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Unipolar Bistable Switching of Organic Non-Volatile Memory Devices with Poly(styrene-co-styrenesulfonic acid Na)

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We demonstrated unipolar organic bistable memory devices with 8 × 8 cross-bar array type structure. The active material for the organic non-volatile memory devices is poly(styrene-co-styrenesulfonic acid Na) (PSSANa). From the electrical measurements of the PSSANa organic memory devices, we observed rewritable unipolar switching behaviors with a stable endurance and narrow cumulative probability. Also the PSSANa memory devices exhibited a uniform cell-to-cell switching with a high ON/OFF ratio of $\sim 10^5$ and good retention time of $\sim 10^4$ seconds without significant degradation.

Keywords: Organic Memory, Non-Volatile Memory, Unipolar Switching.

1. INTRODUCTION

Recently, organic based materials and devices have been researched extensively due to the simple fabrication process, low fabrication cost, light weight, flexibility, and printability on various substrates.[1–4] Particularly, organic electronic devices such as organic light emitting diodes, organic photovoltaic cells, organic thin film transistor, and organic memory devices have been widely investigated due to their good electrical performance and applications.[5–7] Among these organic devices, the organic memory has been considered as an alternative to the conventional inorganic based non-volatile memory devices.[8–16] Organic memory materials and devices have been researched on single or composite organic materials, doner–accepter complex, and hybrid materials with nanoparticles.[17–19] Although, organic memory devices with hybrid materials have been researched due to easily controllable processing factors, the concentration of nanoparticles in the organic host could cause a significant fluctuation of electrical characteristics.

In this respect, single organic material with bistable switching is preferred. In this study, we demonstrate that the poly(styrene-co-styrenesulfonic acid Na) (denoted as PSSANa) can be a promising candidate for organic memory devices. PSSANa is an attractive material for organic electronic devices due to its purity, transparency, and good thermal stability.[20] We fabricated unipolar type non-volatile organic memory devices in 8 × 8 cross-bar array structure using PSSANa as active material. Here, we report the electrical characteristics of PSSANa memory devices which exhibit a stable endurance, good retention time, narrow cumulative probability, and high ON/OFF ratio.

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2. EXPERIMENTAL DETAILS

The unipolar non-volatile organic memory devices were fabricated in the 8 × 8 cross-bar array structure using PSSANa which has good thermal stability up to 264 °C.[20] After cleaning the indium tin oxide (ITO) (sheet resistance of $\sim 8\ \Omega/\square$) coated glass substrate in a typical ultrasonic cleaning process by acetone, methanol, and de-ionized water for 3 minutes in each step, the ITO electrodes with 8 lines of 100 μm line-width acting as bottom electrodes were fabricated by conventional photolithography and a subsequent wet etching process (Fig. 1). PSSANa solution in which 0.1 g of PSSANa dissolved into 10 ml of N,N-Dimethylformamide was spin coated at 500 rpm for 5 seconds and subsequently at 3000 rpm for 40 seconds in a N_2-filled glove box. The thickness of the film was measured as ~ 30 nm by atomic force microscopy. To enhance film uniformity and remove residual solvent from the film, a baking process was conducted on a hot plate

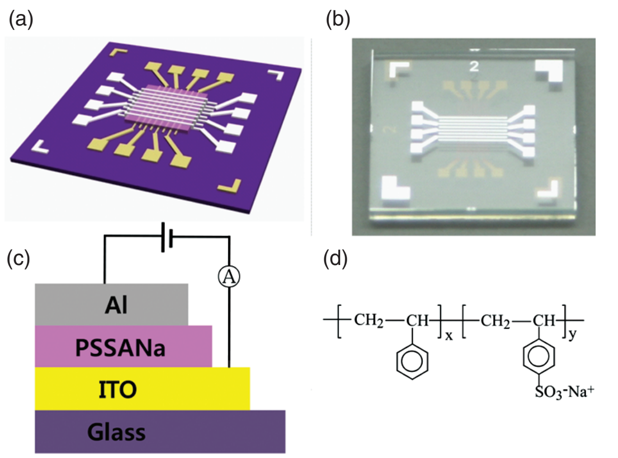

Fig. 1. (a) Schematic and (b) optical image of ITO/PSSANa/Al memory devices in 8 × 8 array structure, (c) Schematic of the cross-sectional view of ITO/PSSANa/Al memory device structure and (d) Molecular structure of PSSANa.

in the N_2-filled glove box at 120 °C for 10 minutes. Then, 50 nm-thick aluminum with 8 line patterns of 100 μm line-width was deposited on the organic film for top electrodes using a shadow mask by an electron-beam evaporator with deposition rate of 0.3 Å/sec at a pressure of $\sim 10^{-7}$ torr. In Figure 1, a schematic of the ITO/PSSANa/Al memory devices in the 8 × 8 cross-bar array structure (Fig. 1(a)), an image of the fabricated memory devices (Fig. 1(b)), a schematic cross-sectional view of ITO/PSSANa/Al (Fig. 1(c)), and the molecular structure of PSSANa (Fig. 1(d)) are shown.

3. RESULTS AND DISCUSSION

Figure 2(a) represents the current–voltage (I–V) characteristics of an organic memory cell in the 8 × 8 cross-bar array devices (total 64 memory cells) composed of the ITO/PSSANa/Al structure. First, we applied the bias from 0 to +5 V with 100 μA compliance current to prevent destroying conducting path during the sweep due to the fluctuation of high current. The current abruptly increased by about three orders of magnitude at around 3 V (set threshold voltage), indicating an electrical resistance transition from a high resistance state (HRS or OFF state) to a low resistance state (LRS or ON state) (1st sweep). When we applied voltage from 0 V to a value higher than the set threshold voltage without any compliances of current, the device still showed the low resistance state until 5 V (reset threshold voltage). However, Over the reset threshold voltage, a gradual decrease in the current was observed, showing a negative differential resistance (NDR) behavior (2nd sweep). Similar NDR phenomenon has been reported in other organic based memory devices.[17,21] When we applied voltage from 0 to 5 V again (3rd sweep), the memory devices exhibited almost the same I–V characteristics of HRS in the 1st

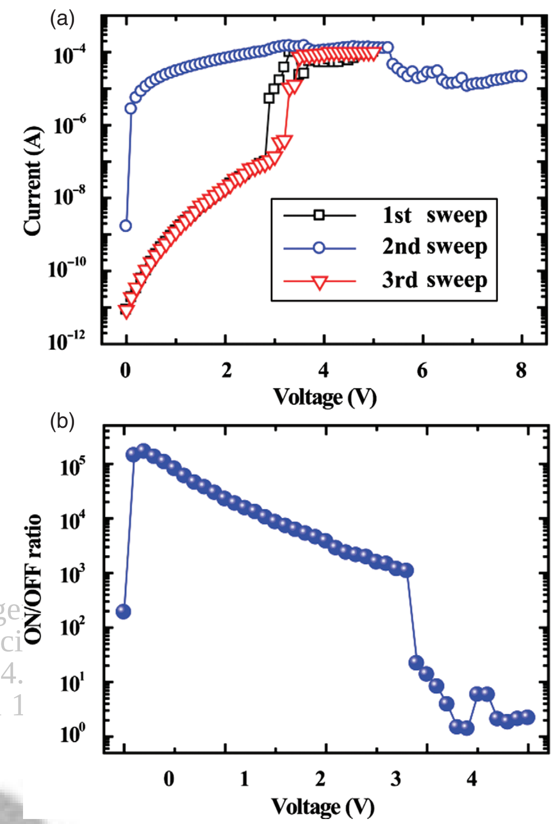

Fig. 2. (a) I–V characteristics and (b) ON/OFF ratio as a function of applied voltage for a ITO/PSSANa/Al memory device.

sweep, demonstrating the rewritable memory effect. With this measurement, the switching behavior was observed by continuous application of voltages in the same polarity. This is a typical unipolar type memory phenomenon. From the I–V characteristics, two stable resistance states (HRS and LRS) can be obtained at a read voltage well below the set threshold voltage. In addition, the memory devices remain stable even without power connection, indicating the non-volatile memory effect.

Figure 2(b) shows ON/OFF ratios as a function of the applied voltage. The ON/OFF ratio was gradually reduced with increasing the voltage and showed a maximum ON/OFF ratio of $\sim 10^5$ around 0.2 V. Thus, we chose this voltage range as the read voltage due to the high performance of ON/OFF ratio near 0.2 V.

Generally, I–V curves have been studied to understand the mechanism of bistable switching in memory device.[22–23] For instance, by investigating the current–voltage relationships of I–V curves on log–log scale, a space charge limited current[24,25] (SCLC) or filamentary type conduction[26] has been considered as a potential mechanism for charge transport in organic devices. As shown in Figure 3(a), at a low voltage (region 1) the current is linearly proportional to the voltage as a result of the thermally generated free carriers. The slope of ~ 2 (region 2), i.e., the quadratic relationship of I–V curve indicates that

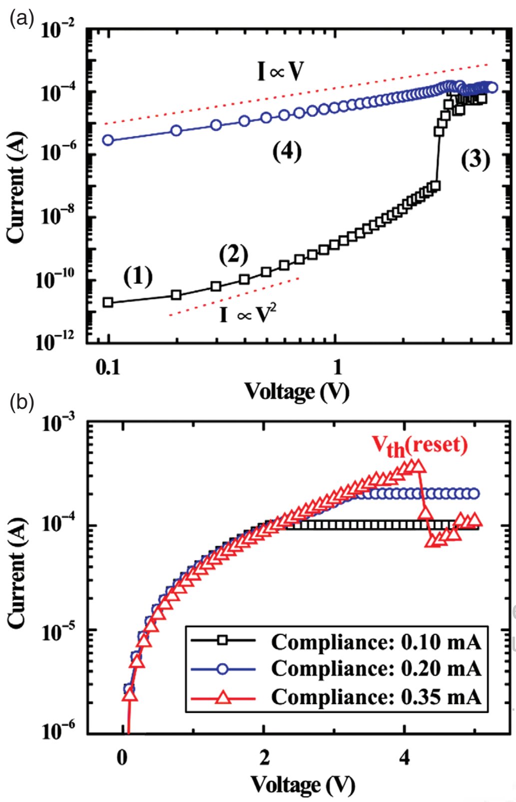

Fig. 3. (a) Logarithmic plot of *I–V* characteristics and (b) memory operation as a function of compliance current for a ITO/PSSANa/Al memory device.

the currents are due to SCLC in which the transport mechanism can be explained with trap states.[27] According to a model of ionomer morphology, ions in PSSANa aggregate to form multiplets, which are features containing several ion pairs in a rigid noncrystalline form with high packing efficiency of Na-sulfonate due to the strong interactions between Na-sulfonate ionic groups. PSSANa has lots of clusters consisting of these multiplets surrounded by a region of chain material and these clusters may act as charge trap centers. The diameter of multiplet and cluster is known as ca. 6 Å and ca. 26 Å, respectively.[28] In the transition region (region 3), a rapid increase in current is observed. In the ON state region, the memory device shows the typical Ohmic behavior with a slope of ∼1 (region 4) which is related with the typical filamentary conduction characteristics.

Figure 3(b) explains the memory operation according to the compliance current. Once the ON state is formed, the OFF state can be obtained only in the case when enough compliance current was applied to the memory devices. As shown in Figure 3(b), the device did not return to the OFF state unless the compliance current was set up to 350 μA. In contrast, the device turned to OFF state only when the compliance current was set to 350 μA or higher. A similar compliance dependency has been reported for other organic memory devices.[29] This compliance dependent phenomenon is associated to the filamentary conduction model. In particular, the memory devices showed a noise fluctuation beyond the NDR region (see Figs. 2(a) and 3(b)). The noise is closely related with rupturing and reconstruction of conducting filaments inside the PSSANa polymer.[30]

To realize practical memory device application, a study on the cell-to-cell uniformity of organic memory devices is required. Figure 4(a) shows the cumulative probability data of the memory devices, showing a good cell-to-cell uniformity. As shown in Figure 4(a), the memory devices exhibit a narrow distribution in both ON and OFF states. Also, the performance test of the memory devices was conducted in terms of retention time and endurance cycles, as shown in Figure 4(b). The memory device exhibited good retention characteristics over $\sim 10^4$ s without significant current change, while sustaining the ON/OFF ratio of $\sim 10^5$. The inset of Figure 4(b) exhibits the sweep endurance result tested from the memory device. The ON and OFF states of the device were determined by measuring the current at a read voltage of 0.3 V. Two stable resistance states with high ON/OFF ratio were also achieved. All these memory properties can present a good bistable switching capability of PSSANa organic memory devices by accurate control of ON and OFF states.

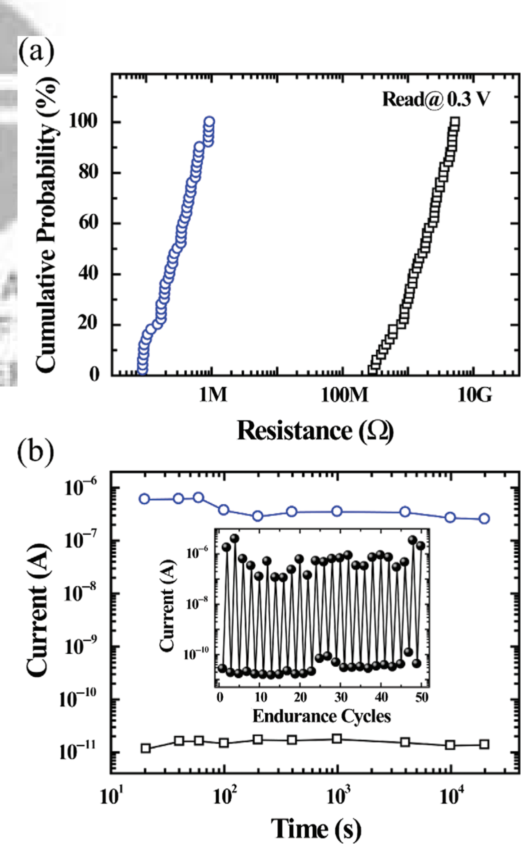

Fig. 4. (a) Cumulative probability of ITO/PSSANa/Al memory devices showing good cell-to-cell uniformity and (b) Retention time characteristics of ON and OFF states at a read voltage of 0.3 V. Also, the inset shows the endurance cycles obtained by repetitive sweeping.

4. CONCLUSION

We fabricated unipolar type, rewritable non-volatile organic memory devices in 8×8 cross-bar array structure using an organic material of poly(styrene-co-styrenesulfonic acid Na) (PSSANa). The PSSANa organic memory devices exhibited a high ON/OFF ratio of $\sim 10^5$ at a read voltage of 0.3 V, uniform cell-to-cell switching, stable endurance cycles, and good retention time of $\sim 10^4$ seconds without significant degradation, all of which feature a potential application for non-volatile memory devices.

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