Reliable Organic Nonvolatile Memory Device Using a Polyfluorene-Derivative Single-Layer Film

Tae-Wook Kim, Seung-Hwan Oh, Hyejung Choi, Gunuk Wang, Hyunsang Hwang, Dong-Yu Kim, and Takhee Lee

***Abstract*—This letter describes the reversible switching performance of metal–organic–semiconductor (MOS) memory devices containing a polyfluorene-derivative single-layer film. The space-charge-limited current contributes to the switching behavior of WPF-oxy-F memory devices. The polyfluorene derivative reported here provides a significant advance to the field of organic semiconductors because it provides a type of organic memory material for nonvolatile memory devices. The following properties are responsible for its memory capabilities: its use of a single-layer film, a large on/off ratio ($I_{\rm on}/I_{\rm off} \sim 10^4$), a long retention time (more than 10 000 s), acceptable thermal stability up to 120 °C, and an excellent device-to-device switching uniformity.**

***Index Terms*—Organic memory device, polyfluorene derivative, reversible switching.**

I. Introduction

DUE to the various merits of organic electronic devices, including low cost, easy fabrication, and printing capability, there has been a significant amount of research on various organic electronic applications based on conjugated polymers [1]–[5]. Examples include organic light-emitting diodes (OLEDs), memory, photovoltaic cells, sensors, and thin-film transistors. Among them, organic bistable memory appears highly attractive, owing to its potential application in data storage [6]–[11]. Although various types of organic memory materials and device structures have successfully demonstrated reversible switching behavior [6]–[11], there have been few reports on thermal stability and device-to-device uniformity. These types of analyses on organic electronics comprised of conjugated polymers have been difficult for many reasons. For example, they have unstable properties under thermal and ambient conditions. Furthermore, multilayers or a blend of nanoparticles in the organic host contribute to difficulties in electronics processing as they affect film uniformity. In addition, memory device performance is significantly affected by film thickness, nanoparticle size, and degree of dispersion of nanoparticles in organic hosts [6]. In contrast, a single layer of the polyfluorene derivatives, which are conjugated polymers for organic devices, are promising candidates for OLEDs and also nonvolatile memory devices due to their processability and endurance against oxidation [12], [13].

In this letter, we report on a high-performance, reliable, and thermally stable organic nonvolatile memory using a single layer of polyfluorene derivative (WPF-oxy-F) film. The WPF-oxy-F memory device exhibited reversible resistance switching between the high and low resistance states (HRS and LRS). We propose a switching mechanism of the WPF-oxy-F memory devices from the analysis of the current–voltage (I–V) characteristics and present detailed discussions of the memory performance in terms of on/off ratio, retention time, thermal stability, and device-to-device switching uniformity.

II. Experimental Section

The single-component polyfluorene derivative memory devices in MOS structures were fabricated on a heavily doped p-type (100) silicon substrate (0.001–0.015 Ω cm). After the typical ultrasonic cleaning processes with acetone, methanol, and DI water, the substrates were treated via a diluted HF-last process to remove the native oxide layer. The polyfluorene derivative (WPF-oxy-F), schematically shown in Fig. 1(a), was synthesized by a palladium-catalyzed Suzuki coupling reaction method [14]. WPF-oxy-F was dissolved in methanol (5 mg/ml) and then spin coated on the substrate (2000 r/min for 30 s). The resulting thickness was measured to be around 30 nm. Subsequently, postbaking was performed at 150 °C for 20 min on a hotplate. The top electrodes of devices were made with a shadow mask that had square patterns of 50 μm × 50 μm. A 100-nm-thick Ag layer was deposited as the top electrode using a thermal evaporator under a pressure of 10^{-6} torr. The electrical characterization was carried out using a semiconductor parameter analyzer (HP4155C).

III. Results and Discussion

Fig. 2(a) shows the I–V characteristic of a WPF-oxy-F memory device. When a positive bias from 0 to 5 V was applied to the top electrode (stage 1), the transition to the resistance state of WPF-oxy-F memory devices was observed at ∼4 V, thereby showing a sharp increase of current. After transition from HRS to LRS of memory, the device remained in the LRS (stage 2). When we applied a negative bias in the direction from 0 to −3 V (stage 3), the device transitioned to the HRS again (stage 4). Fig. 2(b) shows the on/off ratios as a function of applied bias. We observed an on/off ratio of $\sim 10^3$ at 0.3 V.

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The authors are with the Heeger Center for Advanced Materials, Department of Materials Science and Engineering, Gwangju Institute of Science and Technology, Gwangju 500-712, Korea (e-mail: twkim77@gist.ac.kr; shoh317@gist.ac.kr; choihj@gist.ac.kr; kgunu@gist.ac.kr; hwanghs@gist.ac.kr; kimdy@gist.ac.kr; tlee@gist.ac.kr).

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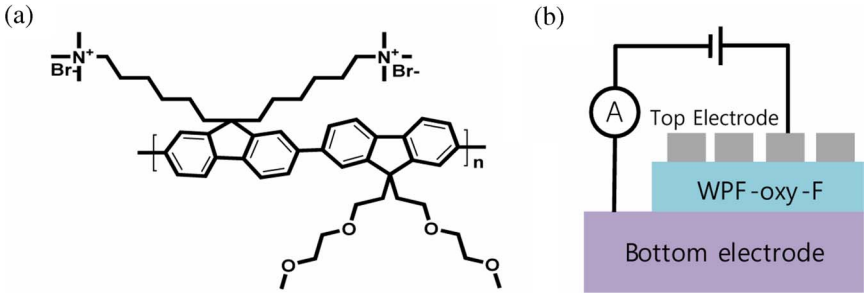

Fig. 1. (a) Chemical structure of the WPF-oxy-F polyfluorene derivative. (b) Schematic of MOS-type WPF-oxy-F memory devices.

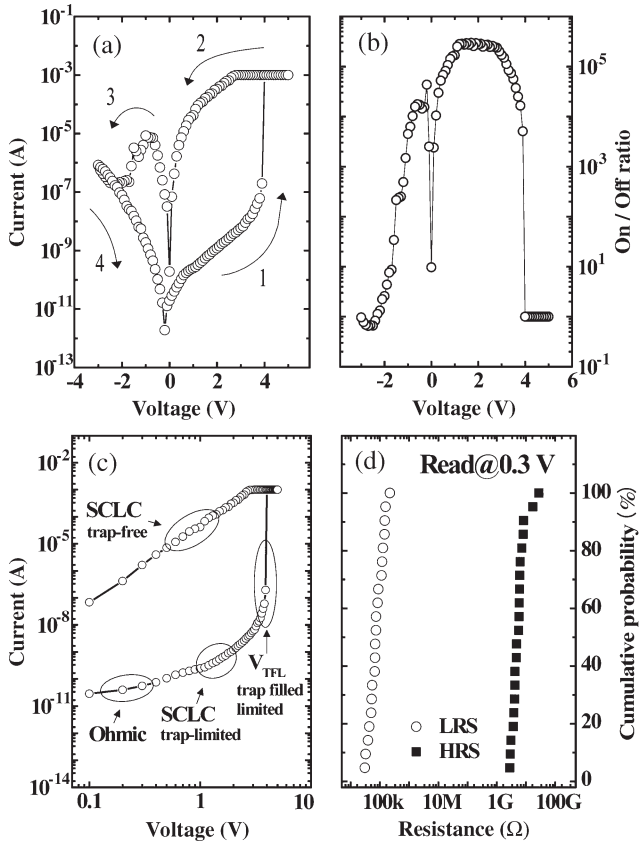

Fig. 2. (a) I–V characteristics of a WPF-oxy-F memory device on a semilog scale. The sweep rate was 50 mV/s without hold time. (b) On/Off ratio of WPF-oxy-F memory device as a function of applied bias. (c) I–V characteristics of a WPF-oxy-F memory device on a log–log scale. (d) Cumulative probability data set for WPF-oxy-F memory devices (21 devices), showing a good device-to-device switching uniformity. The resistance value is the reciprocal ratio of current and a voltage of 0.3 V.

To examine the possible switching mechanism of WPF-oxy-F, we investigated the I–V curve on a log–log scale. Fig. 2(c) shows a log–log plot of the I–V curve in the positive-bias region for a WPF-oxy-F memory device. In the figure, there are four distinct regimes of charge transport behavior, which can be explained by the number of trap sites in the polymer layer that are occupied by carriers, i.e., the space-charge-limited current (SCLC) model [15]–[18]. The transition from the SCLC trap-limited regime (traps are partially filled) to the SCLC trap-free regime (traps are completely filled) is primarily responsible for the switching behavior of WPF-oxy-F [15]–[18]. In the SCLC trap-limited regime, the current is low (OFF-state) because the carriers are trapped at the trap site. On the other hand, in the SCLC trap-free regime, the current is high (ON-state) because the carriers flow without being influenced by the trap sites [15]–[18]. However, recent reports on the switching mechanism of organic memory devices have exhaustively described the formation of metallic filaments due to the migration of metal ions from the top of either silver or copper electrodes [18], [19]. In our case, it is expected that the filamentary conduction may also play a role in the reversible switching behavior. Fig. 2(d) shows the distributions of resistance states for HRS and LRS at 0.3 V for WPF-oxy-F memory devices. The resistance values of 90% of the measured devices were found to be distributed within an order of magnitude, which indicates excellent device-to-device switching uniformity. WPF-oxy-F can be one of the potential active materials for organic memory devices due to the structural characteristics of WPF-oxy-F. This material contains ethylene oxide side groups and bromide ions. The migration of bromide ions *via* the ethylene oxide groups in WPF-oxy-F results in a large amount of space charge [14].

To evaluate the performance of WPF-oxy-F memory devices, measurements of the switching cycle with alternative voltage pulses and retention characteristics were investigated. Fig. 3(a) shows the endurance of a WPF-oxy-F memory device with consecutive single voltage pulses. During 60 repetitions of voltage pulses, our memory device operated well, exhibiting an $I_{\rm on}/I_{\rm off}$ ratio of more than $\sim 10^3$ read at 0.3 V. The retention characteristic test was performed under ambient conditions at room temperature (RT). Both HRS and LRS of the WPF-oxy-F memory device were maintained for 10 000 s without showing any degradation [Fig. 3(b)]. The difference in resistance values between Fig. 3(a) and (b) may be due to both the difference in switching method and the device-to-device variation. To estimate the thermal stability of the WPF-oxy-F memory device, a temperature-variable I–V sweep was performed. Fig. 3(c) shows the resistance values of two resistance states. Their resistance ratios were measured in a temperature range from RT to 120 °C using a 20 °C step. During the thermal stability test, a memory device was heated for 20 min at each temperature then measured. The two resistance states (HRS and LRS) were well separated with a high resistance ratio $(R_{\rm HRS}/R_{\rm LRS})$ of over 10^4 up to 120 °C. After cooling down to RT, the device returned to the HRS, LRS, and $R_{\rm HRS}/R_{\rm LRS}$ values of the initial condition (before the heating). Furthermore, the device did not show any significant degradation of reversible switching behavior. This result indicates excellent thermal stability of the WPF-oxy-F memory devices. Moreover, the switching behavior with high on/off ratio under ambient conditions was stable for one

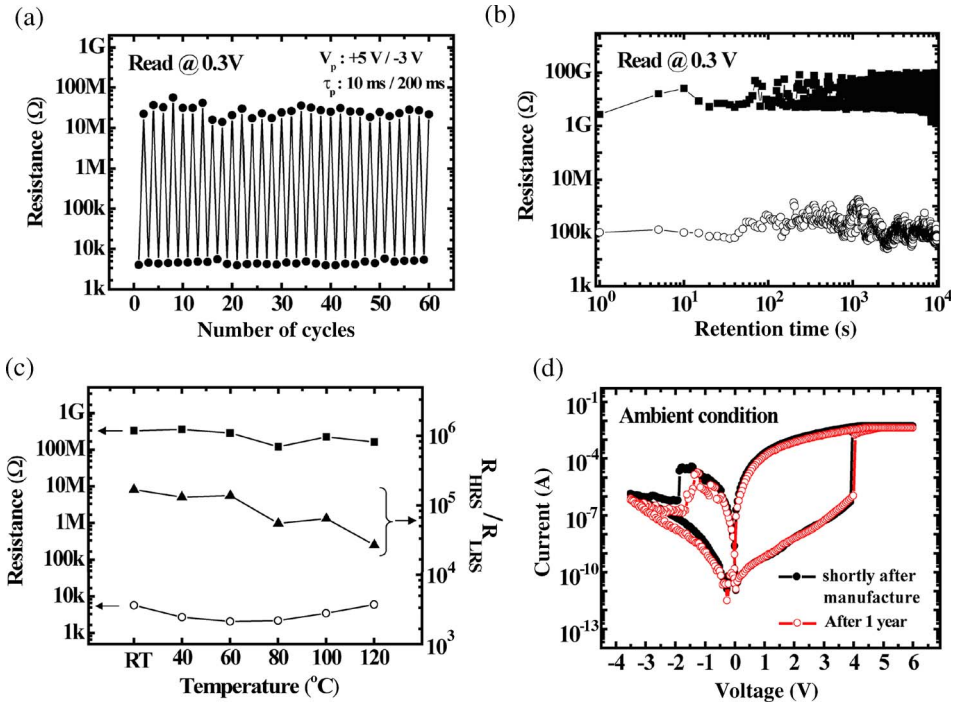

Fig. 3. (a) Switching cycle of a WPF-oxy-F memory device by consecutive voltage pulses (V_p). Low resistance and high resistance states were alternated via a 5-V pulse (writing process) and a −3-V voltage pulse (erasing process) with pulse duration times τ_p of 10 and 200 ms, respectively. (b) Retention characteristics of the two resistance states measured at RT. The data for LRS or HRS are a set of sequential measurements after a single set or reset operation. (c) Resistance values of the two resistance states and their ratio $(R_{\mathrm{HRS}}/R_{\mathrm{LRS}})$ as a function of temperature. (d) I–V characteristics measured shortly after manufacture and after being stored in ambient air for one year demonstrate long-term stability of switching behavior under ambient condition.

year, as shown in Fig. 3(d). This stability of a WPF-oxy-F memory device under ambient conditions may be due to the resistance against oxidation of polyfluorene derivatives [12], [13].

IV. Conclusion

In conclusion, single-layer organic memory devices have been fabricated using a polyfluorene derivative (WPF-oxy-F). SCLC contributes to the switching behavior of WPF-oxy-F memory devices. The memory devices showed excellent reversible switching performance for nonvolatile memory devices, as demonstrated by the following data: a large on/off $(I_{\mathrm{on}}/I_{\mathrm{off}})$ ratio of more than 10^4, a long retention time of more than 10 000 s, a thermally stable switching behavior up to 120 °C, and a good switching uniformity even in ambient conditions. The stable and uniform switching of a WPF-oxy-F device shows the potential for its use in a highly reliable nonvolatile organic memory application.

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