A flexible polymer memory device

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Abstract

A flexible polymer memory device is demonstrated in a sandwich structure of polypyrrole/P6FBEu/Au. Conductance switching at a voltage of about 4 V, with an ON/OFF current ratio up to 200, was observed in this flexible memory device. At the low-conductivity state, current density–voltage ($J-V$) characteristics of the device were dominated by a charge injection current. At the high conductivity state, $J-V$ characteristics were dominated by a space-charge-limited current. Both the ON and OFF states are stable up to $10^6$ read cycles at a read voltage of 1 V. The device can be used as a write-once read-many-times (WORM) memory with good electronic stability.

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1. Introduction

Due to the rapid development of information technology, considerable attention has been paid to overcome the miniaturization challenges facing the traditional Si, Ge, and GaAs semiconductor industry [1]. Organic materials are potential candidates for future molecular-scale device applications [2]. Several types of organic electronics and devices, including light-emitting diodes [3], transistors [4], photovoltaic cells [5] and switches [6], have been realized. Recently, flash-type memory and write-once read-many-times (WORM)-type memory based on polymeric materials have also been demonstrated [7,8]. Polymer memories exhibit simplicity in structure, good scalability, low-cost potential, 3D stacking capability and large capacity for data-storage. Rather than encoding “0” and “1” as the amount of charge stored in a cell in silicon devices, polymer memory stores data, for instance, based on the high and low-conductivity response to an applied voltage [9]. Electroactive polymers and organics are usually deposited by ink-jet printing, spin-coating or vacuum evaporation on a variety of rigid metal, metal oxide and inorganic substrates in the fabrication of memory and other devices [7–10]. The use of conductive polymer films [11–13]
as substrate electrodes offers an opportunity for the preparation of flexible devices.

In this work, we report on a flexible polymer memory device based on the conjugated copolymer of 9,9-dihexylfluorene and benzoate with chelated europium–thenoyltrifluoroacetone ligand complex (P6FBEu, structure shown in Fig. 1a [14]). A conducting polypyrrole (PPy) film is used as the flexible substrate for the memory device, instead of the rigid metal or metal oxide electrodes commonly reported in the memory architectures [7,8,10]. Conductance switching, with an ON/OFF current ratio up to 200, was observed in this flexible memory device.

2. Experimental

2.1. Preparation and characterization of P6FBEu

The copolymer, P6FBEu, containing both the electron–donor (9,9′-dihexylfluorene) and electron-acceptor (europium complex) groups, was synthesized via the Suzuki coupling copolymerization, hydrolysis of the benzoate units, and post-chelation [14]. The Eu complex is known to exhibit memory effects [15]. The number-average molecular weight of P6FBEu was around 41800, with a polydispersity index of about 2.70 and a Eu weight content of 3.61%, corresponding to a molar ratio of 0.92/0.08 for the dihexylfluorene units to the benzoate units containing the Eu complex. From cyclic voltammetry, the energies for the highest occupied molecular orbital ($E_{HOMO}$) and the lowest unoccupied molecular orbital ($E_{LUMO}$) of P6FBEu were calculated to be $-5.66$ eV and $-3.23$ eV, respectively. P6FBEu exhibited good thermal stability, with an onset decomposition temperature above $310^\circ C$, and a glass transition temperature of about $120^\circ C$. With long alkyl substituents on the fluorene group, P6FBEu was soluble in common organic solvents, such as THF, toluene and chloroform. It could be

Fig. 1. (a) Molecular structure of the conjugated copolymer P6FBEu having the composition of $x:y = 0.92:0.08$. (b) Schematic diagram of the memory devices consisting of a thin film (~50 nm) of P6FBEu sandwiched between a flexible PPy film substrate (~40 μm in thickness) and gold top electrodes (~0.2 μm in thickness). $J$–$V$ characteristics of the (c) PPy/P6FBEu/Au device with a $0.4 \times 0.4$ mm$^2$ gold electrode and (d) with a $0.15 \times 0.15$ mm$^2$ gold electrode.
cast into transparent and uniform thin films from solutions. Ionic aggregation and phase separation associated with the rare earth complex [16] were absent in the present copolymer film because the Eu complexes were covalently bonded to the polymer chains.

2.2. Fabrication and characterization of the devices

As shown in Fig. 1b, the flexible memory device has the simple structure of a P6FBEu film (∼50 nm in thickness) sandwiched between a PPy bottom electrode (∼40 μm in thickness) and a gold top electrode (∼0.2 μm in thickness) (PPy/ P6FBEu/Au). For the fabrication of the memory device, the PPy substrate was electrochemically polymerized in an electrolyte solution of pyrrole and toluene-4-sulfonic acid in acetonitrile containing 1 vol.% water, as reported in the literature [17]. A toluene solution of P6FBEu (10 mg/ml) was spin-coated onto PPy film of conductivity of about 60 S cm⁻¹, followed by solvent removal in a vacuum chamber at 10⁻³ Torr and 50 °C for 12 h. Gold top electrodes of 0.4 × 0.4 mm² and 0.15 × 0.15 mm² in areas were thermally evaporated onto the polymer surface at about 10⁻⁷ Torr using a shadow mask. The devices were characterized on a Hewlett-Packard 4156A semiconductor parameter analyzer equipped with an Agilent 16440A SMU/pulse generator under ambient conditions.

3. Results and discussion

The conductance switching effect of the flexible PPy/P6FBEu/Au memory device is shown in the current density–voltage (J–V) characteristics in Fig. 1c and d, for active device areas of 0.4 × 0.4 mm² and 0.15 × 0.15 mm², respectively. Initially, the as-fabricated PPy/P6FBEu/Au device was in its low-conductivity state (OFF state). The current density in the low-voltage range (0–4 V) on the first sweep was low, in the orders of 10⁻⁶–10⁻⁵ A/cm², at 1 V. J increases progressively with the applied voltage (sweep 1). When a switching threshold voltage of about 4 V was applied, an abrupt increase in J from 10⁻⁴ to 10⁻² A/cm² was observed, indicating the device transition from a low-conductivity state (OFF state) to a high conductivity state (ON state). This electrical transition from the OFF state to the ON state served as the “writing” process for the memory device. The device exhibited good stability in this high-conductivity state during the subsequent forward and reverse voltage scans. It remained in the ON-state even after turning off the power and in the subsequent voltage scans: sweep 2 (0 to +5 V) and sweep 3 (0 to −5 V). This flexible memory device could not be returned to the low-conductivity state by turning off the power and application of a reverse bias of the same magnitude (sweep 3, from 0 to −5 V) after it had been switched on. Thus, this device exhibits the write-once read-many-times (WORM) memory behavior. The memory device based on P6FBEu and flexible PPy film substrate is able to achieve an ON/OFF current ratio of about 200, which is comparable to those of the contemporary single layer molecular switching devices [18]. As shown in Fig. 1c and d, the current density and WORM memory effect of this flexible memory device are independent of the metal electrode area. Thus, contributions from the filament effect [19] and dielectric breakdown to the observed memory behaviour of P6FBEu can be ruled out.

It is well known that the lanthanide complexes distinguish themselves from the transition metal complexes by a high (up to 12, due to larger ionic radii) and variable coordination number (3–12, due to weaker crystal fields) [20]. The coordination number of the europium complex in P6FBEu is 8. Thus, it is an electron-deficient complex and can act as an electron acceptor [21,22]. The device based on P6FBEu was in its low-conductivity state in the low voltage range during the first sweep (0 to +5 V) since there were not much free charge carriers in P6FBEu before all the traps were filled. When the voltage was increased to the switching threshold voltage of about 4 V, the conjugated polymer became doped by the high electric field. The charge carriers can now migrate freely and the device is switched from the low-conductivity state to the high conductivity state. For P6FBEu, the neighboring fluorene groups can only assume a “shoulder-to-shoulder” conformation through position 2 and 7 [Fig. 1a] due to the rigid nature of the π-bond and steric hindrance. It is difficult for the fluorene groups to form insulating charge transfer complexes [10] with the europium complexes. Charge in polyfluorene composites with internal donor/acceptor heterojunction can be separated and migrated through the conjugated system. P6FBEu can thus retain its doped state. As a result, the device based on P6FBEu remains in the high conductivity state even after turning off the power (sweep 2) and does not return to the low-conductivity state upon applying a negative bias (sweep 3).
As a comparison, a similar device having the structure of ITO/P6FBEu/Au was also fabricated. The $J-V$ characteristics of the ITO/P6FBEu/Au device are shown in Fig. 2. The ITO/P6FBEu/Au device switches from the low-conductivity (OFF) state to the high-conductivity (ON) state at about 1 V, with an ON/OFF current ratio of about 80 (sweeps 1 and 2). As indicated by the $J-V$ curve of the ITO/P6FBEu/Au device, it cannot be returned to the OFF state by the application of a reverse bias of the same magnitude (sweep 3) after it has been switched on, and is thus also a WORM device similar to the PPy/P6FBEu/Au device.

The use of flexible PPy substrate in the memory device, instead of the rigid ITO glass, has resulted in an increase in the switching voltage. The phenomena may have resulted from the difference in surface resistance of the PPy film and ITO glass substrate. The surface resistance of PPy film is about $10^3 \Omega \text{ sq}^{-1}$ while the surface resistance of ITO glass is about $20 \Omega \text{ sq}^{-1}$. Furthermore, the mobility of charge carriers in PPy films is very slow [23]. Thus, a high field is required to drive the charge carriers in a PPy film. Taking into account of the high surface resistance and low-carrier mobility in PPy, a higher switch-on voltage is required for the PPy/P6FBEu/Au device than for the ITO/P6FBEu/Au device. In ITO/P6FBEu/Au and PPy/P6FBEu/Au devices, the lowest energy barrier (0.56 eV) is between the work function ($\Phi$) of Au (–5.1 eV) and the highest occupied molecular orbital (HOMO) of P6FBEu, indicating that hole injection from Au into the HOMO of P6FBEu (corresponding to Au as the anode), is the favored process. Electron injection from ITO ($\Phi = -4.8 \text{ eV}$) or PPy ($\Phi = -4.5 \text{ eV}$) [24,25] into the lowest unoccupied molecular orbital (LUMO) of P6FBEu will be much more difficult because of the high energy barrier (1.57 eV for ITO, or 1.27 eV for PPy). Thus only hole injection dominates the conduction process.

To further understand the device transition from the OFF state to the ON state in WORM-type memory behavior, the $J-V$ curves in both states were analyzed in terms of theoretical models. For the OFF-state, the $J-V$ curve can be fitted by the Schottky emission model [26]:

$$J \propto T^2 \exp \left( \frac{-a \sqrt{V}}{T - q \Phi_B / kT} \right).$$

![Fig. 2. $J-V$ characteristics of the ITO/P6FBEu/Au device.](image1)

![Fig. 3. Experimental and fitted $J-V$ curves of the PPy/P6FBEu/Au device: (a) OFF state with the Schottky emission model and (b) ON state with a combination of the space-charge-limited model and the Ohmic model (the former is predominant).](image2)
wherein, $T$ is room temperature (298 K), $a = \sqrt{q/(4\pi\varepsilon_a d)}$, $\phi_B$ is the barrier height, $\varepsilon_i$ is the dynamic permittivity of the insulator, and $d$ is the film thickness. As shown in Fig. 3a, the current before the transformation from the OFF state to the ON state was controlled by charge injection from the electrode. For the ON state, the $J-V$ curve can be simulated by a combination of the space-charge-limited model and the Ohmic model as follows [26]:

$$J \approx \frac{8\varepsilon_i \mu V^2}{9d^3} + V \exp(-c/T),$$

wherein, $\mu$ is the mobility of carriers and $c$ is a positive constant independent of $V$ or $T$. The $J-V$ characteristic in Fig. 3b suggests that, after the electrical transition, the current through the device changed from a charge injection current to a predominantly space-charge-limited current [27].

Besides the switching capability, stability is always an important issue in memory device performance. The performance of the WORM device based on PPy/P6FBEu/Au was evaluated under ambient conditions. First, the effect of continuous read pulses (with a read voltage of 1 V) on the ON and OFF states was investigated. More than one million read cycles were conducted on the PPy/P6FBEu/Au device. As shown in Fig. 4a, no current degradation was observed for the ON and OFF states. Thus, both states are insensitive to read cycles. The stability of the device under a constant stress of 1 V is shown in Fig. 4b. An ON/OFF current ratio of about $10^2$ can be maintained when projected to one year.

4. Conclusions

In summary, a flexible polymer memory device is demonstrated in a sandwich structure of PPy/P6FBEu/Au. Conductance switching at a voltage of about 4 V, with an ON/OFF current ratio up to 200, was observed in this flexible memory device. After the device was switched to the high conductivity state, it remained in the ON state even when swept negatively. The device can be used as a write-once read-many-times (WORM) memory with good electronic stability. With the advantage of the flexible and conductive PPy substrate, the present polymer WORM memory is expected to meet the demand for data storage in memory devices of unique spatial construct or architecture.

References