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Effect of metal ions on the switching performance of polyfluorene-based organic non-volatile memory devices

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ABSTRACT

We investigated the switching behavior of the polyfluorene-derivatives (WPF-oxy-F) with and without metal ions (Ca^{2+} and Na^{+}). Basic memory behavior (e.g., current–voltage sweep, cumulative probability and retention) was not significantly affected by the metal ions, and the materials displayed an on/off ratio of more than three orders of magnitude, as well as good device-to-device uniformity and $>10^4$ s of retention time. However, the threshold voltage of Na-WPF-oxy-F containing Na^{+} was found to be lower than that of Ca-WPF-oxy-F containing Ca^{2+}, due to the looser binding between the sodium ion and the ethylene oxide unit in Na-WPF-oxy-F. Both Ca-WPF-oxy-F and Na-WPF-oxy-F showed area dependence in the low resistance state, implying that localized current flow is assisted by metal ions. In addition, the response time of Ca- and Na-WPF-oxy-F was faster than that of WPF-oxy-F, suggesting possible modulation of memory performance by the addition of metal ions in the polymer layer.

1. Introduction

Recently, organic based electronic devices have been intensively studied due to their flexibility, low cost, ease of fabrication and printing capabilities [1–5]. With the rapid development of information technology, the demand for inexpensive and high density data storage media has increased. Organic non-volatile memory devices have been some of the most promising candidates for next generation storage media [6–17].

There have been many efforts to develop optimal structures and fabrication methods for organic non-volatile memory devices [6–17]. Many research groups have tried to develop novel organic materials or mixtures of host polymer material and metallic nanoparticles that exhibit good memory performance [13,15–17]. Recently, we demonstrated sub-micron scale polymer non-volatile memory devices fabricated using a scalable via-hole structure that showed potential for high density polymer non-volatile memory applications [18]. In addition, combined transistor and organic memory device (one transistor and one resistor, 1T-1R) and combined organic diode and organic memory device (one diode and one resistor, 1D-1R) structures were shown to prevent random accessibility in organic non-volatile memory applications [19,20]. Although they showed satisfactory switching behavior, the devices lacked the performance necessary for realistic memory applications without sophisticated control of the switching parameters or an understanding of the switching mechanism. Joo et al. determined operation voltage threshold behavior in organic based memory devices by controlling ionization of a copper electrode [21], and showed the memory behavior dependence on field strength and temperature. Ma et al. reported organic non-volatile memory devices with controlled copper–ion concentrations within the organic layer [22]. However, the specific effects of metal ions on the switching behavior of organic memory

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devices have not been thoroughly investigated, and it is possible that addition of metal ions in organic memory devices could be used to control switching parameters.

In this study, the effects of metal ions on memory performance and specific switching parameters were investigated. Our results show that while the basic current–voltage characteristics of the polyfluorene-derivative were not significantly affected by the addition of metal ions, studies on the change in threshold voltage, area dependence of each resistance state and transient responses indicated that metal ions assisted localized conduction and induced faster responses.

2. Experimental

Single component polyfluorene-derivative memory devices were fabricated in metal–insulator–metal (MIM) structures on heavily doped p-type (1 0 0) silicon (p^+ Si) substrates (0.001–0.015 Ω cm). After the typical ultrasonic cleaning processes with acetone, methanol, and DI water, silicon wafers were treated with diluted HF to remove the native oxide layer and eliminate the possible role of interfacial SiO_2 layer on the switching behavior. Poly[(9,9-bis((6′-(*N*,*N*,*N*-trimethylammonium)hexyl)-2,7-fluorene)-alt-(9,9-bis(2-(2-methoxyethoxy)ethyl)-fluorene)] dibromide (denoted WPF-oxy-F) and its derivatives (Ca-WPF-oxy-F and Na-WPF-oxy-F) was used as an active layer, schematically shown in Fig. 1 [23]. The three kinds of polyfluorene-derivatives were first dissolved in methanol at a concentration of 10 mg/ml, and then were spin coated on the highly doped p-type silicon substrate. Typically, spin-coating was performed at 2000 rpm for 30 s, and the resulting thickness of the films was ~60 nm. To improve the film uniformity and eliminate the solvent from the films, the films were baked at 150 °C for 20 min on a hotplate in a nitrogen-filled glove box. The top electrodes of the MIM devices were patterned with a shadow mask with square patterns of four different sizes: $50 \times 50\ \mu m^2$, $100 \times 100\ \mu m^2$, $200 \times 200\ \mu m^2$ and $400 \times 400\ \mu m^2$. A 100 nm thick Ag layer was deposited as the top electrode using a thermal evaporator under a pressure of $\sim 10^{-6}$ torr. The memory device structure is schematically shown in Fig. 1d.

X-ray photoelectron spectroscopy (XPS) measurements were carried out using a MultiLab2000 (THERMO VG SCIENTIFIC) system equipped with monochromatised Mg Kα radiation at $h\nu = 1253.6$ eV at a pressure of 1×10^{-9} Pa ($\sim 7.5 \times 10^{-12}$ torr). The binding energies were calibrated to the C1s peak at 285 eV. Both room temperature current–voltage (*I*–*V*) measurements and pulsed *I*–*V* measurements were conducted using a semiconductor parameter analyzer (HP4155C). Additionally, transient voltage response tests were performed with a two-channel pulse generator (Agilent Technology 81104A) and a two-channel oscilloscope (Tektronix TDS 3054B), which were connected to a PC with a general purpose interface bus (GPIB) using a Labview program. The Ag top electrode was connected to a signal line, and the bottom electrode was used as a grounding electrode. All electrical characterization was performed under ambient conditions.

3. Results and discussion

To investigate the effect of metal ions on memory performance, we used WPF-oxy-F and its derivatives bound with mobile metal ions (sodium and calcium) [23]. Chemical structures are shown in Fig. 1. These materials were denoted Na-WPF-oxy-F when containing sodium ions and

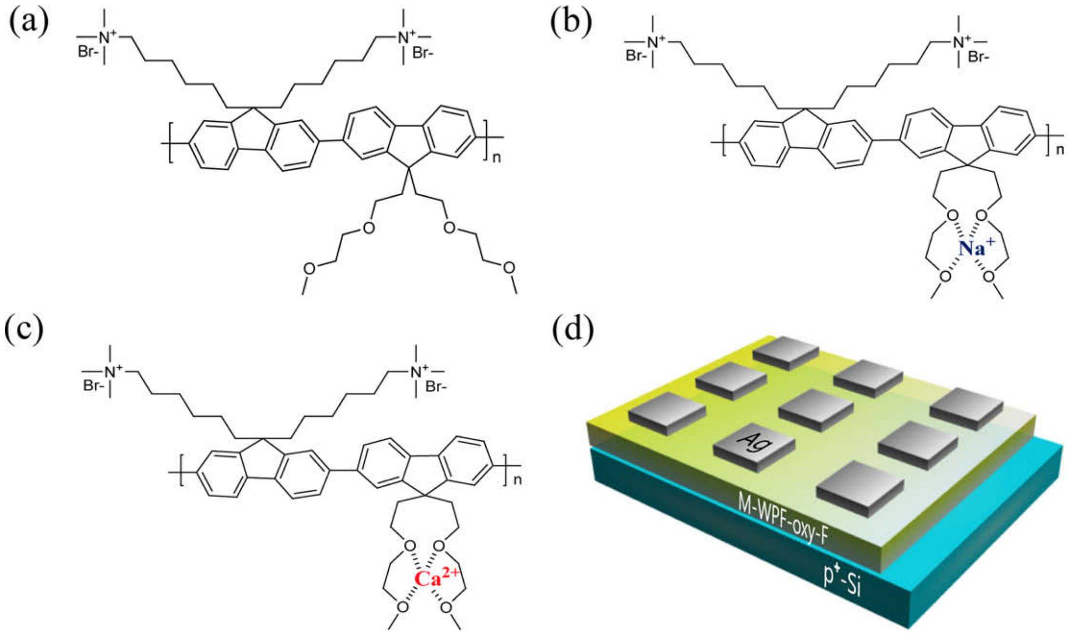

Fig. 1. Chemical structures of polyfluorene-derivatives (a) WPF-oxy-F, (b) Na-WPF-oxy-F and (c) Ca-WPF-oxy-F. (d) Schematic of MIM-type organic nonvolatile memory device.

Ca-WPF-oxy-F when containing calcium ions. The polyfluorene-derivatives with and without metal ions were used as active layers in metal–insulator–metal (MIM) type polymer non-volatile memory devices. To verify the existence of metal ions in M-WPF-oxy-F (where M indicates a metal ion), we performed X-ray photoelectron spectroscopy (XPS) analysis. Fig. 2 shows the XPS spectra of the oxygen 1s (O 1s) peak for each polyfluorene-derivative. For WPF-oxy-F, the O 1s peak equaled ~533 eV, indicating no binding between metal ions and the ethylene oxide unit. On the other hand, the M-WPF-oxy-F series with Na and Ca ions showed Na^+–O and Ca^{2+}–O binding in the O1s spectra as shown in Fig. 2, indicating binding between Na^+ or Ca^{2+} ions and the ethylene oxide unit [24,26]. Because Ca^{2+}–O has a higher binding energy than Na^+–O, binding between Ca^{2+} and the ethylene oxide unit is stronger than that of Na^+ [27].

The MIM polymer memory device structure is shown in Fig. 1d. In our previous work, we reported current–voltage (*I*–*V*) characteristics of WPF-oxy-F in an MIM structure [17]. Reversible switching behavior was observed within the range of 5 to −3 V. The initial state of the polymer memory devices was a high resistance state (HRS). When a positive bias was applied to the top electrode, the current began to increase gradually, and then abruptly jumped to around 3–4 V as the material changed from a HRS to a low resistance state (LRS), as shown in Fig. 3. Conversely, when a reverse voltage sweep was performed on the devices from 5 to −3 V, the current was maintained at a LRS and then decreased somewhat abruptly, indicating a change from a LRS to a HRS. Despite structural differences among these polyfluorene-derivatives, switching behavior was relatively uniform (Fig. 3).

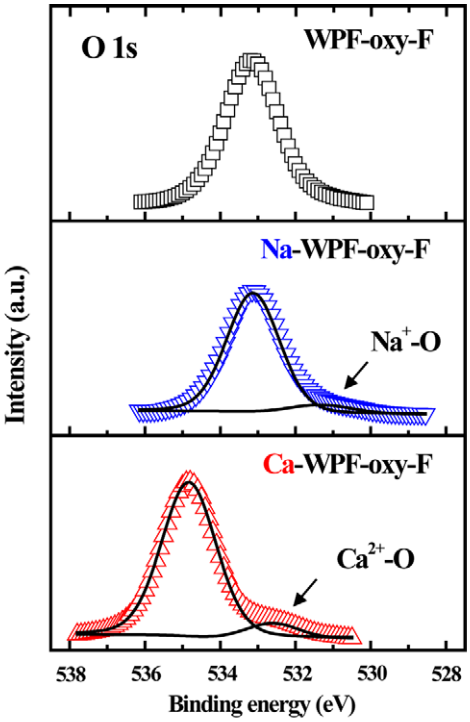

Fig. 2. XPS spectra of oxygen 1s peaks for WPF-oxy-F, Na-WPF-oxy-F and Ca-WPF-oxy-F.

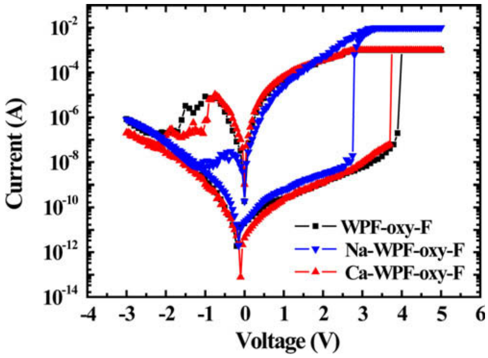

Fig. 3. Semi-log scale *I*–*V* characteristics of WPF-oxy-F, Na-WPF-oxy-F and Ca-WPF-oxy-F with a cell size of 50 × 50 μm².

To investigate the effects of metal ions on polyfluorene-derivatives, we characterized their basic memory performance. Fig. 4a shows the cumulative probability of resistance values (cell size of 50 × 50 μm²). We measured a total of 81 memory devices (20 WPF-oxy-F devices, 37 Na-WPF-oxy-F devices and 24 Ca-WPF-oxy-F devices). The HRS of the three polymer memory devices showed very narrow resistance distributions. The distributions of the LRS were within two orders of magnitude, a slightly wider distribution than that of HRS. However, on/off ratios

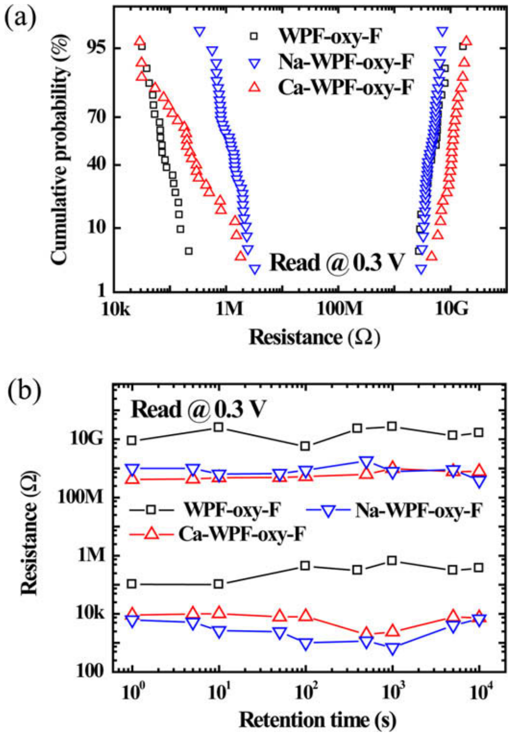

Fig. 4. (a) A Cumulative probability data sets of WPF-oxy-F, Na-WPF-oxy-F and Ca-WPF-oxy-F. (b) Retention characteristics of WPF-oxy-F, Na-WPF-oxy-F and Ca-WPF-oxy-F measured at room temperature.

of mean resistance values for each type of polymer memory devices were still more than three orders of magnitude, indicating excellent device-to-device uniformity in these polyfluorene-derivatives. Fig. 4b shows the retention characteristics of each polymer memory device. Written and erased data were held more than 10^4 s while maintaining on/off ratios of more than three orders of magnitude during the retention characterization. The metal ions did not show any distinct effects on basic memory performance (i.e., *I*–*V* sweeps, device-to-device uniformity and retention characteristics).

We also investigated the effect of metal ions on the threshold voltages and on/off ratios. Fig. 5a shows the distributions of threshold voltage (i.e., the voltage when changing from a HRS to LRS) for each polymer memory device. Although the three kinds of polyfluorene-derivatives had different average threshold voltages, most devices were within the voltage range of 2.5–4.0 V. For example, when we plot the histogram on the threshold voltage for Na-WPF-oxy-F (inset of Fig. 5a), we see a distribution of threshold voltages within 1 V around 2.8 V, indicating reliable switching performance. The other memory devices also showed similar distributions (data not shown). A previous study on the effect of metal ions on switching behavior reported that switching behavior is controlled by two processes: metal ionization and ion drift [21]. Electric field strongly influences the switching behavior, and the switching probability increases sharply around the threshold electric field [21]. In M-WPF-oxy-F containing metal ions, the metal ions are incorporated into the ethylene oxide side groups (see Fig. 1). It is well known that the ethylene oxide unit can be used as a channel for transport of mobile ions even in solid state [24,25]. Hence, when the devices are in the writing process, it is expected that the mobile ions in the ethylene oxide units are rearranged with an applied bias and form conducting current path [27]. This would affect the threshold voltage of the polymer memory devices. The looser bond between the ethylene oxide unit and Na^+ ion (as compared to Ca^{2+} ions, as explained in Fig. 2) results in Na^+ ions moving more easily than Ca^{2+} ions under the same bias conditions. Therefore, Na-WPF-oxy-F displayed a lower threshold voltage than Ca-WPF-oxy-F.

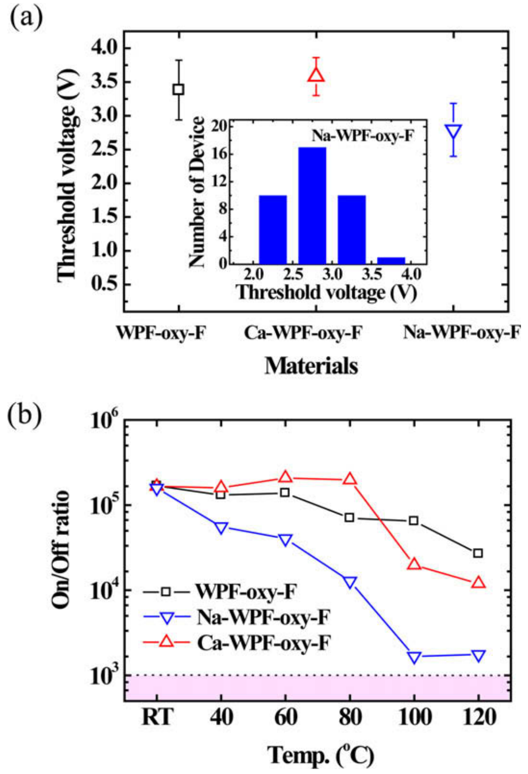

Fig. 5. (a) Distributions of threshold voltage of organic non-volatile memory devices with WPF-oxy-F, Na-WPF-oxy-F and Ca-WPF-oxy-F. Inset shows the histogram of threshold voltage for Na-WPF-oxy-F. (b) Comparisons of on/off ratios of three kinds of polyfluorene-derivatives measured at various temperatures.

Fig. 5b shows the on/off ratios of polymer memory devices at different temperatures. The on/off ratios were measured by the voltage sweep method and read at 0.3 V. In the initial state (at room temperature), all the memory devices showed on/off ratios of more than five orders of magnitude. Although the on/off ratios started to decrease after 60 °C, they retained on/off ratios of more than three orders of magnitude, indicating reliable switching behavior. Only WPF-oxy-F showed a gradual decrease in its on/off ratio. This decrease was due to the increase of leakage current in the HRS, which is enhanced by the hopping current as temperature increases [28]. The on/off ratios of Ca- and Na-WPF-oxy-F reduced considerably near 80 °C due to both hopping current increases and high-temperature activated metal ion movement through the ethylene oxide side groups. Na-WPF-oxy-F showed more rapid on/off ratio reduction with increasing temperature than Ca-WPF-oxy-F. This phenomenon is also related to the different binding energies between the ethylene oxide unit and the Na^+ and Ca^{2+} ions.

To help understand the switching mechanism, we characterized the size dependence of the resistance values of both the HRS and the LRS, as shown in Fig. 6a. The resistance of the polyfluorene-derivative with metal ions (Ca- and Na-WPF-oxy-F) clearly scaled with the reciprocal of the cell size, indicating that the current flowed through the whole cell area in the HRS [28]. This suggests that the metal ions, which exist in polymer layer randomly, allow the current to flow through the whole area in the HRS. On the other hand, dispersed metal ions in each polymer layer are arranged by applied bias and arranged metal ions act as a main current path in the LRS. Most of current flows happen through this current path. Hence the low resistance values of the two polymer materials with metal ions did not change significantly with cell size [29]. One should consider that ionic conduction also partially contributes to the current flow in metal ion based polymer materials. However, unlike Ca- and Na-WPF-oxy-F, the resistance of the WPF-oxy-F did not show any clear size dependence in both LRS and HRS, as can be seen in Fig. 6a. Especially, the slope of log (R)–log (area) at high resistance states observed below 1. This behavior implies that current flows in WPF-oxy-F are affected by not only localized current flows but also space charge limited conduction [17].

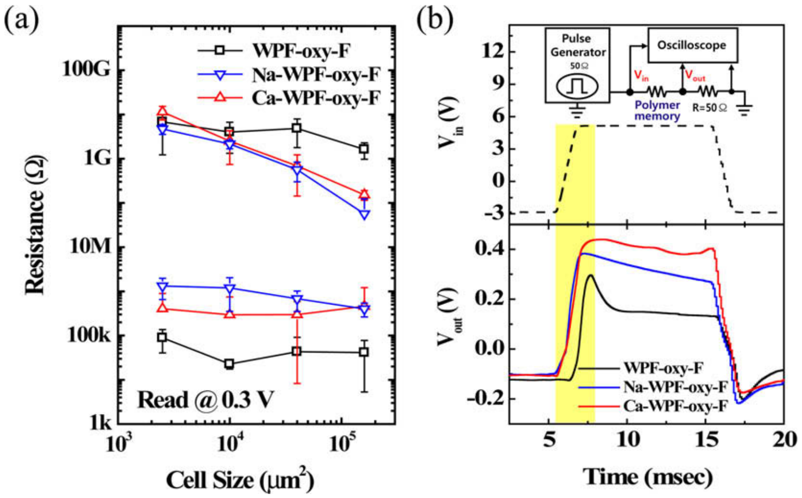

Fig. 6. (a) Resistance values of the on and off states of the three kinds of polyfluorene-derivative memory devices as a function of junction area. (b) Transient response characteristics of the three kinds of polyfluorene-derivative memory devices. The inset shows the circuit of measurement method.

Table 1
Summary of basic switching properties of organic non-volatile memory devices with WPF-oxy-F, Ca-WPF-oxy-F and Na-WPF-oxy-F.

	Band gap [24] [eV]	On/off ratio	*V*th [V]	Response time [μs]	Retention time [s]	Area dependence of HRS
WPF-oxy-F	~2.8	$\sim 10^4$	3.4 ± 0.5	~2000	$\sim 10^4$	No
Ca-WPF-oxy-F	~2.8	$\sim 10^4$	3.6 ± 0.3	~10	$\sim 10^4$	Yes
Na-WPF-oxy-F	~2.8	$\sim 10^4$	3.0 ± 0.4	~10	$\sim 10^4$	Yes

To further study the effects of metal ions on memory performance, we measured pulse delay times for the three kinds of polymer memory devices. The inset in Fig. 6b shows a schematic of the transient response measurements. We monitored input and output voltage pulses using an oscilloscope, and the data are shown in Fig. 6b. By monitoring output voltage (V_{out}) through a 50 Ω external resistor, we estimated the response times for each polymer memory device with cell size of 50 × 50 μm². In this analysis, the response time was the delay time between when an input voltage pulse was applied to the device in the HRS and when it switched to the LRS, as shown in the yellow region of Fig. 6b. The transient responses of Ca- and Na-WPF-oxy-F were very similar (~10 μs writing process). On the other hand, the transient response of WPF-oxy-F was ~2 ms, a much slower writing process response. This difference in response time is mainly due to the metal ions that make current paths in the polymer layer.

The properties of the three polymer memory devices are summarized in Table 1. While they show similar memory characteristics (e.g., similar *I*–*V* hysteresis, room-temperature on/off ratio and retention time), considerable differences can be seen in the threshold voltages, on/off ratios as temperature increases, area dependences and response times. Thus, metal ions in the polymer layer can play an important role in the design of polymer memory devices with low voltage operation and fast response. One can expect more sophisticated control of polymer memory device performance with use of various metal ions.

4. Conclusions

We synthesized polyfluorene-derivatives (WPF-oxy-F) with and without metal ions (Ca^{2+} and Na^+) and compared the switching behaviors of each polyfluorene-derivative. Although basic memory behavior (current–voltage characteristics, cumulative probability and retention) was not significantly affected by the metal ions, Ca-WPF-oxy-F and Na-WPF-oxy-F showed area dependence in the high resistance state, implying that metal ions assist localized current flow. The threshold voltage of Na-WPF-oxy-F was lower than that of Ca-WPF-oxy-F because of more efficient Na^+ movement in Na-WPF-oxy-F. In addition, the Ca- and Na-WPF-oxy-F response time was faster than that of WPF-oxy-F, indicating that memory performances could be controlled with the addition of metal ions in the polymer layer.

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