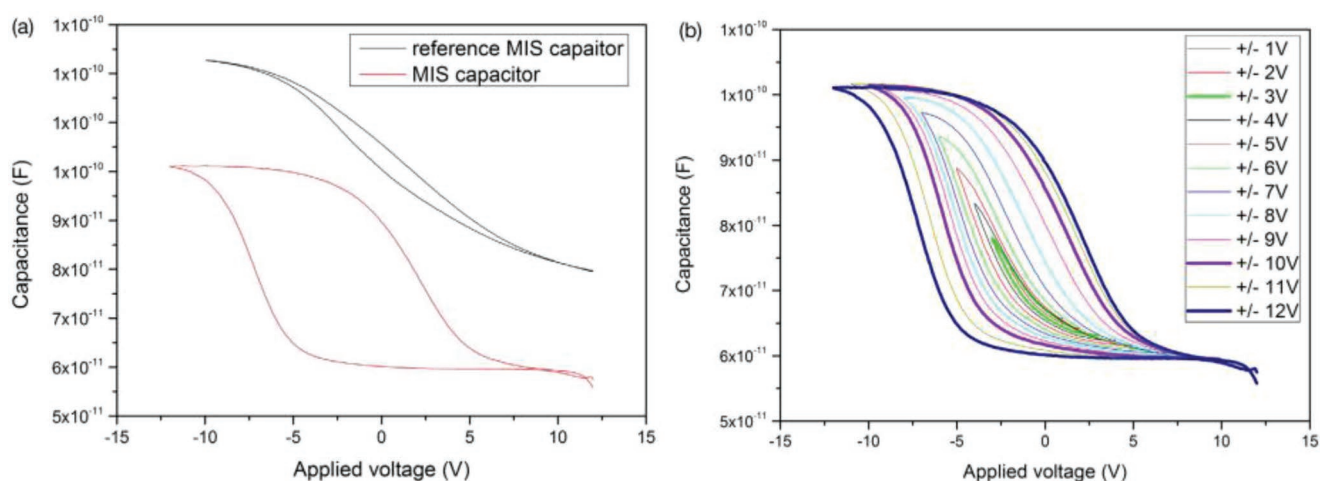


Figure 8. a) The reference device capacitance–voltage behavior shown in comparison to the devices with silicon nanowire. This demonstrates the charge storage ability of the nanowires and the charge build. b) The right image shows how the curve and the hysteresis thereof is depend on the voltage sweep window, demonstrating a kind of voltage scaling behavior. This image is reproduced under the terms of the Creative Commons Attribution 4.0 International License.^[99] Copyright 2016, The Author(s), Published by Springer Nature.

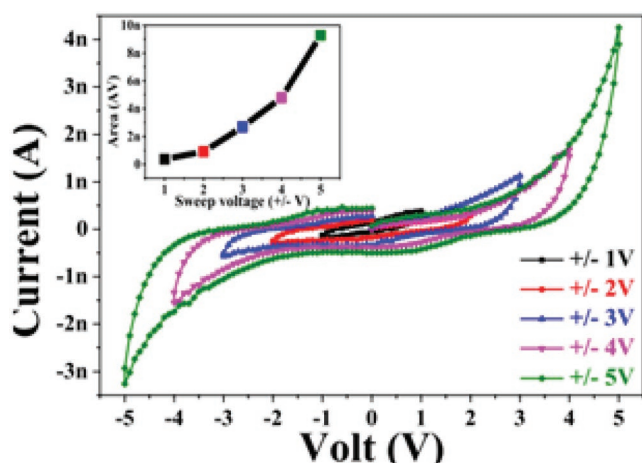


Figure 9. The IV behavior change with increasing voltage sweep window. The inset shows how the area under the curve increases with the voltage sweep window. This image is reproduced with permission.^[93] Copyright 2017, Cambridge University Press.

Another method to follow up on the works that have been published is by focusing on the choice of material. For example, Bozano's work^[45,55] with Alq₃ has been replicated in many studies and have resulted in quite interesting results. Some interesting observation can be followed through from Table 2, like the observation made by Reddy et al.^[49,51,78] and by Busby et al.^[48] in regards to the effect of rate of evaporation on the device behavior. Interestingly, Reddy et al.'s^[49,51,78] devices exhibit charge storage switching mechanism, while Busby et al.^[48] reports the observation of filamentary conduction. Busby et al.^[48] reported that the electrode diffusion, not the interface stress (as is popularly claimed) seems to affect the switching. The electrode diffusion was found to be depend on the evaporation rate of the electrode, wherein lower rate of evaporation led to a decrease in the metal porosity. On the other hand, Reddy et al.^[49,51,78] reported that a lower evaporation rate in the tri-layer structure resulted in the formation of NPs with oxide layer insulation which is favorable for the polymer-doping type charge storage switching behavior. Other works that have been reported for Alq₃ have also been reported in the Table 1.

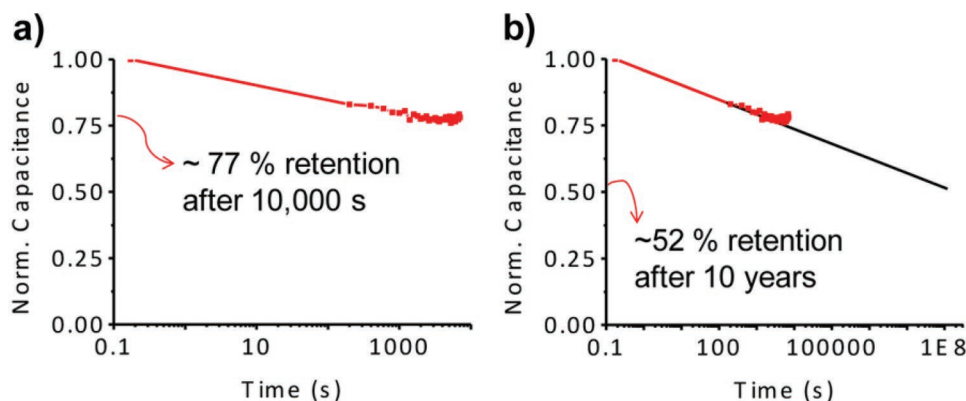


Figure 10. Device charge storage retention results by Suresh et al.^[102] showing retention for a) 10 000 s and b) more than 10 years of extrapolated charge retention. Reproduced with permission.^[102] Copyright 2015, American Chemical Society.

There have been several more works that have taken place in OMDs but they will be referred in the next section the results from the studied will be investigated in the context of the different parameters that affect the switching mechanism.

6. Influencing Factors to Bistable Switching

A closer look at the history of the development of the OMDs reveal that the same structure and often consisting of the same material design is capable of exhibiting mutually distinct behavior. This kind of behavior can only be understood by paying attention to some of the factors that can contribute to the bistable switching process. These factors will be analyzed in this section: 1) Nanoparticle contribution, 2) Ligand molecule contribution, 3) Nanoparticle concentration contribution, 4) Preconditioning/forming contribution, 5) Electrode contribution, and 6) Organic layer contribution

6.1. Nanoparticle Contribution

The role of the interlayer has been the center of a lot of discussion since the last two decades. Ma et al.^[107] discussed about this layer as being indispensable for switching and that no bistable switching was found to occur without it. However, it was also observed that bistability was observed only when the interlayer was more than a critical value of 10 nm. Bozano et al.^[55] too found that the interlayer was an integral part for bistable switching. However, two major differences marked this work from that of Ma et al.,^[67,69,71,74] in which they obtained a N-curve switching, as opposed to the bipolar S-curve switching in the former case. The second major observation by Bozano et al.^[55] was that, for a reliable switching behavior, the interlayer must not be more than 10nm. This was almost contrary to the initial findings, but the reason specified by them was that the prerequisite for device switching was the discrete nature of the NPs, so that they can act as charge traps.

The effect of the interlayer thickness was further investigated in 2009 by Reddy et al.^[49,78] Reddy et al.^[49,78] investigated the interlayer on an indium doped tin oxide (ITO)/Alq₃/Al/ Alq₃/Al device structure with different inter layer thickness ranging

Table 2. Shows a detailed description of the works from Table 1; These works have been further classified depending on the type of curves that have been observed and the performance of the device that have been reported.

Switching type	Device structure	Switching mechanism	ON/OFF ratio	Retention	Ref.
Switching by either polarity, NDR	Al/Alq3/Al/Alq3/Al,Cr,Cu,ITO,Au,Ni	Simmon-Verderber-like switching	–	–	[45]
	Al/Alq3/Ag,Cr,Mg,Cu/Alq3/Al	Simmon-Verderber-like switching	–	–	[45]
	Ag,Al,Au/Alq3/ITO,Au	–	–	–	[103]
	Al/Alq3/Ni/Alq3/Al	SCLC, Thermionic-field-emission	10^3	–	[46]
	Al/ α -NPD/Alq3/Ni/Alq3/ α -NPD /Al	SCLC	$\approx 10^2$	≈ 10 years	[47]
	ITO/Alq3/Ag	CF formation	$\approx 10^5$	2 years	[48]
	Al/Alq3/Al/Alq3/ITO	Fowler Nordheim tunneling (ON state) Poole-Frenkel (OFF state)	$> 10^5$	> 3500 s	[49,50]
	Al/Alq3/MoO ₃ NPs/Alq3/ITO	Thermionic emission (OFF state) Ohmic conduction (ON state)	$\approx 10^3$	≈ 4500 s	[51]
	Al/Alq3/Al,Au,ITO	–	–	–	[104]
	Au/Alq3/Au,Al/Alq3/Al	SCLC	10^4	4 h	[105]
WORM	Al/Alq3/Al/Alq3/Al	Thermionic emission (ON state)	$\approx 10^4$	8000 s	[52]
	Al/ZnSe/Al/Alq3/Al	Ohmic conduction (OFF state)	–	–	–
	Al/Alq3/Al	CF formation	10^5	≈ 20 min	[53]
	ITO/Alq3/Ag	CF formation	–	–	[106]

from 5 to 20 nm using tunneling electron microscope (TEM). It was found that the ON current increased with an increase in the interlayer thickness, but so did the OFF current. But after a critical thickness, any increase in the interlayer thickness led to the decrease in the ON and OFF current (shown in **Table 3**). The real impact of the interlayer was accessed by the ON/OFF current ratio. This revealed a pattern of optimum thickness until which the ratio increased proportionally with the thickness of the layer. But beyond this thickness, which was found to be around 10 nm; the currents ratio began to fall.

The TEM analysis revealed a core-shell like structure, where aluminium NPs were surrounded by an oxide shell (see **Figure 11**). The thickness-dependent ON/OFF current was observed to be a consequence of different NP sizes in these interlayers. It was found that at lower thicknesses the size of the NPs were too small and this gave rise to lower current values due to the higher coulombic energies that needed to be overcome. But as the thickness increased the NPs sizes increased to a considerable size where the charging energies were lower than before and hence the ON–OFF currents

increased correspondingly. But with an even greater interlayer thickness (beyond 10 nm), the NPs were found to coalesce and form a continuous film which did not “hold” any charges and hence the switching collapsed. This study brought two key points in the study of the role of the interlayer in the bistable switching of the device. The first point was that the switching was depend, not so much on the intermediate “layer;” instead it was the presence of discrete NPs within the interlayer that made the switching possible. The second point was that the switching depended on the ability of the NPs to store charges and also to retain it. This was the reason why the NPs needed to be isolated from each other. The reduction in the ON/OFF ratio with the coalescing of the NPs demonstrated the necessity of keeping the NPs isolated from each other.

Tondelier et al.,^[75] observed that the interlayer was not as necessary as reported earlier. Device switching even in the absence of the interlayer, and the OFF-state to ON-state switching was concluded to be due to “field- induced-percolation of the NPs, thus forming nano- filamentary pathways through the organic film.”^[75] Studies by Nau et al.^[96] in 2014, was focused to address this issue of whether or not the interlayer was truly integral for the switching. Nau et al.^[96] studied ITO/Alq₃/Al/Alq₃/Ag device structure to analyze the interlayer and its contribution to the switching process. It was observed that the switching of the device was independent to the presence or absence of the interlayer. Photoconduction measurements and ac measurements were taken to find the equivalent circuit of the device. The measurements revealed that the switching was accompanied by a change in the value of shunt resistance by a few orders. The conclusion, therefore, was that the unipolar switching (that was observed in these devices) had nothing to do the charging effect, but was instead due to filament formation. No attention, however, was paid to the interface between the electrode and the active layer. It has been observed recently, that insulating

Table 3. The table denoting the relation of the ON/OFF ratio with the interlayer thickness. The ON/OFF ratio increases with the increase in the thickness until an optimum thickness (around 10 nm), after which any further increment in interlayer thickness results in a decrease of the ON/OFF ratio. Reproduced with the permission.^[78] Copyright 2009, AIP Publishing.

Thickness (nm)	I_{OFF} (A)	I_{ON} (A)	I_{ON}/I_{OFF}
0	9.49×10^{-11}	1.29×10^{-9}	13.6
5	1.43×10^{-10}	3.89×10^{-8}	2.72×10^2
10	2.17×10^{-10}	4.14×10^{-5}	1.91×10^5
15	3.69×10^{-7}	5.69×10^{-5}	1.54×10^2
20	7.72×10^{-5}	1.02×10^{-4}	1.32

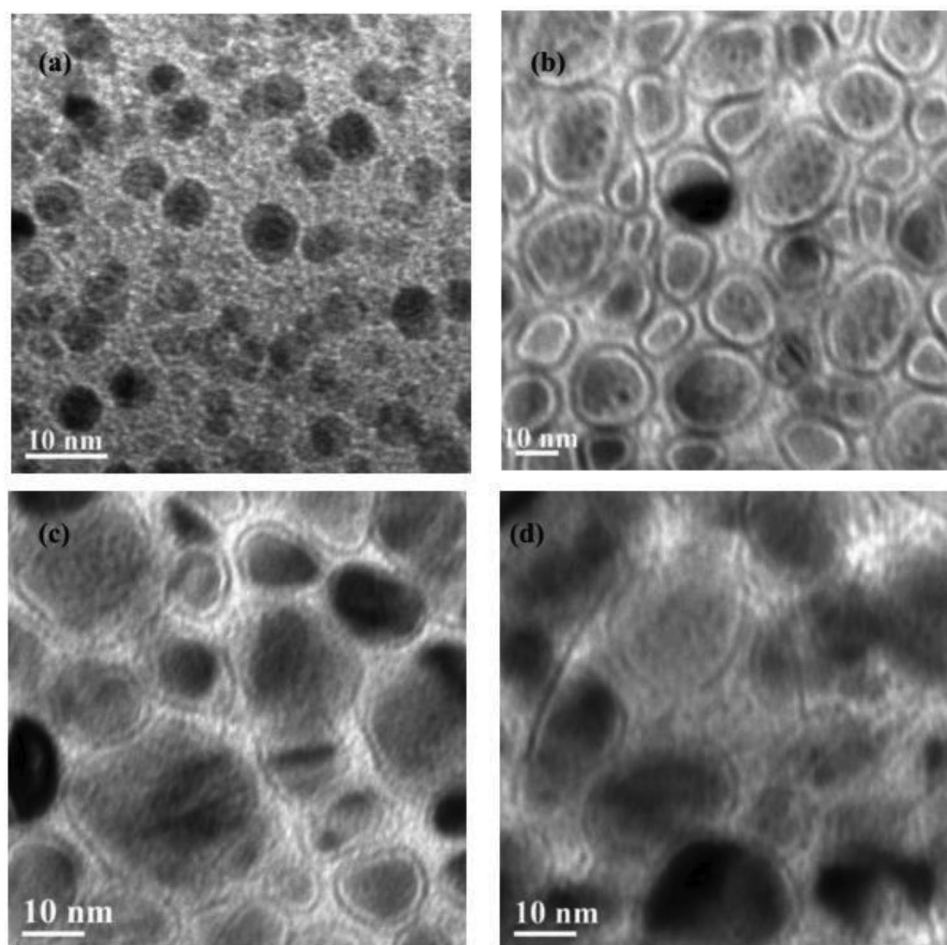


Figure 11. The above image shows the interlayer at various thicknesses- a) 5 nm, b) 10 nm, c) 15 nm, d) 20 nm. a,b) At lower thicknesses, the inter-layer mostly consists of discrete aluminium nanocrystals that are coated by an ultra-thin (≈ 1.5 Å) layer of aluminium oxide, which helps to isolate one nanocrystal from the other. This was proposed to increase the charge storage capability and hence lead to increased ON/OFF ratio. c,d) But as the interlayer thickness is increased, the nanocrystals begin to coalesce with each other and form bigger and bigger lumps, thereby decreasing the ON/OFF ratio. The discrete nanocrystal of smaller dimensions was found to be ideal for achieving high values of ON/OFF ratios. Reproduced with the permission.^[78] Copyright 2009, AIP Publishing.

layer undergoes soft breakdown, to varying degrees, due to metal doping.^[106–109]

Zhang et al.^[98] investigated a planar structure in 2019, to investigate the Joule's heating process that the device underwent during electroforming; and the effect this process had on the nanoparticles. It was found that the device under test, required an electroforming process before they exhibited bistable switching with ON/OFF ratio of three to four orders. The images from before and after electroforming revealed precious insight on how the forming process affected the nanoparticles. It was observed that the NPs had coalesced with each other under the enhanced thermal conditions and has become four times bigger than their initial sizes. (refer **Figures 12** and **13**).

Raman analysis on the devices from before and after the forming revealed further changes in the structural morphology of the device. The broadening of several peaks into a convoluted peak indicated the presence of amorphous sp^2 carbon in the device (see **Figure 14**).

The switching mechanism was concluded to be due to SV mechanisms, and that the NPs were playing a crucial role in the charge trapping and hence contributing to the switching by influence a change in the electrical conduction. But the conduction in the ON state was concluded to be due to the combination of charge trapping due to the NPs and the amorphous sp^2 carbon.

6.1.1. Ligand Molecule Contribution

The ligands are molecules that are added to stabilize the NP surface and to prevent them from agglomerating with each other. The ligands prevent the NPs from coalescing together and they also shield the NP from interacting with the conjugated polymer molecules in the active layer.^[88] But contributions from the ligands, referred as “ligand effect”^[88] was found to be too important to ignore. Ouyang^[88] investigated this effect in devices with the same structure, but differing from

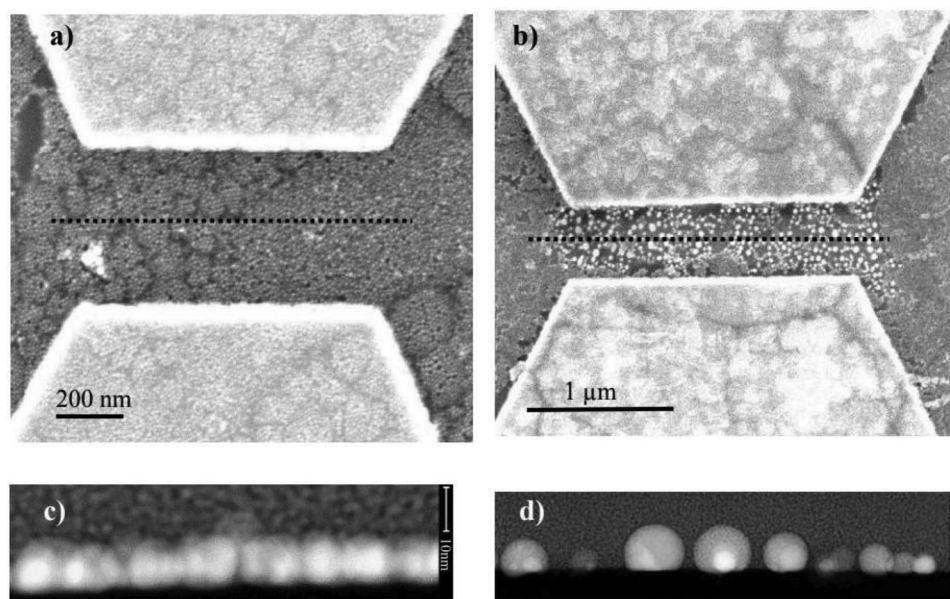


Figure 12. a,b) SEM images of the device before and after the forming. c,d) A cross sectional image, showing the nanoparticle size increase by almost four times the initial size. The image is reproduced with permission.^[98] Copyright 2018, Royal Society of Chemistry.

each other only in the ligands that terminated the NPs. Gold nanoparticles were used with different capping molecules, like 1-dodecanethiol (DT),^[77,84] 2-benzeneethanethiol (BET),^[108] 2-naphthalenethiol (2NT),^[84] and polyaniline (PANI).^[83] All the above-mentioned molecules were used as ligands and PANi functioned as a nanocomposite matrix while stabilizing the nanoparticles.

Ouyang et al. reported his work in 2004,^[77] when he reported a multiple cycle switching device which Au-NPs terminated with DT. But the effect of ligands became noticeable when the Au-NPs were capped using 2-NT.^[84] The most significant difference between this device, Al/Au-2NT NP+PS/Al and the rest of the devices was that it was a WORM device. It could be switched from OFF state to ON state, but the device could not

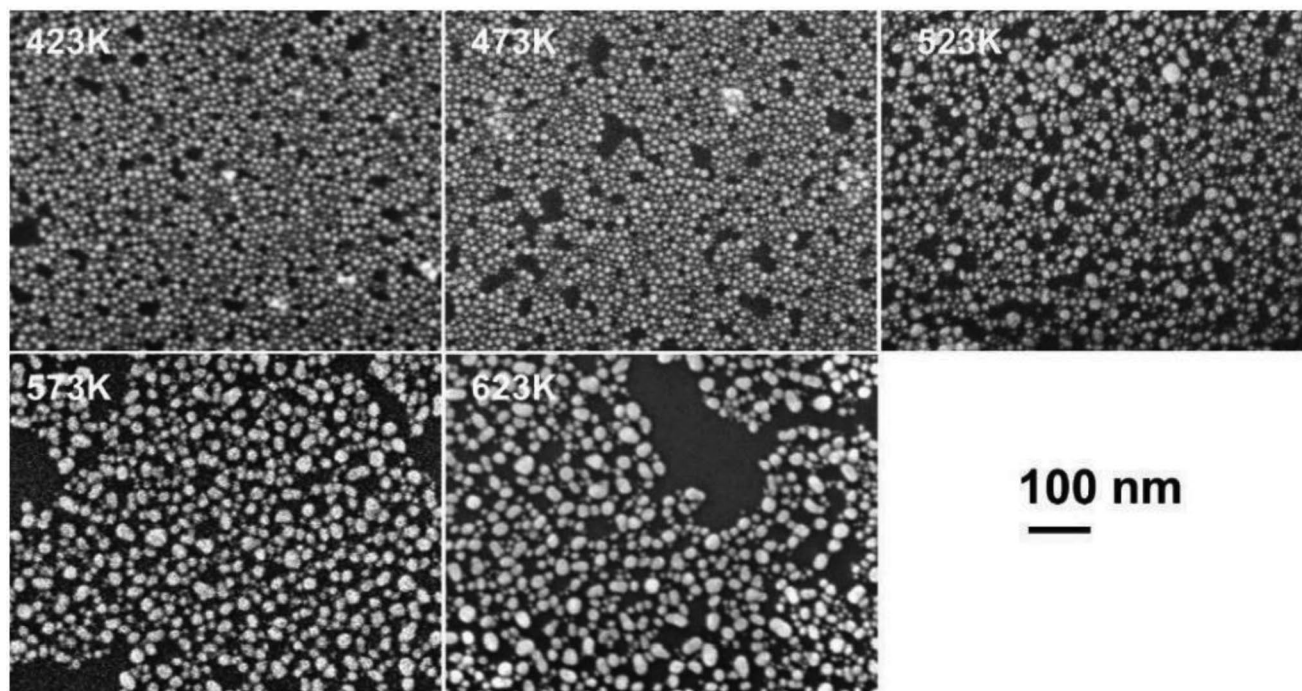


Figure 13. Images of the nanoparticles at different temperatures through the annealing. The size of the nanoparticles can be observed to increase with increase in temperature, indicating a coalescing of the nanoparticles. The image is reproduced with permission.^[98] Copyright 2018, Royal Society of Chemistry.

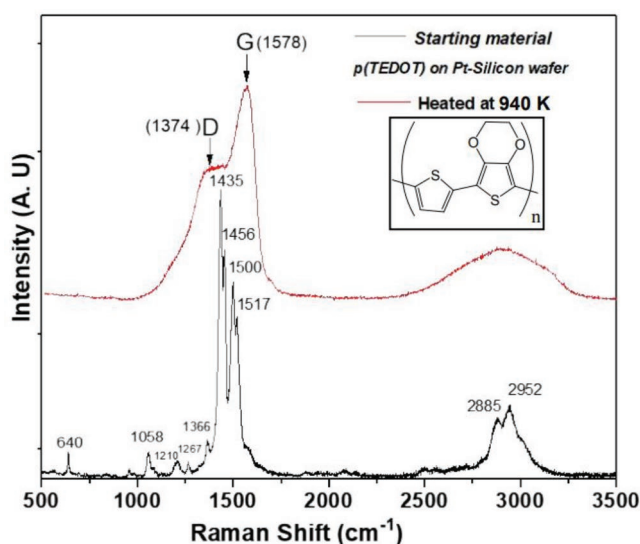


Figure 14. The image shows the Raman spectra of p(TEDOT) polymer before and after annealing. The spectrum after annealing shows a spread-out peak, indicating the presence of amorphous sp^2 carbon bonds. The image is reproduced with permission.^[98] Copyright 2018, Royal Society of Chemistry.

be turned back to the OFF state. This is particularly interesting, because the device with the same structure, but capped with BET (Al/Au-BET NPs+PS/Al), could be switched reversibly. The switching was attributed to the electric-field enhanced charge transfer between the ligands and the NPs. However, a proper understanding of the process is still not achieved. The Au-2NT device was also found to have a gradual switching, unlike the Au-BET device which exhibited the characteristic threshold voltage where the current rises abruptly from low-conduction state to high-conduction state.

Another noticeable contribution of the ligands can be noticed when PANi was used to make a nanocomposite device in polyvinyl alcohol (PVAc) matrix.^[83] In this case the PANi attached to the NPs and induced charge transfer between NPs under the influence of an external electric field. But when the switching was tested, the Au-PANi devices exhibited a unipolar switching with the NDR observed at voltages greater than 3 V.

This goes on to demonstrate that the bistability in nanocomposite devices depend on the ligands too. While some induce a WORM behavior, others help repeatable switching. A careful investigation of the field requires a meticulous comparison of result to achieve a better understanding of the ligand contribution in the device conduction switching.

6.1.2. Nanoparticle Concentration Contribution

Another important factor that must be considered in the analysis of the switching mechanism is the nanoparticle distribution in the polymer matrix. A study by Prime and Paul^[89] investigated the effect of the distribution density of the nanoparticle in the switching behavior of the device. An MIM device structure was investigated with gold nanoparticles dispersed in polystyrene (PS) matrix. The gold nanoparticles were stabilized

and passivated using capping molecule, octadecylamine and tri-*n*-octylphosphine oxide (Q-Au); the switching mechanism was based on a charge transfer between Q-Au nanoparticles and a molecule, 8-hydroxyquinoline (8HQ).^[89] The switching techniques and the charge retention capabilities were studied for Al/Q-Au NPs+8HQ+PS/Al devices, where the concentration of Q-Au was varied for each device.

It was observed that the devices with lower concentrations switched reversibly and repeatedly, although it took a few voltages sweeps to stabilize the IV curve. The device was found to retain the charge for more than 10 000 read pulses; thereby demonstrated that the Q-Au nanoparticles were able to successfully trap the charges for longer time periods. But for the devices with really high Q-Au concentration, the device was found to successfully switch from a low conduction state to a high conduction state only once. The device was a WORM device, and no transition could be achieved from the high conduction ON state to low conduction OFF state.

Other than being a WORM device, the ON current was a few orders higher than the OFF current compared to the previous devices. It was concluded that the different switching pattern was caused by different switching mechanisms operating in the same structure due to the closer proximity of nanoparticles; the reversibly switching devices were concluded to be due to charge trapping by Au-NPs, but the WORM device switching was due to non-reversible filamentary formation under the influence of the applied electric field. This claim was based on the capacitance-voltage (CV) curve, which showed the storage of charges in the device as a shift in the reverse sweep. While the former device showed an increase in the capacitance during the voltage sweep, the sudden drop of capacitance in the WORM device at the point of switching, indicated the short-circuiting of the device between the top and the bottom electrode. The increase in the conduction with increase in the NP concentration can be examined by the works of Schon and Simon,^[41] where it has been noted that the closer NP distribution could increase the chances of electron wave coupling and thereby lead to increasing conduction due to the delocalization-effect of electrons (more information can be found in Section 7.1.4.). The increased temperature due to the high current densities could act as a positive feedback loop for further increase in current until the NPs coalesce together to form a permanent filament within the device cross section. This kind of behavior is not exclusive to nanoparticles-based devices.

Majumdar et al.^[109] noted a similar kind of behavior in fullerene-based bistable devices too. At low fullerene concentrations, the device did not undergo any switching and the current levels were a few orders lower than when the C-60 molecule concentrations were increased. At higher concentrations the device switched successfully, but when the C-60 concentrations were increased even further, the device became a WORM device and switched only once. The WORM behavior at higher concentration levels were concluded to be due to the fullerene molecules having formed “conductive networks” within the device.^[109]

6.2. Pre-Conditioning/Forming Contribution

The behavior of the device switching and the mechanism depends much on if and how, the device has been “conditioned.”

This pre-conditioning of the device has been observed repeatedly by researchers, but only a few have reported it. For example, Dimitrakis et al.^[110] investigated the gold nanoparticle OMDs, and observed that out of the devices that exhibited an N-curve behavior, most of them were exerted under a forming process. The testing procedures and the scheme of testing sequences were rigorously detailed in the report; such attention to detail can be a model for works that document the device behavior. Without crucial details like the need for electroforming, the actual device behavior can be mistaken easily. As detailed in Section 6.1., Zhang et al.^[98] reported how high currents could lead to high temperature generation, which in turn was capable of altering the device morphology and the switching properties in ways that did not exist in the pristine form. These works together demonstrate how the device behavior can be altered differently depending on the preconditioning that the device has been exerted to.

The effect of preconditioning has been studied far extensively in inorganic systems, but these results can be borrowed to understand and elaborate some of the unclear behaviors that have been observed in the organic systems. For example, it has been reported that the ON state conduction and the electronic behavior (semiconductor or metallic) of nickel oxide (NiO) based devices depends on the current density used in the forming process of the device. Nickel oxide has been known to exhibit conductive filament (CF) switching by cation-based switching. And even though this kind of switching behavior has been examined in detail in Section 8.1.1., some of the results will be borrowed here. It has been observed, that a small current used in the forming process will yield a semiconducting behavior in the ON state, while high forming currents will facilitate the formation of metallic-type conducting filament.^[90] This observation is based on the measurements that while one device that has been preconditioned with a low forming current led to the ON state which exhibited sensitivity to the ambient conditions,^[111] a different study observed metallic behavior in NiO-based devices that was preconditioned with high forming current.^[112,113] This might perhaps address the differences in the temperature-dependent conduction that were observed, or suggest further avenues of research in this direction. For example, can this reconcile differences like the semiconducting ON-state behavior observed by Ma et al.^[68] and the “metallic” ON-state observed on the same device structure when investigated by Tondelier et al.^[75]

6.3. Electrode Contribution

The role of electrode in the bistable switching has been the focus in many studies.^[20,25,30] The suspected contribution of the electrode is particularly imperative, since a direct involvement of the electrode can at times, if not always, make it difficult to ascertain that the switching behavior observed in the device is truly a property of the nanocomposite species (nanoparticles or acceptor-donor molecules) under investigation. Tondelier et al.^[75] observed that the aluminium interlayer was not necessary for the switching. This led to the conclusion that the switching that were being reported was not due because of charge storage, but instead because of the metal diffusion occurring from the electrode.

Paul and Salaoru^[23] investigated the role of the electrode in the switching mostly focusing on the device ON/OFF ratio. The O-curve observed in the previously fabricated devices^[79,86,89,92] generally exhibited much lower ON/OFF ratio than the publications that reported on the same systems. But in this study, the result from a device consisting of a layer of PVAc deposited between two aluminium electrodes were compared with a device that had additional aluminium oxide on the bottom electrode (see Figure 15). The IV behavior of these devices revealed the extent to which electrode and the native oxide on them can contribute to the switching behavior of the device. While the device with no aluminium oxide was tested to find little or no hysteresis at all, the device with a native oxide exhibited huge differences between the ON state and the OFF state. The ON/OFF ratio was observed to be about 3 orders of magnitude, and even the behavior of the curve was found to be different. While the other devices exhibited O-curve, this device exhibited an S-curve with a region of saturation. This demonstrated that the switching that was witnessed was not a bulk-limited property, but interface-limited. It has been pointed out that such interface-limited switching is not electronic property of the molecule, but dominated by thermally activated components.^[30] Nau et al.,^[96] also reported such switching behavior and concluded that the switching was due to conductive pathways. Such parasitic contributions of the electrode and the oxides must, therefore, be taken into consideration when a device is being investigated, so that the electrode-dependent factor may not undermine the far smaller molecular interactions and the electronic effects.

6.4. Organic Layer Contribution

The organic materials used to fabricate the memory devices, in the reported literature, are having various purposes. Sometimes it is intended to be the conducting medium, wherein semiconductor layers are electrically modulated the conductance of the material.^[68,74] At other times, these may simply be intended as a matrix, that holds the embedded molecular or macromolecular entity and maintained its physical isolation, in terms of physical proximity from each other. But nonetheless, the organic active layer does have an impact on the behavior of the device to a greater or lesser degree.

In a detailed discussion of OMDs, Kim^[32] mentions that almost all the fundamental properties that the organic materials are sought after, find their origin in the molecular structure and the interaction within the molecule. The characteristic softness and plasticity of the polymer, which can be attributed to the weak van der Waal interaction and intermolecular coupling; also favors high energetic disorder. Due to this reason, the thin film organic layers themselves have a high density of charge traps; the problem though is not the traps themselves, but the ability (or inability) to control it.

Non-volatile polarization due to electric charge trap and molecular re-alignment under the influence of an external applied voltage is observed in certain polymers.^[32] This effect has been prominently observed in organic field effect transistors and the rogue hysteresis, which is bias direction-dependent has been investigated extensively.^[114–119] Tsai et al.^[114] reported

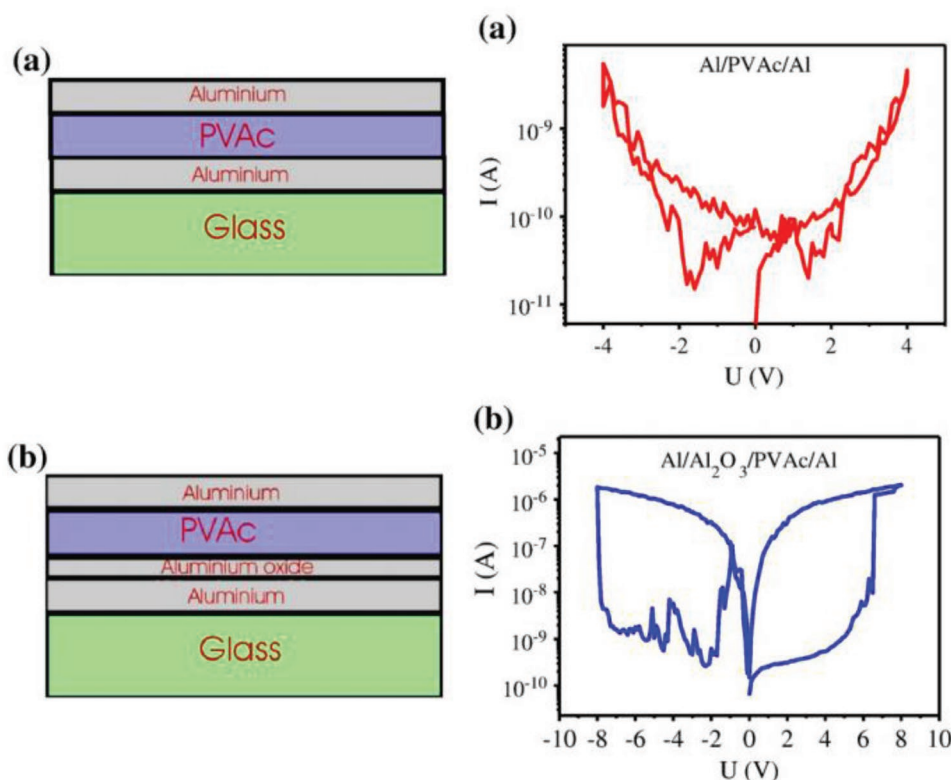


Figure 15. The image indicates the effect of the aluminium oxide on the IV behavior of the device. The characteristic S-curve switching can be seen in the device with aluminium oxide. Reproduced with permission.^[23] Copyright 2017, Elsevier.

such “bias-dependent-hysteresis” in polyvinyl-alcohol (PVA) devices, where the electronegativity due to the hydroxyl group ($-\text{OH}$) lead to the build-up of a false field. This electric-field was reported to be due to the gradual alignment of the $-\text{OH}$ group in the direction of the applied bias along the interface, such that a net charge polarization is observed. The polarization that developed across the gate terminal due to such molecular alignment, resulted in the false switching of the device (see **Figure 16**). Egginger et al.^[115] referred to such property as the metastable polarization in non-ferroelectric materials; the difference between the thermodynamically favored ferroelectric

polarization being that this effect was a mere consequence of slow dielectric response of the molecule to the external bias. Apart from the slow molecular movement, Egginger et al.^[115] held factors like charge injection from the semiconductor into the organic dielectric material, mobile ions in organic material, slow emptying of the minority and majority trap states in the organic materials and others, responsible for the bias-induced-hysteresis in organic devices.

These hysteresis windows might be misunderstood to be “memory behavior” if not careful and can lead to misinterpretation of what is organic layer trap-induced noise.

Other works have noted that certain polymer undergo electric-field-induced phase transformation due to conformational changes.^[120,121] In molecules such as polymers containing pendant carbazole group, it has been observed that under the influence of an external electric field, disordered structures rearrange themselves into a π - π stacked order. Such a change from disordered phase to ordered phase can lead to a switching of the device from a low conduction state to a high conduction state.^[7]

Summary: From the discussion above, this section aims to point out several examples of contributing factors that might have parasitic influence on the final behavior of the device. Based on these examples, it becomes clear that the confusions that persists in this field might complicated due to the several factors that weigh-in on the final behavior. This may result in the lack of repeatability of devices even when a work might be exactly replicated.

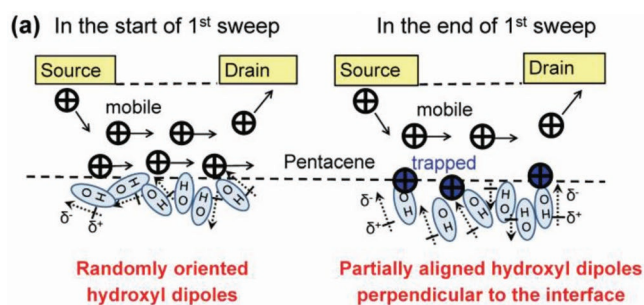


Figure 16. The image shows how the molecular electronegativity in PVA molecule can align according to the direction of the applied external bias. This molecular alignment can induce false device switching (see the right image) due to the net polarization build-up. Reproduced with permission.^[114] Copyright 2013, John Wiley and Sons.

6.5. Switching Mechanisms

Having discussed so far the background of the field and the several factors that have an influence on the switching of the devices, it seems imperative to point out the myriad of switching mechanisms that exist in the literature. In this section, these mechanisms will be discussed in varying degree of detail. Charge trapping mechanism has been covered in great depth to disentangle the myriad of model that have come to claim charge trapping as the main reason for the conduction switching. However upon closer inspection reveal several finer detail that distinguish one model from the other. Similarly other mechanisms have been covered too, for example, the filamentary mechanism has been deconstructed to the several categories to enunciate the differences in each mechanism. Furthermore the filamentary conduction in polymers have been pointed out too, in order to point out the several features of these mechanisms in different materials and contexts.

7. Charge Trapping Mechanism

Many articles have discussed the charge trapping mechanism in the bistable switching process more often focusing on the materials used and a broad discussion of the commonly agreed mechanisms for the switching.^[25,30,32,17] But while charge trapping can be attributed to cause bistable switching, a lot of confusion exists in this area. This review article is intended to focus mainly on the differences within the broadly defined “charge trapping” mechanism used when explaining the behavior of the memory devices. It is important to address the fine differences as it will bring clarity and clear distinction within the many nuances of the charge trapping mechanism; a lack of which often lead to misunderstandings and misinterpretations of results and the device behaviors.

7.1. Polymer Doping Model

It was first reported by the Yang group^[12,68,69,71,74,122,123] from UCLA, to address the device behavior which was observed then. Their devices displayed an ON/OFF ratio of 6 orders; the ON and OFF states appearing stable until an external stimulus (erase signal) was applied. And even though the exact mechanism behind such behavior was unclear, the metal interlayer was found to be integral in the process (refer Section 6.1. for more details). The IV behavior, sometimes referred to as, the “diode memory characteristics,”^[32] had an S-curve and was dependent on the presence of aluminium oxide over the metal interlayer was deemed integral for the isolation of the metal clusters and the retaining of the trapped charges.^[69,71]

This model of polymer doping (PD) was proposed after a theoretical model was developed in 2004,^[123] to address the switching behavior. The theoretical model was based on the assumption that the conduction occurred due to the hopping of charges, the metal interlayer playing a sensitive role in the resonant tunneling of charges.^[123] The metal interlayer thickness contributed critically according to the theoretical model, where at lower thicknesses it was predicted, conduction could

not occur. On the other hand, any deviation over the critical thickness, was proposed to result in exponential decay in the transmission probability of charge tunneling. These predictions were reported to corroborate with the further testing that were carried out on the devices.^[71] The metal interlayer was claimed to be sensitive to the “metal-insulator transition” process^[69] due to the charge storage that occurred in it; the charge redistribution in the nanoparticles thereafter leading to a positive-negative region.^[69,123] It was proposed that the charge storage and the subsequent redistribution led to the “doping of the organics.”^[69] The device bistable switching from ON state to OFF state and vice versa were proposed to be the result of this doping. Just like a forward bias facilitated the formation of a channel in a transistor, the doping of the organic layer was proposed to assist the device switching from the low conduction OFF-state to a high conduction ON-state. The device switched back from the ON-state to OFF-state, under this model, when the reverse bias forced the trapped charges out from the NPs.

The metal interlayer, however, was not considered as a single continuous layer embedded between organic layers. It was assumed to be consisting of a group of metal nanoclusters that were separated from each other by a thin (≈ 16 Å) layer of aluminium oxide.^[69] The oxide presence was prescribed as being imperative for the formation of the nanoclusters; the hopping model predicting the thin insulator layer to be perfect for tunneling between the nanoclusters. The second instance where the oxide layer was reported to play an important role in the switching was when metal-organic compounds were observed to form at the metal electrode-organic interface whenever hot metal was claimed to be deposited over cold organic layer.^[71]

This model was able to successfully address the S-curve bistable switching behavior of the device. But it did not address if the oxide layer, in itself contributed to the switching behavior; in ways other than was assumed. The high ON-state current levels were not taken into consideration; as Joule’s heating becomes predominant in such current regimes. And even when Al_2O_3 was already known to contribute in filamentary conduction, this wasn’t taken into consideration. This charge- hopping model was proposed by ignoring the prospect of thermal contributions that might lead to unintentional contributions from other mechanisms in the switching, as was demonstrated by Paul and Salaoru.^[23]

7.2. Simmons and Verderber Mechanism

The Simmons and Verderber (SV) model represents the works that have been done above 50 years ago, in terms of explaining the switching behavior of devices. The model has been commonly cited so, in reference to the publication that Simmons and Verderber reported in 1967; which however was merely one of the many reports that they published in the area.^[70,124] Their work with thin film insulators sandwiched between metal electrodes, demonstrated that the device exhibited N-curve behavior after electroforming. Their results led to the proposal that the presence NDR and a hysteresis in the IV curve due to the presence of nanoparticles that had detached from the electrodes and migrated into the insulator layer in the presence of an applied electric field.^[70] Since then, numerous

reports have attributed the bistable switching of the devices to the SV mechanism.^[45,55,57–60,73,103,125–132] Owing to the popularity of the SV model and the number of publications that have cited the device behavior to be similar to the SV model, it seems imperative to analyze the features of the SV model. Some of the highlights of the SV model are as follows: a) The studies by Simmons and Verderber were conducted initially on silicon monoxide (SiO) thin film insulator placed between metal electrodes.^[72] While the switching behavior of the thin film insulator was studied extensively, it was noted that the electroforming process was a prerequisite before any switching behavior could be observed.^[64,124] Electroforming process involved applying a very high field (typically about 10 V across 200 nm thick insulator) for a very short time frame (approximately a few seconds),^[45] where the positive bias was applied over the gold electrode^[63] and various other materials were used for the other electrode.^[124] The “forming” process was found to condition the device, and was performed at low pressure conditions (0.1 Torr pressure at room temperature). b) The forming process was found to be an electrode-specific. For example, while Au/SiO/Au could be formed perfectly well, the same was found to be quite incapable for Al/SiO/Al device. It was therefore concluded that the switching process depended on the diffusivity of the electrode in the insulating matrix. The ability of gold nanoparticles to diffuse into the sea insulator was concluded to be the reason for such a behavior. c) The IV behavior showed an N-curve behavior, wherein the current displayed a local maxima followed by a local current minima.^[36] The region followed by the local current maxima was called the negative differential resistance (NDR), due to the negative slope that arise as current decreases even with increment in voltage. The NDR region, as explained under SV model, was assumed to be due to the band of impurity energy levels that the gold atoms introduced in the insulator matrix. Under the SV model, the impurity levels promoted the charge flow, thereby leading to the increase in the current flow, as the trap levels begin to gradually “fill up.”^[70] As the trap levels get completely occupied, the local current maxima is observed in the device; beyond this level further charge injection is reduced due to the opposition experienced by the space-charge field generation. d) The device conduction reported by the SV publications observed an almost temperature-independent device conduction. The temperature dependence in the devices was found to be inadequate to be considered as being thermally driven. The conduction was, therefore, concluded to be due to the tunneling of charges.

The SV model has been successful in addressing most of the device behavior and switching features, but there are a few open questions that are admittedly unclear.^[73] Under the SV model, as long as the trap levels are unoccupied, the conduction will be high and the device will be in the ON-state. The current reduction and the NDR region occurs only after the NPs are completely occupied^[43] and further charge injection experiences an opposition due to the space-charge field inhibition.^[55] One of the clear differences between the PD model and the SV model is seen here as they predict contrasting effect on the device conduction due to the charge trapping in the NPs. While the PD model predicts that the charge injection in the NPs lead to enhanced device conduction and consequently assist the OFF-state to ON-state transition; the SV model predicts that the

continued charge injection into the NPs will eventually result in the decrease of the device conduction and lead to the ON-state to OFF-state switching. This however, results in an open question: If a device will completely unoccupied trap levels initially yield high conduction ON-state, then why is it that a pristine device with no occupied energy levels begin conduction in the low conduction OFF-state? This prediction from the SV model continues to maintain inconsistency with the experimental device behavior observation.

Another point of contention is the electroforming process. The SV model makes it clear that the forming process was imperative for the switching behavior to be observed. The effect of electroforming has been briefly mentioned in Section 6.2.; the large number of additional variables that the process adds to the systems has been presented. The electroforming process adds many uncertainties, especially about the impurity level prediction, as the nanoparticle size and position in the polymer matrix would vary on the forming procedure.^[55] And for this reason, it has been suggested that while NPs can be created by driving metal electrodes into the organic layer, by the forming process; it may not be recommended due to the uncontrollable nature of the process and the non-uniform distribution of the particles.^[43]

Having discussed the features of the SV model and the challenges, it may be advised that due considerations be paid to the abovementioned points before a device behavior is classified under the SV model. Since the model was based on the initial works of Simmons and Verderber, it can be safely assumed that any work that attributes an SV-like switching in their devices, affirms that the device behavior aligns with all the SV model features, unless explicitly mentioned otherwise. The works by Bozano et al.^[45,55] can be taken as an example in this context. The device behaviors were not only analyzed for the unipolar switching or the NDR region, but the temperature-based conduction and the electrode-independent switching were analyzed. And while the work attributed the switching behavior of the device to the SV-like behavior, care was taken to mention the points where the device behavior was distinct from the original SV works. This included explicitly mentioning that the switching behavior was observed without forming. Such detailed investigation can be considered a model for future publications in the exploration of the device behavior; especially since opportunities for investigations still exist

7.3. Electric-Field-Induced-Charge Transfer

The electric-field-induced-charge transfer is a proposed mechanism that relies on charge transfer to explain the switching behavior of the devices. Proposed first by Ouyang et al.^[77] in 2004, this mechanism comes closer in explaining how the nanoparticles and the device structures influence the behavior of the device switching. Ouyang et al.^[77] utilized ligand-stabilized nanoparticle and 8HQ in a polymer matrix to achieve device switching. In this model, the nanoparticles are electron-acceptors and 8HQ acts like electron-donors.

Under the proposed mechanism, the bistability is a consequence of electron exchange between the electron-donors and acceptor. This model was demonstrated once again with PANi



Figure 17. TEM image of Au nanoparticles in PANi nanofibers. The black dots are Au-NP of ≈ 1 nm diameter. Reproduced with permission.^[83] Copyright 2005, American Chemical Society.

nanoribbons and Au nanoparticles.^[83] But unlike the previous devices,^[77,84,108] PANi was used as an electron donor and a matrix to keep the nanoparticle isolated along with PVAc (see Figure 17).^[83]

The change in the conductive state of the device was proposed using the charge transfer that occurs between the donor–acceptor species when an external potential was applied across the device. The switching of the device from low conductance to high conductance state was explained to be due to the loss of electrons in the polymer (PANi) which was similar to an oxidation reaction. The oxidation of the polymer was proposed to be the reason for the change in the device conductance.^[90] But as the polarity of the applied signal was reversed, the charge transfer occurred in the opposite direction, hence reverting the device in the original low conductance OFF state. This explained why the pristine devices always started with the low conductance state.

Here again, the polymer matrix is not simply an insulator. It acts more like a modulated conductor, where the charge-transfer assists in the switching of the insulator. This would work well with certain polymers, but more work would be needed to understand the switching mechanism in polymers that are inert and act as insulators. Although it must be noted that this mechanism is quite different from the redox-based conducting filament mechanism. Here, none of the molecular

component is expected to migrate- the flow of the electrons is merely assisted by the charge transfer happening between the donor–acceptor pair.

7.4. Charge Trapping and Internal Field Mechanism

The internal field mechanism is based on the electron-in-a-box model, where a metal nanoparticle acts like a columbic trap and is embedded within an insulator matrix.^[41,42] Paul et al.^[85,86] examined the switching behavior of the device consisting of a fullerene molecule along with 8HQ in a polystyrene matrix, and treated it as an electron trap to explain the behavior with a great degree of success. Many works have been published since, with a similar treatment to explain the bistable behavior of several other devices.^[27,55,87,90,91,95,97,98,133–136] For the same reason, it seems reasonable that the nuances of this model be examined so as to identify its key features.

This model has also been referred as the “dipole model”^[93] and it stresses on the charge accumulation/charge separation in a manner that a surplus internal field can be sustained. Paul et al.^[86,87] discussed this model to explain the bistable switching behavior of the devices when he investigated 8HQ and C-60 molecule consisting device; 8HQ acted like the electron donor and C60 like electron acceptor. While several existing models focused on the effect of the charge transfer on the polymer layer, Paul et al.^[86,87] focused on the effect of charge transfer in the building up of charge and the consequently the net internal field. Raman analysis of the fullerene molecule evidenced charge transfer through a peak shift. But this system was further simplified by Prime and Paul^[92] when the gold nanoparticle charging was demonstrated when a bias was applied by an EFM tip and the charge retention of the nanoparticle was investigated. These results, demonstrated that the internal field model was a valid hypothesis and required due investigation to understand the change in conductivity phenomenon. Further studies with the same system, except with a layer of thermally grown oxide showed an S-curve instead of the normal O-curve which was seen in the previous studies.^[23] This further strengthened the claim that the oxide contribution could shift the device behavior from an O-curve to an S-curve system; a factor that wasn’t paid much attention to. The unreasonable attention to ON/OFF ratio was brought to question against the objective to understand the device behavior. The ON/OFF ratio approach to device building was further raise when it was demonstrated that the gold nanoparticle concentration could be varied to replicate the behavior with high ON/OFF ratio.^[89] But the CV measurements revealed a short-circuiting due to the filamentary growth. Several studies have since then been published to understand the physics behind the conduction switching and the material interacts with lesser focus on the ON/OFF ratio. The core question, as Salaoru et al.^[91] puts it is to investigate the question of what happens when charges are forced through a device in the presence of a field build-up.

The electron trapping takes place when a “write” voltage is applied to the device. The write voltage is chosen to optimally facilitate the tunneling of charges through the thin insulator layer into the nanoparticles, thereby populating it with charges.^[97] Once the charges are trapped (electrons in this case),

removing the external bias results in continuing the trapping as long as two essential requirements are satisfied: First ensuring that the NP is perfectly isolated (or embedded) in the insulator matrix and second, ensuring that the trapped electrons in the NPs do not have enough energy to escape the quantum trap.^[41] The filling up of the nanoparticles with charged particles results in a gradual building up of an electric field inside the device. Thus, an internal field is built up within the device due to the accumulation of the charges within the nanoparticle. The change in the ON-state and OFF-state conduction, according to this model, results from this internal field.^[87] As a result, to revert the device conduction back to the initial condition, an “erase” function is executed, wherein a reverse polarity bias is applied to expel the trapped charges.

The charging and trapping of the charges have been utilized by Saranti et al.,^[99,100] by demonstrating the bistability in nanowires (refer **Figure 18**).

Due to the abovementioned reasons, the role of the polymer layer is distinctly different in this mechanism. In this model, the polymer matrix solely functions in the isolation of the charges. This pre-requisite, also invalidates any active contribution from the polymer matrix in the switching. It must be noted that it doesn't mean that leakage current from the polymer layer is not taken into consideration. In fact, the leakage conduction is attributed to be one of the reasons for the loss of the trapped charges and the reduction of the charge retention. However, what this does imply is that the polymer must be chosen to be an inert candidate; even the operating conditions (voltage sweep window, voltage sweep rate, etc.) must carefully optimized to ensure the polymer doesn't play any role in the bistable switching.

Such pre-conditions are placed to ensure that the effects witnessed are not due to thermally-dominated mechanisms like the filamentary conduction. The preservation of the integrity of result is integral to verify that the switching is due to the internal field surplus and not due to some kind of soft breakdown of the polymer as observed in several other systems.^[23,89] But more importantly, the thermal contribution can affect the device behavior. The use of the nanoparticles is encouraged to utilize the quantum confinement effects of the nanoparticles.^[133] The discretization of the energy levels in the nanoparticles, ensure that the trapped charges will not escape, unless the thermal energy is less than the charging energy ($E_c > k_B T$).^[133] What it implies is that, the detrimental effect of heat is avoided as much as possible by ensuring a low current operation of the

device. This does lead to lower values of ON/OFF ratios in these devices, although sticking to a lower current regime ensures reliability and repeatability. Utmost care is taken to preserve the pristine nature of the device by carefully biasing it within the low-current regime, so as to prevent any Joule's heating of the device.

The question of the conduction shift through internal field generation can therefore be broken down into segments like techniques to sustain the internal field, the choice of materials used, the choice of insulator, thickness investigation, and many more. Several macromolecular materials have been investigated included metal nanoparticles,^[57,89,92,97] ferroelectric nanocomposites,^[134] nanowires,^[99,100] and other organic and inorganic molecules.^[135] Several insulators have been studied, including organic (PS),^[136] inorganic (SiO_2 , Si_3N_4)^[100,137] and ferroelectric materials.^[85,138] The deposition techniques by which the device were fabricated include Langmuir-Blodgett technique,^[76] Solution-based technique,^[23] PECVD,^[97] thermal evaporation,^[100,139] and chemical processing with semiconductor processing compatibility.^[140] Approaches to sustain field or to increase charge retention has been achieved by investigating the nanoparticle dispersion concentration to prevent delocalization of trapped electron through the “coupling of the electron waves (wave propagation).”^[41,42]

7.5. Molecular REDOX-Based Switching

This mechanism was first brought to the attention with Chen et al.'s^[141] work on benzene-based compounds in 1999. In this work, nitro and amine-based compounds that were placed between metal electrodes, exhibited the N-curve with an increase of current by around 3 orders before dropping to the initial OFF state. It was proposed that the switching behavior observed was due to a two-step reduction process in the active material. As the voltage is increased the addition of an electron was proposed to induce the first reduction process, which resulted in the high conduction ON state. Further increasing the voltage resulted in the second-step reduction, the active material thereby resisting further flow of charges and the conduction drops to the low conduction OFF state. The active was concluded to be responsible when nitro-group-absent materials were testing; not only was the NDR region found to be missing, but the electrochemical reduction peaks were missing too in the voltage range.^[141] Similar reliance on the nitro-group for conduction switching were found by Reed et al.^[142]

Other materials like Rose Bengal^[143–145] and poly(p-phenylenevinylene)^[146] were also investigated for bistability. In these cases too, it was found that π -conjugated polymers were favorable for conduction switching, with the prerequisite being that the molecule must have the ability to undergo voltage-induced electrochemical reduction.^[143,145,146] However doubts regarding the actual switching mechanism were raised when Jakobsson et al.,^[147] investigated Rose Bengal for bistability. Systematic measurements on Rose Bengal revealed that the only a small area of the device participated in the switching and was observed to have a hot spot over the same space. This raised question as to whether other mechanisms (like filament

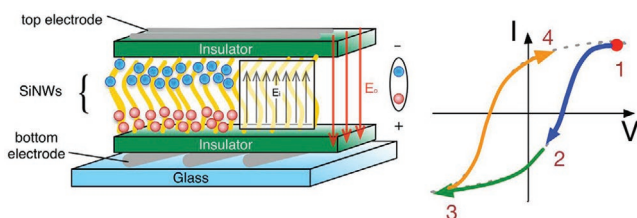


Figure 18. Saranti et al.^[99] demonstrated the internal field generation and charge separation for bistable memory operation in silicon nanowire devices. This image is reproduced under the terms of the Creative Commons Attribution 4.0 International License.^[99] Copyright 2016, The Author(s), Published by Springer Nature.

formation) were contributing to the switching along with the proposed mechanism.^[36]

Another example of electrochemical reactions causing conduction switching is when polypyrrole (PPy) layer was deposited under Titanium oxide (TiO_2) layer.^[148] The device structure $\text{SiO}_2/\text{PPy}/\text{TiO}_2/\text{Au}$ was observed to undergo reduction-oxidation to attain charge accumulation. The PPy layer was proposed to undergo doping when the positive electrode was biased, the TiO_2 , on the other hand reduced to release extra electrons into the system; resulting in the OFF-ON state transition. Applying the reverse bias was observed to reset the device in the initial low conduction OFF state.^[30,148]

It must be noted that this mechanism is exclusive from the electrochemical metallization (ECM) where the electrode plays an active role in forming a conductive filament (see Section 8.1.2.). Even though both the mechanisms depend on electrochemical reduction-oxidation processes, here the active material does not interact with the electrode electrochemically.

8. Other Switching Mechanisms

The charge storage mechanism has been only one of the several switching mechanisms that have been reported to explain the device switching behavior. In this section, the other switching mechanisms will be looked into.

8.1. Conductive Filament Based Switching

The CF-based switching mechanism addresses the switching behavior of the device to be due to the formation of conductive pathways formed across the device cross section. The conductive pathways are formed when the device undergoes forming procedure and thereby switches from high resistance to low resistance states (LRSs) and vice versa by forming and rupturing of the conductive pathways respectively. The forming process activates the switching behaviors in the device,^[20] which would otherwise be challenging to observe in a pristine device. The high current densities that can be observed in the devices lead to the formation of thermally-activated ions, which thereafter follows an electrochemical reduction and oxidation process to migrate to and fro within the device cross section.^[13,20,149] The exact mechanism of the formation and rupturing of the CFs vary broadly across two kind of switching mechanism. These redox-based, switching mechanisms can be broadly classified as: 1) Anion-based switching, 2) cation-based switching.

8.1.1. Anion-Based Switching

Anion-based switching deals with the device switching that originate from oxygen ions. Oxides such as, TiO_x ,^[150–154] NiO_x ,^[155,156] TaO_x ,^[157,158] Al_2O_3 ,^[159,160] Fe_2O_3 ,^[161] WO_3 ,^[162,163] MnO_x ,^[164] HfO_x ,^[165–168] Gd_2O_3 ,^[169] CoO_x ,^[170] etc., or nitrides like aluminium nitride^[171] or nickel nitride^[172,173] have been reported to exhibit resistive switching. In anion-type switching, oxygen vacancies are formed when a potential is applied across the electrode. These ions are formed mostly at the interfaces,

where non-uniformity is inherent and unavoidable. These interfaces, thus become sites for generating oxygen vacancies. The switching behavior in these devices is achieved by generating vacancies and by the migration of the oxygen-ion that was released from the vacancy. Another method of realizing reliable switching is to create a region within the device that can act like an oxygen reservoir.^[13] The oxygen reservoir can be an extra thin layer of material that is oxygen deficient compared to the rest of the device and can act like a tank to store the oxygen, so that it can contribute to the erasing function, when the device switches from high conductance state to low conductance state. For example, some studies have reported using an ultra-thin layer of TaO_{2-x} like an oxygen-ion reservoir in a device consisting of $\text{Ta}_2\text{O}_{5-x}$ layer as a switching layer.^[174] Due to the dependence on the oxygen vacancy generation and the oxygen-ion migration, this type of switching is sometimes referred to as the valence change memory in the literature.^[18,175–177]

This type of switching has been studied widely, through the study of alternate high-k dielectric materials and their behavior under high electric field. Oxides like WO_x , HfO_x , TaO_x , and AlO_x have been investigated for their switching behavior through oxygen migration and is an attractive option due to their compatibility with traditional semiconductor fabrication technology. This is a huge area of study and a whole discussion of it is beyond the scope of this review article. However, the anion-type switching can be broadly understood through the switching behavior of p-type semiconductor like NiO_{1+x} and n-type semiconductor such as, TiO_{2-x} .^[90,113]

The origin of conductive filament formation is material-specific, and is unique for p-type semiconductors and n-type semiconductors. Let us consider the switching in TiO_x switching system as an example. Being a n-type semiconductor, the electrons are injected from the cathode and the oxygen vacancy move from the anode to cathode. The oxygen vacancies move in the opposite direction to the oxygen ion, and assisted by the Joule's heating, the conducting filament progresses from the cathode interface to the anode interface.^[90] The device is reset to the low conductance state by applying a voltage pulse in the opposite polarity. The conductive filament, in this case breaks at the thinnest region and the device reverts to the low conductance state.

On the contrary, a p-type semiconductor such as, NiO experiences the most Joule's heating originating from the anode due to the intense hole injection at the anode interface. The immense temperature promotes the generation of the oxygen vacancies; the loss of oxygen in these regions leading to the generation of Ni interstitials. With an increasing generation of oxygen vacancy, the large accumulation of the metal interstitial agglomerate to form a metallic filament. This conducting filament then progresses from the anode to the cathode, at which point the device switches from low conduction to high conduction state. To achieve the reverse switching, an opposite polarity voltage pulse is applied to the device, wherein the filament breaks at the weakest point and the high conduction state is achieved.

8.1.2. Cation-Based Switching

The electrochemical switching in devices can occur in another variant of CF formation wherein, the electrodes diffuse and the

metal ions migrate in the matrix to form metallic filaments; effectively short-circuiting the device. Also known as ECM, one of the primary requirements to design such a system is to have an electrode that is electrochemically active.^[90,178] The electrochemically active electrode is called the active electrode (AE) and its inert counterpart is known as the counter electrode (CE). Over the years, many metals have been studied for desirable electrochemical properties that suit an active electrode like Ni,^[172] Zn,^[173] Nb,^[174] Ti,^[175] Au,^[176] and other metals.^[170,177–181] But two metals stand out among others, Ag and Cu, as the favorite for the studying the cation-based switching.^[179–182]

The filamentary formation for these metals has been investigated intensively. For example, Sun et al.^[183] investigated the device (Ag/SiO₂/Pt) cross section using high resolution transmission electron microscopy. As can be seen in **Figure 19**, the diffusion of silver (Ag) nanocrystals were observed, and this was found to coincide with the switching of the device. The reversible forming and rupturing of these conductive filaments (CFs) were also investigated by Yang et al.^[184] The reason for such preference in electrode choice lies in the electrochemistry of the metals. First, the standard reduction potential for both Ag and Cu is relatively low. Compared to the reduction potential of Au (1.69 V), Ag and Cu have values, $E_0(\text{Ag}^+/\text{Ag}) = 0.7993$ V and $E_0(\text{Cu}^{2+}/\text{Cu}) = 0.339$ V, respectively.^[90] This goes to demonstrate how both these are electrochemically soluble. But simply being able to dissolve doesn't suffice, the ability to make and break the filament must also be present. The Gibb's free energy of oxide formation for Ag and Cu is -11.21 and -129.7 kJ mol⁻¹, respectively.^[90] Comparing these values with that of Ni (-211.7 kJ mol⁻¹) and Al (-527.4 kJ mol⁻¹) gives a comparative

reasoning as to how the weak interaction with anion, enables Ag and Cu ions to migrate easily and form metal filaments.^[90]

The mechanism of metal filamentary formation on a is as follows, when a potential is applied across the electrodes, the metal loses an electron and forms an ion due to the oxidation reaction ($\text{M} \rightarrow \text{M}^+ + \text{e}^-$). This ion migrates under the influence of the applied electric field toward the control electrode (CE). On reaching the CE, the metal ion undergoes a reduction reaction to form metal atom, thereby undergoing a precipitation at the electrode interface with the dielectric. This precipitation further continues until the accumulating metal atoms form a metallic filament, which ultimately reaches the AE. At this point, the metallic pathway, triggers the devices to switch from low conduction OFF state to high conduction ON state. To reset the device back to the OFF state, a polarity of the applied voltage is reversed, thereby triggering the reaction in the reverse order. The metallic filament begins to dissolve gradually until the filament breaks at the thinnest region of cross section (refer **Figure 20**).

The redox-based switching has gained a lot of impetus in the recent years due to the involvement of materials which are compatible to the semiconductor technology processes. However, there are several challenges that need to be overcome before these devices can be commercialized; reproducibility being a great challenge. The wide range of distribution in the switching of the device makes it imperative to have a huge ON/OFF ratio.^[13] Second, the issue of scalability is a great challenge;^[20] the issue being related to the manner in which conductive filaments progress through the dielectric. The forming process, leads to localized conduction by induced non-homogeneity in

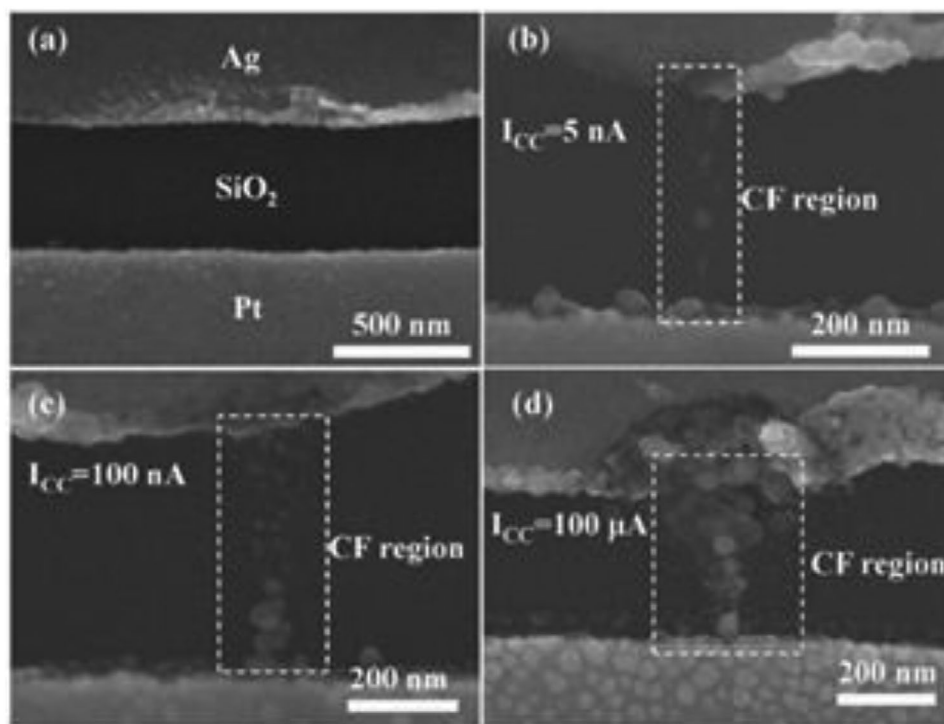


Figure 19. Image showing the formation and progression of conductive filament in comparison with the current magnitude that flowed through the device. Reproduced with permission.^[183] Copyright 2014, John Wiley and Sons.

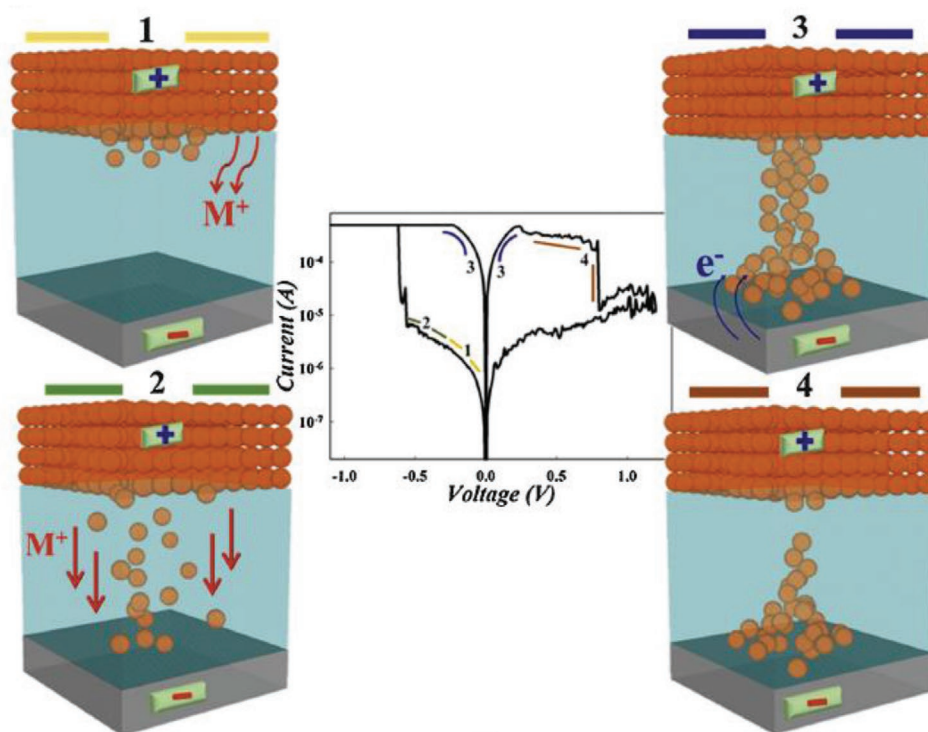


Figure 20. Schematics showing the filamentary formation mechanism. Reproduced with permission.^[13] Copyright 2015, Elsevier.

the interface. These non-uniformity or voids may lead to a concentration of electric field at some local areas within the total device area. It has been observed that the problem can be traced to the edge-effect where the electric field is concentrated at the edges of the electrode; referred in the literature as the “fringing effect.”^[185]

8.2. Carbon-Based Switching

Carbon-based memory devices have recently gained a lot of attention in the recent past, where amorphous hydrogenated carbon (a:C–H) is observed to be bipolar in nature,^[13] with the device first beginning the operation in low conduction OFF state. The OFF to ON transition is marked by the “write” voltage, whereas the ON to OFF transition is achieved by applying an “erase” voltage, which has an opposite polarity compared to the “write” signal. The switching mechanism has been found to be a result of the dehydrogenation and hydrogenation of H atoms.^[13] The proposed mechanism points out to the carbonization of the polymer to be the cause of the OFF to ON transition, where large fractions of sp^2 carbon form conductive paths after the forming process. These paths provide the high conduction to the device that characterizes the ON state. To revert the device to the low conduction OFF state, a reverse electric field is applied. This initiates the hydrogenation of the carbon and the transition of the carbon from highly conductive sp^2 form to an insulating sp^3 hybridization form (see Figure 21).^[13,25]

This filament formation is similar to the metal filament formation; however, the metal filaments are not formed in the

same manner of chemical transformation that is witnessed in the carbon films (refer Figure 21).

Another manner of switching has been observed in carbon-rich graphene oxide (GO) films. Choi et al.^[186] observed that devices using GO between aluminium electrodes (Al/GO/Al) exhibited a unique manner of switching (shown in Figure 22). When aluminium electrodes were used as electrodes, the device exhibited a switching with an ON/OFF ratio of 100 and retention of 10^5 s. The same material (GO) however, showed no switching with an inert electrode such as gold. The switching was finally found to a result of an interfacial amorphous layer that formed due to a redox reaction between the thermal evaporation of aluminium over GO. This interfacial layer posed a wide barrier between the electrode and GO, but as the electric field was applied to the device, the external electric field initiated a migration of oxygen ions into the GO layer. This migra-

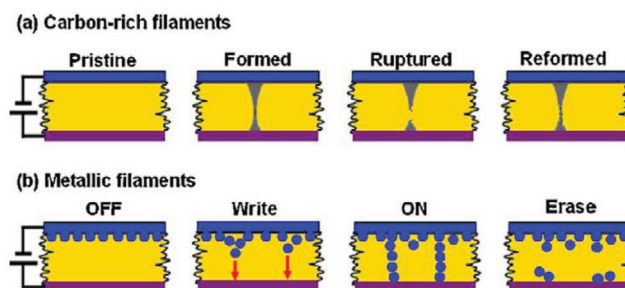


Figure 21. Schematic showing the filamentary formation in inorganic systems and in carbon-rich organic systems. Reproduced with permission.^[25] Copyright 2008, Elsevier.

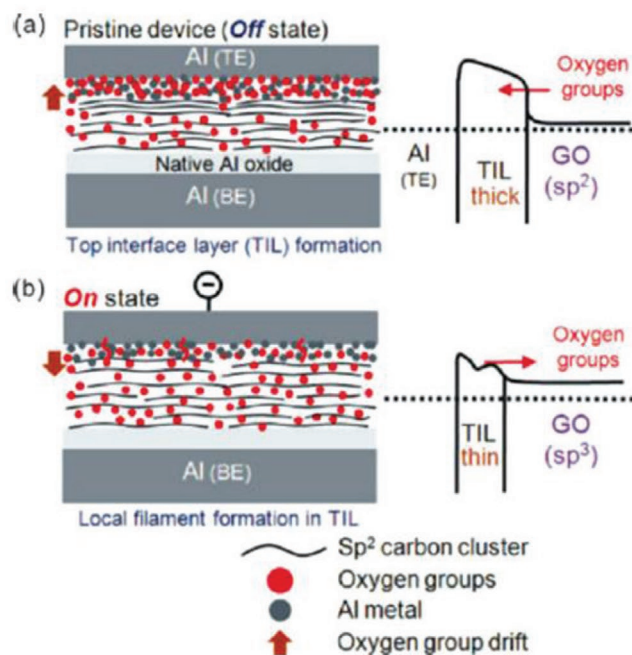


Figure 22. Schematics depicting the switching mechanism for graphene oxide-based device where oxygen migration leads to broadening and depletion of the barrier. Reproduced with permission.^[186] Copyright 2010, American Chemical Society.

tion of oxygen ions impacted the energy barrier such that it got thinner, thereby facilitating the flow of carriers through the device and leading to the transition from OFF state to ON state for the device. The conduction has also been attributed to the fraction of sp^2 carbon in the film that can be changed back and forth to sp^3 form by an application of electric field.^[186] There have been studies that have also shown that GO are able to trap charges similar to fullerene molecule.^[187–189]

8.3. Metal Oxide Electrode-Based Switching

Resistive switching has been observed various materials, which cannot be covered entirely in a short review article as this. There are dielectric materials, binary oxides, perovskite material, semiconducting materials, which have displayed resistive switching, but the whole mechanism of these materials have not been completely understood. Some of these have been covered in this section.

The first and perhaps the most widely known materials for conductive filament switching is the binary transition metal oxides (TMOs). Other TMOs like VO, MnO, FeO, and some others have been reported to be Mott insulator; exhibiting the insulator-to-metal transition, commonly referred to as the Mott transition.^[190] The reason for the distinction of the Mott insulators from the resistive switching TMOs originates from the source of the switching. The Mott transition is considered to be an electronic transition, whereas the filamentary conduction is a defect-based-mechanism that relies on the thermal effects for the switching. Large bandgap dielectrics that have been

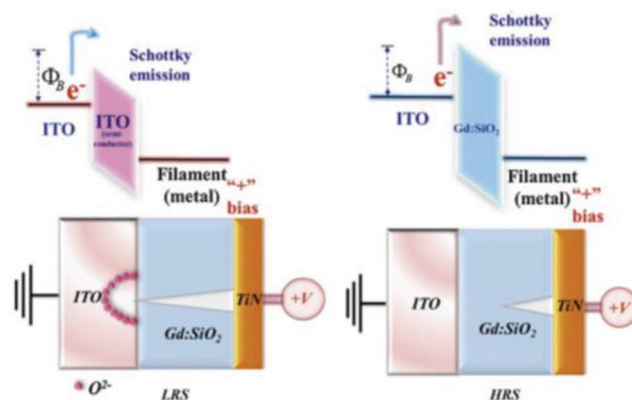


Figure 23. Schematics showing the switching mechanism due to metal oxide-based electrodes like ITO, where the oxygen migration forms a depletion region in the ITO, forming a Schottky-type barrier. Reproduced with permission.^[13] Copyright 2015, Elsevier.

investigated for high-k properties have been reported to exhibit resistive properties. Many publications have reported the resistive switching in Al_2O_3 ; materials like Gd_2O_3 too, have been observed to exhibit switching.^[20]

There have been works that have reported switching based on electrodes like indium tin oxide (ITO).^[13,192] However, the switching mechanism is not typical of the other materials discussed so far. The observed switching has been reported due to an indirect influence of the ITO electrode on the device. Zhang et al.^[192] has reported such switching on a ITO/ $Gd:SiO_2$ /TiN device which reported a data retention of 10^4 s and an endurance of 10^9 pulses. The proposed mechanism, utilizes the property of ITO being an excellent oxygen reservoir exceeding the oxygen storage ability of other metal oxides. The electrical analysis of the switching behavior of the device showed the conduction mechanism to be Schottky conduction. The proposed mechanism describes the OFF to ON switching of the device to be motivated by the high difference of the oxygen gradient in the metal oxide and the ITO, enhanced by the applied electric field. During the switching, the oxygen ions are propelled into the ITO electrode, thereby creating the conductive filament. The migration of the oxygen into the ITO electrode, leads to an oxygen-depleted region even within the ITO electrode, leading to the creation of a Schottky contact between the metal-like ITO and the semiconductor-like ITO (see **Figure 23**). This Schottky-like conduction facilitates a low-voltage switching of the device, which in this case was 0.7 V. The ON–OFF switching is initiated by the oxidizing of the conductive filament, which exposes the ITO to the insulating dielectric SiO_2 layer.

8.4. Coexistent Switching

There have been reports of coexistent switching behaviors inside a single system, like Jeong et al.^[152] who reported the existence of both unipolar and bipolar in Pt/ TiO_2 /Pt memory cells. This is interesting, as different mechanisms work together in the same system, the output being thus a combination of more than one behavior, or perhaps the result of a dominating

behavior. Salaoru et al.^[191] reported the simultaneous switching of resistance and capacitance in Pt/TiO₂/Pt devices.

It was found that devices had a high capacitance state and a low capacitance state along with the reported high resistance state and LRS. But this behavior is not exclusive to the inorganic materials, Zhang et al.^[98] observed that the heat generated during the forming process had resulted in the annealing of the polymer film and the presence of sp_s conductive filaments were observed. The conduction in the ON-state was contributed to the combined contribution of the NPs and the conductive sp² amorphous polymer. Studies have also demonstrated localized transformation in graphene oxide layer during forming, which have been claimed to be able to trap electrons in a fullerene-like manner.^[186–188]

This goes to demonstrate that perhaps a lot of the works that report high ON/OFF ratios with several orders could be observing a coexistence of partial soft breakdown of the device along with the charge storage or even unintended involvement from other switching mechanisms. The differences of conduction mechanisms reported by various works, even when investigating the same system, must be indicative of factors that have already been outlined like, the current level during forming, the rate of voltage sweep, the concentration of the NPs, and much more. The use of high magnitudes of the currents, it seems to lend a sort of unpredictability to the system; the uncertainty born out of multiple mechanisms at work at elevated temperatures, low device thicknesses, and the resultant high electric field.

9. Future Scope

The field of macromolecular memory devices is evolving rapidly, especially with easier fabrication techniques to deposit organic and polymer thin films and the ability to achieve equally competitive performance, huge potential for growth lies ahead. However, many questions continue to remain open-ended in regards to the switching mechanisms. The success of the field and the commercialization of it, depends on the maturing of the field. And, this can only happen if further research is focused toward the systematic investigation of these questions and endeavor to achieve a unifying picture of the switching mechanisms and the conduction mechanisms in the devices. The past results, devices and systems require to be revisited with closer investigations to attain a holistic understanding of the physics that is acting on the various aspects. For example, what are the influencing factors in a system that when inclined one way or the other, lead to completely different results?

Furthermore, attempts must be undertaken to identify the coexistence of multiple switching mechanisms, the factors that contribute and how these can be eliminated. These would also bring a consensus to the various competing theories of switching mechanism and a clarity in regards to the material behavior. Several mechanisms have been put forward to explain similar behavior and sometimes even with the same device structure. A better understanding in this regard would require an alliance of engineers, physicist and chemist to uncover the various facets of this issue to gain a consensus.

Some of the pressing issues that can be understood is that the field of OMD is that it is still at a stage of infancy when compared to other fields like organic light emitting diodes or organic photovoltaics. The device performance are not competitive with the inorganic or silicon-based memory devices. This would require further attention in this direction to push this field forward.

Another pressing issue is the lack of large-area manufacturing capability as is the case with Si-based memory devices. Developing a roll-to-roll manufacturing technique with highly reliable devices is another direction that the field must advance. This can be made possible with further research that focusses on a lab to industry technology with a simple, low-cost, and high-volume manufacturing capability.^[7]

10. Conclusion

Organic and polymer-based nanocomposite devices hold promising future for electronic devices. With niche applications that wearable and flexible technologies, organic devices are placed favorably for future commercialization. Although much work is needed before that can happen; answers regarding the switching mechanism and material properties are required before the reliable and superior devices can be fabricated. Many parameters that can affect the switching behavior of the device have been examined. And for this reason, further publications must think of these questions before publishing the results. For example, what preconditioning has been used on the devices?

The internal field mechanism has been proposed through the many devices that have been fabricated through the past decade and the results that have been borrowed from it. Several other competing proposals addressing the charge storage of the nanoparticle and the switching mechanisms have been compared too. While most of the other charge mechanism, diverge in regards to the reason of the conduction switching, the internal field mechanism, stresses on the coulombic forces to be the primary cause for the bistability. This is further supported by the manageable ON/OFF ratios and how they fit well within the scope of the model. The necessity of such a model has risen from the general propensity in the past to focus on mere ON/OFF ratio to judge the device operation of a memory device. Other mechanisms too, have been examined in brief; focusing on the differences therein and the switching mechanisms too.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

capacitive memory and nanoparticles based memory, conduction mechanism, nanocomposite, non-volatile memory, polymer memory, resistive memory

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- [1] F. Garnier, R. Hajlaoui, A. Yassar, P. Srivastava, *Science* **1994**, 265, 1684.
- [2] C. W. Tang, S. A. VanSlyke, *Appl. Phys. Lett.* **1987**, 51, 913.
- [3] G. Yu, J. Gao, J. C. Hummelen, F. Wudl, A. J. Heeger, *Science* **1995**, 270, 1789.
- [4] Z. Lin, Y. Huang, X. Duan, *Nat. Electron.* **2019**, 2, 378.
- [5] K. Nomura, H. Ohta, A. Takagi, T. Kamiya, M. Hirano, H. Hosono, *Nature* **2004**, 432, 488.
- [6] Y. Li, C. Zhang, Z. Shi, C. Ma, J. Wang, Q. Zhang, *Sci. China Mater.* **2021**, <https://doi.org/10.1007/s40843-021-1771-5>.
- [7] Y. Li, Q. Qian, X. Zhu, Y. Li, M. Zhang, J. Li, C. Ma, H. Li, J. Lu, Q. Zhang, *InfoMat* **2020**, 2, 995.
- [8] Q. Zhang, *Front. Phys.* **2021**, 16, 13602.
- [9] M. Di Ventra, Y. V. Pershin, *Mater. Today* **2011**, 14, 584.
- [10] N. Derhacopian, S. C. Hollmer, N. Gilbert, M. N. Kozicki, *Proc. IEEE* **2010**, 98, 283.
- [11] A. Chen, *Solid-State Electron.* **2016**, 125, 25.
- [12] Y. Yang, J. Ouyang, L. Ma, R. Tseng, C. Chu, *Adv. Funct. Mater.* **2006**, 16, 1001.
- [13] T. C. Chang, K. C. Chang, T. M. Tsai, T. J. Chu, S. M. Sze, *Mater. Today* **2016**, 19, 254.
- [14] S. Lombardo, B. De Salvo, C. Gerardi, T. Baron, *Microelectron. Eng.* **2004**, 72, 388.
- [15] Z. Liu, C. Lee, V. Narayanan, G. Pei, E. C. Kan, *IEEE Trans. Electron Devices* **2002**, 49, 1614.
- [16] Z. Liu, C. Lee, V. Narayanan, G. Pei, E. C. Kan, *IEEE Trans. Electron Devices* **2002**, 49, 1606.
- [17] K. Qian, V. C. Nguyen, T. Chen, P. S. Lee, *J. Mater. Chem. C* **2016**, 4, 9637.
- [18] E. W. Lim, R. Ismail, *Electronics* **2015**, 4, 586.
- [19] T. Lee, Y. Chen, *MRS Bull.* **2012**, 37, 144.
- [20] D. S. Jeong, R. Thomas, R. S. Katiyar, J. F. Scott, H. Kohlstedt, A. Petraru, C. S. Hwang, *Rep. Prog. Phys.* **2012**, 75, 076502.
- [21] D. B. Strukov, G. S. Snider, D. R. Stewart, R. S. Williams, *Nature* **2008**, 453, 80.
- [22] E. S. Reich, *Nature* **2013**, 495, 17.
- [23] S. Paul, I. Salaoru, *Thin Solid Films* **2010**, 519, 587.
- [24] Y. Fujisaki, *Jpn. J. Appl. Phys.* **2013**, 52, 040001.
- [25] Q. D. Ling, D. J. Liaw, C. Zhu, D. S. H. Chan, E. T. Kang, K. G. Neoh, *Prog. Polym. Sci.* **2008**, 33, 917.
- [26] S. Gao, X. Yi, J. Shang, G. Liu, R. W. Li, *Chem. Soc. Rev.* **2019**, 48, 1531.
- [27] J. C. Scott, *Science* **2004**, 304, 62.
- [28] J. S. Meena, S. M. Sze, U. Chand, T. Y. Tseng, *Nanoscale Res. Lett.* **2014**, 9, 526.
- [29] I. S. Devisé, et al., *Int. Devices Syst.* **2018**.
- [30] P. Heremans, G. H. Gelincik, R. Müller, K. J. Baeg, D. Y. Kim, Y. Y. Noh, *Chem. Mater.* **2011**, 23, 341.
- [31] B. Hwang, J.-S. Lee, *Adv. Electron. Mater.* **2019**, 5, 1800519.
- [32] C. H. Kim, *Nanoscale Horiz.* **2019**, 4, 828.
- [33] A. Makarov, V. Sverdlov, S. Selberherr, *Microelectron. Reliab.* **2012**, 52, 628.
- [34] G. I. Meijer, *Science* **2008**, 319, 1625.
- [35] T. Mikolajick, M. Salinga, M. Kund, T. Kever, *Adv. Eng. Mater.* **2009**, 11, 235.
- [36] D. Prime, S. Paul, *Philos. Trans. R. Soc., A* **2009**, 367, 4141.
- [37] C.-U. Pinnow, T. Mikolajick, *J. Electrochem. Soc.* **2004**, 151, K13.
- [38] R. K. Cavin, P. Lugli, V. V. Zhirnov, *Proc. IEEE* **2012**, 100, 1720.
- [39] D. Tsoukalas, *Philos. Trans. R. Soc., A* **2009**, 367, 4169.
- [40] J. S. Lewis, Z. Barani, A. S. Magana, F. Kargar, “capacitive memory,” **2019**.
- [41] G. Schön, U. Simon, *Colloid Polym. Sci.* **1995**, 273, 101.
- [42] G. Schön, U. Simon, *Colloid Polym. Sci.* **1995**, 273, 202.
- [43] T. W. Kim, Y. Yang, F. Li, W. L. Kwan, *NPG Asia Mater* **2012**, 4, e18.
- [44] S. R. Forrest, *Nature* **2004**, 428, 911.
- [45] L. D. Bozano, B. W. Kean, V. R. Deline, J. R. Salem, J. C. Scott, *Appl. Phys. Lett.* **2004**, 84, 607.
- [46] W. Nam, S. Seo, J. Park, *Electrochem. Solid-State Lett.* **2011**, 14, 277.
- [47] W. Nam, S. Seo, K. Park, S. Hong, G. Lee, J. Park, *Curr. Appl. Phys.* **2010**, 10, e37.
- [48] Y. Busby, S. Nau, S. Sax, E. J. W. List-Kratochvil, J. Novak, R. Banerjee, F. Schreiber, J.-J. Pireaux, *J. Appl. Phys.* **2015**, 118, 075501.
- [49] V. S. Reddy, S. Karak, S. K. Ray, A. Dhar, *Org. Electron.* **2009**, 10, 138.
- [50] V. S. Reddy, S. Karak, A. Dhar, *Appl. Phys. Lett.* **2014**, 94, 173304.
- [51] T. Abhijith, T. V. A. Kumar, V. S. Reddy, “Organic bistable memory devices based on MoO₃ nanoparticle embedded Alq₃ structures,” **2017**.
- [52] K. Onlaor, B. Tunhoo, T. Thiawong, J. Nukeaw, *Curr. Appl. Phys.* **2012**, 12, 331.
- [53] C. Tu, Y. Lai, D. Kwong, *IEEE Electron Device Lett.* **2006**, 27, 354.
- [54] P. Lee, T. Chang, S. Chen, *Org. Electron.* **2008**, 9, 916.
- [55] L. D. Bozano, B. W. Kean, M. Beinhoff, K. R. Carter, P. M. Rice, J. C. Scott, *Adv. Funct. Mater.* **2005**, 15, 1933.
- [56] M. Xie, K. C. Aw, M. Langlois, W. Gao, *Solid State Commun.* **2012**, 152, 835.
- [57] D. Prime, S. Paul, P. W. Josephs-Franks, *Philos. Trans. R. Soc., A* **2009**, 367, 4215.
- [58] J. Chen, L. Xu, J. Lin, Y. Geng, L. Wang, D. Ma, *Appl. Phys. Lett.* **2006**, 89, 083514.
- [59] Y. T. You, M. L. Wang, H. N. Xuxie, B. Wu, Z. Y. Sun, X. Y. Hou, *Appl. Phys. Lett.* **2010**, 97, 233301.
- [60] S. M. Islam, P. Banerji, S. Banerjee, *Org. Electron.* **2014**, 15, 144.
- [61] T. W. Hickmott, *J. Appl. Phys.* **1965**, 36, 1885.
- [62] T. W. Hickmott, *J. Appl. Phys.* **1962**, 33, 2669.
- [63] R. R. Sutherland, *J. Phys. D: Appl. Phys.* **1971**, 4, 468.
- [64] D. P. Oxley, *Electrocomponent Sci. Technol.* **1977**, 3, 217.
- [65] C. A. Hogarth, T. Iqbal, *Int. J. Electron.* **1979**, 47, 349.
- [66] T. Iqbal, C. A. Hogarth, *Int. J. Electron.* **1988**, 65, 957.
- [67] L. Ma, J. Liu, S. Pyo, Y. Yang, *Appl. Phys. Lett.* **2002**, 80, 362.
- [68] L. Ma, J. Liu, S. Pyo, Q. Xu, Y. Yang, *Mol. Cryst. Liq. Cryst. Sci. Technol., Sect. A* **2002**, 378, 185.
- [69] L. Ma, S. Pyo, J. Ouyang, Q. Xu, Y. Yang, *Appl. Phys. Lett.* **2003**, 82, 1419.
- [70] J. G. Simmons, R. R. Verderber, *Proc. R. Soc. London, Ser. A* **1967**, 301, 77.
- [71] S. Pyo, L. Ma, J. He, Q. Xu, Y. Yang, Y. Gao, *J. Appl. Phys.* **2005**, 98, 054303.
- [72] R. R. Vekderber, B. Eales, J. G. Simmons, *Philos. Mag.* **1967**, 16, 1049.
- [73] J. C. Scott, L. D. Bozano, *Adv. Mater.* **2007**, 19, 1452.
- [74] J. He, L. Ma, J. Wu, Y. Yang, *J. Appl. Phys.* **2005**, 97, 064507.
- [75] D. Tondelier, K. Lmimouni, D. Vuillaume, C. Fery, G. Haas, *Appl. Phys. Lett.* **2004**, 85, 5763.
- [76] S. Paul, C. Pearson, A. Molloy, M. A. Cousins, M. Green, S. Kolliopoulou, P. Dimitrakakis, P. Normand, D. Tsoukalas, M. C. Petty, *Nano Lett.* **2003**, 3, 533.

- [77] J. Ouyang, C. W. Chu, C. R. Szmanda, L. Ma, Y. Yang, *Nat. Mater.* **2004**, 3, 918.
- [78] V. S. Reddy, S. Karak, A. Dhar, *Appl. Phys. Lett.* **2009**, 94, 88.
- [79] D. Prime, S. Paul, *Mater. Res. Soc. Symp. Proc.* **2007**, 997, 21.
- [80] R. J. Tseng, C. Tsai, L. Ma, J. Ouyang, C. S. Ozkan, Y. Yang, *Nat. Nanotechnol.* **2006**, 1, 72.
- [81] Q.-D. Ling, S.-L. Lim, Y. Song, C.-X. Zhu, D. S.-H. Chan, E.-T. Kang, K.-G. Neoh, *Langmuir* **2007**, 23, 312.
- [82] C. W. Chu, J. Ouyang, J. Tseng, Y. Yang, *Adv. Mater.* **2005**, 17, 1440.
- [83] R. Tseng, J. Huang, J. Ouyang, R. B. Kaner, Y. Yang, *Nano Lett.* **2005**, 5, 1077.
- [84] J. Ouyang, C. W. Chu, D. Sieves, Y. Yang, *Appl. Phys. Lett.* **2005**, 86, 123507.
- [85] A. Kanwal, S. Paul, M. Chhowalla, *Mater. Res. Soc. Symp. Proc.* **2005**, 830, 349.
- [86] S. Paul, A. Kanwal, M. Chhowalla, *Nanotechnology* **2006**, 17, 145.
- [87] S. Paul, *IEEE Trans. Nanotechnol.* **2007**, 6, 191.
- [88] J. Ouyang, *Emerging Resistive Switching Memories*, Springer, Cham **2016**, p. 1, <https://doi.org/10.1007/978-3-319-31572-0>.
- [89] D. Prime, S. Paul, CIMTEC 2008 – Proc. 3rd Int. Conf. Smart Mater. Struct. Syst. – Smart Mater. Micro/Nanosystems **2008**, Vol. 54, p. 480.
- [90] J. Ouyang, *Emerging Resistive Switching Memories*, 1st ed., Springer, Berlin **2016**, p. 1, <https://doi.org/10.1007/978-3-319-31572-0>.
- [91] W. L. Leong, P. S. Lee, S. G. Mhaisalkar, T. P. Chen, A. Dodabalapur, *Appl. Phys. Lett.* **2007**, 90, 042906.
- [92] D. Prime, S. Paul, *Appl. Phys. Lett.* **2010**, 96, 043120.
- [93] I. Salaoru, S. Alotaibi, Z. A. Halafi, S. Paul, *MRS Adv.* **2017**, 2, 195.
- [94] S. P. Iulia Salaoru, *Mater. Res. Soc. Symp. Proc.* **2010**, 1250, 1.
- [95] D. C. Prime, Z. A. Halafi, M. A. Green, I. Salaoru, S. Paul, *ECS Trans.* **2013**, 53, 141.
- [96] S. Nau, S. Sax, E. J. W. List-Kratochvil, *Adv. Mater.* **2014**, 26, 2508.
- [97] S. Alotaibi, K. N. Manjunatha, S. Paul, *Appl. Surf. Sci.* **2017**, 424, 330.
- [98] T. Zhang, D. Guérin, F. Alibart, D. Troadec, D. Hourlier, G. Patriarche, A. Yassin, M. Oçafrain, P. Blanchard, J. Roncali, D. Vuillaume, K. Lmimouni, S. Lenfant, *Nanoscale Adv.* **2019**, 1, 2718.
- [99] K. Saranti, S. Alotaibi, S. Paul, *Sci. Rep.* **2016**, 6, 27506.
- [100] K. Saranti, S. Paul, *ACS Appl. Electron. Mater.* **2019**, 1, 2018.
- [101] B. Naydenov, J. J. Boland, *Nanotechnology* **2013**, 24, 275202.
- [102] V. Suresh, D. Y. Kusuma, P. S. Lee, F. L. Yap, M. P. Srinivasan, S. Krishnamoorthy, *ACS Appl. Mater. Interfaces* **2015**, 7, 279.
- [103] W. Tang, H. Z. Shi, G. Xu, B. S. Ong, Z. D. Popovic, J. C. Deng, J. Zhao, G. H. Rao, *Adv. Mater.* **2005**, 17, 2307.
- [104] A. K. Mahapatro, R. Agrawal, S. Ghosh, *J. Appl. Phys.* **2004**, 96, 3583.
- [105] X. Liu, Z. Ji, L. Shang, H. Wang, Y. Chen, M. Han, C. Lu, M. Liu, J. Chen, *IEEE Electron Device Lett.* **2011**, 32, 1140.
- [106] F. Santoni, A. Gagliardi, M. A. der Maur, A. Pecchia, S. Nau, S. Sax, E. J. W. List-Kratochvil, A. Di Carlo, *IEEE Trans. Nanotechnol.* **2015**, 15, 60.
- [107] L. P. Ma, J. Liu, Y. Yang, *Appl. Phys. Lett.* **2002**, 80, 2997.
- [108] J. Ouyang, C. W. Chu, R. J. H. Tseng, A. Prakash, Y. Yang, *Proc. IEEE* **2005**, 93, 1287.
- [109] H. S. Majumdar, J. K. Baral, R. Österbacka, O. Ikkala, H. Stubb, *Org. Electron.* **2005**, 6, 188.
- [110] P. Dimitrakakis, P. Normand, D. Tsoukalas, C. Pearson, J. H. Ahn, M. F. Mabrook, D. A. Zeze, M. C. Petty, K. T. Kamtekar, C. Wang, M. R. Bryce, M. Green, *J. Appl. Phys.* **2008**, 104, 044510.
- [111] K. Oka, T. Yanagida, K. Nagashima, T. Kawai, J.-S. Kim, B. H. Park, *J. Am. Chem. Soc.* **2010**, 132, 6634.
- [112] K. M. Kim, C. S. Hwang, *Appl. Phys. Lett.* **2009**, 94, 122109.
- [113] K. M. Kim, D. S. Jeong, C. S. Hwang, *Nanotechnology* **2011**, 22, 254002.
- [114] T. Tsai, J. Chang, T. Wen, T. Guo, *Adv. Funct. Mater.* **2013**, 23, 4206.
- [115] M. Egginger, S. Bauer, R. Schwödau, H. Neugebauer, N. S. Sariciftci, *Monatsh. Chem.-Chem. Mon.* **2009**, 140, 735.
- [116] W. Xu, C. Guo, S.-W. Rhee, *J. Mater. Chem.* **2012**, 22, 6597.
- [117] K. Baeg, Y. Noh, H. Sirringhaus, D. Kim, *Adv. Funct. Mater.* **2010**, 20, 224.
- [118] W. L. Leong, N. Mathews, S. Mhaisalkar, Y. M. Lam, T. Chen, P. S. Lee, *J. Mater. Chem.* **2009**, 19, 7354.
- [119] S. Han, Y. Zhou, C. Wang, L. He, W. Zhang, V. A. L. Roy, *Adv. Mater.* **2013**, 25, 793.
- [120] H. Wang, F. Zhou, L. Wu, X. Xiao, P.-Y. Gu, J. Jiang, Q.-F. Xu, J.-M. Lu, *Polym. Chem.* **2018**, 9, 1139.
- [121] S. Liu, P. Wang, Q. Zhao, H.-Y. Yang, J. Wong, H.-B. Sun, X.-C. Dong, W.-P. Lin, W. Huang, *Adv. Mater.* **2012**, 24, 2901.
- [122] Y. Yang, L. Ma, J. Wu, *MRS Bull.* **2004**, 29, 833.
- [123] J. Wu, L. Ma, Y. Yang, *Phys. Rev. B* **2004**, 69, 115321.
- [124] J. G. Simmons, R. R. Verderber, *Radio Electron. Eng.* **1967**, 34, 81.
- [125] R. J. Tseng, J. Ouyang, C.-W. Chu, J. Huang, Y. Yang, *Appl. Phys. Lett.* **2006**, 88, 123506.
- [126] J. Lin, D. Ma, *J. Appl. Phys.* **2008**, 103, 124505.
- [127] C.-H. Tu, D.-L. Kwong, Y.-S. Lai, *Appl. Phys. Lett.* **2006**, 89, 252107.
- [128] M. Lauters, B. McCarthy, D. Sarid, G. E. Jabbour, *Appl. Phys. Lett.* **2006**, 89, 10.
- [129] H. Houili, E. Tutiš, R. Izquierdo, *Org. Electron.* **2010**, 11, 514.
- [130] S. Song, J. Jang, Y. Ji, S. Park, T.-W. Kim, Y. Song, M.-H. Yoon, H. C. Ko, G.-Y. Jung, T. Lee, *Org. Electron.* **2013**, 14, 2087.
- [131] D. Lee, H. Choi, H. Sim, D. Choi, H. Hwang, M.-J. Lee, S.-A. Seo, I. K. Yoo, *IEEE Electron Device Lett.* **2005**, 26, 719.
- [132] J. D. Lee, H. M. Seung, K. C. Kwon, J. G. Park, *Curr. Appl. Phys.* **2011**, 11, e25.
- [133] P. Dimitrakakis, *Charge-trapping non-volatile memories* **2017**, 2.
- [134] I. Salaoru, S. Paul, *J. Optoelectron. Adv. Mater.* **2008**, 10, 3461.
- [135] I. Salaoru, S. Paul, *Thin Solid Films* **2010**, 519, 559.
- [136] D. Prime, S. Paul, P. W. Josephs-Franks, *IEEE Trans. Dielectr. Electr. Insul.* **2008**, 15, 905.
- [137] K. Saranti, S. Paul, in *Charge-Trapping Non-Volatile Memories* (Ed: P. Dimitrakakis), Springer, Berlin **2017**, p. 55.
- [138] D. Black, S. Paul, I. Salaoru, *Nanosci. Nanotechnol. Lett.* **2010**, 2, 41.
- [139] I. Salaoru, S. Paul, *Mater. Res. Soc. Symp. Proc.* **2008**, 1114, 100.
- [140] S. Koliopoulou, P. Dimitrakakis, P. Normand, *J. Appl. Phys.* **2003**, 94, 5234.
- [141] J. Chen, M. A. Reed, A. M. Rawlett, J. M. Tour, *Science* **1999**, 286, 1550.
- [142] M. A. Reed, J. Chen, A. M. Rawlett, D. W. Price, J. M. Tour, *Appl. Phys. Lett.* **2001**, 78, 3735.
- [143] A. Bandyopadhyay, A. J. Pal, *Chem. Phys. Lett.* **2003**, 371, 86.
- [144] A. Bandyopadhyay, A. J. Pal, *Appl. Phys. Lett.* **2003**, 82, 1215.
- [145] S. K. Majee, A. Bandyopadhyay, A. J. Pal, *Chem. Phys. Lett.* **2004**, 399, 284.
- [146] S. K. Majee, H. S. Majumdar, A. Bolognesi, A. J. Pal, *Synth. Met.* **2006**, 156, 828.
- [147] F. L. E. Jakobsson, X. Crispin, M. Cölle, M. Büchel, D. M. de Leeuw, M. Berggren, *Org. Electron.* **2007**, 8, 559.
- [148] S. Barman, F. Deng, R. L. McCreery, *J. Am. Chem. Soc.* **2008**, 130, 11073.
- [149] J. J. Yang, M. D. Pickett, X. Li, D. A. A. Ohlberg, D. R. Stewart, R. S. Williams, *Nat. Nanotechnol.* **2008**, 3, 429.
- [150] D.-H. Kwon, K. M. Kim, J. H. Jang, J. M. Jeon, M. H. Lee, G. H. Kim, X.-S. Li, G.-S. Park, B. Lee, S. Han, M. Kim, C. S. Hwang, *Nat. Nanotechnol.* **2010**, 5, 148.
- [151] B. J. Choi, D. S. Jeong, S. K. Kim, *J. Appl. Phys.* **2005**, 98, 033715.
- [152] D. S. Jeong, H. Schroeder, R. Waser, *Electrochem. Solid-State Lett.* **2007**, 10, G51.

- [153] I. Salaoru, T. Prodromakis, A. Khat, C. Toumazou, *Appl. Phys. Lett.* **2013**, 102, 013506.
- [154] D. Carta, I. Salaoru, A. Khat, A. Regoutz, C. Mitterbauer, N. M. Harrison, T. Prodromakis, *ACS Appl. Mater. Interfaces* **2016**, 8, 19605.
- [155] H. Shima, F. Takano, H. Akinaga, Y. Tamai, I. H. Inoue, H. Takagi, *Appl. Phys. Lett.* **2007**, 91, 012901.
- [156] S. Seo, M. J. Lee, D. H. Seo, S. K. Choi, D.-S. Suh, Y. S. Joung, I. K. Yoo, I. S. Byun, I. R. Hwang, S. H. Kim, B. H. Park, *Appl. Phys. Lett.* **2005**, 86, 093509.
- [157] A. C. Torrezan, J. P. Strachan, G. Medeiros-Ribeiro, R. S. Williams, *Nanotechnology* **2011**, 22, 485203.
- [158] J. E. Stevens, A. J. Lohn, S. A. Decker, B. L. Doyle, P. R. Mickel, M. J. Marinella, *J. Vac. Sci. Technol., A* **2014**, 32, 021501.
- [159] Y. Wu, S. Yu, B. Lee, P. Wong, *J. Appl. Phys.* **2011**, 110, 094104.
- [160] W. Kim, S. Il Park, Z. Zhang, S. Wong, *IEEE Trans. Electron Devices* **2014**, 61, 2158.
- [161] S. B. Lee, S. C. Chae, S. H. Chang, C. Liu, C. U. Jung, S. Seo, *J. Korean Phys. Soc.* **2007**, 51, 96.
- [162] S. Kim, K. P. Biju, M. Jo, S. Jung, J. Park, J. Lee, W. Lee, J. Shin, S. Park, H. Hwang, *IEEE Electron Device Lett.* **2011**, 32, 671.
- [163] W. C. Chien, Y. C. Chen, E. K. Lai, Y. D. Yao, P. Lin, S. F. Horng, J. Gong, T. H. Chou, H. M. Lin, M. N. Chang, Y. H. Shih, K. Y. Hsieh, R. Liu, C.-Y. Lu, *IEEE Electron Device Lett.* **2010**, 31, 126.
- [164] S. Zhang, S. Long, W. Guan, Q. Liu, Q. Wang, M. Liu, *J. Phys. D: Appl. Phys.* **2009**, 42, 055112.
- [165] S. Yu, H.-Y. Chen, B. Gao, J. Kang, H.-S. P. Wong, *ACS Nano* **2013**, 7, 2320.
- [166] Y. S. Lin, F. Zeng, S. G. Tang, H. Y. Liu, C. Chen, S. Gao, Y. G. Wang, F. Pan, *J. Appl. Phys.* **2013**, 113, 064510.
- [167] Z. Fang, H. Y. Yu, W. J. Liu, Z. R. Wang, X. A. Tran, B. Gao, J. F. Kang, *IEEE Electron Device Lett.* **2010**, 31, 476.
- [168] C. Walczyk, D. Walczyk, T. Schroeder, T. Bertaud, M. Sowinska, M. Lukosius, M. Frasccke, D. Wolansky, B. Tillack, E. Miranda, C. Wenger, *IEEE Trans. Electron Devices* **2011**, 58, 3124.
- [169] X. Cao, X. Li, X. Gao, W. Yu, X. Liu, Y. Zhang, L. Chen, X. Cheng, *J. Appl. Phys.* **2009**, 106, 073723.
- [170] H. Shima, F. Takano, Y. Tamai, H. Akinaga, I. H. Inoue, *Jpn. J. Appl. Phys.* **2007**, 46, L57.
- [171] Z. Zhang, B. Gao, Z. Fang, X. Wang, Y. Tang, J. Sohn, H.-S. P. Wong, S. S. Wong, G.-Q. Lo, *IEEE Electron Device Lett.* **2014**, 36, 29.
- [172] H.-D. Kim, M. J. Yun, S. M. Hong, T. G. Kim, *J. Nanosci. Nanotechnol.* **2014**, 14, 9088.
- [173] H.-D. Kim, M. J. Yun, S. M. Hong, T. G. Kim, *Nanotechnology* **2014**, 25, 125201.
- [174] M.-J. Lee, C. B. Lee, D. Lee, S. R. Lee, M. Chang, J. H. Hur, Y.-B. Kim, C.-J. Kim, D. H. Seo, S. Seo, U.-I. Chung, I.-K. Yoo, K. Kim, *Nat. Mater.* **2011**, 10, 625.
- [175] J. J. Yang, I. H. Inoue, T. Mikolajick, C. S. Hwang, *MRS Bull.* **2012**, 37, 131.
- [176] R. Waser, R. Dittmann, C. Staikov, K. Szot, *Adv. Mater.* **2009**, 21, 2632.
- [177] U. Celano, A. Fantini, R. Degraeve, M. Jurczak, L. Goux, W. Vandervorst, *AIP Adv.* **2016**, 6, 085009.
- [178] S. Munjal, N. Khare, *J. Phys. D: Appl. Phys.* **2019**, 52, 433002.
- [179] Q. Liu, J. Sun, H. Lv, S. Long, K. Yin, N. Wan, Y. Li, L. Sun, M. Liu, *Adv. Mater.* **2012**, 24, 1844.
- [180] W. Guan, M. Liu, S. Long, Q. Liu, W. Wang, *Appl. Phys. Lett.* **2008**, 93, 223506.
- [181] L. Ma, Q. Xu, Y. Yang, *Appl. Phys. Lett.* **2004**, 84, 4908.
- [182] W. Devulder, K. Opsomer, A. Franquet, J. Meererschaut, A. Belmonte, R. Muller, B. De Schutter, S. Van Elshocht, M. Jurczak, L. Goux, C. Detavernier, *J. Appl. Phys.* **2014**, 115, 054501.
- [183] H. Sun, Q. Liu, C. Li, S. Long, H. Lv, C. Bi, Z. Huo, L. Li, M. Liu, *Adv. Funct. Mater.* **2014**, 24, 5679.
- [184] Y. Yang, P. Gao, L. Li, X. Pan, S. Tappertzhofen, S. Choi, R. Waser, I. Valov, W. D. Lu, *Nat. Commun.* **2014**, 5, 4232.
- [185] C. Nauenheim, C. Kuegeler, A. Ruediger, R. Waser, *Appl. Phys. Lett.* **2010**, 96, 122902.
- [186] H. Y. Jeong, J. Y. Kim, J. W. Kim, J. O. Hwang, J.-E. Kim, J. Y. Lee, T. H. Yoon, B. J. Cho, S. O. Kim, R. S. Ruoff, S.-Y. Choi, *Nano Lett.* **2010**, 10, 4381.
- [187] G. L. Li, G. Liu, M. Li, D. Wan, K. G. Neoh, E. T. Kang, *J. Phys. Chem. C* **2010**, 114, 12742.
- [188] G. Liu, X. Zhuang, Y. Chen, B. Zhang, J. Zhu, C.-X. Zhu, K.-G. Neoh, E.-T. Kang, *Appl. Phys. Lett.* **2009**, 95, 253301.
- [189] B. Zhang, Y.-L. Liu, Y. Chen, K.-G. Neoh, Y.-X. Li, C.-X. Zhu, E.-S. Tok, E.-T. Kang, *Chem. - Eur. J.* **2011**, 17, 10304.
- [190] INTERNATIONAL ROADMAP FOR DEVICES AND SYSTEMS, "Beyond CMOS: Emerging Research Devices (ERDS)", **2016**, p. 1.
- [191] I. Salaoru, A. Khat, Q. Li, R. Berdan, T. Prodromakis, *Appl. Phys. Lett.* **2013**, 103, 233513.
- [192] R. Zhang, T.-F. Young, M.-C. Chen, H.-L. Chen, S.-P. Liang, Y.-E. Syu, S. M. Sze, K.-C. Chang, T.-C. Chang, T.-M. Tsai, S.-Y. Huang, W.-J. Chen, K.-H. Chen, J.-C. Lou, J.-H. Chen, *IEEE Electron Device Lett.* **2014**, 35, 630.



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