

Synthesis and Dynamic Random Access Memory Behavior of a Functional Polyimide

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Polyimides (PIs) have been widely used in microelectronics, owing to their excellent mechanical, dielectric, thermal, and chemical properties.¹ In recent years, PIs have also been explored for applications in organic electronics, such as light-emitting diodes,² photovoltaics,³ and xerography.⁴ Polymer memories exhibit simplicity in structure, good scalability, low-cost potential, 3D stacking capability, and large capacity for data storage.⁵ In the pioneering works on polymer memories, polymers were used as polyelectrolytes, matrixes of dyes or nanoparticles, or components of charge transfer (CT) complexes in doped or mixed systems.^{6–10} The design and synthesis of polymers that can provide the required memory properties within a single molecule is an alternative approach.¹¹ Taking into account the demand for thermal stability in polymeric materials,¹² the present work explores a thermally stable PI for memory applications. The present memory device is based on a functional PI containing both electron-donor (D) and electron-acceptor (A) moieties within a single macromolecule (TP6F-PI, Figure 1). Differing from that of the widely reported nonvolatile flash and write-once read-many-times polymer memories, the device based on TP6F-PI exhibits dynamic random access memory (DRAM) behavior.

The functional PI was synthesized by the reaction of 4,4'-diaminotriphenylamine with hexafluoroisopropyl bis(phthalic dianhydride), to form the corresponding poly(amic acid).¹³ Imidization gave rise to TP6F-PI with a number-average molecular weight of 4.16×10^4 and a polydispersity index of 3.70 (see Supporting Information). TP6F-PI exhibited excellent thermal stability, with a 10% weight-loss temperature of 524 °C and a glass transition temperature of 316 °C. The memory device consisted of a NMP solution spin-coated TP6F-PI film (~50 nm in thickness) sandwiched between an indium-tin oxide (ITO) bottom electrode and a 0.3 μm-thick Al top electrode (Figure 1).

The memory effect of TP6F-PI is shown in the current density–voltage (J – V) characteristics of Figure 2. In the 1st sweep from 0 to 4 V, an abrupt increase in J was observed at a switching threshold voltage of about 3.2 V, indicating the device transition from a low-conductivity (OFF) state to a high-conductivity (ON) state (the “writing” process). The device remained in this high-conductivity state during the subsequent positive scan (the second sweep). The distinct bielectrical states in the voltage range of 0 to 3.2 V allowed a voltage (e.g., 1.0 V) to read the “0” or “OFF” signal (before writing) and “1” or “ON” signal (after writing) of the memory. In the third sweep from 0 to –4 V, an abrupt decrease in J was observed at a threshold voltage of about –2.1 V, indicating the

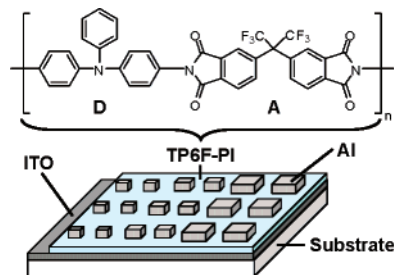


Figure 1. Molecular structure (top) of the functional PI (TP6F-PI) and schematic diagram (bottom) of the single-layer memory devices.

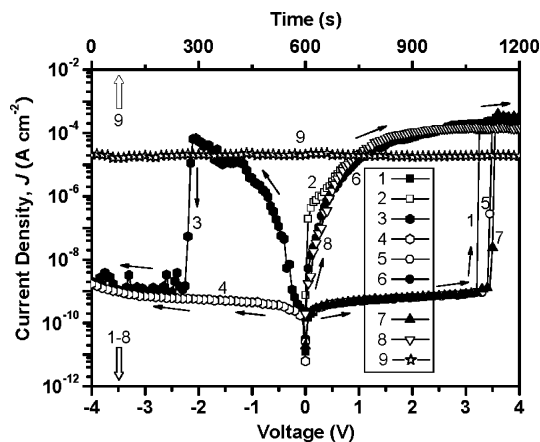


Figure 2. Current density–voltage (J – V) characteristics of a 0.16 mm² Al/TP6F-PI/ITO device. The ON state was maintained by refreshing at 1 V every 5 s. Sweeps 1, 2, 5, 6, 7, and 8: 0 to +4 V (with power off for 1 min for sweeps 6 and 7). Sweeps 3 and 4: 0 to –4 V.

device transition from the ON state back to the OFF state. This electrical transition served as the “erasing” process for the memory device. The device remained in the OFF state after this erasing process, as indicated by the subsequent negative sweep (the fourth sweep). The erased (“0”) state could be further written to the stored (“1”) state when the switching threshold voltage was reapplied, indicating that the memory device was rewritable (the fifth and sixth sweeps). The seventh sweep was conducted after turning off the power for about 1 min. It was found that the ON state had relaxed to the steady OFF state without an erasing process. The short retention time of the ON state indicated that the memory device was volatile. However, the device could be reprogrammed to the ON state (the seventh and eighth sweeps). The unstable ON state could be electrically sustained by a refreshing voltage pulse of 1 V in every 5 s (the ninth trace).

The J – V characteristics were repeatable with good accuracy, and device degradation was not observed. The current magnitude

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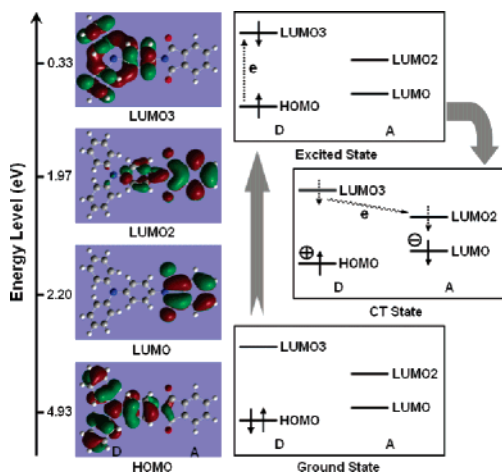


Figure 3. Molecular orbitals (left) of the basic unit of TP6F-PI and the transitions (right) from the ground state to the CT state induced by the electric field.

was proportional to the device area, that is, J was independent of this parameter. This ability to write, read, erase, and refresh the electrical states fulfils the functionality of a DRAM.

The mechanism of field-induced conductivity is probably similar to that of the photoinduced CT in photoconductive PIs.¹⁴ The incorporation of Ds has been known to enhance the photocurrent in PI by several orders of magnitude, arising from the improved CT complex formation in the PI backbone.¹⁵ In the present TP6F-PI, triphenylamine acts as a D, while phthalimide acts as an A to promote the CT complex formation. Molecular simulation of the basic unit of TP6F-PI was carried out at the DFT B3LYP/6-31G(d) level with the Gaussian 03 program package.¹⁶ Figure 3 shows the resulting HOMO and LUMOs, and the plausible electronic processes. The calculated energy levels are comparable to the HOMO (-5.13 eV) and LUMO2 (-2.03 eV) energy levels of TP6F-PI, measured by cyclic voltammetry (see Supporting Information). The HOMO is located on D, while the first and second LUMOs are located on A. At the threshold voltage, one of the electrons transits from the HOMO to the LUMO3 within D to form an excited state. Excitation of D leads to a decrease in ionization potential and consequently promotes intra- or intermolecular CT at the excited state. CT can occur indirectly from the LUMO3 of D to the LUMO2, then to the LUMO of A, or directly from the HOMO to the LUMO2 and LUMO at the excited state, to form a conductive complex. These processes are supported by the electronic absorption spectrum of TP6F-PI. The respective absorption maximum and absorption edge at ~ 290 nm (4.28 eV) and ~ 400 nm (3.10 eV) correspond to the HOMO \rightarrow LUMO3 (4.60 eV, highest probability) and HOMO \rightarrow LUMO2 (2.96 eV, low probability) transitions (see Supporting Information). The charges can be further segregated under an electric field and delocalized to the conjugated triphenylamine, thus stabilizing the CT state to some extent. However, the ON state of TP6F-PI could not be sustained due to limited delocalization in the triphenylamine moieties. A reverse bias of about -2.1 V, or removal of the electric field, can dissociate the CT complex and return the device to the initial OFF state.

Figure 4(a) shows the dependence of ON/OFF current ratio on V and the stability of the device. An ON/OFF current ratio up to 10^5 (which increases slightly due to the increase in ON-state current with bias) promises minimal misreading error. At a constant stress of 1 V, no obvious change in J for the OFF state was observed. Although a slight degradation in J for the ON state was observed

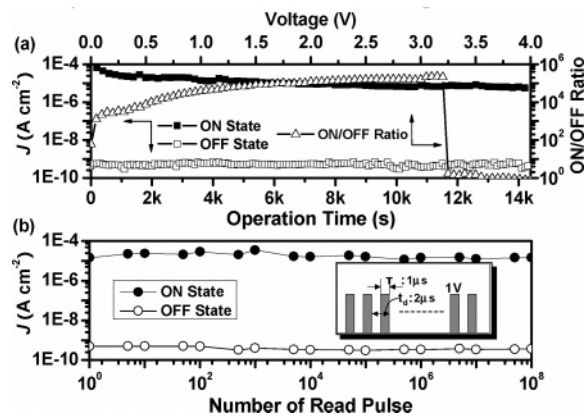


Figure 4. (a) ON/OFF current ratio and effect of operation time and (b) read pulses on the device in the OFF state and ON state. The inset in (b) shows the pulses used for the measurements.

for the first 0.5 h, an ON/OFF current ratio of $\sim 10^4$ was maintained during the long-term testing under ambient conditions. No obvious degradation in J was observed for the ON and OFF states after more than 10^8 read cycles at a read voltage of 1 V (Figure 4(b)). Thus, both states were stable under the voltage stress and were insensitive to read pulses.

In summary, a plastic DRAM, based on a donor-functionalized PI (TP6F-PI), exhibited an ON/OFF current ratio up to 10^5 . Both the ON and OFF states were stable under a constant voltage stress of 1 V and survived up to 10^8 read cycles at 1 V. A PI memory device distinguishes itself from other polymer devices by its superior thermal and chemical properties, while still possessing good processability and scalability.

Supporting Information Available: Details on polymer synthesis and characterization, molecular simulation, device fabrication, and ref 16. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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