Stackable Resistive Memory Device Using Photo Cross-linkable Copolymer
Wei Lek Kwan, Ricky J. Tseng, Wei Wu, Qibing Pei, and Yang Yang*

Department of Materials Science and Engineering, University of California, Los Angeles
Los Angeles, CA 90095-1595 *Email: yangy@ucla.edu

Abstract

A multi-stackable memory device was fabricated using a photo cross-linkable copolymer. Once cross-linked, the polymer film became insoluble, making multi-level stacking possible. It can also be directly patterned using a photomask, reducing the numbers of processing steps. The memory device consisted of a polymer film sandwiched between two electrodes. The device could be switched from a high resistive state to a low resistive state using 4 V pulse, and back to its high resistive state using a 9 V pulse. Our device showed stable performance achieving more than 4000 times of write/erase cycles.

Introduction

Since the report of the first organic electrical bistable device by Ma et al, there had been tremendous interest in organic memory devices (1). Its simple structure, usually an organic film sandwiched between two electrodes, coupled with its high write/read speed and non-volatility, makes it an ideal choice to replace the existing flash memory technology. Ouyang et al had further demonstrated that crossbar memory structures could be fabricated using a solution processable polymer (2). Many other groups had since come out with different polymer systems, demonstrating the potential of the polymer memory (3-6).

The crossbar structure is ideal for polymer memory devices due to its simplicity and ability to achieve very high density. However, to reach very high density, exotic patterning technique is required, thereby increasing the cost of manufacturing. Alternatively, the same high memory density could be realized using conventional photolithography if multi-level stacking of the crossbar structure is possible. The polymer must then be robust enough to withstand lithographic processes that are used in the patterning of the electrodes. It must also not be dissolved by its own solvent again once the bottom layer polymer film is formed. However, most polymer blend or copolymer systems reported so far are soluble in common solvent and are therefore not compatible with photolithography or multi-level stacking. Thermally cross-linkable polymer can be used to solve this problem (5). Recently, Cho and co-workers reported a memory device that used a thermally cured polyimide:PCBM composite film as the active layer (7). Once the imidization process is completed, the polymer film became insoluble and was processable using photolithography. Multi-level stacking of the devices was also achieved. However, such blend systems are prone to phase separation which may cause problems when the device size is further scaled down. One way to overcome this problem is to use a single copolymer which contains the necessary functional groups for the memory device (4). Müller et al reported a photo cross-linkable oxetane-functionalized co-polymer system for the application in polymer light-emitting diodes (8). Here, we made use of the oxetane group for the photo cross-linking process. This copolymer system can be solution processed and yet robust enough to withstand the lithography process after the cross-linking process. Since this polymer can be cross-linked using UV light, direct patterning of the polymer film is possible using a photo mask, thus further reducing the cost of fabrication.

Experiments and Results

Photo cross-linkable copolymer (PFN-C, Fig. 1) was synthesized using Suzuki polycondensation. To demonstrate the patterning capability of the cross-linkable PFN-C, the spin-cast film of the polymer solution (3.0 wt% PFN-C, 0.4 wt% PAG 203(photocid generator from Ciba Specialty Chemicals) in 1,2dichlorobenzene) was irradiated with UV light (wavelength 254nm) through a photo mask. The substrate was then placed on a 90 °C hot plate for 2 min and

Figure 1: (a) Chemical structure of photo cross-linkable polymer, PFN-C (b) After cross-linking, a network of polymer chain is formed, increasing its robustness.
rinsed in toluene. It was finally baked on the hot plate at 150 ºC for 30 min to complete the cross-linking process. Fig. 2 shows the profile trace of the patterned thin film by a Dektak 6M profiler. This shows that the copolymer film could be directly patterned using a photomask without additional etching steps. Thermogravimetric analysis (TGA) of PFN-C (Fig. 3) showed that it remained stable up to 200 ºC after cross-linking.

A device with lithographically patterned electrodes was then fabricated. A silicon wafer with thermally grown oxide was used as the substrate. The bottom Au electrode was first patterned using the lift-off technique. The polymer solution was then spin-coated on the substrate and cured using UV light. The thickness of the film was about 65nm. As PFN-C became insoluble after the cross-linking process, the lift-off method could be used to pattern the top Al electrode deposited on the polymer film (Fig. 4).

All devices were tested in a probe station under vacuum with the top electrode biased as the reference electrode. The I-V curve of the lithographically patterned device is shown in Fig. 5. In the initial sweep, the current remained low until about 3 V, where there was an abrupt increase in the current. The current reached a maximum at about 5 V to 6 V after which the device exhibited negative differential resistance (NDR) characteristics. In the reverse sweep, the device remained in the high conductive state even when the voltage dropped below 3 V. In the next voltage sweep from 0 V to 3 V, the device remained in the high conductive state. After applying a 9 V pulse to the device, it reverted back to its low conductive state as shown in the figure. The device can also be switched to its high conductive mode using a 4 V pulse (Fig. 6). Electrical pulses as short as 500ns could be used to switch the devices. The conductive state of the device could...
be read by applying a small voltage pulse (Fig. 7). The read time could be less than 500ns.

Since the conductive states of the device were stable (for more than a month, Fig. 8) even when all biases were removed, it could be used as a non-volatile memory device. A cyclic write-read-erase-read test was conducted on the device using 4 V, 9 V, 0.6 V as the write, erase and read voltages respectively. More than 4000 cycles, with on-off ratio of 10 times or more, were achieved (Fig. 9).

Next, a double stacking memory array was fabricated. The bottom aluminum electrode was first deposited on a glass substrate using a shadow mask. The bottom polymer film was then spin-cast and cross-linked using the steps mentioned earlier. The same processes were then repeated for the middle electrode, the top polymer film and the top electrode. Fig. 10 shows the I-V curves of the bottom and top layer devices. Both devices showed similar characteristics as the single layer device.
Conclusion

A new material system for memory application is reported. Due to its robustness achieved through the cross-linking process, multi-level stacking of the device is possible. It is also compatible with conventional photolithographic processes. Since all the functional groups are included in a copolymer system, the problem of phase separation is also eliminated. We have also shown that direct patterning of the polymer film is possible using the photo cross-linkable copolymer.

References