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Enhancement of resistive switching behavior of organic resistive random access memory devices through UV-Ozone treatment

Joong Hyeon Park1, Sobia Ali Khan1, Mehr Khalid Rahmani1, Jihwan Cho∗ and Moon Hee Kang1,2,∗

1 School of Electronics Engineering, Chungbuk National University, Cheongju, 28644, Republic of Korea
2 R&D Center, Jinoid, Seoul, 08507, Republic of Korea
∗ Author to whom any correspondence should be addressed.

E-mail: moonhee@chungbuk.ac.kr

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Abstract

We fabricated organic resistive random-access memory (RRAM) devices using a low-cost solution-process method. All the processes were performed at temperatures below 135 °C under ambient atmospheric conditions. The RRAM resistive switching layer was formed from a polymer-fullerene bulk heterojunction using poly(3-hexylthiophene-2,5-diyl) (P3HT) and (6,6)-phenyl C61 butyric acid methyl ester (PCBM). The fabricated organic RRAM device exhibited typical nonvolatile bipolar resistive switching behavior with an ON/OFF ratio of ~40, but it provided a low endurance of 27 cycles. Therefore, for enhanced stability, simple UV–Ozone (UVO) treatment was applied to the P3HT:PCBM organic bulk heterojunction layer. The organic RRAM device with UVO treatment exhibited an enhanced performance with an ON/OFF ratio of ~400 and an endurance of 47 cycles. In addition, complementary resistive switching behavior was observed. The conduction mechanisms of the organic RRAM device were investigated by fitting the measured I–V data to numerical equations, and Schottky emission and Ohmic conduction were the main conduction mechanisms for the high-resistance and low-resistance states for the RRAM device with or without UVO treatment.

1. Introduction

Organic resistive random access memory (RRAM) devices have attracted attention as promising next-generation non-volatile memory devices owing to their material variety, high mechanical flexibility, low power consumption, low fabrication cost, and scaling benefits [1–4]. A RRAM device has a simple sandwich structure composed of a resistive switching (RS) layer between the two electrodes. The RS layer for the organic RRAM device can be composed of polymers, small molecular compounds, and hybrid organic/inorganic nanocomposites [5–7]. Among the diverse organic materials, poly(3-hexylthiophene-2,5-diyl) (P3HT) and (6,6)-phenyl C61 butyric acid methyl ester (PCBM), which are widely used in organic solar cell fabrication [8–10] were used in this study to form the RS layer of the RRAM device. Although P3HT is a donor semiconducting polymer material, it has a superior coordination of hetero-sulfur atoms, which could be beneficial for the formation of metallic filaments, facilitating conduction in the RS layer [11]. However, organic RRAM devices do not exhibit high stability because of the low stability of organic materials. Ji et al reported polyimide (PI) and PCBM based memory device with write-once-read-many characteristics [12]. Jin et al reported P3HT:PCBM based RRAM for nonvolatile memory device applications. They fabricated a RRAM with a structure of Al/PI/Au/P3HT:PCBM/Au and it exhibited an endurance of over 100 cycles and ON/OFF ratio of 102 to 103 [13]. Our recent research on RRAM with P3HT single layer demonstrated endurance cycle up to ~1,000 and ON/OFF ratio of ~10 [14]. Sagar et al emulated synaptic functions with low operation voltage from P3HT based RRAM device [15]. Our previous works on RRAM with poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS) single layer demonstrated ~16 cycles endurance and ON/OFF ratio of ~20 [16]. However, this low endurance was significantly increased up to 140 cycles by using different commercial grade PEDOT:PSS, which has more PSS in PEDOT:PSS [17]. As the performance and stability of the organic RRAM is strongly dependent on the materials,
performance enhancement may come from optimization of the materials including modification of the chemical composition or the chemical treatment.

In this study, to address the low environmental stability and performance enhancement of organic RRAM devices, the impact of UV-Ozone (UVO) treatment on the solution-processed organic RRAM devices was investigated [18, 19]. This is because UVO treatment was reported to be beneficial to the performance of the inorganic or organic devices. The UVO may enhance the RS behavior, reliability, stability, and ON/OFF ratio of the devices [20–22].

2. Experimental

Organic RRAM device fabrication starts with a commercially available indium tin oxide (ITO)-coated glass substrate (figure 1). ITO (thickness of 150 nm, sheet resistance of 10 Ω sq⁻¹) was used as the bottom electrode of the RRAM device. The substrate was cleaned using acetone and isopropyl alcohol for 10 min in a sonicator, followed by UVO (λ = 184.9/253.7 nm, power = 20 mW cm⁻²) for 10 min to achieve hydrophilic surfaces and cleaning [23]. The organic RS layer of the RRAM device was formed from a solution containing 15 mg of P3HT and 12 mg of PCBM in 1 ml of 1,2-dichlorobenzene. This solution was then stirred overnight at 65 °C and then deposited onto ITO by spin coating at 1000 rpm for 80 s. Subsequently, the organic P3HT:PCBM RS layer was treated again with UVO for 2 min and then annealed at 135 °C for 10 min. UVO was irradiated in the direction of the P3HT:PCBM organic RS layer. Finally, an Al top electrode was formed on the organic RS layer by thermal evaporation using a shadow mask (100 um diameter circle). Electrical I–V measurements were performed using a semiconductor device parameter analyzer (Keithley 4200A-SCS), and cross-sectional scanning electron microscopy (SEM) images and atomic force microscopy (AFM) images were obtained using the Hitachi S-4800 and Bruker Dimension Icon, respectively.

3. Results and discussion

3.1. Geometrical structure of the fabricated organic RRAM device with ITO/P3HT:PCBM/Al structure

Figure 2(a) shows the geometrical structure of the fabricated organic RRAM device with ITO/P3HT:PCBM/Al structure. ITO and Al were used as the bottom and top electrodes, respectively, while the P3HT:PCBM bulk heterojunction organic layer was used as the RS layer of the RRAM. During the I–V measurements, the ITO bottom electrode was grounded, and a DC bias was applied to the Al top electrode. Figure 2(b) shows a cross-sectional SEM image of the fabricated organic RRAM device. The thicknesses of the ITO, P3HT:PCBM organic RS layer, and Al electrode were 152 nm, 234 nm, and 45 nm, respectively.

UVO may have an impact on the surface roughness of the underlying layer [24] which can be detrimental to nanoscale thin-film devices. Therefore, we measured the surface roughness of the P3HT:PCBM organic layer before and after the UVO treatment using AFM. As shown in figure 3, there was no significant change in the surface roughness after the UVO treatment. The average surface roughness values were 0.672 nm and 0.182 nm.
for the organic layers with and without UVO treatment, respectively. Therefore, UVO treatment of the organic layer may not be detrimental to the surface roughness.

3.2. Enhancement of RS behavior of organic RRAM device through UVO treatment

To investigate the RS behavior of the fabricated organic RRAM device, current-voltage (I–V) measurements were performed (figure 4). Current compliance (CC) was applied during the I–V measurements to prevent device breakage. The electroforming process is not required, which is beneficial for practical operations [25]. First, a positive bias sweep from 0 to 2 V was applied, and the resistance of the RRAM device switched from a high resistance state (HRS) to low resistance state (LRS) when the voltage reached $\sim 0.5$ V. This process is called the SET process. Subsequently, the current reached a saturated CC level. Following the second sweep from 2 V to 0 V, the RRAM device maintained its LRS. After the third sweep from 0 to $-1.2$ V, the device switched its resistance from LRS to HRS. This process is called the RESET process. Following the final bias sweep from $-1.2$ to 0 V, the RRAM device maintained its HRS. It should be noted that the SET and RESET voltages were low, at only $\sim 0.5$ and $\sim -1$ V, respectively. These low operating voltages are beneficial for low-power applications.

As shown in figure 4, the RRAM devices with and without UVO treatment provided non-volatile bipolar resistive switching (BRS) with ON/OFF ratios of $\sim 400$ and $\sim 40$, respectively. It is worth noting that complementary resistive switching (CRS) behavior can be observed in the negative bias region of RRAM devices that received UVO treatment. Figures 4(c) and (d) shows the endurance characteristic of the RRAM with UVO and without UVO treatment. The organic RRAM without UVO treatment sustained its stability for up to 27 cycles (figure 4(c)), while the organic RRAM with UVO treatment sustained its stability for up to 47 cycles (figure 4(d)). The resistance value during the endurance test was read at a voltage of 0.1 V. From these I–V measurements, it is clear that UVO treatment enhances the RS behavior and the slight enhancement of stability of the RRAM device.
However, endurance for both RRAM was not impressive compared to the RRAM with inorganic materials. Our previous research demonstrated only 16 cycles endurance from RRAM with PEDOT:PSS RS layer [16]. However, this low endurance was enhanced up to 140 cycles [17] by using different grade PEDOT:PSS [17]. Our recent research on RRAM with P3HT single layer demonstrated endurance up to ∼1,000 cycles [14]. As the stability of the organic material is strongly dependent on the either material or synthesis condition, further stability enhancement may arise from the investigation of the materials. This may include optimization of the synthesis condition (varying wt% of P3HT and PCBM in the solution) or chemical treatment.

Figure 4. I–V curve and endurance test of the organic RRAM (a), (c) without UVO and (b), (d) with UVO treatment.

Figure 5. Statistical distribution of the (a) SET and (b) RESET voltages of the organic RRAM devices without and with UVO treatment.

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Figure 5 shows the statistical distribution of the SET and RESET voltages for the organic RRAM device with and without UVO treatment. As can be seen in figure 5, there was no significant difference in the SET and RESET
voltages for RRAM devices with and without UVO treatment. The average SET voltage was 0.47 and 0.52 V for organic RRAM devices without and with UVO treatment, respectively. The average RESET voltage was the same to as that for organic RRAM devices without and with UVO treatment. These statistical plots indicate that the UVO treatment did not significantly affect the average SET and RESET voltages. However, as can be seen in figure 5 for UVO treated sample, there was an outlier (dot in the box plot), which has a value far different from other values. This may because UVO was not irradiated evenly for all the cells, and some cells were over or under exposed.

3.3. Conduction mechanism of P3HT:PCBM-based organic RRAM device
To investigate the conduction mechanism of the fabricated organic RRAM device, I–V curve fitting was performed, and the slope values for ln(V) versus ln (I) during the HRS and LRS were obtained. As can be seen in
Figure 6, there was no difference in the conduction mechanisms for the organic RRAM devices without and with UVO treatment. As the slope was 1.19 and 1.47 for HRS, Schottky emission was the dominant mechanism while when the slope was 0.88 and 1.03 for LRS, Ohmic conduction was the dominant conduction mechanism for the P3HT:PCBM-based organic RRAM device without and with UVO treatment, respectively. Schottky emission is an electrode-limited conduction mechanisms \[26\], while Ohmic conduction is a bulk-limited conduction mechanisms \[27\].

Figure 7 shows the energy band diagram of the P3HT: PCBM-based RRAM device \[28\] with a work function of both electrodes and lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO) for organic materials. As shown in Figure 7, the asymmetric energy level of the both electrodes can result in asymmetric RS behavior for both polarities. In addition, based on the materials what we were used, a feasible RS mechanism in our RRAM device can be electrochemical metallization mechanism (ECM) \[29\]. In ECM, RS behavior is based on the formation and rupture of the metallic conductive filament (CF). For example, in our organic RRAM devices, Al (active metal) can form metallic CF. Figure 7(b) indicates that a positive bias was applied to the Al top electrode. At a positive bias, Al can be oxidized into Al$^{3+}$ ions, and under a high electric field, these ions can start to move towards the ITO bottom electrode, which is grounded. In addition, electrons injected from the ITO can move towards the Al electrode. Owing to this process, Al$^{3+}$ ions can be reduced to Al atoms by recombination with electrons. As the intensity of the positive bias increases, these Al atoms become thicker and longer and finally form CF. The formation of this CF results in easy movement of electrons, and the RRAM device undergoes the SET process, switching its state from HRS to LRS. In contrast, when a negative bias is applied to the Al top electrode, the RRAM device changes its state from LRS to HRS in a process called the RESET process. During the RESET process, the formed Al CF is ruptured and returns to its original site owing to a reverse polarity bias, and RRAM devices changes its state from LRS to HRS.

4. Conclusion

In this study, solution-processed low-cost organic RRAM was fabricated using the bulk heterojunction P3HT: PCBM. The fabricated organic RRAM demonstrated non-volatile BRS behavior. Organic RRAM devices operate at a low voltage of $\sim 0.5$ and $\sim 1$ V for SET and RESET operations, respectively, making them suitable for low-power memory device applications. In addition, for further performance enhancement, a few minutes of UVO treatment was applied to the P3HT:PCBM-based organic RRAM device. As a result, the ON/OFF ratio and endurance cycle increased from 40 to 400 and 27 to 47 cycles, respectively. In addition, CRS behavior was observed in organic RRAM with UVO treatment. A study of the conduction mechanism revealed that the Schottky emission was dominant for HRS and Ohmic conduction was dominant for LRS, irrespective of whether the devices underwent UVO treatment.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

ORCID iDs

Joong Hyeon Park  ⓒ https://orcid.org/0000-0003-2099-7971
Moon Hee Kang  ⓒ https://orcid.org/0000-0002-9485-2006

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