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# Electrical bistability, negative differential resistance and carrier transport in flexible organic memory device based on polymer bilayer structure

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ABSTRACT

Bistable nonvolatile memory devices containing two different layers of polymers, viz. MEH-PPV (poly[2-methoxy-5-(2′-ethyl-hexyloxy)-1,4-phenyl vinylene]) and PEDOT:PSS (poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate)) has been fabricated by a simple spin-coating technique on flexible polyimide (PI) substrates with a structure Al/MEH-PPV/PEDOT:PSS/Ag-Pd/PI. The current–voltage measurements of the as-fabricated devices showed a nonvolatile electrical bistability with electric field induced charge transfer through the polymer layers and negative differential resistance (NDR) which is attributed to the charge trapping in the MEH-PPV layer. The current ON/OFF ratio between the high-conducting state (ON state) and low-conducting state (OFF state) is found to be of the order of $10^3$ at room temperature which is comparable to organic field effect transistor based memory devices. We propose that such an improvement of rectification ratio (ON/OFF ratio) is caused due to the inclusion of PEDOT:PSS, which serves as a conducting current path for carrier transport; however, NDR is an effect of the trapped charges in the MEH-PPV electron confinement layer. The device shows excellent stability over $10^4$ s without any significant degradation under continuous readout testing in both the ON and OFF states. The carrier transport mechanism of the fabricated organic bistable device has been explained on the basis of different conduction mechanisms such as thermionic emission, space-charge-limited conduction, and Fowler–Nordheim tunneling. A band diagram is proposed to explain the charge transport phenomena. These bilayer structures are free from the drawbacks of the single organic layer based memory devices where the phase separation between the nanoparticles and polymers leads to the degradation of device stability and lifetime.



## 1. Introduction

In recent years a lot of interest is found in conducting polymer based electronic devices due to its unique advantages such as simple device structures, easy processing, low fabrication costs, high-mechanical flexibility, versatility, good controllability of the material and so on compared to existing inorganic semiconductors. For next generation electronic and optoelectronic applications, devices such as organic light emitting diodes [1–3], organic field effect transistors [4,5], solar cells [6–9], and sensors [10] have been found to contribute profoundly along with memory devices based on organic polymers [11,12]. Recently, organic non-volatile memory devices and its current bistability behavior have been extensively reported [13–16]. The fundamental characteristic of a memory device is to show electrical bistability behavior, i.e. two different resistance states at the same applied voltage. In these devices, various active materials such as small molecules, organic polymers, and hybrid organic/inorganic nanocomposites have been widely utilized.

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It is found from the literature that organic memory devices are based on single organic layer (SOL) and for storing the charges self-assembled semiconductor nanoparticles (NPs) embedded in a polymer matrix [17–19], metallic NPs embedded in polymer layer [20,21] or hybrid organic/inorganic nanocomposites [16,22,23] were mostly used. In organic/inorganic nanocomposite based memory devices the electrical bistability originates from inorganic nanoparticles [23,24]. In these devices the negative differential resistance (NDR), i.e. decrease in current with increasing applied voltage has also been observed in the current–voltage characteristics.

Single organic layer based memory devices using various materials such as (poly[2-methoxy-5-(2′-ethyl-hexyloxy)-1,4-phenyl vinylene]) (MEH-PPV) [25,17], PEDOT:PSS [26–28], poly(3-hexylthiophene) [20], poly(N-vinylcarbazole) [29,21], poly(methyl methacrylate) [30], and even organic donor–acceptor based memory systems [16,22] have been found in the literature. Recently Ouyang et al. reported the electrical bistability and memory effect using a blend of gold NPs and organic donor polymer embedded in a polystyrene matrix [31]. However, phase separation takes place between the organic polymer material and the metallic NPs, which reduces the device stability as well as degrades its long operating lifetime.

For NPs embedded SOL based hybrid memory devices, the inorganic NPs are dispersed indiscriminately into the polymer matrix. The high density of NPs leads to the degradation of current through the device in the ON state. When the electrons are captured by the NPs, coulomb interaction becomes significant due to the reduction of interparticle separation. Here the mutual repulsion between the charges promotes the discharging phenomena to happen. As a result, the current degrades with applying reading voltage in case of NPs incorporated SOL based memory devices. This in turn lowers the device retention and stabilization through the discharge process [29]. Again, in the SOL based memory devices there exists several parasitic conduction paths. Even the contact at the interface between hybrid layer and the metal electrode always cannot be ensured as ohmic. Moreover, in case of NPs a lot of challenges are involved in terms of synthesis as well as its stability and repeatability.

Thus, in this work, we have introduced organic bilayer structure using PEDOT:PSS and MEH-PPV where the former is a conducting agent and the later one acts as charge storing element through electron confinement. Earlier PEDOT:PSS has been used in write-once-read-many times (WORM) memory devices [32,33]. However, the memory effect and carrier transport mechanism of organic bistable devices (OBDs) consisting of organic bilayer structure on a flexible substrate have not yet been reported in terms of operating mechanism, charge trapping, storing, and emission of carriers related to various electronic state as explained through the band diagram.

In this paper, we report the fabrication of an electrically bistable nonvolatile flexible organic memory device using MEH-PPV and PEDOT:PSS polymer on polyimide (PI) substrate for OBD application in flexible electronic devices. Current–voltage ($I$–$V$) measurements were carried out to study the electrical behavior of the device. A suitable energy band diagram has been proposed to understand the electronic transitions corresponding to the operating mechanism of programming (writing) and erasing processes, i.e. ON and the OFF-states, respectively, for the device.

## 2. Experimental

The organic nonvolatile memory devices were fabricated on PI substrates of thickness 60 μm. The substrates were cleaned for 3 min in de-ionized water and annealed in vacuum of $5 \times 10^{-6}$ torr at 200 °C. A low resistance ohmic contact on the PI substrate as bottom electrode was created by thermal evaporation technique using silver–palladium (Ag–Pd) alloy at a base pressure of $4 \times 10^{-6}$ – $3 \times 10^{-6}$ torr. Ag–Pd anode was partially masked for future metal contact before subsequent processing. An aqueous solution of PEDOT:PSS (1.3 wt.% dispersion in $H_2O$, conductive grade Sigma–Aldrich) was spun onto the substrates as a hole conducting polymer initially at 500 rpm for 10 s and then at 3000 rpm for 45 s. Subsequently the films were baked on a hot plate at 95 °C in air for 10 min. This was followed by coating MEH-PPV on PEDOT:PSS at 3000 rpm for 60 s. Moreover, MEH-PPV was synthesized in-house according to the procedure reported by Heeger and Braun [34]. The material was also characterized by IR, $^1$H NMR and elemental carbon and hydrogen analyses. The average molecular weight of the polymer was 330,000 with polydispersity index of 2.7 as determined by a gel-permeation chromatography with respect to monodisperse polystyrene standard. The solution of MEH-PPV was made on dissolving it in tetrahydrofuran (THF) at about 3% volume. To evaporate away the entire solvent the whole device was then subjected to anneal in vacuum at 50 °C for another 120 min. The thickness of the films was measured using Gaertner Ellipsometer (model L-117) and found to be 50 nm and 200 nm, respectively, for PEDOT:PSS and MEH-PPV. The top electrode having a thickness of 200 nm was made by evaporation of Al on MEH-PPV layer through a metal shadow mask with square patterns of 600 μm × 600 μm areas at a vacuum of $2 \times 10^{-6}$ torr. The devices were studied under standard laboratory condition at room temperature, whereas, some of the devices (control) are fabricated and studied inside a glove box (Labstar, Mbraun Inc., Germany, Model MB10 Compact) under inert condition (argon filled; moisture and oxygen content less than 1.0 ppm) by using freshly synthesized MEH-PPV. In Fig. 1 the schematic diagram of a device structure is shown. The current–voltage ($I$–$V$) characteristics of the devices were carried out using Keithley 2400 source

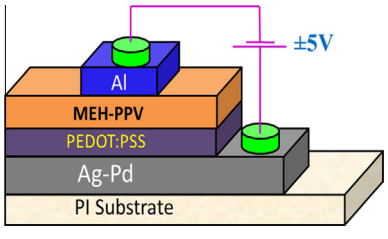


**Fig. 1.** A schematic diagram of device structure.