

Resistive-switching and current-conduction mechanisms in F8BT polymer resistive switch

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Poly[(9,9-di-n-octylfluorenyl-2,7-diyl)-alt-(benzo[2,1,3]thiadiazol-4,8-diyl)] (F8BT) polymer has been investigated to elucidate the resistive-switching properties in a sandwiched structure of indium tin oxide (ITO)/F8BT/aluminium (Al). An active layer of F8BT polymer was deposited on the ITO-coated polyethylene terephthalate through spin coating. Morphologically, the layer was characterised with field emission scanning electron microscope. The fabricated sample showed resistive-switching properties within ± 5 V with an OFF/ON ratio of 10:1. The switching characteristics were attributed to the transition of trap-limited space charge-limited conduction (SCLC) to trap-filled SCLC. It is shown through energy band diagram that memory effects in the fabricated sample were due to the trapping of electrons in the F8BT active layer that were injected from the top Al electrode.

1. Introduction: Resistive switching is a resistance-based switching in contrast to a charge-based switching. Resistive-switching devices have emerged as potential candidates for memory and electrical switching elements due to their small size, high speed, and simple device structure [1–3]. They are capacitor-type metal–insulator–metal (MIM) structures that possess at least two different resistance states when they are being forced by a voltage source at its electrodes [4, 5]. These different resistance states of the MIM sandwiched structures could be exploited to be used for ON and OFF states of electrical switching as well as to represent 1 and 0 s for memory purposes [6–13]. Different organic and inorganic materials have been used as a switching layer to fabricate these novel devices [14]. In the recent past, quite a few materials inherent emissive properties have been researched for its switching layer. These materials are quite significant in optical readout applications [15]. Poly[(9,9-di-n-octylfluorenyl-2,7-diyl)-alt-(benzo[2,1,3]thiadiazol-4,8-diyl)] (F8BT) is one of the frequently used polymers to fabricate the emissive layer of light emitting devices [16–19]. F8BT has been utilised as an emissive layer for light emitting diodes in a recent research work [20]. F8BT has not been used to elucidate the resistive-switching properties and therefore, its resistive-switching and current-conduction mechanisms have not been researched.

In this Letter, resistive-switching and current-conduction mechanisms are investigated in a F8BT polymer resistive switch with a sandwiched structure of indium tin oxide (ITO)/F8BT/aluminium (Al). To elucidate the resistive-switching properties in F8BT polymer, the polymer was spin coated on ITO-coated polyethylene terephthalate (PET). The active layer of F8BT has been morphologically characterised. Resistive-switching properties of the fabricated sandwiched structure are measured by current–voltage (I – V) curves. The switching characteristics observed in the sample are correlated with the different current-conduction mechanisms. Finally, resistive-switching mechanism in the fabricated device is concluded based on energy band diagram.

2. Experimental details: F8BT powder with average $M_w \approx 20,000$ and ITO-coated PET with thickness around 100 μm were purchased from Sigma-Aldrich. The surface resistivity of the ITO

is 60 Ω/sq . The tetrahydrofuran (THF) solvent was purchased from Daejon Chemical and Metal Co. Ltd, Republic of Korea.

Prior to the fabrication of sandwiched structure of ITO/F8BT/Al, ITO-coated PET was rinsed with ethanol to remove contaminations and processed with ultraviolet light for 5 min. The solution of F8BT was prepared with a concentration of 1:1 in THF solvent. The active layer of F8BT was deposited on ITO-coated PET by spin coating at 2000 rpm for 30 s. After the deposition of F8BT layer on the ITO-coated PET, the sample was cured at 110 $^{\circ}\text{C}$ for 1 h. The layer morphology of the F8BT layer was checked by the field emission scanning electron microscope that shows the smooth and uniform deposition of the F8BT polymeric layer with no porosity as shown in Fig. 1.

The film thickness of the F8BT layer was measured with K-MAC ST4000-DLX non-contact machine and it was observed to be around 60 nm. Roughness of the active film was analysed by using a Nano View high accuracy three-dimensional (3D) non-contact surface profiler. Roughness of the active film has strong impact on the device performance. The average roughness of the active film was found to be 19.5 nm as shown in Fig. 2. Finally, the top electrode of Al was deposited by thermal evaporation in a circular shape with thickness of around 100 nm, thereby concluding the device.

3. Resistive switching: Characteristics: Agilent B1500A semiconductor device analyser was used to perform the I – V measurements in order to examine the switching characteristics of the fabricated sample. Fig. 3 shows the I – V characteristics of the device. All the measurements were obtained by double sweeping the voltage source within ± 5 V as shown in the lower inset of Fig. 3. It is clear from Fig. 3 that the device started operating in low resistance state (LRS)/ON state during the forward voltage sweep from +5 to -5 V. However, as the voltage sweep crossed -2 V, the device started switching its LRS to high resistance state (HRS)/OFF state and completely switched to HRS at -5 V. During the reverse voltage sweep from -5 to +5 V, initially the device was in HRS but as the voltage sweep crossed +4 V the device changed its HRS to LRS. The I – V characteristics show

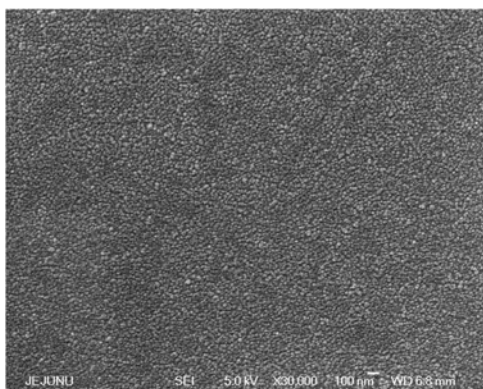


Fig. 1 Field emission scanning electron microscopic image of the F8BT polymer on the ITO-coated PET

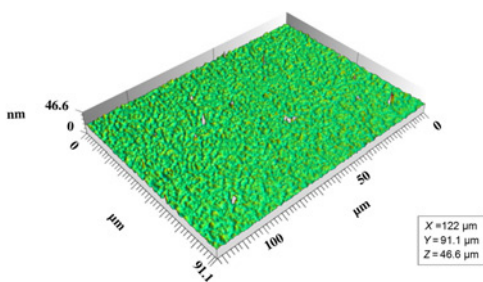


Fig. 2 Nano View 3D surface profiler image of the F8BT polymer on the ITO-coated PET

that the device exhibited lissajous pinched hysteresis loop with two distinct states: HRS and LRS with an OFF/ON ratio of 10:1. It is evident from Fig. 3 that there exit a larger memory window on the negative side of the voltage polarity as compared with the positive side of the voltage polarity. The behaviour of the fabricated device was also checked against multiple voltage sweeps. The upper inset of Fig. 3 shows the robustness test. The graph shows that the device behaved exceptionally well against multiple voltage stresses over 100 cycles with a reasonable OFF/ON ratio of 10:1.

4. Current-conduction mechanism: Current-conduction mechanisms in the fabricated device are concluded through straight line fittings in the log-log scale on the negative side of the voltage polarity due to its prominent memory window on this side as

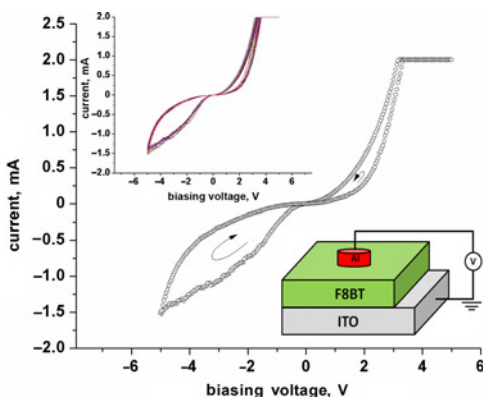


Fig. 3 I - V characteristics of the ITO/F8BT/Al sandwiched device. The upper inset shows the endurance test for the ITO/F8BT/Al sandwiched device over 100 cycles and the lower inset shows the biasing polarity of the device

shown in Fig. 4. As shown in the graph, four different current conductions are found in the I - V characteristics. In the start at the LRS of the device until -0.5 V, the slope is calculated to be around 1 which concludes that the current is due to the Ohmic conduction where the current is directly proportional to the voltage. The Ohmic conduction normally occurs by virtue of the transport of intrinsic background carriers present inherently in the material (F8BT in this case) as reported in the literature [21]. This low field conduction is due to the bulk effects, so, it dominates where there is absence of injected carriers from the electrodes. The current density in this low bias region can be described as

$$J = qn_0\mu V/d \quad (1)$$

where q is the electronic charge, n_0 is the density of free carriers, μ is the carrier mobility, V is the applied voltage, and d is the thickness of the F8BT layer.

As the applied voltage across the device is increased in a negative side, the injected carriers started accumulating near the top electrode. Due to the mutual repulsion amongst the injected carriers, space charge built-up near the top electrode which further reduced the injection of carriers from the top electrode. The observed phenomenon is quite in line with the reported literature [22]. The injected carriers exercised their role and thereby transforming the Ohmic current conduction initially into space charge-limited conduction (SCLC) where the current is directly proportional to the square of the applied voltage and then Ohmic conduction. The current due to the injected carriers was decreased by several orders due to the presence of traps in the layer. After -0.5 until -1.5 V, slope is measured to be 2 which concludes that the current conduction is due to SCLC. After -1.5 until -5 V, the slope is turned to be around 1 that shows the current conduction is modulated into Ohmic conduction from SCLC. Current density in the SCLC is described by the Mott-Gurney law as described in the following equation

$$J = 9\epsilon\epsilon_0\mu\Theta V^2/d^3 \quad (2)$$

where ϵ is the dielectric constant of the F8BT polymer, ϵ_0 is the permittivity of the free space, and Θ is the trapping fraction.

Eventually almost all carriers were trapped within the switching layer once the inherently present traps in the F8BT layer were filled with the injected carriers (electrons) from the top Al electrode. In this case, the current in the F8BT layer is due to the trap charge-limited conduction (TCLC) where the current increases exponentially with the voltage and the onset of VTFL (trap-filled voltage) describes the density of traps N_t as given in the following equation

$$N_t = 3\epsilon\epsilon_0 V_{TFL}/2qd^2 \quad (3)$$

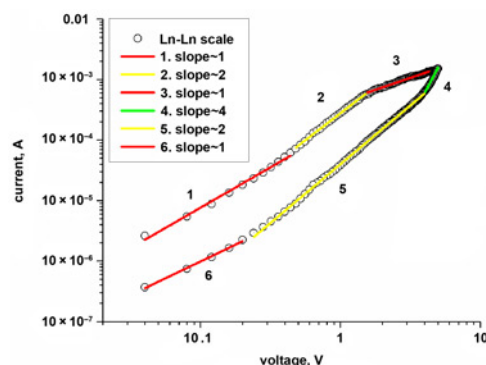


Fig. 4 Double logarithmic I - V graph of the ITO/F8BT/Al sandwiched device in a negative cycle of the sweeping voltage indicating different current-conduction mechanisms in the forward and reverse directions of the voltage polarity

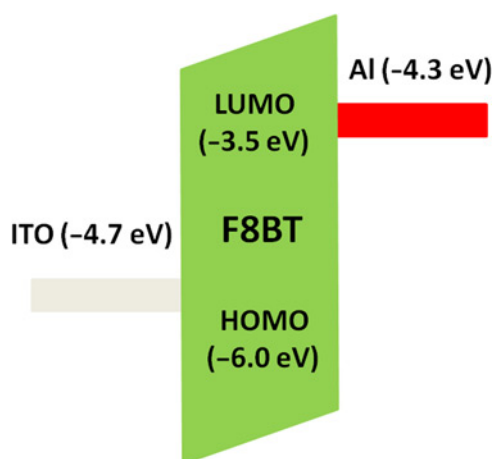


Fig. 5 Energy band diagram of the ITO/F8BT/Al sandwiched device supporting electrons injection from the top Al electrode on the basis of difference in energy levels

Therefore, in the reverse direction of voltage polarity in the HRS of the fabricated device, the current conduction is concluded as TCLC based on slope calculation of around 4 from -5 to -4 V. The appearance of TCLC conduction after SCLC conduction is very common as reported in literature [21–23]. In some reported literature, during the transition of trap-limited SCLC to TCLC there is abrupt jump of current but it is not considered as normal because it causes the failure of the device.

Subsequent to the filling of trap sites within F8BT layer there must be another region which is trap-filled SCLC after TCLC. From -4 to -0.3 V, the current conduction is governed by trap-filled SCLC as the slope is around 2. Again at lower voltage in the HRS of the device, the current is conducted as a result of Ohmic conduction which is due to the transport of intrinsic background carriers in the F8BT layer as slope is around 1 from -0.2 V to onward.

On the basis of the above discussion and analysis of the log–log graph, the charge transport in F8BT-based resistive switch is attributed to the transition from trap-limited SCLC to trap-filled SCLC.

5. Resistive-switching mechanism: Energy band diagram of the fabricated device is demonstrated in Fig. 5 to show its operating mechanism. The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of F8BT are -6.0 and -3.5 eV, respectively. The work functions of Al top electrode and ITO bottom electrode are -4.3 and -4.7 eV, respectively. As shown in the energy band diagram, the difference between the work function of Al and the LUMO of F8BT (0.8 eV) is much lower than that between the work function of ITO and the HOMO of F8BT (1.3 eV). This difference in energy obviously supports electrons injection from the top Al electrode into the F8BT active polymeric layer. These injected electrons trap into the F8BT layer and induce high electric field. Therefore, the trapped charges are actually responsible for the change in the conductance level of the F8BT layer. Furthermore, the injection of electrons from the top electrode is also a reason of the ample memory window on the negative voltage polarity. The traps formed within the F8BT layer are shallow because of the difference of band energy which is only 0.8 eV. Hence, the trapped charges could easily be released by the voltage stresses on the reverse direction and hence memory effects are shown.

6. Conclusion: Resistive switching within ITO/F8BT/Al sandwiched structure has been demonstrated over 100 cycles with an OFF/ON ratio of 10:1. Transition from trap-limited SCLC to trap-filled SCLC is found to be the major source of resistive-switching characteristics in the fabricated device. It is concluded that memory effects are because of the electrons

injection from the top Al electrode into the F8BT active layer due to the minimal difference between the work function of Al electrode and LUMO of F8BT. Memory effects are prominent on the negative side of the voltage polarity due to the fact that Al metal supports electrons injection instead of holes injection. Results and analysis show that the fabricated resistive switches could be implemented in polymer-based electronics.

7 References

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