Gold nanoparticle charge trapping and relation to organic polymer memory devices

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Nanoparticle-based polymer memory devices (PMDs) are a promising technology that could replace conventional silicon-based electronic memory, offering fast operating speeds, simple device structures and low costs. Here we report on the current state of nanoparticle PMDs and review some of the problems that are still present in the field. We also present new data regarding the charging of gold nanoparticles in metal–insulator–semiconductor capacitors, showing that charging is possible under the application of an electric field with a trapped charge density due to the nanoparticles of \(3.3 \times 10^{12} \text{ cm}^{-2}\).

Keywords: gold nanoparticle; organic polymer memory device; metal–insulator–semiconductor capacitor; trapped charge density

1. Introduction

In the field of electronics, boundaries are continually being expanded, with a constant drive to produce devices that are faster, smaller and cheaper than those of the previous generation. Indeed, this trend has persisted throughout the history of electronics, with the famous Moore’s law being used to describe how the number of transistors in an integrated circuit doubles approximately every 2 years (Intel 2005). It is not known how long this trend can continue, but eventually conventional electronics will reach the fundamental limits of the atomic scale. One promising new technology that is currently receiving extraordinary levels of interest is organic electronics, which could offer cheaper electronics and simpler device architectures compared with those based on silicon. Recent advances in devices such as organic field-effect transistors and organic light-emitting diodes (OLEDs), and the commercialization of organic-based devices such as OLED-based flat panel displays (Sony 2008), have shown that organic electronics can compete with silicon in certain areas. However, in others, such as organic-based electronic memories, progress has been slower. High-profile articles such as that published by Scott (2004) have clearly highlighted a need for a ubiquitous memory.
device that can replace current memory technologies such as hard disk drives (HDD), flash and random access memory (RAM), each of which has their inherent disadvantages as outlined by Scott.

One possible organic memory architecture that could offer the performance characteristics of RAM, combined with the non-volatile nature of flash and the price of HDDs, is the metal nanoparticle-based polymer memory device (PMD), in which a polymer matrix containing metal nanoparticles and other small molecules is sandwiched between a cross-point array of electrodes as shown in figure 1. These devices store data by existing in either a high- or low-conductivity state, which can be set by applying either a write or erase voltage across the memory cell (usually of opposite polarities). The state can then be sensed by reading out the current when an intermediate read voltage is applied across the cell.

The first devices to incorporate discrete nanoparticles in this way were studied by Ouyang et al. (2004), but these were just the latest in a progression of devices going back to the ones investigated by Ma et al. (2002a,b,c), which used a discontinuous evaporated metal layer in the middle of the polymer layer to trap charge. While these memory devices have been shown to exhibit rewritable and non-volatile characteristics, they still have not progressed to commercialization, due in part to the fact that there are still large amounts of uncertainty and associated debate over the exact mechanisms that are responsible for the large change in conductivity between the on and off states of the devices. So far, some of the main theories that are still discussed in the literature may be broken down into the following categories: charge transfer between nanoparticles and an electron-donating species (such as 8-hydroxyquinoline) (Ouyang et al. 2004), conductive filament formation (Tondelier et al. 2004) and charge trapping leading to space-charge inhibition of injected current (Bozano et al. 2004).

This paper aims to give an overview of the main results that have been published, which can be classed as nanoparticle-based memories, as well as highlighting some of the inconsistencies in the field. It will then go on to present some new experimental data that shed light on possible mechanisms that have been proposed for PMDs.

2. Nanoparticle memory review

First, it is important to highlight that, even among device structures that are supposedly identical, differing research groups do not necessarily report identical characteristics. This is most evident in the shape of the current–voltage (I–V)
curves that are often reported. The vast majority of papers fall into either S-shaped or N-shaped characteristics, where a sudden switch occurs leading to a higher conductance state as shown in figure 2a,b. One of the main differences between the two types is the region of negative differential resistance (NDR) that is present in the N-shaped characteristics. There are also several variations in these two shapes, with some devices exhibiting asymmetrical behaviour, in which the erase and write voltages are of opposite polarity, while in symmetrical devices, all the functions can be performed with a single polarity and tend to show the same characteristics in the negative voltage region. There is also a third type of device that simply shows hysteresis within the $I-V$ characteristics, with no sudden switching or NDR.

As mentioned previously, the first devices that can be classed as nanoparticle based were proposed by Ma et al. (2002a,b,c, 2003), He et al. (2005) and Pyo et al. (2005) and consisted of a trilayer structure of organic/metal-nanocluster/organic sandwiched between two aluminium electrodes (named three-layer organic bistable devices, 3L-OBDs). 2-Amino-4,5-imidazoledicarbonitrile (AIDCN), an organic semiconducting polymer, was used for the organic layers. The metal-nanocluster layer was formed in these devices by evaporating a thin metal layer in the presence of oxygen or AIDCN, forming discontinuous metal nanoclusters. It was proposed that charge could be stored at either side of the nanocluster layer, thereby doping the AIDCN layers and significantly increasing the conductivity of the devices, allowing ‘digital bits’ of information to be stored. Many permutations of metals (Ma et al. 2002a,b,c) and various layer thicknesses (Pyo et al. 2005) were studied, with on/off ratios in the devices ranging from four to six orders of magnitude, depending on the structure studied. He et al. (2005) showed that switching mainly occurs in the bottom organic layer, postulating that this was due to the organometallic complex formed by evaporating the top contact, giving rise to an asymmetric device structure. It is also shown in this paper that devices can be made symmetric by deliberately introducing an Al$_2$O$_3$ layer under the top electrode. 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 NDR region, except for that of He et al. (2005), which showed asymmetric S-shaped characteristics.

Similar structures have also been fabricated by Bozono et al. (2004), with the mechanisms for bistability being investigated in greater detail. They also related electrical characteristics to those found in electroformed metal–insulator–metal (MIM) diodes, such as those studied by Simmons & Verderber (1967), concluding...
that similar mechanisms were likely to be responsible for the two memory states in modern devices. However, despite supposedly the same structure being investigated, Bozano et al. found NDR to be present in their devices, leading to symmetric N-shaped characteristics, highlighting that characteristics can also be dependent as much on the research group and methodology used, as on the device structure. Subsequent investigations by Tondelier et al. (2004) also studied the same 3L-OBD structure as well as devices without the middle metal-nanocluster layer (calling them 1L-OBDs), finding that similar switching behaviour was present even without the middle metal layer. They concluded that metal nanoparticles were included in the polymer layer due to 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.

A subsequent evolution in the device structure came by including ready-made nanoparticles in the devices, rather than relying on nanoparticles self-assembling during fabrication of the devices. Paul et al. (2003) demonstrated the first of these devices by incorporating a monolayer of gold nanoparticles via the Langmuir–Blodgett technique into the insulating layer of metal–insulator–semiconductor (MIS) capacitors. Capacitors including nanoparticles were found to show hysteresis in their 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, charging the nanoparticles and allowing data storage. Similar results were also demonstrated in MIS structures more recently by Leong et al. (2007, 2008); however, they attributed the hysteresis to holes injected onto the nanoparticles. While the devices demonstrated in these papers are not used directly as PMDs, it does show that the principle of using nanoparticles as charge storage elements is feasible.

The first paper to include discrete nanoparticles into MIM memory structures was presented by Ouyang et al. (2004), who demonstrated that devices with discrete nanoparticles would behave in a manner similar to the metal-nanocluster devices previously studied by Ma et al. The devices comprised an admixture of gold nanoparticles capped with 1-dodecanethiol (Au-DT) and 8-hydroxyquinoline (8HQ) molecules in a polystyrene matrix, with the change in conductivity in these devices attributed to the transfer of electrons from the 8HQ molecules to the Au-DT. This positive and negative charging of the 8HQ and Au-DT, respectively, leads to a change in the conduction properties of the insulating film. 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. Further evidence for the charge transfer between 8HQ and Au-DT devices was presented in the form of electrical force microscopy (EFM) images of the polymer layer, without the top electrode. By using the EFM tip to bias the film with positive and negative voltages, the different conductivity states could be induced and then sensed by scanning over the whole area at a read voltage. The images presented showed pronounced EFM signals between the different pre-biased areas of the substrate.

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

Work investigating the effect of nanoparticles using different metals, as well as the position of the nanoparticles in the structure and electrode material, has also been carried out by Bozano et al. (2005), with bistability shown to be a common phenomenon among the materials chosen and the structures investigated. All the devices used semiconducting organic material as the organic layers of the device, with compositions similar to those studied by Ma et al. (2002a,b,c) and Ouyang et al. (2004). However, once again Bozano et al. reported N-shaped $I$–$V$ characteristics, in stark contrast to 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 once again characteristics were broadly similar to those reported by Simmons & Verderber (1967) in their work on electroformed MIM structures and concluded that similar conduction mechanisms are responsible. The main difference is that in the Simmons–Verderber model Au atoms introduced from the electrodes create charge transport and trapping sites in the insulator, whereas in Bozano et al. 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 nanoparticles and 8HQ admixtures have also been investigated by Prime & Paul (2007, 2008). In these devices, loop-shaped characteristics were reported, with no abrupt transition between the on and off states.

Other structures based on gold nanoparticle charge-transfer complexes have also been studied, with poly(3-hexylthiophene) (P3HT) (Prakash et al. 2006), poly($N$-vinylcarbazole) (PVK) (Song et al. 2007; Lai & Chen 2008) and 4-cyano-2,4,4-trimethyl-2-methylsulphanylthiocarbonylsulphanyl-poly(butyric acid 1-adamantan-1-yl-1-methyl-ethyl ester) (PCm) (Lin et al. 2007), being used as both the electron donor material and the polymer matrix material. Similar S-shaped characteristics were reported in all the papers; however, Prakash et al. (2006) reported that the on state current fitted well with the Poole–Frenkel emission, based on field-enhanced thermal emission of trapped charges.

There have also been attempts to ensure that nanoparticles are well dispersed in the devices, with Tseng et al. (2006) incorporating platinum nanoparticles into the tobacco mosaic virus (TMV), finding that bistability occurred only when the nanoparticles were present, with the mechanism again being attributed to charge transfer, this time between the TMV and the nanoparticles.

Recent articles by Kim et al. (2008) and Lai & Chen (2008) both draw the conclusion that charge transfer onto the nanoparticles is responsible for the change in conductivity of the devices, but, in their devices, conclude that carrier transport is via hopping of holes along the PVK polymer chains, rather than via electron tunnelling through the nanoparticles, as has been the more popular theory in the majority of papers.

A detailed investigation into switching in fluorene-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.

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contact and to 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.

3. Nanoparticle charging experiments

Unfortunately, owing to the variety of devices studied by different research groups (semiconducting or insulating polymer matrices, different nanoparticle capping ligands, differing metals, etc.), differences in the implementation of electrical testing methods and differences in the manufacturing procedures for different laboratories, it is very difficult to draw any one conclusion for a likely mechanism that could be responsible for every single case. However, if we take the proposed theory of nanoparticle charging, where carriers become trapped on the nanoparticles, then experiments based on capacitance measurements of MIS capacitors are much more sensitive to changes in trapped charge than \( I-V \) measurements of MIM devices. Similar experiments have been conducted by Paul et al. (2003) and Leong et al. (2007); however, here the experiments are extended and related back to conventional semiconductor theory to gain an understanding of the magnitudes of charges that are being trapped.

The nanoparticles used in the fabrication of the MIS capacitors and the structure of the capacitors are shown in figure 3.

In order to assess the quality and coverage of the gold nanoparticle layer, atomic force microscopy (AFM) images were taken of the Langmuir–Blodgett deposited layer before the final insulator and gate contacts were fabricated. In figure 4, the gold nanoparticle layer is clearly visible as the light areas on the darker substrate. From the analysis of the image, the surface coverage of nanoparticles is approximately 80 per cent. Scans of other areas of the substrate also confirm that this level of coverage is consistent across all the devices.

In conventional semiconductor MIS theory, the amount of trapped charges that are present in the insulating layer can be measured by studying the flatband voltage shifts of experimental capacitors compared with theoretical ones (Nicollian & Brews 1982). Here we are deliberately introducing gold nanoparticles

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in the MIS capacitors, which will act as trap sites and so induce large flatband voltage shifts depending on whether the nanoparticles are charged or uncharged. By placing the nanoparticles close to the semiconductor interface, any charge that is stored on them will have the greatest possible effect on the flatband voltage, relating to the largest possible amount of hysteresis. By considering the position of the nanoparticles in the capacitor and assuming that they remain immobile when an electric field is applied, the amount of charge stored can be modelled closest by using the equations relating to oxide-trapped charge \((Q_{\text{ot}})\) (Sze 1981), so the charge due to the nanoparticles \(Q_{\text{np}}\) can be calculated from

\[
Q_{\text{np}} = -\Delta V_{\text{FB}} \times C_{\text{ins}}. \tag{3.1}
\]

As the device geometry is known, it is possible to calculate the density of charges per unit area. As can be seen from figure 5, which shows typical \(C-V\) curves for the gold nanoparticles in the MIS capacitors, as the voltage scanning window is increased, the amount of hysteresis also increases. This large amount of hysteresis can be attributed to charge trapping and de-trapping of the gold nanoparticles; when nanoparticles are not present in the capacitors, very little hysteresis can be seen (figure 5, inset).

Figure 6 shows the large increase in the average hysteresis in the MIS capacitors when nanoparticles are included, with error bars showing the standard error for all data collected (error bars on the devices without nanoparticles are too small to show in the figure). This clearly illustrates the remarkable effect that the nanoparticles have on the levels of trapped charge that are present in the capacitors.

From the amount of hysteresis present in the \(C-V\) curves during the maximum gate voltage sweep, the density of trapped charges attributed to the nanoparticles is approximately \(3.3 \times 10^{12} \text{cm}^{-2}\). This level of charge density is of the same order of magnitude as that found by Prime et al. (2008) for the magnitude of

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mobile trapped charges in their investigations into insulator-trapped charges in polystyrene MIS capacitors. It is reasonable to assume that the poly(4-vinylphenol) (PVP) insulator used here will have a similar level of mobile trapped charges; however, we rule out the possibility of mobile charges being responsible for any of the hysteresis present here for two reasons. First, mobile charges take many minutes to move through the polymer layer under constant voltage stress, rather than the immediate effect that can be seen in the flatband voltage shifts here. Second, owing to the slower movement of mobile charges through the insulator, the whole curve, including positive and negative voltage sweeps, moves, rather than showing hysteresis between the positive and negative sweeps.

The large amount of hysteresis that is present in the $C-V$ curves not only provides data on the magnitudes of the trapped charges, but also can, in fact, be used itself as a memory device. The basic requirement for digital memory is that it is able to exist in two distinct states at a particular read voltage.
Figure 7. Retention characteristics of nanoparticle MIS capacitor. Inset shows capacitance difference between the on (grey) and off (black) states. The erase, read and write voltages were −7, −0.5 and +7 V, respectively.

The inset of figure 7 clearly shows that, at the read voltage, there is a clear difference between the on and off capacitances, with initial on and off capacitances being 10 and 48 pF, respectively, after applying write and erase voltage pulses of +7 and −7 V. A constant read voltage of −0.5 V was then applied to the capacitor for approximately 6 h in both the on and off states as shown in figure 7, with a discernible difference being present at all times.

As would be expected, the off-state capacitance remains reasonably constant, as this is the case in which the nanoparticles are discharged, whereas the on-state capacitance slowly increases as the nanoparticles discharge with time. It is believed that by refining the device structure, it would be possible to minimize the discharge, further improving the retention times of the memory.

4. Experimental

Nanoparticle MIS capacitors were fabricated via the following procedure: clean p-type silicon with a thin layer (approx. 3 nm) of SiO$_2$ and an ohmic aluminium back contact was silanized, followed by deposition of a layer of gold nanoparticles (dodecanethiol capped, purchased from Sigma Aldrich) via Langmuir–Blodgett deposition. A PVP insulating layer approximately 50 nm thick was then evaporated on top of the nanoparticle layer, followed by evaporation of an aluminium gate electrode. All evaporations were carried out in an Edwards Auto 306 evaporator at a pressure below 5 × 10$^{-6}$ Torr. All C–V measurements were performed on an HP4192A impedance analyser under computer control. All C–V scans were performed by starting the scan with a positive gate voltage (inversion region for a p-type semiconductor). In order to ensure accurate C–V measurements, the leakage current through the capacitors was measured in the range of gate voltages used. Leakage currents of MIS capacitors in the voltage ranges used were measured on an HP4140B picoammeter and were found to be below 1 nA in all cases.
In conclusion, in the field of nanoparticle-based PMDs, there is still uncertainty over the exact mechanism that is responsible for the large change in conductivity present between the on and off states, with many questions remaining unanswered. Currently, the most prolific theory for this change is based on nanoparticle charging, thereby changing the properties of the polymer matrix material. We have shown here the charging properties of the nanoparticles using MIS capacitor structures, which are much more sensitive to trapped charges than studying MIM structures, calculating the trapped charge density to be approximately $3.3 \times 10^{12} \text{cm}^{-2}$ due to the nanoparticles. Because of the differences in device structures between MIS capacitors and MIM PMDs, this does not conclusively prove that nanoparticle charging is responsible for the change in conductivity of PMDs. However, we have fabricated memory devices based on an MIS structure containing gold nanoparticles, in which the capacitance difference between the on and off states can be directly attributed to nanoparticle charging.

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