Multilevel Nonvolatile Flexible Organic Field-Effect Transistor Memories Employing Polyimide Electrets with Different Charge-Transfer Effects

An-Dih Yu, Wei-Yao Tung, Yu-Cheng Chiu, Chu-Chen Chueh, Guey-Sheng Liou,* Wen-Chang Chen*

The electrical memory characteristics of the n-channel organic field-effect transistors (OFETs) employing diverse polyimide (PI) electrets are reported. The synthesized PIs comprise identical electron donor and three different building blocks with gradually increasing electron-accepting ability. The distinct charge-transfer capabilities of these PIs result in varied type of memory behaviors from the write-one-read-many (WORM) to flash type. Finally, a prominent flexible WORM-type transistor memory is demonstrated and shows not only promising write-many-read-many (WMRM) multilevel data storage but also excellent mechanical and retention stability.

1. Introduction

Organic memories have attracted extensive interests because of the advantages of low-cost and simple manufacture, lightweight, and flexibility. Among various kinds of organic memories, the field-effect transistor (OFET) type is the most striking and has been widely investigated recently due to its nondestructive read-out property, single-transistor realization, and good compatibility with the complementary metal oxide-semiconductor devices. Compared with the typical OFET structures, the OFET memory requires an electret layer to modulate the charge density of the conducting channel for the memory operation, which correlates closely with the materials nature. To date, several organic electrets, such as organic ferroelectric materials, polymer composites, and nonconjugated polymers have been demonstrated with strong charge-storage properties. Lately, polyimides (Pis) become another emerging materials to serve as the electrets owning to their excellent thermal, mechanical, and electrical properties. We recently showed that the donor–acceptor (D–A)-type PIs could be employed as effective electrets for OFET memories and the memory behaviors can be modulated by their constituent units accordingly.

To address the scaling issue for the next-generation memory devices, a transistor memory with a multilevel data storage capability has attracted significant scientific interest recently. Two main concepts were applied for multilevel data storage, as described in the following. A dielectric layer embedded with highly ordered metallic nanoparticles was reported effective by controlling the trapping levels as well as trap sites. The other approach selected an electret material with an appropriate energy level, compacted molecular shape, and single-carrier-accumulating nature, for example, star-shaped triphenylamine in our previous report. However, the
manipulation on the multilevel data storage using PI-based electrets have not been explored yet.

In this work, new PIs, polyimidithioether[4,4′-(diaminodiphenylsulfide)bismaleimide-2,5-bis(mercaptomethyl)-1,4-dithiane] [PITE(BMI-BMMD)], poly[bis-[4-aminoanilfonyl]-sulfide-oxydiphthalimide] [PI(APS-ODPA)], and poly[bis-[4-aminophenyl]-sulfide-biphtalimide] [PI(APS-BPA)], were designed and explored as the electrets for n-type N,N′-bis(2-phenylethyl)perylene-3,4,9,10-tetra-carboxylic diimide (BPE-PTCDI) transistor memories (Scheme 1). An identical electron-donating moiety of phenylene sulfide moiety is couple with three different building blocks, including neutral (BMMD), weak (ODPA), and strong (BPA) electron acceptors, which enables different charge-transfer (CT) capability of the studied PIs to modulate the OFET memory characteristics. The effects of charge-transfer and bending characteristics on the OFET memory characteristics were explored and correlated with chemical structures.

2. Experimental Section

2.1. Materials

The detailed materials, synthesis, and characterization of the Experimental Section are shown in Figures S1–S3 (Supporting Information) and described briefly in the following. The 1 H NMR spectrum of the synthesized PITE(BMI-BMMD) is shown in Figure S1(Supporting Information). The proton resonance peaks at 2.51–3.30 and 4.15–4.30 ppm are assigned to the alicyclic and methylene groups of BMMD and succinimide moieties. The signals between 7.28–7.40 and 7.58–7.42 ppm are attributed to the phenyl groups of phenylene sulfide moiety. The elemental analysis (EA) results of C, H, N, and S contents are in a fair agreement with the theoretical content. The number-average molecular weight and polydispersity index are 1.45 × 10⁴ g mol⁻¹ and 2.37, respectively. The completed imidizations of PITE(APS-ODPA) and PITE(BMI-BMMD) after thermal curing were confirmed using IR spectra. The IR spectra (Figure S2, Supporting Information) of the prepared PIs exhibit the characteristic imide absorption bands at the following peaks: 1776 (symmetrical C=O stretching), 1372 (C–N stretching), and 730 cm⁻¹ (imide ring formation). The number-average molecular weights of the polyamic acids, PAA(APS-ODPA) and PAA(APS-BPA), are 23.6 × 10⁴ and 19.6 × 10⁴ g mol⁻¹. The thermal decomposition temperature of PITE(BMI-BMMD), PI(APS-ODPA), and PI(APS-BPA) are 284, 513, and 517 ºC, respectively, as shown in Figure S3 (Supporting Information). The above results suggest the successful preparation of the target PIs.

2.2. Device Fabrication and Measurement

Classic OFET memory devices were fabricated with a top-contact configuration as shown in Scheme 1 that wafer with a thermally grown 300-nm thick SiO₂ dielectric on highly doped n-type Si was selected as the device substrate. Solutions of PITE(BMI-BMMD) and PAs in DMAc were filtered through a PTFE membrane syringe filter (pore size, 0.22 μm) and spin-coated at 1000 rpm for 60 s on a precleaned wafer. The polymer films were baked at 150 ºC to remove extra solvent for 20 min. Noted that PAA films were further put through a thermal curing process (90, 150, 250, and 300 ºC for 1 h each) for the transformation to PI films. The thicknesses of PITE and PI films were determined around 50 nm. Semiconductor BPE-PTCDI thin films (50 nm) were thermally evaporated and deposited on PI and PI surfaces at about 10⁻⁷ Torr with the maintenance of substrate temperature at 90 ºC. Gold source and drain top contacts (channel length and width were defined as 50 and 1000 μm, respectively) of about 80 nm in thickness were subsequently deposited through the shadow mask at a rate of 0.5 nm s⁻¹.

Flexible OFET memory device was fabricated on an indium-tin oxide (ITO)-coated PEN substrate. DMAc solution of PITE(BMI-BMMD) (100 mg mL⁻¹) was also filtered through a PTFE membrane syringe filter and spin-coated on the ITO-PEN substrate for a 650 nm thick film. The following BPE-PTCDI layer and gold electrodes were deposited in the same way as described in the previous paragraph. The characteristics of the OFET memory devices were measured using a Keithley 4200-SCS semiconductor characterization system under an inert condition at room temperature. The capacitance (C) of individual polymer

Scheme 1. Schematic illustration of the studied n-type OFET memory devices and the molecular structures of the studied PIs.
layer was carried out with a simple sandwich structure of ITO/polymer layer (650 nm)/gold electrode using Keithley 4200-SCS analyzer equipped with a digital capacitance meter (model 4210-CVU). Note that the estimated average capacitances of PITE(BMI-BMMD), PI(APS-ODPA), and PI(APS-BPA) films with the thickness of 650 nm are 4.28 × 10⁻⁹, 3.84 × 10⁻⁹, and 3.81 × 10⁻⁹ F cm⁻². Fundamental OFET parameters, such as field-effect mobility (μ), threshold voltage (V_{th}), were estimated using the conventional characterization equation in the saturation regime:

\[ I_{ds} = \frac{W C_{tot} \mu}{2L} (V_{gs} - V_{th})^2 \]

where \( C_{tot} \) is the capacitance per unit area of total dielectric layer, \( I_{ds} \) is the drain-to-source current, and \( V_{th} \) is threshold voltage.

### 3. Results and Discussion

#### 3.1. Polymer Properties

The related optical and electrochemical properties of the PIs are listed in Table 1 and the spectra are shown in Figure S4 (Supporting Information). Alicyclic PIs have higher transparencies compared with aromatic PIs mainly due to the weak electron-withdrawing ability of alicyclic imide moieties (e.g., succinimide in this work) and also less chain–chain interactions. The charge transfer between electron-donating and accepting moieties often results in deep-color PI films. The red-shifted absorption peaks of PI(APS-ODPA) and PI(APS-BPA) show a clear charge-transfer (CT) effect[6] from 265 nm (PI(BMI-BMMD)) to 306 nm (PI(APS-ODPA)) and 332 nm (PI(APS-BPA)). Following the trend of the electron-accepting strength (BPA > ODPA > BMMD), the optical bandgap of the resultant PIs is in the order of PI(APS-BPA) (3.10 eV) < PI(APS-ODPA) (3.49 eV) < PITE(BMI-BMMD) (3.76 eV). The CV results of these three polymers show the irreversible oxidation behavior and have a similar highest occupied molecular orbital (HOMO) level of ~5.69 to ~5.82 eV, due to the identical donor moieties of the phenylene sulfide. The lowest unoccupied molecular orbital (LUMO) level of PITE(BMI-BMMD), PI(APS-ODPA), and PI(APS-BPA) estimated by the difference between the optical bandgaps and the HOMO energy levels are ~1.93, ~2.31, and ~2.72 eV, respectively. PI(APS-BPA) exhibited the lowest LUMO energy levels among the three polymers, due to the large charge-transfer effect.

#### 3.2. OFET Memory Characteristics

The OFET memory constructed with the studied PI electrets is characterized in a bottom gate/top-contact configuration, as shown in Scheme 1. Figure 1 illustrates the OFET memory characteristics of the studied devices. All the PI electrets show smooth surfaces, indicating the minimized amount of interface-traps between the dielectric electrets and semiconducting layers (Figure S5a–c, Supporting Information). BPE-PTCDI on those PIs exhibits similar nanorod surface textures with average length of ~230 nm and diameter of ~75 nm, due to the alike hydrophobic nature and smooth surfaces of the seeding PIs (Figure S5d–f, Supporting Information). These highly crystalline structures suggest the well crystal growth of BPE-PTCDI on those PIs, which is beneficial for the high mobility and memory operation.

All the devices exhibit typical unipolar n-type accumulation mode with an estimated mobility around 10⁻³–10⁻⁴ cm² V⁻¹ s⁻¹ (Table 1), suggesting no ambipolar behavior induced by the PI electrets. After the writing procedure of applying a gate pulse of ~100 V for 1 s, all the transfer curves are substantially shifted toward the negative bias direction and result in the written threshold voltages (V_{th}) of ~58 (PITE(BMI-BMMD)), ~54 (PI(APS-ODPA)), and ~55 (PI(APS-BPA)) V. The results suggest the good charge storage capabilities of those PI electrets.

However, after the erasing procedure of applying a gate pulse of 100 V for 1 s, only the devices using PI(APS-ODPA) and PI(APS-BPA) electrets show apparent erasable actions. Their transfer curves shift toward the positive bias direction with the erased V_{th} of 7.0 and 26.5 V. Different to

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**Table 1.** Optical and electrochemical properties of the studied polyimides and their electrical characteristics of their OFET memory.

<table>
<thead>
<tr>
<th>Polymides</th>
<th>( \lambda_{max} ) [nm]</th>
<th>( E_g ) [eV]</th>
<th>HOMO [eV]</th>
<th>LUMO [eV]</th>
<th>Mobility [cm² V⁻¹ s⁻¹]</th>
<th>On/off ratio</th>
<th>Memory window [V]</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>PITE(BMI-BMMD)</td>
<td>265</td>
<td>3.76</td>
<td>~5.69</td>
<td>~1.93</td>
<td>5.7 × 10⁻³</td>
<td>9.0 × 10⁵</td>
<td>64.39</td>
<td>WORM</td>
</tr>
<tr>
<td>PI(APS-ODPA)</td>
<td>306</td>
<td>3.49</td>
<td>~5.80</td>
<td>~2.31</td>
<td>1.3 × 10⁻³</td>
<td>9.3 × 10⁴</td>
<td>61.22</td>
<td>Flash</td>
</tr>
<tr>
<td>PI(APS-BPA)</td>
<td>332</td>
<td>3.10</td>
<td>~5.82</td>
<td>~2.72</td>
<td>6.0 × 10⁻⁴</td>
<td>4.6 × 10⁴</td>
<td>81.49</td>
<td>Flash</td>
</tr>
</tbody>
</table>

\( E_g \) Estimated from the onset of the UV–vis absorption spectrum; \( HOMO = E_g + E_g \)
these two PI electrets, the device derived from PITE(BMI-BMMD) electret exhibits an inerasable characteristic with an ignorable $V_{th}$ shift (around 3 V). The invariability of the written transfer curve indicates the OFET memory is likely to being converted to the write-one-read-many (WORM) from the flash type. The retention time testing of the studied devices was recorded in Figure S6 (Supporting Information). All the devices showed excellent stability over $10^4$ s without a significant decay, which indicated the nonvolatile nature of the studied devices. Therefore, we can define the PI(APS-ODPA)- and PI(APS-BPA)-based devices as nonvolatile flash memories, while the PITE(BMI-BMMD)-based device is nonvolatile WORM memory according to their corresponding writing/erasing behaviors. The multiple switching stability of the studied flash memory was evaluated by write-read-erase-read (WRER) cycles (Figure S7, Supporting Information). All these two devices showed the on/off current ratios of more than $10^3$ during the WRER cycles, suggesting the good resolution for memory operation. Also, the device can be operated over 100 cycles with excellent stability and reversibility.

The conversion from flash type to WORM type of the studied OFET memory is necessarily related to the CT capability of the PI electrets. As depicted in Figure 1d, the rich-sulfur-containing main chain together with the nonconjugated alicyclic succinimide of PITE(BMI-BMMD) suggests its respectable electron-donating ability, leading to the highest energy levels among these three PIs. Moreover, as shown in Figure 2 (calculated by B3LYP/6-31G(d, see Supporting Information), the intramolecular CT is not found between HOMO and LUMO orbitals of PITE(BMI-BMMD) due to the insignificant electron-withdrawing ability of BMMD moiety, while the PIs containing ODPA or BPA moieties possess obvious intramolecular CT. Besides, the dominant CT states extended to LUMO+3 of PI(APS-BPA) implies the strongest electron-accepting characteristic among those three used building blocks. For all studied OFET memories, large amounts of holes will be generated in the BPE-PTCDI layer, while the negative gate bias pulse is applied. These accumulated holes in the BPE-PTCDI will be gradually transferred to the PI electrets, and leads to the hole injections across the shallow energy barrier due to the appropriate interface energetics. The captured holes in the electret will naturally raise the electron density of BPE-PTCEI and result in the significant shifting of transfer curves toward the more negative direction and denoted as the written state. Since the electron-donating segment is identical for all PIs, the devices possess similar written capability, showing similar $V_{th}$ shifts in the negative direction. However, after the erasing process, the written transfer curve of the device derived from PITE(BMI-BMMD) shows a irerasability, suggesting a WORM-type memory behavior as a result of its prominent electron-donating nature. This irreversible shifts can be envisioned by the lack of recombination of
the holes trapped in the PITE(BMI-BMMD) electret due to its poor electron-withdrawing property and the large energy barrier between the LUMOs of BPE-PTCDI and PITE(BMI-BMMD). It can be confirmed by the measured transfer curves of the fabricated devices under a dual sweep (forward and backward) mode (Figure S8, Supporting Information). The lack of electrical hysteresis of the transfer curve during the backward scanning reveals the negligible electrons trapped by the PITE(BMI-BMMD) electret.

Compared with the PITE(BMI-BMMD) electret, the written transfer curves of the devices based on PI(APS-ODPA) and PI(APS-BPA) electrets can be easily erased, showing flash-type memory characteristics. It can be attributed to the enhanced intramolecular CT features of PI(APS-ODPA) and PI(APS-BPA), arising from the electron-accepting moieties of ODPA and BAP, which will facilitates the formation of CT complexes. Given this, the induced electrons in the BPE-PTCDI layer is likely to be captured by the accepting moiety (ODPA and BAP) of the PI electret, while applying an erasing pulse. Considering the facilitation of the CT complex of those PIs, the transferred electrons will neutralize the stored holes in the electrets and complete the erasing actions. Due to the higher electron affinity of the BPA segment, the PI(APS-BPA) shows an better intermolecular CT and stronger electron trapping ability as compared with PI(APS-ODPA), resulting in a more positively shifted curve of about 20 V of the former (Figure 1). Meanwhile, the faster decay of PI(APS-BPA) than PI(APS-ODPA) in the backward sweep of the electrical hysteresis loops (Figure S8, Supporting Information) also demonstrates the more efficient electron-accepting ability of the former. Notably, the enhanced CT feature of PIs also affects the mobility of the devices by simultaneously lowering the barrier of electron injection and decreasing the density of negative carriers in the BPE-PTCDI layer, especially under the positive gate bias (saturated regime), as summarized in Table 1.

The WORM-type OFET memory with similar device structure was further explored on a flexible substrate, in which ITO replaces the silicon oxide as the gate electrode as shown in Figure 3. As shown, the flexible OFET memory also demonstrates the similar inerasability. An inerasable negative-shift around 80 V occurred after applying a writing gate pulse of −100 V. The large on/off current ratio ($V_g = 0$) over $10^3$ suggest the good resolution of the device. The retention testing presented in Figure S9 (Supporting Information; flat condition) demonstrates the excellent data preservation ability of the device up to $10^5$ s with no energy consumption of gate bias. In addition, the broad resistance difference for over $10^3$ confirms the distinguishable resolution from misreading. Figure 3b show the transfer curves with fixed drain voltage of 100 V under different gate voltage sweeping.
range from $-20$, $-40$, $-60$, $-80$ or $-100$ V to 100 V. It shows a tendency of the negatively shifted starting point and $V_{th}$, which broadens the memory window of the device and suggest the multilevel nonvolatile memory behavior. To further demonstrate this multilevel storage characteristic, a various programing (writing) gate pulses of $-80$ to $-140$ V are applied successively as illustrated in Figure 3c. As can be seen, the transfer curve moves to a specific state and defined as the “read” curves after each writing step by the programed voltage. As a result, the capability of multilevel data storage of the studied flexible memory is successfully demonstrated in the Figure 3d, in which the drain current is continuously collected under the drain bias of 100 V, while the gate bias starts from 0 to $-140$ V.

The multilevel inerasable data storage could be attributed to various degrees of traps captured in the PITE(BMI-BMMD) electret under different gate biases and this property enables the original WORM-type memory to become a write-many-read-many (WMMR)-type memory.[24]

The bending durability of the studied flexible PITE(BMI-BMMD)-based OFET memory devices are also characterized after being physically fixed with a vernier caliper under different bending conditions as shown in Figure 4a. Specifically, the device is bent from a flat configuration to curves with radii of curvature of 30, 20, 10, and 5 mm. To simplify the examination of the effect of physical bending, only $-100$ V gate bias is selected for the writing process. The memory characteristics under different bent conditions are described in Figure S10 (Supporting Information) and the related statistical analyses

Figure 3. a) Transfer characteristics of the studied flexible OFET memory using PITE(BMI-BMMD) electret. Transfer curves of the device with b) different sweeping ranges and c) various programmed voltages (solid marks) and the corresponding reading curves (empty marks). d) The multilevel current responses read at gate voltage of $-10$ V when applied various programmed gate voltages. All currents were collected under $V_d = 100$ V.

Figure 4. a) The studied flexible PITE(BMI-BMMD)-based OFET memory device in flat and various bent states. b) Variations of on/off ratio, $V_{th}$ shifts, and mobility of the studied flexible memory device with different bending radii.
(collected from five cells) are summarized in Figure 4b. Parameters such as on/off current ratio ($V_g = 0$), memory window, and electron mobility are recorded to trace the device stability under different degrees of mechanical bending stress. All parameters of the flexible memories show great stability after bending, suggesting the flexible device does not deform or crack upon bending. Meanwhile, the retention characteristics of the flexible device bent to a radius of curvature of 5 mm (Figure S9, Supporting Information) can be steadily maintained for $10^5$ s, indicating the reliable performance even when the substrates are severely bent. The result demonstrates the great potential of the studied PI as the electret for the flexible memory devices.

4. Conclusions

We have developed a series of PI as the electrets for n-channel OFET memories. The memory characteristics are found to be highly related to the CT features of the studied PIs. The PITE(BMI-BMMD) electret with strong electron-donating ability enables the device to exhibit a hole-trapping-only behavior, resulting in the inerasable WORM-type memory. For D−A type PI(APS-ODPA) and PI(APS-BPA) electrets, the derived memory devices exhibit programmable flash-type characteristics. It indicated that the performance of transistor memory could be modulated by controlling the CT features of the electrets. Finally, a prominent flexible WMRM transistor memory with multilevel memory behavior is demonstrated by using PITE(BMI-BMMD) electret, showing excellent stability even under severe bend radius of 5 mm. The demonstration here reveals a promising high-capacity flexible memory in the future.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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