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Electrical stabilities and memory mechanisms of organic bistable devices fabricated utilizing a poly(3,4-ethylene-dioxythiophene): Poly(styrenesulfonate) layer with a poly(methyl methacrylate) buffer layer

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Organic bistable devices (OBDs) based on a poly(3,4-ethylene-dioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) layer with a poly(methyl methacrylate) (PMMA) buffer layer were fabricated on indium-tin-oxide (ITO)-coated polyethylene terephthalate (PET) flexible substrates. Current-voltage curves for the Al/PEDOT:PSS/PMMA/ITO/PET device showed current bistabilities with an ON/OFF current ratio of 1×10^3, indicative of a significant enhancement of memory storage. The endurance number of the ON/OFF switchings for the OBDs was above 1×10^5 cycles showing high potential applications in read only memory devices. The memory mechanisms for the OBDs on the basis of oxidation and reduction operations were attributed to the filament processes. © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4709399]

Organic materials have attracted a great deal of interest because of their potential applications in low-cost electronic and optoelectronic devices with the excellent properties of high-mechanical flexibility.[1–3] In addition, nonvolatile memory devices fabricated using organic materials have become particularly interesting because they exhibit resistive switching effects.[4–7] Among the several types of nonvolatile memory devices, organic bistable devices (OBDs) have currently emerged as excellent candidates for next-generation nonvolatile memory devices due to their relatively simple fabrication processes without additional source and drain regions.[8–12] Some works on the physical properties of the OBDs fabricated using hybrid inorganic/organic nanocomposites containing nanoparticles have been performed.[13–16] However, relatively, few investigations about the fabrication and electrical properties of the OBDs using organic materials have been carried out due to inherent problems of poor device performance with a small memory margin.[17,18] Even though some investigations concerning the memory effects in OBDs fabricated using organic materials on solid state substrates have been performed, very few studies on the electrical bistabilities, the memory stabilities, and the memory mechanisms in OBDs made of a poly(3,4-ethylene-dioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) layer with a poly(methyl methacrylate) (PMMA) buffer layer on flexible substrates have been performed. Furthermore, PEDOT:PSS materials are of current interest because of their easy formation and stability.[19–21]

This letter presents data for the electrical bistability properties, the memory stabilities, and memory mechanisms of OBDs fabricated using a PEDOT:PSS layer with a PMMA buffer layer on indium-tin-oxide (ITO)-coated polyethylene terephalate (PET) flexible substrates. Atomic force microscopy (AFM) measurements were performed in order to characterize the surface uniformity of the PEDOT:PSS layer with and without a PMMA buffer layer. Current-voltage (I-V) and switching measurements were performed to investigate the memory performance of the fabricated devices. Retention measurements were performed to investigate the electrical stability properties of the devices. The ITO-coated PET substrates were alternately cleaned ultrasonically in acetone and methanol. Subsequently, they were thoroughly rinsed in de-ionized water and were treated by using ultraviolet light. The chemically cleaned substrates were dried using N_2 gas with a purity 99.9999% in order to avoid interactions with air. A 3 wt. % PMMA solution was formed by dissolving PMMA in tetrahydrofuran with a ultrasonic treatment for 30 min in order to obtain a uniform solution. The PMMA solution was deposited on ITO-coated PET substrates by spin-coating at 500 rpm for 10 s, 3500 rpm for 30 s, and 1500 rpm for 15 s. Then, the residual solvents within the PMMA layer were removed by heating the samples on a hotplate at 100 °C for 30 min. After the soft baking, the PEDOT:PSS (PH 500) purchased from H. C. Starck Inc. was spin-coated on the formed PMMA layer. After the spin-coating, the film was dried at 100 °C for 30 min. Finally, Al top electrodes with a thickness of 200 nm and a diameter of 500 μm were deposited on top of the PEDOT:PSS/PMMA layers by using thermal evaporation through a metal mask, which prevents any contamination, at a high vacuum system of 1×10^{-6} Torr.

Figure 1 shows (a) a schematic diagram of the fabricated Al/PEDOT:PSS/PMMA/ITO/PET device and the molecular structures of the (b) PEDOT:PSS and (c) PMMA organic materials. The AFM measurements were performed by using an XE-100 atomic force microscope. The I-V and the retention measurements were performed by using an HP 4140B PA meter/dc voltage source in ambient conditions.

The root-mean-square average surface roughnesses of the PEDOT:PSS layers with and without a PMMA buffer layer, as determined from the AFM measurements, were

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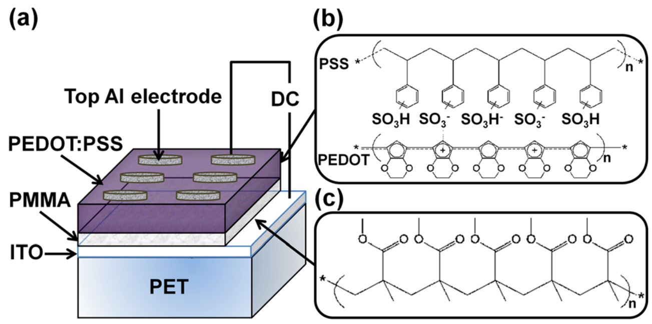

FIG. 1. (a) Schematic diagram of the organic bistable device with a PEDOT:PSS layer formed on a PMMA layer studied in this work. Molecular structures of the (b) PEDOT:PSS and the (c) PMMA organic materials.

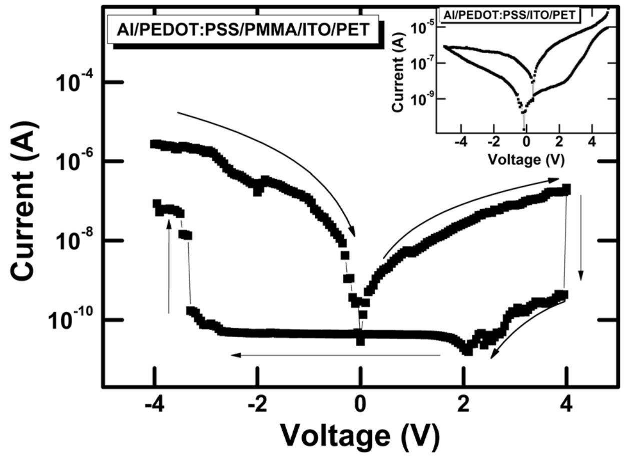

FIG. 2. Current-voltage (I-V) curves for the Al/PEDOT:PSS/PMMA/ITO/PET device. The inset represents the I-V curves for the Al/PEDOT:PSS/ITO/PET device.

1.16 and 1.61 nm, respectively. The AFM images showed that the surface of the PEDOT:PSS layer with a PMMA buffer layer was much more uniform than that without a PMMA layer. The surface of the PEDOT:PSS on the PMMA buffer layer was significantly improved due to the uniform molecular structure of the PMMA, resulting in the achievement of the more uniform interfacial contact between the PEDOT:PSS layer and Al top electrodes.[22,23] This results in the improvement of the device performance due to the decrease of the leakage current. Even though a PEDOT:PSS layer is typically deposited on an ITO-coated substrate at a temperature above 140 °C,[23] the deposition temperature for a PEDOT:PSS layer on a PMMA layer is lower than this temperature. This decrease in the deposition temperature of the PEDOT:PSS layer up to 100 °C prevents the metamorphosis of the PET substrate.[24] The PET substrate at a high temperature of 140 °C receives the strain.[24]

Figure 2 shows the I-V curves for the Al/PEDOT:PSS/PMMA/ITO/PET device. While a bias voltage was applied to the top electrode, the bottom electrode was grounded. These curves were obtained by sweeping the voltage from 4 to −4 V and from −4 to 4 V. The I-V curves for the devices clearly show current hystereses, indicative of memory effects in the nonvolatile memory devices. While the PEDOT:PSS film is typically well known to be a hole-transporting layer,[25] the PEDOT:PSS film with a PMMA buffer layer used in the device acts as a storage region.[19] When the bias voltage was scanned form 4 to −3.5 V, the devices fabricated using a PEDOT:PSS layer with a PMMA buffer layer maintained a low conductivity state with currents between 4.39×10^{-10} and 1.56×10^{-11} A. The conductivity state transitioned from low to high conductivity at −3.5 V and from high to low conductivity at 4 V, which correspond to writing and erasing processes, respectively, as shown in Fig. 2. The ON or OFF state of the device containing a PEDOT:PSS layer with a PMMA buffer layer was maintained until an applied erasing voltage or an applied writing voltage, respectively. The ON/OFF current ratio of the device containing a PEDOT:PSS layer with a PMMA buffer layer was about 1×10^3, which is equivalent to that of a reading process in a digital memory cell. The maximum current difference for the device with a PMMA buffer layer was one order larger than that for the device without a PMMA buffer layer, as shown in the inset of Fig. 2. Furthermore, the current at the ON state for the device with a PMMA buffer layer was typically 5×10 larger than that for the device without a PMMA buffer layer. These results indicate that the charge storage capacity of the PEDOT:PSS layer in the devices was significantly improved by inserting a PMMA buffer layer.

Figure 3 shows the switching characteristics for the Al/PEDOT:PSS/PMMA/ITO/PET device. The writing, reading, and erasing voltage pulses for the current-time (I-t) characteristics were set as −4, +1, and +4 V, respectively, as shown in Fig. 3. The applied voltage time for the writing, erasing, and reading processes was 1 ms. The erasing voltage pulse was applied to change the device from the ON to the

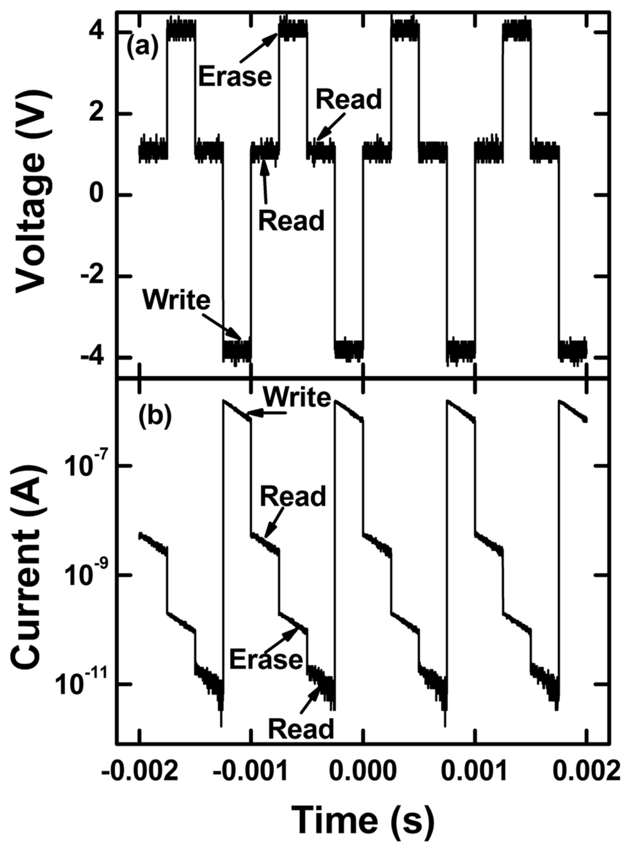

FIG. 3. Switching results of the (a) input voltage and (b) output current for the Al/PEDOT:PSS/PMMA/ITO/PET device.

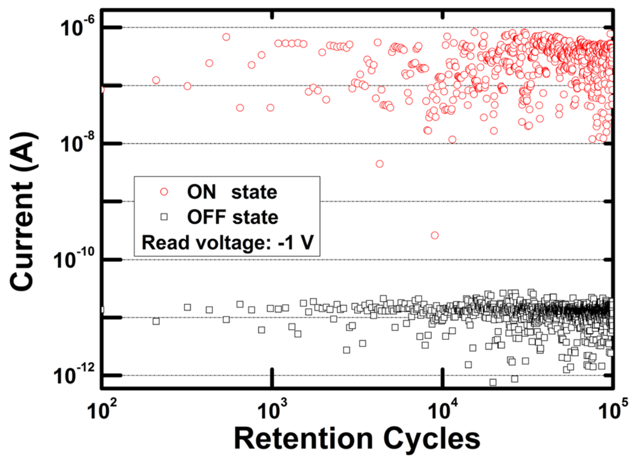

FIG. 4. Retention cycles of the Al/PEDOT:PSS/PMMA/ITO/PET device under a read voltage of −1 V.

OFF state. The current at the reading voltage pulse was approximately 2×10^{-11} A. After the writing voltage pulse had been applied to turn the device from the OFF to the ON state, the current at the reading voltage was approximately 1×10^{-8} A. The significant difference between the ON and the OFF currents indicates that the Al/PEDOT:PSS/PMMA/ITO/PET device has good switching characteristics.

Figure 4 shows the number of cycling stress tests performed at the ON and the OFF states of the device fabricated using a PEDOT:PSS layer with a PMMA buffer layer. After the ON and the OFF states were changed by applying writing voltage of −4 V and erasing voltage of 4 V, respectively, the stability of the ON and the OFF states for the devices under an electrical stress was evaluated by applying repeatedly a reading voltage of −1 V. Even though some fluctuations applied in the data for the ON and the OFF states, no significant degradation was observed until 10^5 cycles of continuous stress, indicative of memory devices with excellent stability. The cycle stress characteristics demonstrate that the OBDs might be useful for potential applications in read only memory (ROM) devices.

The memory mechanisms of the Al/PEDOT:PSS/PMMA/ITO/PET device are attributed to the trapping and the detrapping processes of electrons in the trap sites of the PEDOT:PSS layer, which correspond to the oxidation and the reduction of the PEDOT:PSS layer. When the holes are injected into the trap sites of $PEDOT^0$ from the top electrodes with increasing negative voltage, $PEDOT^0$ is oxidized to $PEDOT^+$. When the number of $PEDOT^+$ chains is sufficiently large, the current paths are formed by $PEDOT^+$. On the other hand, when a positive voltage is applied in the reset process, electrons are injected into $PEDOT^+$, and the formed current paths vanish due to the reduction from the $PEDOT^+$ to $PEDOT^0$.[26,27]

In summary, OBDs based on a PEDOT:PSS layer with a PMMA buffer layer were fabricated on ITO-coated PET flexible substrates. I-V curves for the Al/PEDOT:PSS/PMMA/ITO/PET device showed a current bistability with an ON/OFF current ratio of 1×10^3, which was much larger than that of the device without a PMMA buffer layer. The endurance number of the ON and the OFF states for the devices fabricated using a PEDOT:PSS layer with a PMMA buffer layer was above 1×10^5 cycles, indicative of the potential applications in ROM devices. The memory mechanisms for the Al/PEDOT:PSS/PMMA/ITO/PET device on the basis of oxidation and reduction operations were attributed to the filament processes.

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