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A direct metal transfer method for cross-bar type polymer non-volatile memory applications

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Abstract

Polymer non-volatile memory devices in 8 × 8 array cross-bar architecture were fabricated by a non-aqueous direct metal transfer (DMT) method using a two-step thermal treatment. Top electrodes with a linewidth of 2 μm were transferred onto the polymer layer by the DMT method. The switching behaviour of memory devices fabricated by the DMT method was very similar to that of devices fabricated by the conventional shadow mask method. The devices fabricated using the DMT method showed three orders of magnitude of on/off ratio with stable resistance switching, demonstrating that the DMT method can be a simple process to fabricate organic memory array devices.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Organic electronic devices have attracted much attention due to their various merits, such as low cost, easy fabrication, and printing capability. Organic-based materials have been extensively developed for next-generation electronic devices such as organic light-emitting diodes, thin-film transistor memories, photovoltaic cells, and sensors [1–5]. Among these organic devices, polymer non-volatile memory devices appear highly attractive due to their potential application to data storage. Many efforts have been made to produce polymer non-volatile memory devices exhibiting two different states of resistivity, i.e., a high-resistance state and a low-resistance state [6–17]. Most development of polymer non-volatile memory devices has been focused on the synthesis of new polymer materials [7–10] or the identification of appropriate ratios between well-known polymer materials and metallic nanoparticles [11–13] and the electrical characterization of memory devices fabricated as unit device structures [8–10]. However, there have been relatively few reports on the fabrication of high-density polymer memory devices with cross-bar architecture [12–14]. In particular, due to the use of shadow masks to pattern the top electrodes of polymer non-volatile memory devices in either unit device or array device structures, the memory cell size has generally been larger than 100 μm [12, 15, 16].

Recently, Yang *et al* reported a photo cross-linkable copolymer that can be directly patterned using the conventional photolithography process [17]. With the scalability of adapting a photolithography and lift-off process, they demonstrated the fabrication of 4 μm × 4 μm memory cells to achieve high memory density [17]. However, it is difficult to apply this method to well-known polymer materials that have no robustness against organic solvents due to damage or dissolution of active polymer layers by aqueous solutions during the fabrication process, which results in the failure or degradation of the device's performance. Therefore, it is necessary to introduce an alternative fabrication process that can obtain high memory density and use non-aqueous fabrication methods such as cold-welding [18, 19], micro contact printing [20] or nanoscale transfer printing [21]. Although these processes are good for pattern transfer, some methods require enormous printing pressure for

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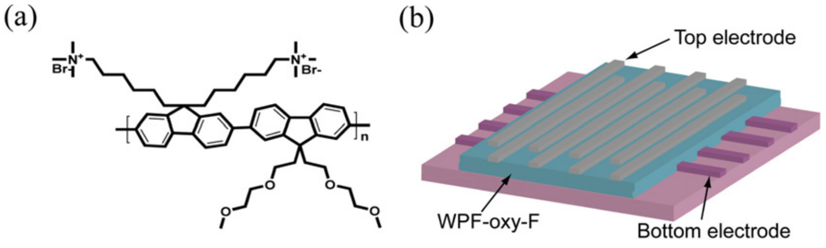


Figure 1. (a) Chemical structure of WPF-oxy-F polyfluorene derivative. (b) Schematics of 8 × 8 cross-bar type polymer non-volatile memory device.

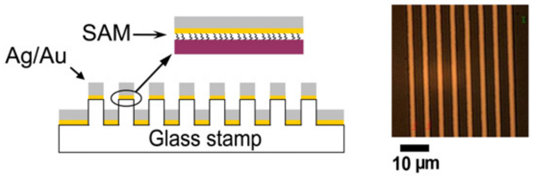
pattern transfer. For example, 290 MPa (∼42 060 psi) pressure was used to transfer dot patterns on an organic layer coated ITO substrate [18] and 190 MPa (∼27 560 psi) was used to transfer metallic line patterns on polymer spin-coated SiO_2 substrates [19]. Such high pressure may damage the active polymer layer. On the other hand, there are other methods which do not require such high pressure [20, 21]. In particular, pattern transfer methods involving poly dimethyl siloxane (PDMS) stamps do not use high pressure and are useful due to its conformal contact at the interface between the stamp and the organic layer. But the PDMS-related process is generally limited in terms of minimum feature size that can be patterned because of the elastic properties of PDMS stamps. Also the PDMS requires additional process steps such as self-assembled ink as an etching mask for subsequent metal etching [20] and a monolayer coating of a chemical linker for chemical bonding between the metal and the substrate [21].

In this paper, we report on the fabrication of cross-bar type polymer non-volatile memory devices using a non-aqueous direct metal transfer (DMT) method with two-step thermal treatment. Using the DMT method, the top electrodes with a linewidth of 2 μm were successfully transferred onto the polymer active layer. The switching behaviour of 8 × 8 array memory devices fabricated by the DMT method was compared with those fabricated by the conventional shadow mask technique.

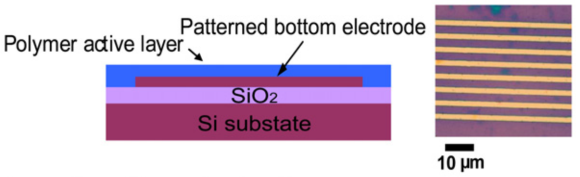
2. Experimental details

As an active polymer layer, poly[(9,9-bis(6′-(N,N,N-trimethylammonium) hexyl)-2,7-fluorene)-*alt*-(9,9-bis(2-(2-methoxyethoxy)ethyl)-fluorene)] dibromide (denoted as WPF-oxy-F), schematically shown in figure 1(a), was synthesized by a palladium-catalysed Suzuki coupling reaction method [22]. Polyfluorene derivatives, which are conjugated polymers for organic devices, can be potential candidates to satisfy the essential conditions for high-performance non-volatile memory devices due to their native properties of good processability and resistance to oxidation [7–10, 23]. In particular, the WPF-oxy-F used as a single active layer in this work has the temperature at 5% weight loss of around 206 °C [22], and WPF-oxy-F memory devices have shown potential for reliable and thermally stable memory performance [9, 10]. Figure 1(b) shows the schematics of a cross-bar type polymer non-volatile memory device. The polymer memory device consists of an active polymer layer (WPF-oxy-F) and 8 lines of both top and bottom electrodes.

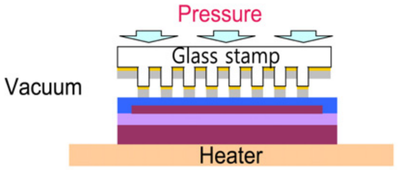
(a) Metal evaporation



(b) Spin-coating polymer film



(c) Transfer of top electrode



(d) Detaching stamp

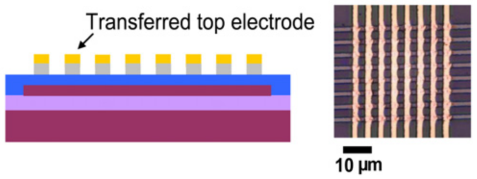


Figure 2. Fabrication process of cross-bar type polymer non-volatile memory devices using the DMT method. (a) Metal evaporation on patterned glass stamp, (b) spin-coating of polymer layer on the patterned bottom electrode, (c) transfer of top electrode, (d) detaching the stamp.

Figure 2 shows a fabrication process for cross-bar type polymer non-volatile memory devices using the direct metal transfer (DMT) method. There are four steps to transfer the top electrode onto the active polymer layer. The first step is the preparation of a glass stamp, as shown in figure 2(a). A transparent glass stamp with a linewidth of 2 μm was prepared by conventional photolithography and a subsequent etching process. Typical ultrasonic cleaning processes with acetone, methanol, and deionized (DI) water were performed to clean the glass stamp. Then, the glass stamp surface was deposited with a monolayer of a releasing material, $CF_3(CF_2)_5(CH_2)_2SiCl_3$ (tridecafluoro-1,1,2,2-tetrahydroctyltrichlorosilane) (purchased from Gelest Inc.) in the vapour phase [24]. After formation of the releasing monolayer on the stamp surface, to detach the metallic layer from the glass stamp easily, a Au layer (35 nm) was deposited on the releasing layer because it has poor adhesion against the releasing layer, and then a Ag layer (40 nm) was deposited on the Au layer using an electron beam evaporator. The right picture in figure 2(a) shows an optical image of the prepared glass stamp with 8 lines of electrodes. The second step is the preparation of the bottom electrode and spin-coating of the active polymer layer, as shown in figure 2(b). The bottom electrodes on the silicon on insulator (SOI) wafer with a linewidth of 2 μm for the DMT method were prepared in the same way as the glass stamp. A heavily doped p-type polycrystalline SOI-type substrate was used to pattern 8 lines of bottom electrodes for the polymer non-volatile memory devices. Optical images of the bottom electrodes are shown in the right picture in figure 2(b). Prior to spin-coating of the active polymer layer, the substrate was treated via a diluted HF-last process to remove the native oxide layer. WPF-oxy-F was first dissolved in a mixture of methanol and water with a volume ratio of 3:7 at a concentration of 5 mg ml^{-1}. Then, the solution was spin-coated on the patterned substrates at 4000 rpm for 30 s, and the resulting thickness of the WPF-oxy-F film was measured to be around 100 nm. To improve film uniformity and to eliminate solvent from the film, post-baking was performed at 150 °C for 20 min on a hotplate prior to the DMT process for the top electrodes. The third step is transfer of the top electrodes by the DMT method, as shown in figure 2(c). The metal-deposited glass stamp was aligned at 90° to the bottom electrodes, and then pressed on the WPF-oxy-F layer, which was first heated to 100 °C with a pressure of 550 psi for 10 min, as shown in figure 2(c). The final step is detaching the glass stamp, as shown in figure 2(d). When the sample was cooled down to 80 °C, the glass stamp was detached from the polymer active layer. The Ag layer was transferred on the WPF-oxy-F layer by easy detachment of the Au layer from the stamp surface. The right picture in figure 2(d) shows the resulting 8 × 8 cross-bar type polymer non-volatile memory devices, indicating that 8 lines of metal top electrodes were well transferred on the polymer layer. Also, we tried to make a smaller size of pattern using the DMT method. In a separate study of the DMT method, 70 nm half-pitch metal lines were successfully transferred on the polymer film from a stamp [25]. Fabrication of polymer memory devices which have nanoscale metal electrodes is currently under study. Further details of the DMT method have been given previously elsewhere [25].

For comparison, similar organic memory devices were also fabricated with the conventional shadow mask method. However, the linewidths of the top and bottom electrodes are typically very large; in our devices made by the shadow mask method, the linewidth was about 100 μm. First, the WPF-oxy-F was spin-coated on the patterned substrate. After the same baking process, a 100 nm thick Ag top electrode with linewidth of 100 μm was deposited as the top electrode with a shadow mask with a thermal evaporator under a pressure of $\sim 10^{-6}$ Torr. The room temperature current–voltage (I–V) measurements of the organic memory devices fabricated both by the DMT method and the shadow mask method were carried out using a semiconductor parameter analyser (HP4155C).

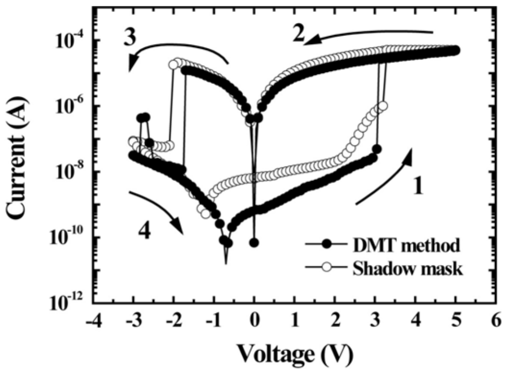


Figure 3. Switching characteristics of memory cells in cross-bar arrays fabricated by the DMT and shadow mask methods. Open circles and filled circles are I–V curves for polymer memory devices made by (a) the DMT method and (b) the shadow mask method, respectively. The sweep rate was 50 mV s^{-1} without hold time.

3. Results and discussion

Figure 3 shows the representative I–V curves of polymer memory devices fabricated by both the DMT and shadow mask methods. Both devices showed similar switching characteristics. When we applied a positive bias from 0 to 5 V to the Ag top electrode, a resistance change was observed. The current increased gradually with the applied bias (stage 1). Then, the device was turned on when the bias was increased beyond a certain transition voltage at ∼3 V, indicating the transition of the organic memory device from a high-resistance state (HRS) to a low-resistance state (LRS). After the transition from an HRS to an LRS, the devices remained in the LRS during the voltage sweep in the negative bias direction from 5 to 0 V (stage 2). When the bias was swept continuously in the negative bias direction from 0 to −3 V (stage 3), the current decreased abruptly, implying another transition of the memory devices from LRS to HRS. After this stage, the device showed a pristine HRS (stage 4). When the bias was applied in the positive bias direction repeatedly, the device showed almost identical I–V characteristics at the range between −3 and 5 V, indicating reversible resistance switching behaviour. Both devices showed electrical bistability with a high on (LRS)/off (HRS) ratio (e.g., $I_{on}/I_{off} \sim 10^3$ at 0.5 V).

To identify the switching behaviour of individual cells in the cross-bar arrays of organic memory devices, I–V characteristics of all of the individual memory cells were obtained with voltage sweep in the range between 5 and −3 V. While measuring a specific memory cell in the 8 × 8 memory cell array, the other cells were kept in the HRS. As mentioned before, both devices showed similar reversible switching behaviour in spite of the different patterning methods (DMT and shadow mask). Although some cells in the cross-bar array devices did not show switching behaviour, a sufficient

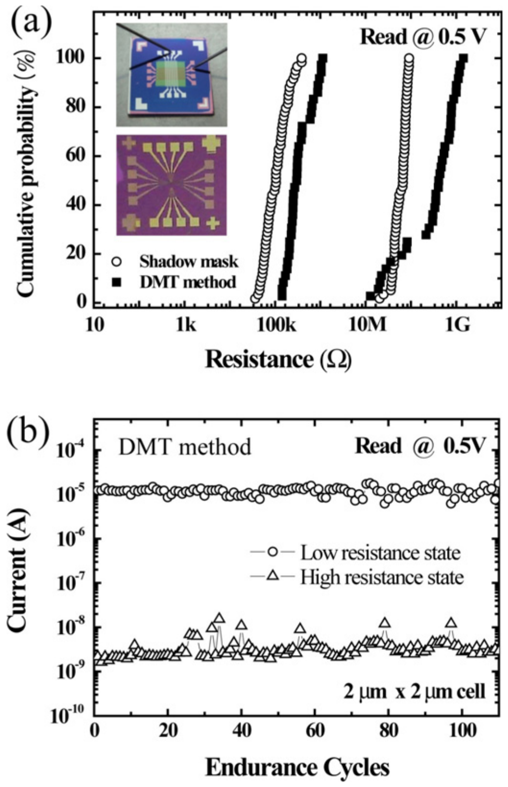


Figure 4. (a) Cumulative probability data set for 8 × 8 cell array memory devices fabricated by the DMT and shadow mask methods. The inset figures show optical images of fabricated array devices made by the DMT method (lower picture) and the shadow mask method (upper picture). (b) Sweep endurance of cross-bar type polymer memory devices made by the DMT method.

number of cells in the arrays successfully operated as non-volatile memory devices; for example, 42 out of 64 cells (64%) and 60 out of 64 cells (90%) operated properly in 8 × 8 memory cell arrays fabricated by the DMT and shadow mask methods, respectively, suggesting the possibility of high-density organic memory applications using WPF-oxy-F. Note that the estimation of device yield depends on how we define the working devices. For example, we actually observed that all the 64 cells made by the DMT method showed switching behaviour, but only 42 devices showed sufficient on/off ratio ($\sim 10^3$). Although the other 22 cells also showed switching behaviour, the on/off ratio was lower than an order of magnitude at a read voltage of 0.5 V. These cells were regarded as 'non-working' devices.

Figure 4(a) shows device uniformity in memory arrays fabricated by both methods. In the devices made by the conventional shadow mask method, the distributions of both the LRS and the HRS are within an order of magnitude, and the difference between the HRS and the LRS was found to be more than two orders of magnitude. In the case of the devices made by the DMT method, the HRS showed somewhat wider distributions, but the difference between the HRS and the LRS was still more than one order of magnitude, indicating reasonably good reversible switching characteristics for non-volatile memory applications. in particular, we evaluated the switching stability of the devices fabricated by the DMT method with a sweep endurance test, as shown in figure 4(b). Repeated sweeps in the voltage range between 5 and −3 V were performed. The tested memory device within the array showed an on/off ratio of four orders or magnitude and good resistance switching cycles over more than 100 trials. These results suggest that WPF-oxy-F can be a potential reliable switching material [9, 10] and that the DMT method also can be a good fabrication method in a non-aqueous process for producing high-density polymer non-volatile memory devices.

4. Conclusions

In summary, we have successfully demonstrated that the DMT method is a potential process for fabrication of polymer non-volatile memory devices with cross-bar architecture. The fabricated memory devices in 8 × 8 arrays with cell size of 2 μm × 2 μm showed almost three orders of magnitude of on/off ratio with stable switching of more than 100 cycles. Although the memory performance needs to be further improved, the scalability by the DMT method may be promising for high-density non-volatile polymer memory applications.

Acknowledgments

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