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Multi-layer stackable polymer memory devices

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Multi-layer stackable polymer memory architecture is an interesting new direction for polymer memory. The memory density can be increased by increasing the number of stacked layers without reducing the minimum feature size. To achieve multi-level stacking, the polymer used must be able to be cross-linked so that it will not be dissolved upon deposition of additional layers. This requirement also makes the polymer robust enough to withstand conventional lithographic processes. In this paper, the various approaches to achieve cross-linkable polymer memory are discussed. Device fabrication and performance are also reported.

Keywords: polymer memory; organic memory; cross-linkable polymer; stackable memory

1. Introduction

Polymer memory devices show fast switching speed and non-volatile characteristics (Ma et al. 2002; Ouyang et al. 2004; Scott & Bozano 2007), and are therefore ideal candidates to replace existing memory technologies. However, in order for polymer memory to achieve commercial success, there are a few hurdles that need to be overcome. Besides requirements for device performance, which were comprehensively covered in a recent review article by Scott & Bozano (2007), polymer memory has to be highly scalable and compatible with the existing patterning techniques.

To achieve high memory density, a cross-bar array is highly desirable because each memory cell size is only $4F^2$, where $F$ is the minimum feature size. Even higher memory density can be achieved by stacking multiple layers of memory arrays. The cell size can be reduced to $4F^2/n$, with $n$ being the number of layers stacked. Furthermore, as noted in the review of Scott & Bozano (2007), a practical memory device has to be less than 1 μm². For such a small scale, a shadow mask cannot be used for defining the area for the electrodes. Although special techniques like imprint lithography (Chen et al. 2003; Green et al. 2007) are available for patterning very fine metal lines on chemically sensitive materials like polymers and small molecules, conventional photolithography is still highly desirable owing to the scalability of the technique, and the availability of expertise

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and tools. Therefore, for practical memory applications, the polymer used has to be robust enough to withstand multi-layer stacking and photolithography processes.

However, polymers used in memory devices are usually soluble in organic solvents (because the polymers are chosen to be soluble for ease of processing) and are therefore not compatible with photolithography or multi-layer stacking. Thermally curable or photo cross-linkable polymer systems have been developed to overcome such problems. During the curing process, cross-linkages are formed between polymer chains, resulting in reduced solubility of the polymer.

There are many strategies to achieve cross-linking in a polymer, but it is important to choose a method that is simple and flexible, yet able to maintain the desirable electrical functionalities of the polymer. So far, three different approaches (Beinhoff et al. 2005; Cho et al. 2006; Kwan et al. 2007) have been applied to polymer memory devices. In the next section, we will discuss the relative merits of these three methods. In §§3 and 4, we will report on the performance of our devices fabricated with a photo cross-linkable polymer system and discuss the issues related to device fabrication using photolithography.

2. Strategies to achieve cross-linkable polymer memory systems

(a) Thermally cross-linkable polymers using 4-phenylethenyl end-cap groups

Thermally cross-linkable polyfluorene (Klärner et al. 1999), polyarylamine (Chen et al. 2000) and poly(biphenylmethylene) (Beinhoff et al. 2005) had been synthesized by end-capping the polymers with 4-phenylethenyl groups. After spin-coating the polymer onto a substrate, the film was heated at 150°C in an inert environment to complete the cross-linking process. The process was monitored by measuring the optical absorption of the film before and after dipping into a solvent. If the cross-linking step was successful, the film was able to retain most of the absorption.

The advantage of using 4-phenylethenyl end-cap groups is that the cross-linking process can be achieved under relatively mild conditions, while retaining the electrical properties of the polymers. Also, no undesirable byproduct is formed. A wide variety of polymers with different electrical and optical properties can be synthesized using this method.

Memory devices fabricated with these cross-linkable polymers blended with gold nanoparticles showed excellent stability (Bozano et al. 2005). Multi-layer device architectures can also be fabricated using these polymers, thereby increasing the design flexibility of these devices.

(b) Thermally cured polyimide composite

Polyamic acid, a precursor of polyimide, can be converted to polyimide by heating it to over 300°C. The polyimide formed is a thermally robust, chemically inert and insoluble polymer. Recently, Samsung (Cho et al. 2006) demonstrated that by blending polyimide with [6, 6]-phenyl-C61 butyric acid methyl ester, a thermally robust polymer memory could be realized. A first demonstration of a two-layer stacked device was fabricated using the composite film. Multi-level programming was also demonstrated by using different pulsing voltages.
Since the film was able to withstand over 300°C of thermal budget, it was compatible with complementary metal oxide semiconductor (CMOS) back-end processes, therefore paving way for polymer-CMOS hybrid devices (Sezi et al. 2003).

(c) Photo cross-linkable polymer with oxetane group

Müller et al. (2003) reported a photo cross-linkable polymer system with oxetane side groups for polymer light-emitting diodes application. Applying similar concepts, our group developed a photo cross-linkable polymer for memory application (Kwan et al. 2007). The polymer contained an oxetane group, which can react with acid to form cross-linkages. A photoacid generator was blended with the polymer, so that the cross-linking process could be triggered by irradiating UV light on the film. This enabled the direct patterning of the polymer film using a photomask, thereby saving multiple process steps. The polymer, once cross-linked, could resist temperatures up to 200°C and was robust enough to withstand standard lithography processes. Using this polymer, we recently demonstrated a two-layer stackable polymer memory array (Kwan et al. 2007). More layers could be stacked on top of each other to increase memory density without shrinking the cell size. Devices, as small as 4 × 4 μm², were also fabricated using photolithography.

In the subsequent two sections, we will describe the fabrication processes, device performance and related issues.

3. Experimental

Two polymers, one with the oxetane cross-linkable group (PFN-C, figure 1a), and one without (PFN-U, figure 1b), were synthesized using Suzuki polycondensation. Both polymers were dissolved in 1,2-dichlorobenzene to form a 3 wt% solution. Photoacid generator (PAG 203 from Ciba Specialty Chemicals) was added to the PFN-C solution with a weight ratio of 1 : 7.5.

A chromium photomask was used to pattern the polymer film directly. After spin-coating the film onto a substrate, UV light (245 nm) was irradiated on the film through a photomask. It was then heated to 90°C on a hot plate and subsequently rinsed in toluene. The cross-linking process was completed by heating the substrate at 150°C for 30 min. Negative image of the photomask with very well-defined edges was formed after the developing process (Kwan et al. 2007).

To fabricate the memory devices, Al electrodes at the bottom were first deposited onto a cleaned glass substrate. Gold and indium tin oxide were also used as the bottom electrode. The polymer layer was then spin-coated onto the substrate. PFN-C was cross-linked by irradiating the film with UV light. Both PFN-C and PFN-U films were baked at 150°C. The thickness of the polymer film was about 65 nm. Top Al electrodes were then deposited using a shadow mask. PFN-C was used to fabricate multi-layer stackable devices. Additional layers of cross-linked polymer and electrodes were deposited on top of existing films. The spin-coating and UV curing of the polymer films were done inside a nitrogen glove box. No degradation of the electrodes was observed after the curing process.

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For devices with photolithographically patterned electrodes, silicon wafers with 300 nm of thermally grown oxide were used as the substrates. The bottom Au electrode was first patterned using the ‘lift-off’ method. PFN-C was then spin-coated and cross-linked. Finally, the Al top electrode was aligned and patterned using the ‘lift-off’ technique. Devices with area of $4 \times 4$, $10 \times 10$ and $100 \times 100 \mu m^2$ were fabricated.

Current–voltage measurements were performed using an Agilent 4155C semiconductor parameter analyser. An HP 214B pulse generator was used to test the switching speed of the devices. All the devices were tested in a vacuum probe station with the top electrode biased as the reference.

4. Results and discussion

Figure 2 shows the $I-V$ characteristics of a pristine device being swept multiple times from 0 to 15 V. The device showed switching characteristics from the beginning but only became more stable and repeatable after multiple voltage sweeps. This process was similar to the ‘initialization’ or ‘forming’ process reported elsewhere (Jakobsson et al. 2007; Verbakel et al. 2007). The curve in bold shows the $I-V$ curve of the device after the ‘initialization’ process and applied with a 10 V pulse. All $I-V$ curves shown in this paper were measured after similar treatment to the device.

Initially, after a 10 V pulse was applied, the current was low when the bias voltage was swept from 0 to 3 V. The current suddenly increased by a few orders of magnitude when the voltage was swept further, reaching a maximum at about 5 V. The current then started to decrease with increasing voltage (negative differential resistance), reaching a minimum at about 8 V. After 8 V, the current continued to rise again gradually as the voltage was increased. In the reverse sweep direction, the current remained high even when the bias was returned to zero. The device
Figure 2. $I-V$ curves of an Al/PFN-C/Al device. The pristine device was swept multiple times from 0 to 15 V and then applied with a 10 V pulse. The bold curve was obtained after this process. Bold line, after multiple voltage sweeps to 15 V and a 9 V pulse.

Figure 3. $I-V$ curves of devices fabricated with PFN-U (bold line) and PFN-C (unbold line) show very similar characteristics.

could be returned to the low conductivity state by applying a 10 V pulse. It could also be programmed to its high conductivity state by applying a 4 V pulse. Both the low (off) and high conductivity (on) states were very stable even when no bias was applied to the device. Two individually programmed devices were found to retain their original states even after more than a year of storage. Therefore, these devices could be used as non-volatile digital memory devices.

Memory devices using both PFN-C and PFN-U were fabricated. Figure 3 shows the $I-V$ curves of the devices. Both devices showed very similar characteristics so it could be ruled out that the cross-linking process was responsible for the
Figure 4. Device structure of a two-layer stacked polymer memory. The middle electrode acts as a common electrode for both the bottom and top layer cell.

Figure 5. (a) Device structure of first version of photolithographically patterned device. Bottom: SEM image of top electrode of failed device. (b) Device structure of improved version of device. Bottom: SEM image of top electrode after 4000 cycles of write–read erase–read cycles. The scale bars represent 50μm for both SEM images.

memory effect of the devices. Next, a two-layer stackable device was fabricated using PFN-C. The device structure is shown in figure 4. Both the top and the bottom layers had similar electrical characteristics. The number of layers can be more than the two-layer device shown here.

Initially, when the lithographically patterned devices were first tested, the devices failed after only a few cycles of operation. We examined the failed devices using a scanning electron microscope (SEM) and found that the electrode near the edge of the device was damaged (figure 5a). We reasoned that it was due to the sharp edges of the bottom electrode patterned using the ‘lift-off’
technique. We did not notice such failures in devices made with shadow mask-patterned electrodes, since the edges would be smoother due to the shadow effect of the mask.

In order to reduce the effects from the edges, we tried to planarize the surface before spin-coating the polymer. Most of the processes remained the same except an additional step at the beginning. To create a trench for the bottom electrode to fill in, a thin layer of SiO$_2$ was first plasma-etched with the same mask that was used to pattern the bottom electrode (figure 5b). The results were remarkable. The device with the new structure was able to withstand up to 4000 cycles of write–read–erase–read test. SEM image of the device after 4000 cycles showed similar but less severe damages, indicating the imperfection of our planarization technique.

We also measured the write (4 V), erase (10 V) and on and off current (measured at 1 V) of our devices with different dimensions. The results are summarized in figure 6. As expected, the write, erase and on current were not proportional to the device area indicating the presence of localized conductive spots at the on state. From the damages shown on the failed devices, these spots were likely to be concentrated along the edges of the device. If the conduction paths were formed as a result of dust particles (Tang et al. 2005), the on state current would be likely to be proportional to the device area. The off current showed a higher dependence on device area indicating a more uniform conduction mode. From these experiments, we conclude that the uniformity of the electrode and polymer film plays an important role in reliable device operation.

It was observed that aluminium oxide formed between the aluminium electrode and polymer may play an important role in the switching mechanism of the polymer memory device (Cölle et al. 2006). Although we had successfully replaced

Figure 6. Write, erase, on, off current versus device area. The black line indicates the slope when current is proportional to device area. Filled squares indicate write current at 4 V; inverted filled triangles indicate on current at 1 V; filled circles indicate erase current at 10 V; filled triangles indicate off current at 1 V.
aluminium with other metals, e.g. calcium, as the top electrode (results not shown here), we could not completely rule out the possibility of switching in metal oxide. (We were not successful in using gold as the top electrode for our devices due to the diffusion of gold atoms into the thin layer of polymer during the deposition process.) Further experiments are underway to understand how non-uniformity in the electrode could affect the conduction mechanism of our device.

5. Conclusion

We have demonstrated the feasibility of multi-layer stackable polymer memory devices using cross-linkable polymer. However, there are many obstacles ahead before multi-layer, large-array system of polymer memory can be achieved. Although not addressed here, for a large cross-bar array structure to work, it is important to integrate a diode to the polymer memory (Scott & Bozano 2007). (With special programming schemes, diodes may not be necessary; see Lin et al. 2007.) So far, there have been few reports of integrating polymer memory with a diode (Möller et al. 2003; Jakobsson et al. 2005). Furthermore, new interconnect schemes will be needed to connect the multi-layers of memory arrays. Nevertheless, a multi-layer stackable polymer memory device is a promising new direction for hybrid polymer-CMOS and low-cost applications.

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