Understanding the switching mechanism of polymer memory

Wei Lek Kwan, Bao Lei, Yue Shao, Yang Yang*
University of California, Los Angeles, Department of Materials Science and Engineering, Los Angeles, CA 90095, United States

1. Introduction

A typical polymer memory device consists of a polymer active layer sandwiched between two electrodes [1–3]. The resistance of the device can be changed by simply applying voltage pulses across the electrodes. Depending on the material system, both unipolar and bipolar operations have been observed. The resistance, once changed, is stable even when the applied voltage is removed. The two resistive states, which can be different by more than 3 orders of magnitude, can be read non-destructively by applying a smaller bias. By assigning the two resistive states as “1” and “0”, the device can be used as a non-volatile digital memory.

We have observed that the memory effect can be obtained reproducibly if we embedded nanoparticles into a polymer matrix [4–6]. Besides having a simpler device structure, the polymer based device can be solution processed, thus reducing the fabrication cost. In addition to metallic nanoparticles, we have also shown that semiconducting quantum dots and organic acceptors like C-60 can be used [7].

To achieve high density memory arrays, we use a photo-cross-linkable copolymer to fabricate multi-level stacking devices [8,9]. The memory density can be increased by simply increasing the number of layers in the stacked structure. The copolymer that we used is a single component system, so the problem of phase separation is also alleviated. Since the copolymer is cross-linkable using UV light, the film can be patterned using a photomask, thus reducing the number of processing steps. Once the polymer is cross-linked, it becomes robust enough to withstand photolithography. Micro-scaled devices with lithographically patterned electrodes were fabricated. Our device was able to achieve more than 4000 write/erase cycles with retention time of more than a year. However, for further improvements on performance and reliability, the details of its operation mechanism need to be better understood. In this paper, to provide a better picture of our understanding on the working mechanism, our recent work on the mechanism study [9,10] is reviewed. New ideas [11] on improving the endurance of our device are also discussed.

2. Mechanism study

After write–erase cycling tests were performed on the lithographically patterned devices, we observed that damages to the top electrode occurred at the edge of the bottom electrode Fig 1 [9]. This gave us the first hints that the resistive switching happened at localized area along the edges of the bottom electrode. Area dependence study on the current of the device confirmed our observation [9]. The write, erase and on currents of the device have little dependence on the device area. On the other hand, the current at the off state of the device showed a more linear relationship with the area, indicating a more uniform distribution of the current. Temperature dependence study indicates that the off state of the device is associated with the intrinsic conductivity of the polymer [10]. The damage to the top electrode is likely to be caused by the large current that flows through the localized spots during the switching of the device.

* Corresponding author.
E-mail address: yangy@ucla.edu (Y. Yang).
To find out why the switching occurred at the edge of the bottom electrode, a cross-sectional slice of the device after forming was prepared by a focused-ion beam (FIB). The details of the sample preparation and experiments are described elsewhere [10]. It is observed that the switching of the device occurred after a forming process, where a high voltage bias was applied across the device. Compliance current was set to limit the current that flows through the device during forming. Fig 2 shows the dark field scanning tunneling electron microscopy (STEM) images of the cross-section of the device at the edge of the bottom electrode and at a more uniform region. Near the edge, the bottom electrode is protruding and the polymer film is also thinner. The non-uniformity is likely caused by the liftoff process when patterning the electrode. We note that in devices which do not use liftoff patterned electrodes, non-uniformities can still be found in the devices due to variation in polymer thickness [11].

Fig 2c shows that gold can be found deeper into the polymer film at the region where the electrode is non-uniform. This is probably due to the higher electric field at this point. The higher current density and electric field cause the drift of the gold into the polymer film, creating a region higher conductivity. After the device is formed, a smaller voltage is sufficient to switch the device to the on state due to additional contribution from joule heating at the highly conductive regions.

To directly observe the nature of these conductive channels, a 4 μm × 4 μm device was switched on and off alternatively for a few times. Morphological changes to the top electrode due to the high localized current density were observed using a scanning electron microscope. The small size of the device was chosen so the whole device could be examined at high magnification using a scanning electron microscope (SEM). To find out the nature of these conductive regions, a cross-sectional slice of the device was prepared using a focused-ion beam. Fig. 3c and d shows the transmission electron microscopy (TEM) images of a conductive channel. At certain point, the top and bottom electrodes are almost in contact with each other. It is highly likely that most of the current flows through these conductive spots when the device is at the on state. At higher voltages, these spots can be destroyed by joule heating caused by the high current density. A model of the switching mechanism is developed based on these experimental evidences (Fig 4).

3. Controlling switching paths

Our model suggests that the memory effect is due to the formation and elimination of conductive routes at localized points. Our next sets of experiments were done using a commercially available polyfluorene (PFO) to prove the generality of the memory phenomenon and to reduce batch to batch variations [11]. The electrodes used were aluminum and indium tin oxide (ITO).

Fig 5 shows the cross-sectional SEM images of the PFO-based device. Similar to the cross-linkable copolymer based device, the electrodes of PFO-based device are also not uniform at certain regions of the device. Conductive channels are likely to be found at these regions where the electric field is much stronger. The switching may also change the distance of the gap between metals and...
the thickness of conductive paths formed, and consequently causing the variation and history dependence of the switching voltages.

Fig. 6 shows the results of a cycling test with 4 and 10 V as the writing and erasing voltages respectively. After about 70 cycles, the

Fig. 3. (a) Device schematic, (b) Top SEM view of device showing irregularities on the electrode, (c) A cross-sectional slice of the boxed region in (b) was prepared by focused-ion beam. The sample preparation is described in detailed in Ref. [10]. This figure shows the TEM image of the sliced sample. Near the edge of the gold electrode, the top electrode was almost in contact with the bottom electrode. (d) Closed up TEM image of the boxed region in (c). Reprinted with permission from W.L. Kwan, B. Lei, Y. Shao, S.V. Prikhodko, N. Bodzin, Y. Yang, J. Appl. Phys. 105 (2009) 124516. Copyright 2009.

Fig. 4. (a) Metal injection during forming process, (b) filament caused by high electric field and current, (c) destruction of conductive spot when a higher voltage is applied and (d) formation of new filament at old filament site. Reprinted from Ph.D. dissertation of Wei Lek Kwan.

Fig. 5. Cross-section SEM images of the device at different spots. (a) In uniform regions. (b) In non-uniform regions. Reprinted with permission from B. Lei, W.L. Kwan, Y. Shao, Y. Yang, Org. Electron. 10 (2009) 1048. Copyright 2009.
device could not be switched on even after several 4 V pulses. However, the device can be recovered by another forming process. In certain cases when the device cannot be switched off by 10 V, it can be switched off when a larger voltage pulse is used. Based on these observations, we designed a new switching method which dynamically adjusts the switching voltages according to the device condition [11]. When the device cannot be switched by a certain voltage, a larger voltage pulse is used in the next cycle. In this way, the switching endurance was extended to more than 5000 cycles in one of our devices (Fig 7). It is notable that in certain switching cycles, the switch on voltage is larger than the switch off voltage (Fig 7b). This rules out the possibility that the switching is due to a purely electric field induced effect.

We further develop our model to explain the variation in the switching voltages. When the conductive filament is destroyed by joule heating, a new gap is formed between the electrodes. As it is not a well controlled process, the threshold voltage to switch the device may change due to the variations in the new gap distance or the electrode shape. Similarly, a larger voltage may be needed to switch off the device when a thicker filament is formed.

4. Conclusion

We have developed a model for the switching mechanism of polymer memory from strong experimental evidences using cross-section TEM images of the device. The memory phenomenon is due to the non-uniformity unintentionally introduced during the fabrication process. Based on this improved understanding of the device, we developed a programming method which dramatically increases the switching endurance of our devices. The cycling test using this new algorithm also provided additional evidences of the switching mechanism and allowed us to further understand the variations in device characteristics of the polymer memory.

We believe that the yield and device variations can be further improved by better control of the nanostructure of the electrodes and development of new materials. There remain huge obstacles for the commercialization of polymer memory but this improved understanding of the device provides us with the correct direction for future development of the technology.

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