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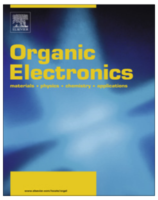

Uniform bipolar organic memory using vapor phase polymerized poly (3,4-ethylenedioxythiophene)

Pranav Y. Kalode, Yong-Eun Koo Lee, Myung M. Sung *

Department of Chemistry, Hanyang University, Seoul 133-791, Republic of Korea

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ABSTRACT

Organic memory device has emerged as an excellent candidate for the next generation storage devices due to its high performance and low production cost. In this paper, we report the fabrication and electrical characterization of an organic memory device made of vapor-phase polymerized PEDOT thin films that are highly uniform and free of PSS and free of unreacted reactants. The PEDOT memory device exhibited a typical bipolar resistive switching with a high ON/OFF current ratio of at least 10^3, which was maintained for more than 10^3 dc sweeping cycles. The device performance was stable for more than 10^5 s. Moreover, the device containing 64 cells has very high cell to cell uniformity as demonstrated by (1) at least 93% of the cells displaying the ON/OFF current ratio of at least 10^3 and (2) the deviation of the set and reset voltages from the average values being less than 0.5 V and 0.4 V, respectively. The maximum current before switching in the reset process was found to increase linearly with increase in the compliance current applied during the set process.

1. Introduction

Conducting organic polymers have attracted great attention in organic electronics due to their mechanical flexibility, tunable optoelectrical properties, and facile fabrication process with good scalability [1–3]. The conducting polymers have shown their great potential in organic light emitting diodes (OLEDs), solar cells, organic memory devices and organic field effect transistors (OTFTs) [4–8]. Especially, the conducting polymer-based memory devices have emerged as an excellent candidate for the next generation memory devices because of their high performance and low cost [9,10]. Poly (3,4-ethylenedioxythiophene) (PEDOT) is one of the most widely used conducting polymers for nonvolatile memory applications. Mollar et al. first observed write-once-read-many times (WORM) memory behavior in PEDOT [11]. Further studies revealed that the PEDOT memory device shows bipolar and unipolar switching behaviors depending on the electrode combinations [12–14]. These studies used the thin films of water-soluble PEDOT:PSS complex instead of those of water-insoluble PEDOT so that the films can be prepared by a simple solution-process method. We note that while the addition of PSS brings an enhanced processability, this compromises the memory device performance because of the following reasons.

First, the solution-processed PEDOT:PSS films usually have large microstructural and electrical inhomogeneities, with morphology and conductivity varying by orders of magnitude over different film regions [15]. For instance, a current sensing AFM study on the PEDOT:PSS films showed that inhomogeneous mixing of PEDOT and PSS could generate different electronic states, resulting in large variations in the current–voltage characteristics, over different regions of the same film [16]. The structural inhomogeneity of the film doubtless leads to poor cell to cell uniformity within the same memory device. Second, PEDOT and PSS may segregate at the interface, leading to the permanent

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* Corresponding author. Tel.: +82 02 2220 2555; fax: +82 02 2220 0762.
E-mail addresses: pranav.kalode@gmail.com (P.Y. Kalode), yeleekoo@gmail.com (Y.-E. Koo Lee), smm@hanyang.ac.kr (M.M. Sung).

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loss of conductivity [17]. This may hinder the use of PEDOT:PSS as a reversible resistive memory element. Note that the reversible switching in PEDOT mainly depends on change in the conductivity of PEDOT, i.e., transition from low conducting state to high conducting state and vice versa. Third, the aqueous PEDOT:PSS complex solution is highly acidic on the account of excess of PSS, corroding metal electrodes, especially at elevated temperatures [18]. Consequently, it is highly desirable to make uniform PEDOT thin films that are free of PSS to enhance the effectiveness of the PEDOT films for the organic memory devices.

Several groups suggested that polymer thin films can also be prepared by vapor phase polymerization method (VPP) [19–21]. The VPP may enable the PEDOT only films to be formed on the device during the synthesis, obviating the requirement to become processible coating materials, i.e., to have good solubility in solvents. Also, VPP may produce the films of lower thickness with better reproducibility than the solution process method. Note that the thin polymer layer permits fast conductance change by efficient transport of charges due to the short distances involved, enhancing their performance as memory devices [22]. Moreover, the VPP has been reported to produce highly uniform films [23]. The memory device utilizing the uniform VPP PEDOT films may have highly uniform performance among cells within the device, which may be useful for high density memory applications [24]. The VPP of the PEDOT involves the polymerization of ethylenedioxythiophene (EDOT) monomer in the presence of $FeCl_3$, an oxidant [25,26]. However, the PEDOT thin films thus formed by VPP may contain unreacted $FeCl_3$ at the bottom of the film, which may cause bad electrical contacts with electrodes and produce noise in the memory operation.

Herein, we developed a high-performance and air-stable nonvolatile memory device with pure PEDOT thin films that are grown by VPP and free of the oxidant, $FeCl_3$. In order to remove the unreacted oxidant at the bottom of the film after VPP, we employed a liquid-bridge-mediated transfer method (LB-mTM) to transfer the thin films upside down from one substrate to another substrate and then rinsed the exposed unreacted oxidant off the films [27]. The prepared PEDOT organic memory device exhibited nonvolatile bipolar switching properties with ON/OFF current ratio of at least 10^3. It also exhibited high cell to cell uniformity – at least 93% of the cells within the same device possessing the on/off current ratio of 10^3 or higher, and the set and reset voltage among cells varying within 0.5 V and 0.4 V from their respective average values. Furthermore, we investigated the effect of compliance current in the set process on the maximum current before switching in the reset process.

2. Experimental

2.1. Materials

Ethylenedioxythiophene (Bytron M of Bayer AG), $FeCl_3{\cdot}6H_2O$ (Aldrich, 98%) and methanol (Aldrich, 98%) were used as received. Polydimethylsiloxane (PDMS, Sylgard 184) was ordered from Dow Corning. Glass substrate used in this study was purchased from JMC Glass, Korea. Deionized water was purified with a Millipore Milli Q plus system, distilled over $KMnO_4$, and then passed through the Millipore Simplicity system.

2.2. Fabrication of PEDOT memory device

The glass substrates, employed as a base for the memory device in this work, were cleaned with acetone and methanol, further rinsed with deionized water, and finally blow-dried with a stream of nitrogen to remove the contaminants. Fig. 1 shows a schematic that illustrates the steps involved in the fabrication of the PEDOT memory device. Initially eight line patterns of aluminum (Al) measuring 100 μm (width) × 100 nm (thickness) was deposited on glass by a thermal evaporator through a shadow mask under a pressure of 10^{-6} torr, so as to serve as a bottom

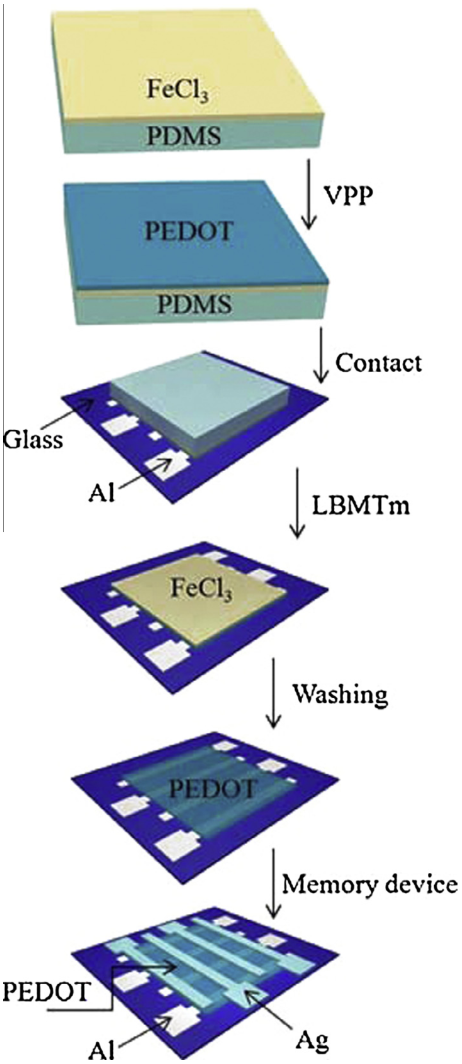

Fig. 1. Schematic illustration of steps involved in the fabrication of PEDOT Organic memory device.