

Effect of Ag Nanoparticles on Resistive Switching of Polyfluorene-Based Organic Non-Volatile Memory Devices

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The effects of Ag nanoparticles on the switching behavior of polyfluorene-based organic non-volatile memory devices were investigated. Polyfluorene-derivatives (WPF-oxy-F) with and without Ag nanoparticles were synthesized, and the presence of Ag nanoparticles in Ag-WPF-oxy-F was identified by transmission electron microscopy and X-ray photoelectron spectroscopy analyses. The Ag-nanoparticles did not significantly affect the basic switching performances, such as the current-voltage characteristics, the distribution of on/off resistance, and the retention. The pulse switching time of Ag-WPF-oxy-F was faster than that of WPF-oxy-F. Ag-WPF-oxy-F memory devices showed an area dependence in the high resistance state, implying that formation of a Ag metallic channel for current conduction.

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I. INTRODUCTION

With recent progress in information technology (IT), organic electronics have attracted great attention due to their low cost, easy fabrication, and printing capability. Organic materials have been intensively developed for next-generation electronic devices, such as organic light-emitting diodes (OLEDs), memories, photovoltaic cells (OPVs), sensors, and thin-film transistors (OTFTs) [1–7]. Among these organic devices, organic memories appear highly attractive, owing to their potential applications in data storage. Many efforts have been made to realize organic bistable memory devices exhibiting non-volatile memory with two different states of resistivity, *i.e.*, a high-resistance state and a low-resistance state [8–15]. Recently, different types of memory devices, such as a homogeneous-polymer-based metal-insulator-metal (MIM) structures [16–18], small-molecule-based MIMs, including molecularly-doped polymers [19], donor-acceptor complexes [20,21], and a blend of nanoparticles (NPs) in organic hosts [22–26] as active organic memory material have been demonstrated.

Among them, blending of nanoparticles (NPs) in organic hosts is one of the widely studied organic materials for organic non-volatile applications due to the simplicity of material preparation, which involves making a mixture of nanoparticles and organic host materials. Furthermore, because organic hosts generally do not have any memory properties without nanoparticles, the aim of these research efforts was to find an optimal ratio of nanoparticles to organic host [22–26]. Hence, there have been few reports on the effects of nanoparticles on the resistive switching behavior of organic materials, which have their own memory property without any nanoparticles.

In this study, we synthesized a polyfluorene derivative (WPF-oxy-F), which has memory property. In order to investigate the effects of Ag nanoparticles on memory properties of WPF-oxy-F, Ag nanoparticles were incorporated into the WPF-oxy-F. From high-resolution transition electron microscopy (HR-TEM) and X-ray photoelectron spectroscopy (XPS) analyses, we observed well-dispersed Ag nanoparticles in the Ag-WPF-oxy-F film. Although the basic memory behavior (current-voltage characteristics, cumulative probability, and retention) was not significantly affected by the Ag nanoparticles, Ag-WPF-oxy-F showed area dependence in the high-resistance state, implying the formation of a Ag metallic channel for current conduction. In addition, the pulse switching time of Ag-WPF-oxy-F was faster than that of WPF-oxy-F, indicating the effect of Ag-nanoparticles on switching behavior of polyfluorene-based organic non-

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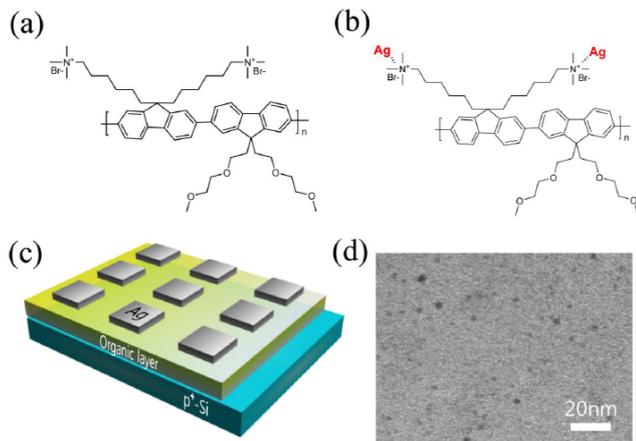


Fig. 1. (color online) Chemical structure of polyfluorene derivatives: (a) WPF-oxy-F and (b) Ag-WPF-oxy-F. (c) Schematic of a MIM-type organic non-volatile memory device. (d) TEM image of Ag nanoparticles in Ag-WPF-oxy-F.

volatile memory devices.

II. EXPERIMENT

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 derivative, containing Ag nanoparticles (Ag-WPF-oxy-F) and schematically shown in Fig. 1(a) and (b), were synthesized via a palladium-catalyzed Suzuki coupling reaction and freeze drying method [27]. Polyfluorene based organic non-volatile memory devices were fabricated in metal-insulator-metal (MIM) structures on heavily-doped p-type (100) silicon (p^+ Si) substrates ($0.001 - 0.015 \Omega \text{ cm}$). After the typical ultrasonic cleaning processes with acetone, methanol, and deionized (DI) water, the substrates were treated with diluted HF to remove the native oxide layer. Both WPF-oxy-F and Ag-WPF-oxy-F were first dissolved in methanol at a concentration of 10 mg/ml and were then spin coated on a highly doped p-type silicon substrate. Typically, spin-coating was performed at 2000 rpm for 30 sec, and the resulting thickness of the films was around 60 nm. To improve the film uniformity and eliminate the solvent from the films, we baked the films 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: $50 \times 50 \mu\text{m}^2$, $100 \times 100 \mu\text{m}^2$, $200 \times 200 \mu\text{m}^2$ and $400 \times 400 \mu\text{m}^2$. A 100 nm thick Ag layer was deposited as the top electrode by using a thermal evaporator under a pressure of $\sim 10^{-6}$ Torr. The memory device structure is schematically shown in Fig. 1(c).

XPS measurement was carried out using a MultiLab2000 (THERMO VG SCIENTIFIC) system

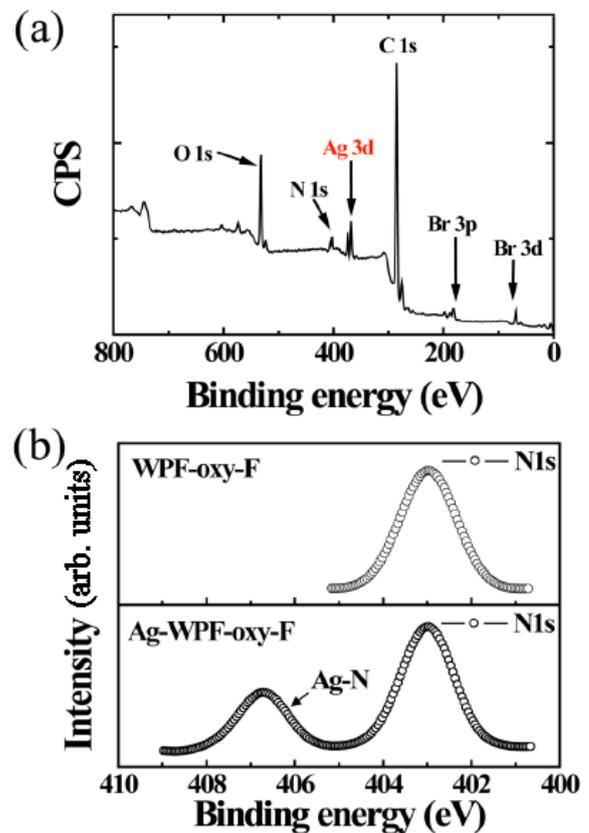


Fig. 2. (color online) (a) XPS spectrum of Ag-WPF-oxy-F. (b) Comparison of XPS spectra of the nitrogen 1s (N 1s) peaks for WPF-oxy-F and Ag-WPF-oxy-F.

equipped with monochromatized Mg K_{α} radiation at $h\nu = 1253.6 \text{ eV}$ at a pressure of $1 \times 10^{-9} \text{ Pa}$ ($\sim 7.5 \times 10^{-12} \text{ Torr}$). The binding energies were calibrated to the C1s peak at 285 eV. The TEM sample was prepared by dropping a polymer solution onto a carbon-coated copper grid and drying at 60°C , and a HR-TEM system (JEOL JEM-2100) operating at 200 kV was used to observe the silver particles. The current-voltage (I-V) measurements were carried out using a semiconductor parameter analyzer (Agilent Technology 4155C) with pulse generator units (Agilent 41501B PGUs). All electrical characterization was performed under ambient conditions.

III. RESULTS AND DISCUSSION

In order to investigate the effect of Ag nanoparticles on the resistive switching of polyfluorene-based organic non-volatile memory devices, we synthesized a polyfluorene derivative with Ag nanoparticles (Ag-WPF-oxy-F). The Ag nanoparticles in WPF-oxy-F were synthesized by using a freeze drying method. These two types of polyfluorene derivatives were used as active layers in metal-

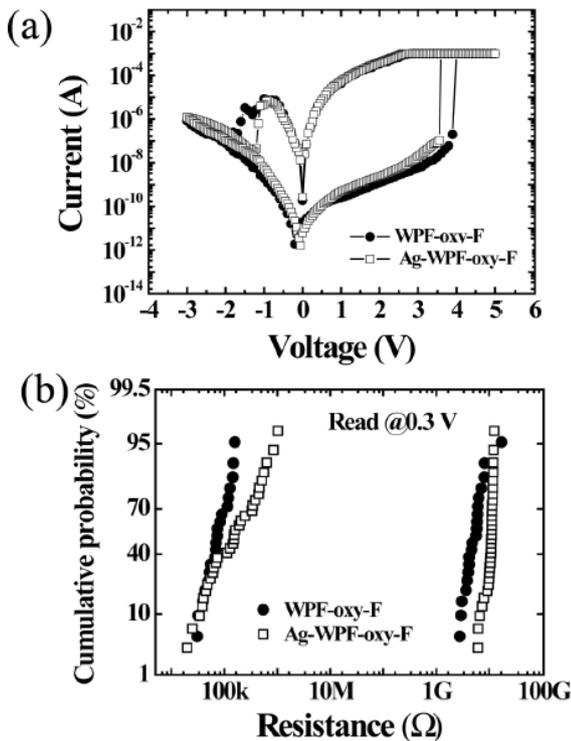


Fig. 3. (a) Semi-log scale I-V characteristics of WPF-oxy-F and Ag-WPF-oxy-F with a cell size of $50 \times 50 \mu\text{m}^2$. (b) A cumulative probability data of the on/off resistances of WPF-oxy-F and Ag-WPF-oxy-F.

insulator-metal (MIM) type organic non-volatile memory devices. To identify the existence of Ag nanoparticles in WPF-oxy-F, we performed both TEM and XPS analyses. Figure 1(d) shows the TEM image of Ag-WPF-oxy-F. We observed that Ag nanoparticles with an average size of about 5 nm were synthesized and are well dispersed over all WPF-oxy-F film without any significant aggregation. Fig. 2 shows the XPS spectra of Ag-WPF-oxy-F. Silver 3d (Ag 3d) peaks are clearly observed within the range between 363 eV and 378 eV, indicating the existence of Ag nanoparticles in WPF-oxy-F. In addition, from comparisons of the nitrogen 1s (N 1s) peaks for the polyfluorene derivatives (WPF-oxy-F and Ag-WPF-oxy-F), we were able to clearly identify the presence of Ag nanoparticles in Ag-WPF-oxy-F.

To investigate the effects of Ag nanoparticles on the switching behavior of WPF-oxy-F, we characterized their basic memory performance. In our previous works, we reported the current-voltage (I-V) characteristics of WPF-oxy-F in a MIM structure [8,9]. Despite differences in the chemical structures between WPF-oxy-F and Ag-WPF-oxy-F, the switching behavior was very similar, as shown in Fig. 3(a). Reversible switching behavior was observed within the range from 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

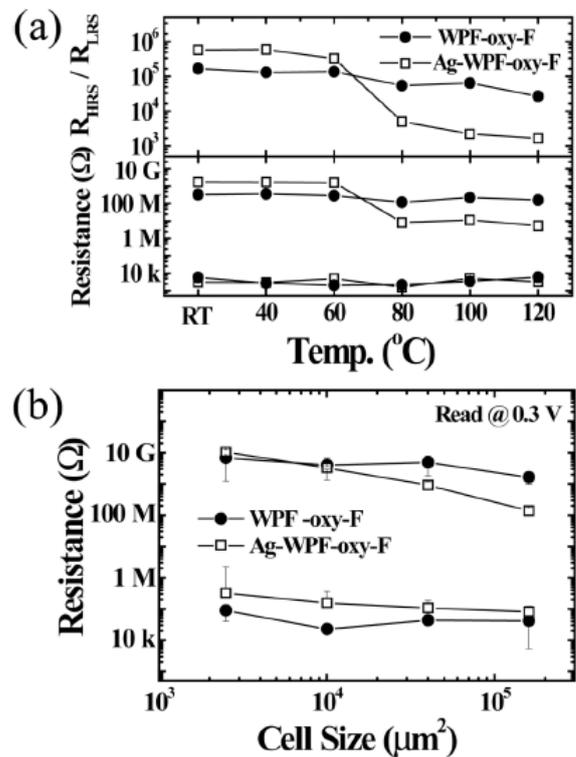


Fig. 4. (a) Comparisons of resistance state and on/off ratios for both WPF-oxy-F and Ag-WPF-oxy-F measured at various temperatures. (b) Resistance values of the on and the off states of the two kinds of polyfluorene-derivative memory devices as a function of junction area.

then abruptly jumped to around 3 – 4 V as the device changed from a HRS to a low-resistance state (LRS). Conversely, when a reverse voltage bias was applied to 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. In addition, in order to evaluate device-to-device uniformity, we measured a total of 53 memory devices (21 WPF-oxy-F devices and 32 Ag-WPF-oxy-F devices). Both the HRS and the LRS of the two organic non-volatile memory devices showed very narrow resistance distributions as shown in Fig. 3(b). The on/off ratios of mean resistance values for both WPF-oxy-F and Ag-WPF-oxy-F were also more than three orders of magnitude, indicating excellent device-to-device uniformity in these polyfluorene derivatives.

For further analysis of the effect of Ag nanoparticles, we observed the on/off ratios of organic non-volatile memory devices at different temperatures, as shown in Fig. 4(a). The on/off ratios were measured by used the voltage sweep method and were read at 0.3 V. As shown in Fig. 4(a), The LRS of both memory devices was not affected by increasing the temperature. In the initial state (at room temperature), both memory devices showed on/off ratios of more than five orders of magnitude as shown in upper figure in Fig. 4(a). Although

Ag-WPF-oxy-F showed on/off ratios of more than three orders of magnitude at high temperatures, that does not mean reliable operation of Ag-WPF-oxy-F under high-temperature conditions. Hence more detailed studies of Ag-WPF-oxy-F are still necessary for reliable memory applications. In the case of WPF-oxy-F, a slight decrease in its on/off ratio due to increasing of leakage current was observed in the HRS, which is enhanced by the hopping current as temperature increases [28]. On the other hand, Ag-WPF-oxy-F showed a significant decrease in the on/off ratios at temperature above 60 °C. This phenomenon may be due to both the increase in the hopping current increases the formation a Ag metallic channel, activated at high temperature, through the Ag-WPF-oxy-F film.

To understand the switching behavior, we characterized the area dependence of the resistance values of both the HRS and the LRS, as shown in Fig. 4(b). The LRSs of both memory devices showed little dependence on cell area. The HRS of WPF-oxy-F did not show any clear size dependence. This behavior in WPF-oxy-F is due to the so-called "space-charge-limited-conduction" and localized current flows [8]. On the other hand, the HRS of Ag-WPF-oxy-F exhibited an obvious dependence on the cell area. The resistance of the HRS increases about 10 times when the area of the devices decreases 10 times, indicating that the current flows through the whole cell area in the HRS [29]. It seems that the Ag nanoparticles, which were well dispersed in WPF-oxy-F, acted as current paths, allowing the current to flow through the whole area in the HRS. In case of the LRS, the resistance values did not change significantly with the cell area due to the formation of localized current paths through Ag nanoparticles in Ag-WPF-oxy-F. Hence, formation of a Ag metallic channel in Ag-WPF-oxy-F is responsible for this filamentary conduction.

To evaluate the memory performance of Ag-WPF-oxy-F, we investigated measurements of the switching cycle with alternative voltage pulses and retention characteristics. In our previous report on WPF-oxy-F, the memory device operated well, exhibiting an I_{on}/I_{off} ratio of more than $\sim 10^3$ read at 0.3 V. The LRS and the HRS were alternated via a 5V pulse (writing process) and a -3 V voltage pulse (erasing process) with pulse duration times τ_p of 10 ms and 200 ms, respectively [9]. However, the Ag-WPF-oxy-F case required a much shorter duration times than WPF-oxy-F, showing a pulse duration time τ_p of 100 μ s for writing process, as shown in Fig. 5(a). It seems that this faster switching may be due to the Ag nanoparticles, which help formation of metallic channels in Ag-WPF-oxy-F. Therefore, Ag-WPF-oxy-F memory devices show much faster switching than WPF-oxy-F devices. Despite 10^4 repetitions of voltage pulses, our memory device operated well, indicating reliable pulse switching behavior of Ag-WPF-oxy-F. In addition, a retention characteristic test of WPF-oxy-F was performed under ambient conditions at room temperature, as shown in Fig. 5(b). Both the HRS and the LRS of the Ag-

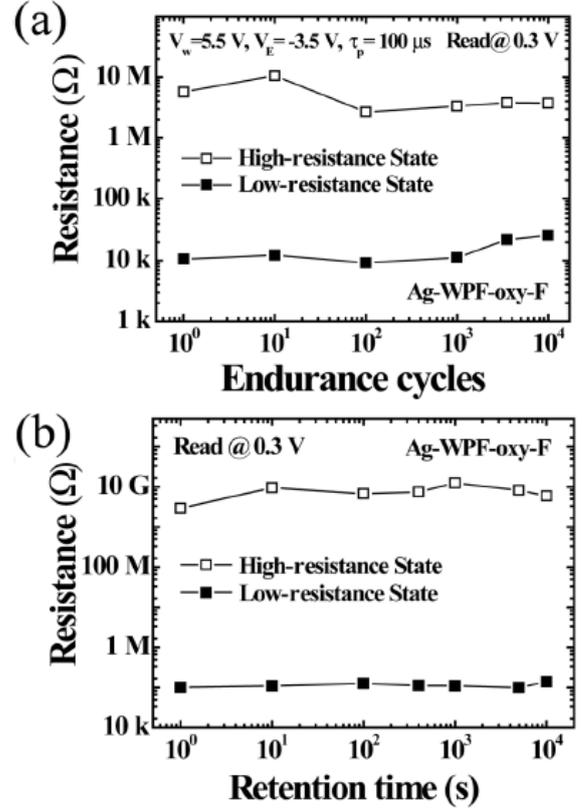


Fig. 5. (a) Switching cycle of a Ag-WPF-oxy-F memory device by consecutive voltage pulses (V_p). (b) Retention characteristics of Ag-WPF-oxy-F measured at room temperature.

WPF-oxy-F memory device were maintained for 10,000 sec without showing any degradation.

IV. CONCLUSION

In summary, we synthesized polyfluorene derivatives (WPF-oxy-F) with and without Ag nanoparticles and compared the switching behaviors of the polyfluorene derivatives. From TEM and XPS analyses, we observed well-dispersed Ag nanoparticles in the Ag-WPF-oxy-F film. Although the basic memory behavior (current-voltage characteristics, distribution of on/off resistance and retention) was not significantly affected by the Ag nanoparticles, Ag-WPF-oxy-F showed area dependence in the high-resistance state, implying the formation of a Ag metallic channel for current conduction. In addition, the pulse switching time of Ag-WPF-oxy-F was faster than that of WPF-oxy-F, indicating the effect of Ag-nanoparticles on the switching behavior of polyfluorene based organic non-volatile memory devices.

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