INTRODUCTION

Overview of organic memory devices

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The demand for more efficient and faster memory structures is greater today than ever before. The efficiency of memory structures is measured in terms of storage capacity and the speed of functioning. However, the production cost of such configurations is the natural constraint on how much can be achieved. Organic memory devices (OMDs) provide an ideal solution, in being inexpensive, and at the same time promising high performance. However, all OMDs reported so far suffer from multiple drawbacks that render their industrial implementation premature. This article introduces the different types of OMDs, discusses the progress in this field over the last 9 years and invokes conundrums that scholars of this field are currently faced with, such as questions about the charging mechanism and stability of devices, contradictions in the published work and some future directions.

Keywords: nanoparticles; molecules; polymer memory devices; charging mechanism(s); stability of memory devices; retention time

1. Introduction

Organic memory technology harbours the potential to radically improve this situation, because it is based on the deposition of low-cost polymer films of an active organic material, by a spin-on or by a dip-coating technique. A simple crossbar structure that determines the fabrication procedure of organic memories can eliminate the requirement of transistors. This in turn can greatly reduce the cost of manufacturing, as the bit-cell array can now be created in a single lithographic step instead of multiple lithographic steps, which would be needed in the presence of the transistors. Furthermore, the expenditure for supporting the crossbar architecture is potentially lower than complementary metal oxide semiconductors, because the substrate material for the bit-cell array does not need to be crystalline silicon; any plastic substrate could suffice. In light of the demonstrably lower production costs of the spin-on (or dip-coating) mechanism, we have the option of moving along the Z-direction,

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an endeavour that is balked by the unacceptably large costs involved in traditional deposition techniques. This opens up the possibility of creating inexpensive three-dimensional memory structures.

It is possible to characterize the organic memory devices (OMDs) that have so far appeared in publications and the literature into one of three broad categories:

(i) resistive switch and ‘write once, read many times’ (WORM) devices, 
(ii) molecular memory devices, and 
(iii) polymer memory devices (PMDs).

It should, however, be understood that these categories are by no means exclusive of each other, with large grey areas between them where some demonstrated devices can fall into two (or possibly even all three) categories.

(a) Resistive switch and write once, read many times devices

These devices potentially offer the simplest device structure, consisting of a cross-point array of top and bottom electrodes, separated by a resistive material as shown in figure 1. Each place where the top and bottom electrodes cross is one memory cell.

Depending on the material that the resistive layer consists of, it can then change in one of two ways when a voltage pulse is applied across the cell. The first type of device will short between electrodes, giving a lower resistance than the pristine state, whereas the second type acts like a blown fuse, giving a higher resistance than the pristine device.

(b) Molecular memories

In a molecular memory, a monolayer of molecules is sandwiched between a cross-point array of top and bottom electrodes, as shown in figure 2, with the molecules being packed in a highly ordered way, so one end of the molecule is electrically connected to the bottom electrode and the opposite end of the molecule is connected to the top electrode. Langmuir–Blodgett (LB) deposition is ideally suited for depositing the molecular layer in these devices.

By applying a voltage between the electrodes, the conductivity of the molecules is altered, enabling data to be stored in a non-volatile manner. The process can then be reversed and the data erased by applying a voltage of the opposite polarity to the memory cell.
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c) Polymer memory devices

PMDs also consist of a layer of organic material sandwiched between a cross-point array of top and bottom electrodes. However, in this structure, the organic layer consists of an admixture of deliberately introduced molecules and/or nanoparticles in an organic polymer matrix, as illustrated in figure 3.

Deposition of the organic layer is usually done by the spin-coating method (or by dip-coating), with all the required constituent materials being dissolved in a solvent, which is then spun onto the substrate. As the solvent evaporates, a thin film of material in the region of tens to hundreds of nanometres thick is deposited on the bottom layer of electrodes. Top electrodes are then deposited as the final step.

The conductivity of the organic layer is then changed by applying a voltage across the memory cell, allowing a bit of data to be stored.

Before an in-depth discussion of previous work is undertaken, it is prudent to add a brief description of the general shapes that have been reported in the current–voltage ($I-V$) characteristics of OMDs, to allow the reader to visualize the descriptive terms used. In the majority of OMDs, the bistability of the devices is demonstrated by investigating the $I-V$ characteristics and showing that for a given read voltage, there exist two different conductivity states and hence two different current responses. The bulk of $I-V$ characteristics published so far can be grouped into one of three general shapes, namely, N-shaped, S-shaped and O-shaped.

N-shaped characteristics (illustrated in figure 4) are typified by a low current up to a certain threshold voltage ($V_T$; region 1), where a sudden increase in current by up to several orders of magnitude becomes apparent (region 2). If the voltage is then reduced, the device stays in this high conductivity state and has a high current response (region 3). However, if voltages higher than $V_T$ are
applied, a phenomenon known as \textit{voltage-controlled negative resistance} (VCNR) is present, where an increase in voltage leads to a reduction in current (region 4). Voltages higher than the VCNR region once again return the device to its low conductivity state. These devices respond symmetrically to applied voltages, so applying negative voltages has the same effect as positive voltages.

S-shaped $I$–$V$ characteristics are similar to N-shaped characteristics with respect to the sudden increase in current at a voltage $V_T$; however, these plots do not show the VCNR region and instead current continues to increase with applied voltage. Both symmetric and asymmetric characteristics are possible, with symmetric devices (figure 5a) switching to the on state with a $V_T$ of either polarity. Some devices revert to the off state when the voltage is reduced to zero, making them volatile memories, whereas in others only a very small voltage of the opposite polarity is needed to switch these devices off. With asymmetric devices (figure 5b), the on state is maintained when the voltage is reduced, with a negative voltage needed to switch back to the low conductivity state.

The final type, O-shaped characteristics, does not show any abrupt increase in current at a specific voltage, but instead shows a simple hysteresis loop. Figure 6 demonstrates this showing an anticlockwise hysteresis loop for a positive voltage applied; however, this loop can also be clockwise, i.e. the \textit{write} voltage can either increase or decrease the conductivity depending on the device studied.

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2. Resistive switch and write once, read many times devices

The field of organic memories is considered to be relatively new, with high profile articles popularizing the field only appearing within the past decade (Scott 2004). However, the origins of the work date back to the early 1960s, when thin films of insulating materials were shown to exhibit electrical switching and, in most cases, regions of VCNR.

The word forming, or the now more common electroforming, became used to describe the process by which the insulating material’s conductivity is altered when a voltage above a certain threshold voltage is applied. Initially, the insulating materials investigated were inorganic insulators such as Al$_2$O$_2$ (Hickmott 1962, 1965; Barriac 1969), SiO (Simmons & Verderber 1967), ZnS (Sutherland 1971) and TiO (Ansari & Qadeer 1985); however, organic and polymeric insulators were soon investigated and also found to exhibit similar electroforming behaviour (Hogarth & Zor 1975; Hogarth & Iqbal 1979). However, there was still much uncertainty over the mechanisms that were responsible, with theories including

(i) metal ion injection from the electrodes, leading to impurity bands in the insulator (Simmons & Verderber 1967);
(ii) conducting filamentary pathways forming owing to electrolytic processes (Barriac 1969);
(iii) formation of filaments from the metallic electrodes (Dearnaley et al. 1970; Sutherland 1971; Hogarth & Iqbal 1979), carbonaceous material from the insulator itself or from sources introduced during manufacture of the devices (Blessing et al. 1981; Biederman et al. 1989); and
(iv) tunnelling between metal islands produced during the electroforming process (Thurstans & Oxley 2002).

The majority of papers published that attempt to explain the phenomena observed in electroformed metal–insulator–metal (MIM) claim that filamentary formation occurs in the insulating material, forming a low conductance pathway between the electrodes (Dearnaley et al. 1970; Sutherland 1971; Hogarth & Iqbal 1979; Ray & Hogarth 1984, 1990; Biederman et al. 1989; Pagnia 1990). However, despite multiple efforts to image filaments using various microscopy techniques such as scanning electron microscopy, transmission
electron microscopy (Pagnia et al. 1987) and scanning tunnelling microscopy (Pagnia 1990; Pagnia et al. 1990; Brauer et al. 1994), there is still only circumstantial evidence for their existence, with Pagnia et al. (1990) concluding that if filaments existed, they could be no larger than the resolution of the imaging instrument being used.

Despite these devices’ ability to function as electronic memory elements, and the proponents of using these devices as such, resistive switching devices have been regarded by several as unsuitable for non-volatile memory applications owing to the large areas of uncertainty in their operation and the possibility that the mode of operation is actually due to a physical breakdown of the device (Pagnia 1994; Thurstans & Oxley 2002).

One exception to this case is when a device is being intentionally and irreversibly damaged to change the state of a memory cell, as is the case with WORM devices. Forrest and co-workers demonstrated a WORM device based on a polymer fuse of poly(3,4-ethylenedioxythiophene) (PEDOT; Moller et al. 2003). The as-deposited device shows high conductance owing to the conducting polymer PEDOT, but when a sufficiently high voltage is applied across the memory cell, the polymer fuses will burn causing a low conductance state.

Applications for this type of device are limited to replacement for programmable read-only-type memories, where data do not need to be rewritten, meaning that the market is much more limited than for a rewritable bistable device.

As discussed earlier, any device showing a VCNR region has a general N-shaped characteristic, as is the case for all the resistive switches discussed here. It therefore seems possible that similar (if not the same) mechanisms are responsible despite the differences in materials used.

3. Molecular memories

The first devices to appear in publication that were claimed to work via electrical switching in monolayers of oriented molecules between two metallic electrodes were demonstrated by Chen et al. (1999). They demonstrated that a benzene-based molecule containing amine and nitro groups could exhibit bistability, concluding that the change in conductivity was due to a two-step reduction process in the molecule, the first reduction supplying an excess electron, providing a charge carrier for electron flow, and hence high conductivity. Upon increasing voltage, a second reduction step takes place, blocking the current flow in the system, leading to low conductivity. Similar results were obtained by Reed et al. (2001), who demonstrated that molecules without the nitro group did not show switching behaviour. Retention times of more than 15 min were possible and multiple memory cycles were shown; however, no mention of the ultimate number of memory cycles is given.

Subsequent papers by Chen et al. (2003a,b) demonstrated that the memory effect was also present at the nanoscale, by fabricating 40 nm² memory cells. These papers were also the first to present data regarding statistical analysis of devices, highlighting variations from 10 to 10⁴ for on/off ratios. Typical on/off ratios of 100 were reported, but quickly decayed to unity after a few hundred cycles at most. Also 50 per cent of the devices only switched once, and those that
did show rewritable behaviour had large variations in switching voltages, ranging from 3.5 to 7 V. Overall, out of 24 8 × 8 matrices analysed, only three showed no catastrophic defects, which emphasizes the need for improvements in these devices before viable memories can be achieved.

Other molecules including DDQ (Bandyopadhyay & Pal 2003a,b), TAPA (Bandyopadhyay & Pal 2003a,b) and Rose Bengal (Bandyopadhyay & Pal 2003a,b; Majee et al. 2004) have been demonstrated to exhibit bistability, with all research groups finding that the required prerequisite for bistability is that the molecule possesses groups that can be chemically reduced when a voltage is passed through them, thus allowing the mechanisms described by Reed et al. (2001) to take place.

Despite the majority of research groups claiming that reduction/oxidation mechanisms are responsible for the switching in these organic memories, there are still some uncertainties, with another possible mechanism being filamentary formation. Jakobsson et al. (2007) conducted systematic experiments on Rose Bengal molecular devices, finding that switching only occurred in a small area of the device and also had an associated heat spot at that position, concluding that switching was owing to repeatable formation of conductive filaments.

The main problem with molecular devices has been the variability between devices, with large differences in characteristics being present, even between devices on the same substrate. This could be a symptom of having a large number of molecules, even in nanoscale devices (approx. 1100 molecules for a 40 nm² device; Chen et al. 2003b).

4. Polymer memory devices

In some respects, many of the devices that fall into the PMD category could be included in the resistive switch category. This is especially true of the devices that consist solely of a polymer layer sandwiched between electrodes, which in many cases show remarkably similar behaviour to those classed as organic resistive switches. Despite the similarities in characteristics, and even in some cases similar proposed mechanisms for the switching phenomenon, the authors themselves do not class their work as resistive switches and also no longer use the term electroforming in relation to the switching. For this reason, most modern devices studied (year 2000 onwards) will be classed as PMDs.

The first device based on this structure was studied by Ma et al. (2000) and consisted of a polymer derivative of anthracene called poly(methylmethacrylate-co-anthracenylmethacrylate) (MDCPAC), in a sandwich structure between gold and aluminium electrodes. By applying various voltages to the devices, the MDCPAC layer conductivity could be changed, resulting in a non-volatile, bistable memory device. It was proposed that the mechanism for the change in conductivity was trap sites in the polymer film being filled upon the application of an electric field, but no conclusive evidence was presented, and the performance of the devices as memory elements was not discussed. It was also noted that the gold bottom electrode was crucial for switching to take place, with no switching occurring when aluminium bottom electrodes were used.

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The next progression in devices came from structures first proposed by the Yang group at the University of California, Los Angeles (Ma et al. 2002a,b,c, 2003; He et al. 2005; Pyo et al. 2005) and consisted of a layered structure of organic/metal-nanocluster/organic deposited between two aluminium electrodes. 2-Amino-4,5-imidazoledicarbonitrile (AIDCN), an organic semiconducting polymer, was used for the organic layers, whereas evaporation of a thin metal layer in the presence of oxygen or AIDCN formed discontinuous metal nanoclusters. The proposed working mechanism involved doping the AIDCN layers, thereby significantly increasing the conductivity of the devices by the storage of charge at either side of the nanocluster layer. Many layer thicknesses (Pyo et al. 2005) and permutations of metals (Ma et al. 2002a,b,c) were also studied with on/off ratios in the range from four to six orders of magnitude. Subsequent investigations by He et al. (2005) used contacts to this middle nanocluster layer to show that switching mainly occurs in the bottom organic layer. It was postulated that this was due to organometallic complexes formed by contact evaporation, giving rise to an asymmetric device structure. It is also shown in this paper that devices can be made symmetric by deliberately introducing an Al₂O₃ layer under the top electrode; however, as Al₂O₃ was one of the first materials found to show resistive switching, this could be playing an important role in the switching mechanism itself. All of the devices based on nanocluster layers (Ma et al. 2002a,b,c, 2003; Pyo et al. 2005) were symmetric S-shaped devices, showing no negative differential resistance (NDR) region, except those (He et al. 2005) that showed asymmetric S-shaped characteristics.

The mechanisms for bistability in these devices were investigated in greater detail by Bozano et al. (2004), while relating the electrical characteristics to those found in early electroformed MIM diodes and also concluding that similar mechanisms were likely to be responsible. However, Bozano et al. found NDR to be present in their devices despite the same structure being investigated, highlighting the problem that characteristics can also be as much dependent upon the research group as on the device structure. Tondelier et al. (2004) studied the 3L-OBD and, in addition, 1L-OBD structures, by which devices were fabricated without the middle metal nanocluster layer. Similar switching behaviour was found even without the middle metal nanocluster layer. They concluded that metal nanoparticles were included in the polymer layer during the thermal evaporation of the top electrode, with metallic filaments of nanoparticles forming in the polymer under high electric fields, giving rise to a high conductivity on state.

Rather than relying on nanoparticles forming during fabrication of the devices, Paul et al. (2003) demonstrated the feasibility of including ready-made nanoparticles in devices. By incorporating a monolayer of gold nanoparticles via LB deposition techniques into the insulating layer of metal–insulator–semiconductor (MIS) capacitors, hysteresis was found in the capacitance–voltage (C–V) characteristics when compared with devices without nanoparticles. This was attributed to electrons being injected onto the nanoparticles from the gate electrode, thereby charging the nanoparticles and allowing data storage. Leong et al. (2007) more recently demonstrated similar results in MIS structures; however, they attributed the hysteresis as being due to holes injected onto the nanoparticles. While the devices demonstrated in these papers are not used directly as PMDs, it is demonstrated that the proposed mechanism of using nanoparticles as charge storage elements is feasible.
The first paper that includes discrete nanoparticles into MIM memory structures was presented by Ouyang et al. (2004), demonstrating that these devices would behave in a manner similar to the metal nanocluster devices previously studied by Ma et al. (2002a, b, c) and Pyo et al. (2005). The devices comprised an admixture of gold nanoparticles capped with 1-dodecanethiol (Au-DT) and 8-hydroxyquinoline (8HQ) molecules in a polystyrene matrix. The change in conductivity in these devices is attributed to the transfer of electrons from the 8HQ molecules to the Au-DT, with 8HQ and gold nanoparticles previously shown to act as electron donors and acceptors, respectively (Castella & Prout 1971; Ipe et al. 2002; Adams et al. 2003). A tunnelling mechanism between 8HQ molecules was proposed as being responsible for the high conductivity on state, with a combination of Fowler–Nordheim and direct tunnelling being fitted to the experimental data.

Ouyang et al. (2005a, b) later studied MIM structures including nanoparticles capped with 2-naphthalenethiol (Au-2NT) embedded in a polystyrene matrix. Here, a transfer of electrons from the capping ligands of the nanoparticles and the nanoparticle core itself is proposed as the charging mechanism, with tunnelling between the nanoparticles responsible for conduction in the on state. These devices were found to only exhibit WORM characteristics, with no transition back to the off state, implying that once the electron transfer has taken place it is irreversible.

Work investigating the effect of different metallic nanoparticles, as well as the position of the nanoparticles in the structure and electrode material, has been carried out by Bozano et al. (2005), with bistability shown to be surprisingly independent of the materials chosen and the structures investigated. However, once again Bozano et al. reported N-shaped I–V characteristics, in disagreement with those of Ma et al. (2002a, b, c) and Ouyang et al. (2004, 2005a, b) who, in all cases, reported S-shaped characteristics. Bozano et al. found that characteristics were broadly similar to those reported by Simmons & Verderber (1967) in their work on electroformed MIM structures and concluded that similar mechanisms were probably responsible. The main differences being that while in the Simmons–Verderber (SV) model, gold atoms introduced from the electrodes create charge transport and trapping sites in the insulator, here, that role is played by the gold nanoparticles. Hence, conduction in the on state is dominated by tunnelling between the nanoparticles.

Devices based on gold nanoparticle and 8HQ admixtures have also been investigated by Prime & Paul (2007, 2008), following the device structure used by Ouyang et al. (2004). In these devices, O-shaped characteristics were reported, with no abrupt transition between on and off states, once again showing differing device characteristics, where the same structure has been investigated by different research groups.

Further materials based on the idea of gold nanoparticle charge transfer complexes have also been studied with poly(3-hexylthiophene) (P3HT; Prakash et al. 2006), poly(N-vinylcarbozole) (PVK; Song et al. 2007) and PCm (Lin et al. 2007), being used as both the electron donor material and the polymer matrix material. S-shaped characteristics were reported in all the papers; however, Prakash et al. (2006) reported that the on-state current fitted well with Poole–Frenkel emission, based on field-enhanced thermal emission of trapped charges, rather than the tunnelling mechanism widely reported in other papers.
In order to ensure that no nanoparticle agglomerations were present in the devices Tseng et al. (2006) incorporated platinum nanoparticles into the tobacco mosaic virus (TMV), finding that bistability only occurred when the nanoparticles were present. The mechanism here was once again attributed to charge transfer, this time between the TMV and the nanoparticles.

Recent articles by both Kim et al. (2008) and Lai & Chen (2008) draw the conclusion that charge transfer onto the nanoparticles is responsible for the change in conductivity of the devices; however, Lai & Chen (2008) conclude that carrier transport is via hopping of holes along the PVK polymer chains.

Table 1 summarizes the main findings of papers based on metal nanoclusters and metal nanoparticles.

The later device structures appearing in publication consist of admixture structures similar to the nanoparticle devices, but use buckminsterfullerene (C60) as an electron-accepting material in place of the metallic nanoparticles. First introduced by Kanwal et al. (2005) at the Materials Research Society (MRS) conference in 2004, these devices also show the required characteristics for bistability and non-volatility. Subsequent devices studied by Majumdar et al. (2005) showed that depending upon the concentration of C60, the devices exhibited either bistability or at higher concentrations WORM characteristics. Latest reports on these devices by Paul et al. (2006) expanded on the work of Kanwal et al. and were the first to show that bistability was also present at the nanoscale by using a conducting atomic force microscope (c-AFM) probe as the top electrode of the device. While current difference between the on and off states at the nanoscale was significantly smaller than at the macroscale, this work did prove that high-density memories could be fabricated, while still retaining memory functionality.

Another novel memory structure demonstrated by Ma et al. (2004) included copper ions introduced into an AIDCN layer. This device switched to a high conductivity state at approximately 0.7 V and switched off again at 2 V. Ma et al. (2004) proposed that electric field-induced migration of the Cu⁺ ions into the polymer layer causes metallization of the polymer layer, resulting in a high conductivity state. At higher voltages, the ions drift all the way across the polymer layer, returning it back to an insulator. Current ratios of three orders of magnitude have been demonstrated with this structure.

Other devices studied, but so far receiving less attention, include memories based on europium-based charge transfer polymers (Ling et al. 2005), polymers with sulphur impurities (Majee et al. 2006) and functionalized carbon nanotubes (Pradhan et al. 2006).

A detailed investigation into switching in fluorine-containing PMDs has also been undertaken by Dimitrakis et al. (2008). In these devices, NDR was observed, and also in most cases a forming process was needed before bistability became evident. Including gold nanoparticles into the structure was found to improve reproducibility, but was not essential for switching to occur, with switching instead being related to the presence of an oxide layer on the bottom aluminium contact and the deposition rate of the top contact. They proposed that filamentary formation did not fully explain all of the characteristics, but that charge transport through nanocrystalline regions in the polymer may better explain the observed characteristics.
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Despite continued research and many papers being published on the subject, there is still much speculation over the exact mechanisms that are responsible for the large change in conductivity that is present in many PMDs. The main theories that have so far been postulated are as follows.

(i) Charge transfer creating internal electric fields: this internal electric field either enhances or diminishes an external voltage applied to the device, thereby giving either high or low conductance.

(ii) Nanoparticle/nanocluster charging leading to a change in material properties: various conduction mechanisms have been proposed including space-charge-limited current, Poole–Frenkel emission, Fowler–Nordheim or direct tunnelling.

(iii) Filamentary formation between electrodes: conductive filaments are formed under electrical stress from either migration of electrode material or alignment of nanoparticles. These filaments can then be ruptured returning the device to a low conductivity state.

Until the working mechanism is understood in greater detail, this is likely to prove a large obstacle in the development and possible commercialization of PMDs.

In the majority of work published to date, bistability and non-volatility are reported, which constitutes the absolute minimum requirements for a device to be called a memory. Other important device characteristics such as on/off ratio, retention times and memory cycles are either omitted completely or show large discrepancies in the reported values. This lack of data regarding long-term memory performance could be a symptom of the general trend in the field to overly concentrate on the on/off ratios of the devices, which have now reached extraordinary levels. Alternatively, it could be that research has been conducted in this area, but possibly does not compare favourably with existing memory technologies.

A summary of the extremes reported for the different characteristics is included in table 2, with the data being limited only to devices containing charge trapping nanoclusters or nanoparticles.

Of these characteristics, the on/off ratio actually raises many questions regarding the working mechanisms of the PMDs. With ratios as high as $10^9$, there are many reported devices that have on-state currents in the microampere range and, in some cases, even milliamperes. When considering that these are organic-based materials with thicknesses of generally less than 100 nm and lateral dimensions of a few millimetres, this results in incredibly high current densities. Scott (2004) argued that any new technology must be able to compete with cutting-edge memory devices in terms of rated memory cycles, power consumption, retention time and price, in order to be considered as a successor to any of the currently available memories; characteristics that so far PMDs fail to match in one or more areas. PMDs also have to offer performance that is at least equal to the foreseeable advances that are likely to be made by the established memory technologies in order to make it economically viable to switch to a new technology. While it is unclear whether PMDs will compete directly with existing memory technologies or find their own niche market where price becomes a driving factor and performance requirements are not so strict, what is certain is that much work still needs to be done to improve performance.
Table 1. Summary of metal nanocluster and nanoparticle PMDs.

<table>
<thead>
<tr>
<th>device structure</th>
<th>$I-V$ shape</th>
<th>switching mechanism</th>
<th>memory performance</th>
<th>reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al/AIDCN/Al/AIDCN/Al</td>
<td>S-shaped</td>
<td>polarization of middle Al nanocluster layer</td>
<td>on/off ratio: $10^6$</td>
<td>Ma et al. (2002a,b,c)</td>
</tr>
<tr>
<td>Al/AIDCN/Al/AIDCN/Al</td>
<td>S-shaped</td>
<td><em>not</em> due to metallic filaments</td>
<td>on/off ratio: $10^6$</td>
<td>Ma et al. (2002a,b,c)</td>
</tr>
<tr>
<td>Al/AIDCN/Al/AIDCN/Al</td>
<td>S-shaped</td>
<td>trapped charges/polarization in the middle metal layer</td>
<td>on/off ratio: $10^4$, retention: several weeks, cycles: &gt;1 million, switching time: 10 ns</td>
<td>Ma et al. (2003), He et al. (2005)</td>
</tr>
<tr>
<td>Al/AIDCN/Al/AIDCN/Al</td>
<td>S-shaped</td>
<td>polarization of middle Al nanocluster layer</td>
<td>on/off ratio: $10^3$, retention: &gt;3 h, cycles: &gt;10000</td>
<td>Pyo et al. (2005)</td>
</tr>
<tr>
<td>Al/AIq3/Al/AIQ3/Al</td>
<td>N-shaped</td>
<td>SV mechanism—charge trapping in metal nanoclusters</td>
<td>not discussed</td>
<td>Bozano et al. (2004)</td>
</tr>
<tr>
<td>Al/pentacene/Al</td>
<td>S-shaped</td>
<td>metallic pathways of nanoparticles; ohmic behaviour in on state</td>
<td>on/off ratio: $10^9$, retention: &gt;1 week, cycles: &gt;100</td>
<td>Tondelier et al. (2004)</td>
</tr>
<tr>
<td>p-Si/SiO$_2$/Au-NP/CdAA/Al</td>
<td>—</td>
<td>charge trapping of electrons on gold nanoparticles</td>
<td>not discussed</td>
<td>Paul et al. (2003)</td>
</tr>
<tr>
<td>n-Si/SiO$_2$/Au-NP/pentacene/Al</td>
<td>—</td>
<td>charge trapping of holes on gold nanoparticles</td>
<td>not discussed</td>
<td>Leong et al. (2007)</td>
</tr>
<tr>
<td>Al/Au-DT+8HQ+PS/Al</td>
<td>S-shaped</td>
<td>charge transfer between 8HQ and Au-DT; on state: tunnelling between 8HQ molecules</td>
<td>on/off ratio: $10^4$, cycles: &gt;5, switching time: &lt;25 ns</td>
<td>Ouyang et al. (2004, 2005a,b)</td>
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<tr>
<td>Al/Au-NT+PS/Al</td>
<td>S-shaped</td>
<td>charge transfer between ligand and Au-NT core; off state: electrode-limited current injection; on state: space-charge-limited current</td>
<td>on/off ratio: $10^3$, retention: &gt;60 h</td>
<td>Ouyang et al. (2005a,b)</td>
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Table 1. (Continued.)

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<tr>
<th>device structure</th>
<th>I–V shape</th>
<th>switching mechanism</th>
<th>memory performance</th>
<th>reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>MIM structures with various electrode metals,</td>
<td>N-shaped</td>
<td>SV mechanism—charge trapping in metal nanoclusters; on state: tunnelling between</td>
<td>on/off ratio: 10–10⁶, dependent as much on the device, than the</td>
<td>Bozano et al. (2005)</td>
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<tr>
<td>nanoparticle metals and polymer matrices</td>
<td></td>
<td>metal nanoparticles</td>
<td>difference between structures</td>
<td></td>
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<tr>
<td>Al/Au-NP+8HQ+PS/Al</td>
<td>O-shaped</td>
<td>charge transfer between 8HQ and Au-NP</td>
<td>on/off ratio: 10, cycles: &gt;3 h, working devices: approximately 90 per</td>
<td>Prime &amp; Paul (2007, 2008)</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>cent retention: &gt;3 h, working devices: approximately 90 per cent</td>
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<tr>
<td>Al/Au-NP+P3HT/Al</td>
<td>N-shaped</td>
<td>charge transfer between P3HT and Au-NP; off state: contact-limited Schottky emission;</td>
<td>on/off ratio: 10³, cycles: &gt;3000</td>
<td>Prakash et al. (2006)</td>
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<tr>
<td></td>
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<td>on state: bulk-limited Poole–Frenkel emission</td>
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<tr>
<td>Al/Au-NP+PVK/Al</td>
<td>S-shaped</td>
<td>charge transfer between PVK and Au-NP</td>
<td>on/off ratio: up to 10⁵, cycles: approximately 50, retention: &gt;5 days</td>
<td>Song et al. (2007)</td>
</tr>
<tr>
<td>Al/Au-NP+PCm/Al</td>
<td>S-shaped</td>
<td>charge transfer between PCm and Au-NP</td>
<td>on/off ratio: 10², cycles: &gt;150, retention: approximately 10 h</td>
<td>Lin et al. (2007)</td>
</tr>
<tr>
<td>Al/TMV-Pt+PVA/Al</td>
<td>S-shaped</td>
<td>charge transfer between TMV and Pt nanoparticles; on state: Fowler–Nordheim tunnelling</td>
<td>on/off ratio: &gt;10³, cycles: approximately 400</td>
<td>Tseng et al. (2006)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>between Pt nanoparticles</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ITO/Au-NP+PS/LiF/Al</td>
<td>S-shaped</td>
<td>charge transfer between capping dendron and Au-NP</td>
<td>on/off ratio: approximately 10²</td>
<td>Kim et al. (2008)</td>
</tr>
<tr>
<td>Al/Au-NP+PVK/Al</td>
<td>S-Shaped</td>
<td>charge transfer between PVK and Au-NP</td>
<td>on/off ratio: up to 10⁹, retention: 42 min</td>
<td>Lai &amp; Chen (2008)</td>
</tr>
</tbody>
</table>
Table 2. Summary of reported device characteristics.

<table>
<thead>
<tr>
<th>characteristic</th>
<th>minimum reported</th>
<th>maximum reported</th>
</tr>
</thead>
<tbody>
<tr>
<td>retention time</td>
<td>&gt;3 h (Pyo et al. 2005)</td>
<td>several weeks (Ma et al. 2003; He et al. 2005)</td>
</tr>
<tr>
<td>memory cycles</td>
<td>approximately 50 (Prime &amp; Paul 2007, 2008; Song et al. 2007)</td>
<td>&gt;1 million (Ma et al. 2003; He et al. 2005)</td>
</tr>
</tbody>
</table>

Failures of devices have received no attention in published work, which can cast doubt on any results obtained. For instance, many research groups publish on-state currents of the order of tens to hundreds of microamperes. In devices that have dimensions of only a few millimetres squared and thicknesses of less than 100 nm, this leads to current densities and electric fields in excess of the published breakdown strengths of many of the polymer materials used. In any device operating under these conditions, there is doubt as to whether the device is actually suffering some form of electrical breakdown, rather than truly reversible bistability.

In summary, several areas of missing or ambiguous data concerning PMDs that will need attention are charging mechanism(s), in-depth electrical study of polymer materials used, failure mechanism and consistency in results obtained by other groups on similar devices.

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References


Phil. Trans. R. Soc. A (2009)
Introduction. Organic memory devices


*Phil. Trans. R. Soc. A* (2009)
Introduction. Organic memory devices


