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Unipolar Switching Characteristics of Non-volatile Memory Devices Based on Poly(3,4-ethylenedioxythiophene):Poly(styrenesulfonate) (PEDOT:PSS) Thin Films

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1. Introduction

Non-volatile memory technology using polymer materials has attracted attention to overcome the limitations of scaling down of silicon devices. Therefore, polymer materials are actively being researched as non-volatile memory. This paper reports on a non-volatile reversible memory device using a PEDOT:PSS thin film. The current-voltage (*I-V*) characteristics of devices were measured. The reversible switching behavior in devices with various top electrode materials is studied.

2. Experiments

Unipolar switching devices were fabricated from Al/PEDOT:PSS/top electrodes (TEs). A 300 nm thick Al bottom electrode was deposited onto SiO_2 (500 nm) wafer. The PEDOT:PSS solution was spun on the substrates. After spin coating, the films were baked on a hot plate at 120 ℃ in ambient air for 10 min. The thickness of the films was determined to be about 60 nm. 200 nm thick TEs of Al, Ti, Cr, Au, Ni, Pd or Pt were deposited through shadow masks on top of the films. The active area of the cells was 1 mm^2.

3. Results and discussions

Fig. 1 shows the current-voltage (*I-V*) characteristics of the Al/PEDOT:PSS/Al devices. The devices initially had the OFF state. After setting the compliance current (CC) at 10 mA, the voltage was scanned from 0 V to 4 V, and the devices switched from the OFF state to the ON state at 2 ~ 3 V. Then the voltage was scanned from 0 V to 1 V without the restriction of the CC, and the devices switched from the ON state to the OFF state (under 10^{-7} A) at about 0.5 V. The maximum current (turn-OFF current) flowing though the devices was about 15 mA at this time.

Unipolar switching characteristics of devices were investigated in detail by applying various CC to the devices (Fig. 2). The turn-OFF current linearly increases from 15 mA to 73 mA as the CC linearly increases from 10 mA to 50 mA. The resistance of the current path in the PEDOT:PSS thin film also decreases linearly from 18 Ω to 6 Ω. Therefore, the turn-OFF current and the resistance of current path in the PEDOT:PSS thin film are affected by the CC.

PEDOT:PSS thin film has a broad redox peak [1], [2] and redox behavior of PEDOT chain due to injection carrier occurs in formation and destruction of current paths in write-once-read-many-times (WORM) memory devices [3], [4]. The unipolar switching of our devices is explained by redox behavior of PEDOT chain and the CC. When a voltage is applied to the electrode, carriers will be injected into the PEDOT:PSS film. The PEDOT chain in the polymer thin film will be oxidized to $PEDOT^+$, and then current paths will be formed by $PEDOT^+$. At this time, the number of injection carriers was limited by the CC. Therefore, the number of oxidized PEDOT chains and the number of current paths were determined by the CC. When a voltage was applied to the electrode without the restriction of the CC, the current flowing through the current path in the device suddenly increased. Since the current was larger than the CC, the current paths were destroyed by the excessive current.

The unipolar switching is not affected only by the CC and the redox behavior of PEDOT chains, however. It seems to be related to a natural thin Al_2O_3 layer that inevitably forms between the organic layer and the Al BE [5]. Fig. 3 is a pair of TEM images of a cross section of an Al/PEDOT:PSS/Al device showing this thin oxide film. This natural thin oxide acts as an energy barrier that interrupts the injection of carriers from the polymer thin film into the BE. When a low voltage (0 V ~ 2 V) was applied to the OFF state devices, carriers could not be injected easily. The current level of the devices was very low (under 10^{-7} A). When the sufficient voltage (2 V ~ 3 V) was applied, it was suddenly easy to inject carriers. The devices were switched from the OFF state to the ON state. Therefore, this natural oxide is probably one of several causes of the unipolar switching.

Fig. 4 shows the results of the write-erase cycle test. The device current changed with the voltages applied during the write-erase cycle. The probe current in the ON state was several orders of magnitude higher (10^4 ~ 10^9) than that in the OFF-state. The device was cycled through such write–erase operations over 27 times.

Fig. 5 shows the current-voltage (*I-V*) characteristics of the Al/PEDOT:PSS/TEs devices. The unipolar switching characteristics of the devices using Al BEs weren't affected by various TE materials. The level of the ON current was 10^{-2} A ~ 2 x 10^{-2} A. The ON voltage was 2 ~ 3V. Also the OFF voltage was relatively constant at about -0.5 V. Because this characteristic is not yet clearly understood, further works are required to study the effect of various TEs.

4. Conclusions

We have fabricated polymer memory devices using PEDOT:PSS thin film with various electrodes. The Al/PEDOT:PSS/TEs devices had unipolar switching characteristics. The unipolar switching occurred due to several factors, such as the CC, redox behavior of

PEDOT:PSS chain and the natural thin oxide, Al_2O_3, sandwiched between PEDOT:PSS thin film and Al BE. Also, the switching characteristics of the devices using Al BEs weren't affected by various TE materials.

Acknowledgements

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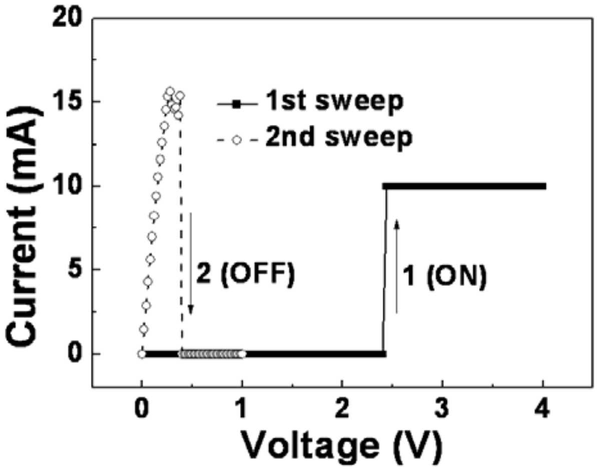

Fig. 1 The current-voltage (*I-V*) characteristics of the Al/PEDOT:PSS/Al devices.

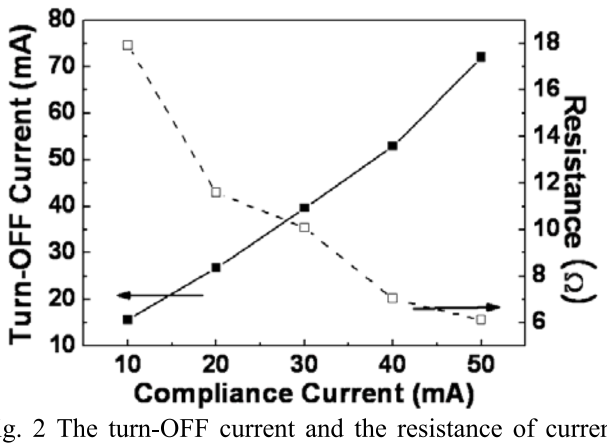

Fig. 2 The turn-OFF current and the resistance of current path in the PEDOT:PSS thin film are dependent on the CC.

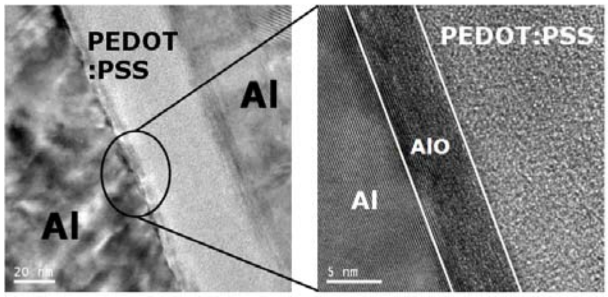

Fig. 3 A pair of TEM images of a cross section of an Al/PEDOT:PSS/Al device.

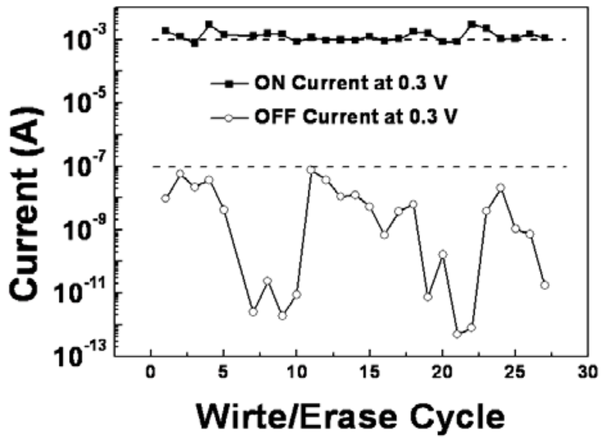

Fig. 4 The results of the write-erase cycle test.

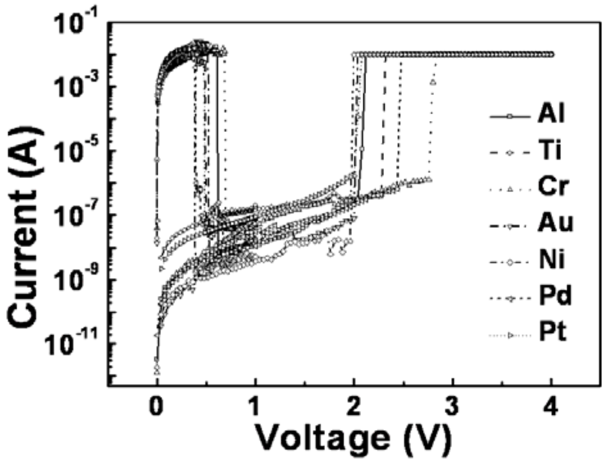

Fig. 5 The unipolar switching characteristics of a PEDOT:PSS film with Al BE and various TEs.