Electrical bistability in a composite of polymer and barium titanate nanoparticles

BY I. SALAORU AND S. PAUL*

Emerging Technologies Research Centre, De Montfort University, Hawthorn Building, The Gateway, Leicester LE1 9BH, UK

Growth in the use of organic materials in the fabrication of electronic devices is on the rise. Recently, some attempts have been undertaken to manufacture polymer memory devices. Such devices are fabricated by depositing a blend (an admixture of organic polymer, small organic molecules and nanoparticles) between two metal electrodes. These devices show two electrical conductivity states (‘high’ and ‘low’) when a voltage is applied, thus rendering the structures suitable for data retention. In this paper, we describe an attempt to fabricate memory devices using ferroelectric nanoparticles embedded in an organic polymer. This paper also discusses issues related to the observed memory effect.

Keywords: ferroelectric nanoparticles; polymers; non-volatile memory devices; conduction mechanism; retention time; stability of polymer memory devices

1. Introduction

In recent years, the use of organic materials (polymers, monomers, etc.) in electronic device fabrication has shown a rapid increase. In this period there have been substantial advances in materials and devices, such as organic light-emitting diodes (Tang & VanSlyke 1987), organic field-effect transistors (Garnier et al. 1994) and solar cells (Yu et al. 1995), with some devices being developed to the point of commercialization. The actors driving this growth can be attributed to the overall low cost of organic devices, material tailoring for specific properties, simple device structures, low-temperature manufacturing processes and compatibility of organic materials with cheap flexible substrates.

In the field of organic memory devices, progress can be broadly split into two categories, namely molecular memory devices and polymer memory devices. In the case of molecular memory, a monolayer of molecules is deposited between metal electrodes (Reed et al. 2001). In a polymer memory device, an admixture (a blend) of small organic molecules and/or metal nanoparticles in a polymer matrix is deposited between metal electrodes to form an array of memory elements (Paul et al. 2006). Both classes of memory devices can be switched

*Author for correspondence (spaul@dmu.ac.uk).

One contribution of 8 to a Theme Issue ‘Making nano-bits remember: a recent development in organic electronic memory devices’.
between two conductivity states upon the application of write and erase voltages, with the state being sensed by an intermediate read voltage. This bistable behaviour of the devices renders them suitable for non-volatile organic memory. Molecular memories have proved difficult to manufacture, with large variations between device characteristics. However, polymer memory devices, in contrast, are typically fabricated by the spin-coating technique and have shown a great deal of promise as a future memory technology.

While significant advances have been made in the field of polymer memory devices, Scott (2004) and Scott & Bozano (2007) highlighted several performance criteria that needed to be addressed before any new memory technologies would be capable of competing favourably with the current silicon technologies. Polymer memory devices may be able to fulfil the criteria highlighted in the aforementioned papers, and so far there have been demonstrations of devices based on metal nanocluster layers by Ma et al. (2003), Bozano et al. (2004) and Tondelier et al. (2004). The use of gold nanoparticles (encapsulated in organic ligands) in hybrid organic/inorganic memory devices has been demonstrated by Paul et al. (2003) and Kolliopoulou et al. (2003). Möller et al. (2003) showed that the combination of organic materials and silicon diodes can be used to produce a write-once read-many-times (WORM) memory device. Devices with gold nanoparticles embedded in a polymer matrix have also been demonstrated by Ouyang et al. (2005) and Prakash et al. (2006). More recently, C_{60}-based devices have been successfully implemented by Kanwal et al. (2005) and Paul (2007).

Albeit there have been a number of demonstrations of polymer and nanoparticle blends in emerging electrical memory devices, their working principle is not as yet very clear. For example, Ouyang et al. (2005) have investigated the memory mechanism in devices in which the active layer is a polymer film consisting of small organic molecules and metal nanoparticles. In this case the memory effect is attributed to electric field-induced charge transfer between the metal nanoparticles and the small organic molecules. Segui et al. (1976) and Henish & Smith (1974) suggested that the switching mechanism (i.e. between the two conductivity states) in their devices is due to the formation of conductive filaments between the top and bottom metal electrodes. There are also a number of reports in which charge transfer between nanoparticles and small organic molecules has been suggested as the cause for the bistability in polymer memory devices (Kolliopoulou et al. 2003; Möller et al. 2003; Paul et al. 2003; Kanwal et al. 2005; Ouyang et al. 2005; Prakash et al. 2006; Paul 2007). For other types of polymer memory devices, the switching mechanism is attributed to chemical rearrangement, conformational change or isomerization. For example, it has been suggested that a conformational change occurs in a ferroelectric polymer (Wang et al. 2003; Scott & Bozano 2007). In addition, from work on polymer and ionic complexes (Krieger et al. 2001; Verbakel et al. 2006), a switching mechanism is proposed on the basis of structural electronic instability of one-dimensional molecular systems, which is caused by the displacement of atoms or molecules by the application of an external electric field.

In this paper, we attempt to answer some of the questions concerning the memory effect by intentionally incorporating electric dipoles (using ferroelectric nanoparticles) in the polymer matrix.

Phil. Trans. R. Soc. A (2009)
2. Experimental

A polymer blend was prepared by dissolving barium titanate (BaTiO$_3$) nanoparticles and polymer in an organic solvent. Polystyrene (PS) and polyvinyl acetate (PVAc) were used as the polymer materials.

The blend was then spin-coated onto glass substrates marked with thin aluminium (Al) tracks, and a top (Al) contact was evaporated onto the blend after drying; this resulted in a metal–polymer–metal (MPM) structure. As-purchased BaTiO$_3$ powder (of particle size between 50 and 100 nm) has a cubic structure and was annealed at 1000$^\circ$C in air for 1 h to obtain the tetragonal phase. Scanning electronic microscopy (SEM) was used to study the effect of annealing on the BaTiO$_3$ nanoparticles. Powder X-ray diffraction (XRD) was also carried out on the BaTiO$_3$ to confirm the phase change from cubic to tetragonal. The current–voltage ($I$–$V$) and capacitance–voltage ($C$–$V$) characteristics of the MPM structures were measured in a screened sample chamber in the dark and at room temperatures, using a PC-driven picoammeter (HP4140B) and an LCR bridge impedance analyser (HP4192A).

3. Results and discussion

Figure 1 shows SEM micrographs of the as-purchased and annealed BaTiO$_3$ nanoparticles. It appears from the micrograph analysis that annealing of BaTiO$_3$ nanoparticles results in larger particle size. This should not affect the electrical behaviour of the devices. The annealing was done to change the nanoparticles from cubic phase to tetragonal. The change in the phase was confirmed by XRD. Figure 2 shows the XRD patterns of as-purchased BaTiO$_3$ (BTO) nanoparticles and the annealed sample.

Two polymer device structures (structures I and II) have been investigated to understand the bistability phenomenon: structure I is based on a polymer sandwich between two metal electrodes (termed Al–polymer–Al); and structure II is based on an admixture of BaTiO$_3$ nanoparticles (annealed at 1000$^\circ$C) in a polymer matrix (termed Al–BTO + polymer–Al). The structures are shown in figure 3a.

Typical $I$–$V$ behaviours of PS–PVAc–Al and Al–PVAc + BTO–Al structures are shown in figure 3b and c. The devices exhibit symmetrical $I$–$V$ characteristics for negative and positive applied voltages. The symmetrical $I$–$V$ characteristics are typical of a bulk-limited mechanism (Paul 2007). The Al–PVAc (or Al–polymer blend) interface does not play any significant role in determining the electrical behaviour of these devices. The structure with nanoparticles shows a significant (when compared with pristine devices) hysteresis in $I$–$V$ behaviour, which is an indication of electrical bistability (or two conductance states) in the devices.

In order to determine if the ferroelectric BaTiO$_3$ nanoparticles play a significant role in causing the electrical bistability in the admixture of BaTiO$_3$ + PVAc, we have investigated the $C$–$V$ behaviour of Al–PVAc–PS + BTO–Si metal–insulator–semiconductor (MIS) structures. The hysteresis in the $C$–$V$ behaviour (figure 4) indicates the dipole rotation in ferroelectric crystalline domains when a high electric field of opposite polarity is applied (Salaoru & Paul 2008). The

*Phil. Trans. R. Soc. A* (2009)
I. Salaoru and S. Paul

Figure 1. Scanning electron micrographs of (a) as-purchased BaTiO₃ nanoparticles and (b) BaTiO₃ nanoparticles annealed at 1000°C in air for 1 h.

Figure 2. XRD patterns of (a) as-purchased BaTiO₃ nanoparticles and (b) BaTiO₃ nanoparticles annealed at 1000°C in air. A comparison of the insets in (a) and (b) indicates that the nanoparticles have changed from cubic to tetragonal phase.

MIS devices consisting of PS and PVAc layers (figure 4a) show a small hysteresis (1.0 V), while the MIS devices with PVAc–PS + BTO (figure 4b) show a hysteresis with a threshold voltage of 5.0 V, indicating that the electrical domains determine the switching behaviour in these devices.

$I–V$ scans were also conducted on pristine devices to determine the dielectric strength of the polymer layer. The write and erase voltages were then selected so as to be significantly lower than the breakdown voltage, thus ensuring that no physical damage took place during read, write and erase (RWE) cycles. The read voltage was then selected to be the point of greatest hysteresis in the $I–V$ curves. To access the memory characteristics of the structures, RWE cycles were performed with write and erase voltages of $+4$ and $−4$ V, respectively, and a read voltage of $+3$ V; these characteristics are shown in figure 5.
Bistability in polymer–$\text{BaTiO}_3$ composite

Figure 3. (a) MPM structures and (b,c) their corresponding current–voltage behaviour: (b) Al/PVAc/Al and (c) Al/PVAc + BTO/Al.

Figure 4. Capacitance–voltage behaviour of (a) Al/PVAc/PS/Si (p-type) and (b) Al/PVAc/PS + BTO/Si (p-type). The $C$–$V$ characteristics were measured at 1 MHz.

In the off state, the typical measured current was of the order of $10^{-6}$ A, while in the on state a typical current of $10^{-5}$ A was measured, giving a measurable current difference between the two states. Memory retention time, as shown in figure 6, was also investigated, with the devices exhibiting a stable on/off current ratio for over 10 000 read cycles over a period of 5 h.

Phil. Trans. R. Soc. A (2009)
The working mechanism of our MPM devices promises to be complex, and a number of mechanisms have already been proposed by various workers (Bozano et al. 2004; Paul et al. 2006; Paul 2007). At the same time, a broad qualitative understanding is possible. It appears likely that BaTiO$_3$ nanoparticles play a significant part in the memory effect. At a certain applied electric voltage, the BaTiO$_3$ nanoparticles embedded in the polymer matrix become polarized. This creates a surplus (or internal) electric field in the device. This leads to the deliberate creation of an internal electric field in the PVAc. A detailed investigation of the memory effect on the basis of electric dipole formation in the polymer matrix can be found elsewhere (Paul 2007), whereas the charging mechanism is briefly discussed in this paper. Figure 5 shows a virgin device that is exposed to a write voltage (+5 V). The applied voltage polarizes the nanoparticles present in the polymer and thus results in the formation of dipoles in the PVAc matrix. This creates an internal electric field, the direction of which is opposite to the externally applied electric field. After the application of a read pulse (+3 V), the effective voltage that appears across the device is less than that of the applied voltage, which results in a reduction in the conductivity; thus, a lower current passes through the device. The erase pulse (−5 V) changes the orientation of the internal electric field (to be in the same direction as that of the applied field),
and thus results in a higher read current. Thus, the working mechanism presented here explains the memory effect in our devices as the difference between the on and off states, as determined completely by the magnitude of the internal electric field.

4. Conclusions

Polymer memory devices based on an admixture of BaTiO$_3$ nanoparticles and a polymer (PS and PVAc) were studied. Both $I–V$ and $C–V$ measurements prove that ferroelectric nanoparticles (or ‘an internal electric field’) play an important role in the electrical bistability mechanism in our polymer memory devices. This further strengthens our previously proposed working mechanism—i.e. the switching between a high- and a low-conductivity state is determined entirely by the value of the internal electric field.

The authors would like to thank EPSRC (grant no. EP/E047785/1) for supporting this work.

References


