Statistical characterization of the memory effect in polyfluorene based non-volatile resistive memory devices

Bao Lei, Wei Lek Kwan, Yue Shao, Yang Yang*
Department of Materials Science and Engineering, University of California, Los Angeles, 420 Westwood Plaza, Los Angeles, CA 90024, USA

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Abstract
Non-volatile resistive memory devices based on a polyfluorene layer sandwiched between two electrodes were studied. The working mechanism was ascribed to the formation of metallic filaments. We characterized the switching probability of multiple devices and the consistency of the switching capability within the same device. Together with cross-section scanning electron microscope images and finite element simulation of electric field distributions, a model was developed to describe the resistive switching phenomenon and explain the variations between devices as well as between switching cycles.

1. Introduction
Polymer based resistive memory has been considered a very promising candidate for the future non-volatile information storage device [1,2]. In addition to its low cost and ease of processing, high switching speeds [3–6], sub-micron scalability [7], and long retention time [8] have been demonstrated, making it favorable for practical applications.

Recently, polymer memory devices based on a photo crosslinkable co-polymer have been developed. Due to the crosslinkable properties of the polymer, it was compatible with conventional photolithography processes and suitable for 3-D integration [9,10]. The system was based on a polyfluorene based co-polymer sandwiched between two metallic electrodes, and the switching behavior has been understood as the formation and destruction of localized conductive channels [11].

Further improvement of the device performance and reliability requires a more detailed understanding of the switching mechanism. Although several comprehensive models were suggested for filament based memory systems [12–15], further theorizing the memory systems, i.e. predicting the electrical characteristics from the fundamental laws of physics, or linking the memory parameters to the material properties of filaments, remains very difficult. The major challenge lies in the difficulty in controlling the filaments. The locations, geometries and amount of filaments formed in response to a switching pulse could be random, and hard to be characterized individually. One result from the randomness is the large variations in the reported memory parameters [16]. Therefore, the stochastic properties associated with filament formations should be better understood, in order to achieve a deeper insight of the memory effect.

Based on the memory devices we made, we found that the memory parameters, e.g. current–voltage characteristics, switching probability, cycling lifetime, varied even for the devices prepared using exactly the same process and under careful control. In this work, we applied...
statistical methods to investigate the filament based memory system. The devices were based on a metal/polymer/metal structure, similar to the crosslinkable devices we reported earlier. Polyfluorene (PFO) with dimethyl-benzyl end capping group was chosen as the polymer active layer. Since it contains no known donor and acceptor pairs and only carbon and hydrogen in its chemical formula, the possibility of occurrence of other reported switching mechanisms [4,17–19] is negligible. Batch to batch variation is also lower in the commercially available polymer. We studied the variations between devices with the same processes and the variations between switching cycles within the same device. We proposed a model to explain the results.

2. Experimental

PFO was purchased from American Dye Source and used without further purification. The polymer was dissolved in chlorobenzene (1 wt% of the solvent), and filtered with a 0.45 μm syringe filter. The polymer solution was spin coated onto the glass substrates with pre-patterned indium tin oxide (ITO). Finally, a 50 nm thick aluminum layer was thermally evaporated on top of the polymer film, at a rate of 0.1 nm per second. The device structure is shown in the inset of Fig. 1. The active area of the device was defined by the overlapped region of the top and bottom electrodes, which is about 0.2 mm².

The current–voltage (IV) characteristics were measured in a vacuum probe station with an Agilent 4155C semiconductor parameter analyzer. The capacitance was measured using an HP 4284A LCR meter. Cross-section scanning electron microscope (xSEM) images were taken by a FEI Nova 600 Nanolab Dualbeam™ SEM/Focused ion beam (FIB).

3. Results and discussion

A typical IV curve, as shown in Fig. 1, had similar shape as previously studied crosslinkable polymer memory devices [9]. Starting from the low conductivity state (OFF state), when the voltage increased to between 3 and 4 V, the device switched abruptly to a high conductivity state (ON state). A negative differential resistance (NDR) region followed and the current reached a minimum at about 6 V. During the reverse sweep, the device stayed at the ON state even when the voltage dropped below 4 V. The device could also be written to the ON state by a voltage pulse of 4 V, and erased to the OFF state by a pulse between 8 and 10 V. The device was read at 1 V, without disturbing its state.

No noticeable differences in the shape of the IV curves were observed when the switching behavior was tested through a temperature range of −20–85 °C. The conductivities of both ON and OFF devices were also stable for more than 20 h at 85 °C. The capacitances of the device at both states were the same, and depended only on the thickness of the polymer film.

It was noticeable that some of the devices, especially the ones with thicker polymer layers, required an initial forming process [20] before the observation of the memory phenomena. These devices were formed by applying a voltage bias higher than the 4 V writing voltage, ranging from 5 to above 20 V, with a 10 μA current compliance (note: during the erasing process, the current compliance was set at 10 mA). The forming process could also be considered as an abnormal writing process which used a higher voltage since the current compliance would keep the device in the ON state. After the forming process, the device could be switched ON by a writing voltage as low as that of the devices which did not require forming, i.e. 4 V.

3.1. Device to device variation

Since the required forming voltage, or the initial writing voltage, varies from device to device, we first analyzed the distribution of the voltages. We define the switching probability as the percentage of devices which can be successfully written to ON state and erased to OFF state at least one time. The ON state is defined as the state with a current above 100 nA at 1 V, and OFF state is below 10 nA at 1 V. All the writing (forming) pulses were limited with a 10 μA compliance. For every device, the initial writing voltage was 4 V, and if it was not successful, the writing (forming) voltage was increased by 1 V until the device was successfully written.

Fig. 2a shows the switching probability as a function of forming voltage for devices with different values of polymer layer thickness. Generally, the switching probability increased with higher forming voltage. The figure also shows that devices with thinner polymer layers were more likely to be switched successfully. Devices with thicker films which did not work at first might work after using a higher forming voltage. However, as shown in Fig. 2b, the probability was not determined by the electric field based on the average thickness of the film. For example, devices with 400 nm thick polymer layers did not have the same switching probability as those with 40 nm thick polymer layers even if 40 V was used. This is consistent with our previous understanding that the switching processes happen at some non-uniform regions within the devices [10].
Next, we studied the non-uniformities of our device using cross-section scanning electron microscope (xSEM). Cross-section slices of the device were prepared using focused ion beam (FIB). In most regions of the device, the polymer film thickness was uniform at 50 nm, as shown in Fig. 3a. However, at a few spots, we observed a much narrower gap between the electrodes (Fig. 3b). Localized electric field at these spots could be much greater than at other regions. Therefore we believe that these spots are crucial for the switching phenomenon, and their existence determines the device switching probability.

According to this observation, we attribute the switching behavior to the formation and rupture of filamentary conductive paths [10,21–23] at localized spots [8] such as the one shown in Fig. 3b, similarly to the switching mechanism proposed for oxide based resistive memories [12]. During the forming and writing processes, a conductive link can build between the electrodes possibly as a result of the ionization and injection of metallic materials into the film under high electric field [22]. The erasing process at 10 V results in a very high current flowing through the conductive link, causing the rupture of the link [10,22,24,25].

The distribution of electric field near the protrusion from the electrode was studied by solving the Poisson equation using the 3D finite element method. The geometries used in our model were based on the xSEM image. The metallic and polymeric films were simplified as parallel plates. The protrusion from the metal was modeled as a hemisphere with 30 nm radius. Using the capacitance data and geometry of our device, we estimated that the dielectric constant of our polymer film to be around 4.

Fig. 4a shows the distribution of electric field for a 40 nm device under a normal writing voltage of 4 V. The maximum local field strength at the tip of the protrusion can reach $4.86 \times 10^8$ V/m, which is more than four times that of the uniform regions. The calculated electric field at localized spots during the writing process is consistent with the data from Cu/P3HT/Al memory system previously reported by Joo et al. [22], which is above $10^8$ V/m.

Fig. 4b shows the simulated electric field distribution for devices with different thickness. The voltages used are determined by the minimum voltage required for the maximum switching probability (Fig. 2a), which are 4 V for 40 nm devices, 16 V for 65 nm devices, 50 V for 160 nm devices, and 100 V for 400 nm devices. In all cases the protrusion is assumed to have a radius of 30 nm. The electric field along the vertical line crossing the protrusion tip has been plotted as a function of vertical position $z$. For 40, 65 and 160 nm devices, the minimum values of the electric field inside the polymer film are about the same, which are above $3.0 \times 10^8$ V/m. Correspondingly in Fig. 2, the three types all gave high switching probability (>80%) with necessary writing voltages. For the 400 nm device, even at 100 V, the electric field in the polymer film is comparatively lower (below $2.5 \times 10^8$ V/m), and this can be correlated with its low switching probability (<20%).
Therefore we suggest that the switching probability may be related to the localized electric field near the protrusions from the electrode. The role of the high electric field might include: (1) producing a high current and localized heating which dissociate the metal ions from the electrode surface, and (2) driving the metal ions to the other electrode to form a conductive link.

3.2. Cycle to cycle variation

For the same device, the switching capability also varied as write-erase cycles were performed on the device. Typically, after several hundreds of write-erase cycles, the devices could not be written to the ON state with a 4 V pulse. When this happened, using the same forming process as mentioned earlier can turn the device back to the ON state. On the other hand, though at relatively lower probability, there were also cases where the devices became more difficult to be erased. In such situations, using a higher erasing voltage, eg. 12 V, could turn the device to the OFF state.

With this in mind, we designed a different cycling test approach which dynamically adjusts both the writing and erasing voltages. Instead of using single values for writing and erasing voltages, we set a range for writing and erasing voltages. In each cycle, the writing process began with the minimum writing voltage in the specified range. We determined the status of the device right after the writing pulse.

![Electric field distribution at a localized switching spot in our model. (a) In a 40 nm device. (b) Along the vertical line crossing the protrusion tip.](image)

![Flow chart for the writing and erasing procedures in the dynamic voltage cycling test.](image)
by measuring the current at 1 V. If the writing process failed, it was repeated with a voltage raised by 0.5 V, until the voltage reaches the upper limit of the range. The erasing process was almost the same, except that the voltage range was different from the one used for writing. A current compliance of 10 µA was set during the writing processes. The flow chart for the writing and erasing procedures are shown in Fig. 5.

This cycling test was applied on devices with 100 nm thick polymer film. The writing voltage ranged from 3.5 to 20 V with 10 µA current compliance, while the erasing voltage was set between 8 and 15 V. Fig. 6a shows that the device worked persistently through 5000 cycles. Fig. 6b reveals the actual voltages used for writing and erasing in each cycle. It was found that the device normally switched at the minimum writing (3.5 V) and erasing (8 V) voltages. However, at certain cycles, higher writing or erasing voltages were needed to ensure a successful switching. These gave rise to the peaks in the recorded voltage values. Fig. 6c shows the distribution of writing and erasing voltages.

We further develop our model in order to explain the dynamic process during repeated switching cycles. After the disconnecting process during erasing, a new gap distance might be established. In normal cases, the new gap should be close enough so that the next writing within 4 V could be successful, as seen in Fig. 6b. However, due to any kind of variations, at certain probability, the gap could be widened and/or the tip could be smoothened, so that in the next cycle, much higher writing voltage would be required, corresponding to the peaks in the writing voltage curve in Fig. 6b. It is also shown in Fig. 6b that there are certain peaks in the erasing voltage curve, which means that at certain cycles, the device could not be erased with 8 V pulse. This could be explained by the variation in the filament thickness formed during each cycle.

4. Conclusion

We have statistically characterized the polyfluorene based memory cells. The switching probability of the devices was linked to the required switching voltage. Based on the variation of required switching voltages among different devices as well as switching cycles, we developed a model which suggests that protrusions from the electrodes are dominating the switching phenomenon, and their varying geometries contribute to the variations in the reproducibility of the memory effect.

The switching sites introduced by the nonuniform geometries have to be better controlled in order to overcome the inconsistency and make the polymer memory devices reproducible and reliable enough for commercialization. In low cost applications where switching speed is less critical and device driving circuit can be more flexibly designed, applying a device programming scheme which dynamically adjusts the switching voltages would be a practical solution. For high end applications, the device structure should be fundamentally improved to minimize the changes of the switching sites. Our future work will include both the memory driving circuit design and device structural optimization to achieve a highly reliable polymer memory system.

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