**Organic Donor–Acceptor System Exhibiting Electrical Bistability for Use in Memory Devices**

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During the past ten years, with the extraordinary advances made in the field of organic materials, organic electronic devices have been demonstrated to be promising candidates for inorganic-dominated electronic and optoelectronic devices, such as light-emitting diodes,[1–2] solar cells,[3] and transistors.[4] A new family of organic electronic devices is organic memory devices, which were demonstrated by Ma et al. in 2002.[5] Their devices, based on a thin film of metallic nanoparticles embedded in an organic layer, attract considerable attention. The organic memory has a nanosecond writing time and exhibits the non-volatile memory effect, which makes it ideal for applications in flash memory. The memory-effect mechanism is attributed to electrically induced charge transfer between nanoparticles, which causes a sudden change in conductivity of the organic thin film.[6] Scott and co-workers demonstrated a similar effect with, alternatively, a much thinner metallic film (5 nm), and attributed the major mechanism of electrical bistability, and hence the memory effect, to charge trapping.[7] More recently, Ouyang et al. demonstrated electrical bistability and the memory effect by blending gold nanoparticles and organic electron-donor molecules in a polystyrene matrix.[8] Electrical bistability and the memory effect have been generalized into trap-engineering inside organic thin films. Despite these encouraging developments, organic electronic memory devices are still in the exploratory stage; their stability is still questionable, preventing them from being used in commercial products. One of the problems of the thin-metal system or the Au nanoparticle system is the phase separation that occurs between the organic (or polymer) material and the metal nanoparticles. This phase separation may prevent the device from having a stable, long operating lifetime.

The motivation for this study is to demonstrate an all-organic thin film (i.e., without the use of metallic nanoparticles) as the active layer for achieving electrical bistability and, thus, memory devices. As described earlier, electrical bistability is caused by a field-induced charge transfer (or trapping); hence, it is critically important to introduce a charge donor and acceptor system into the polymer matrix to replace the metallic nanoparticles. Organic electron-donor and electron-acceptor materials were used to prepare the organic composite thin films. Charge transfer could occur between molecules after applying a voltage pulse, and electrical bistability was observed in the composite film.[9–11] Most organic thin films are fabricated by thermal evaporation in high vacuum and the requirements for the evaporation conditions are very strict. Hence, it is important to develop a process with easily controlled parameters.

In this communication, we report on an electric-field-induced memory effect in devices made of organic composite thin films. The films consisted of polystyrene (PS) as the matrix, methanofullerene 6,6-phenyl C61-butrylic acid methyl ester (PCBM) as the organic electron acceptor, and tetrafluorovalene (TTF) as the organic electron donor. Electrical bistability was demonstrated in a two-terminal structure consisting of an organic composite film (which was prepared by a simple solution process) sandwiched between two metal electrodes. The polymer film was formed by spin-coating a 1,2-dichlorobenzene solution of 1.2 wt-% polystyrene and 0.8 wt-% TTF and PCBM. Both the top and bottom Al electrodes had a width of 0.2 mm, so that the device had an active area of 0.04 mm². The chemical structures of the materials and the device structure are shown in Figure 1. This device can be used as non-volatile organic memory.

![Figure 1. Chemical structures of the organic materials, and layout of the organic memory device.](image)

Typical current–voltage (I–V) characteristics of the devices are shown in Figure 2. (Our device had an electrically symmetrical behavior, so only one bias direction is presented.) The device exhibits two states of different electrical conductivity at the same voltage. During the first bias scan (curve a), a low
current was observed for the device in a bias range from 0 to 2.6 V. A sharp increase in the current, from $10^{-7}$ A to $10^{-5}$ A, took place at around 2.6 V, indicating the transition of the device from a low-conductivity state (OFF state) to a high-conductivity state (ON state). After the transition, the device remained in the ON state, as shown in the subsequent voltage scan (curve b). The conductivity of the device in the ON state was more than three orders of magnitude larger than that in the OFF. The low-conductivity state could be recovered by simply applying a higher bias of either polarity (such as $+9$ or $-9$ V) as indicated by curve c, where the current suddenly dropped from $-10^{-4}$ to $-10^{-5}$ A at $-6.5$ V. Another crucial parameter for memory devices is the switching time. We observed that devices in the low-conductivity state could be changed to the high-conductivity state by applying a 5 V pulse of width shorter than 100 ns. In addition, the high-conductivity state could be converted to the low-conductivity state by applying a $-9$ V pulse of width shorter than 100 ns.

Electrical switching between the low- and high-conductivity states was performed numerous times, as demonstrated in Figure 3. A 5 V pulse induced the device to be in the ON state. This ON state could be read by a 1 V pulse with a current of $\sim 10^{-5}$ A. A negative bias of $-9$ V erased this ON state, to produce the OFF state. The OFF state could be detected by a 1 V pulse with a current of $\sim 10^{-8}$ A. The electrical bistability of the device could be precisely controlled by applying an appropriate voltage pulse numerous times without any significant device degradation. Moreover, once the device switched to either state, it remained in that state for a prolonged period of time. The stability of the devices under stress was measured under continuous-bias conditions. A constant voltage (0.5 V) was applied to the device in the OFF and ON states, and the current was recorded at different times. There was no significant change in the state of the devices in both states even after 12 h of continuous stress testing. In addition, the retention ability was tested by leaving several devices in the ON state without applying a bias in a nitrogen environment. Once we wrote an ON state, the devices remained in that state for several days to weeks. These write–read–erase cycles and the duration test demonstrate that the devices have the basic requirements necessary for binary-information storage and present the potential for operation as non-volatile memory.

The switching mechanism was further studied using an alternating-current impedance, as shown in Figure 4. The device in the OFF state exhibits a capacitance of 30 pF from 20 to $10^6$ Hz that is insensitive to frequency, while the capacitance becomes strongly dependent on frequency when the device is in the ON state. For the device in the ON state, the capacitance in the high frequency range $10^0$–$10^6$ Hz was almost the same as that in the OFF state, then it subsequently increased with decreasing frequency. This suggests that no dielectric breakdown took place, since the dielectric properties of the bulk material between the two electrodes contributes to the device capacitance in this high frequency range. On the other hand, the capacitance in the ON state is higher than that in the OFF state by more than one order by magnitude at low frequencies (frequencies less than 600 Hz). This increased capacitance at low frequencies may be partly caused by the increase in the apparent dielectric constant of the film. The change of apparent dielectric constant is believed to be associated with the field-induced dipole formation between the donor and the acceptor. The dipole formation is further discussed in the following paragraph.

In order to optimize the performance of our devices, we studied the conduction mechanism in both the ON and OFF states. The device exhibited a nonlinear $I$–$V$ relationship before and after the electrical transition. The plot of $\log(I)$ ver-

![Figure 2](image2.png)

**Figure 2.** $I$–$V$ curves of the device with the structure Al/PS:PCBM:TTF/Al. (a–c) The first, second, and third bias scans, respectively. The arrows in the figure indicate the voltage-scanning directions.

![Figure 3](image3.png)

**Figure 3.** Write–read–erase cycles of the device Al/(PS:PCBM:TTF)/Al. The top and bottom curves are the applied voltage and the corresponding current response, respectively. “1” and “0” in the bottom curve indicate the device in the high- and low-conductivity states, respectively.
charge carriers due to impurities existed in the film, so that the film had a low conductivity. A high electric field, however, may facilitate electron transfer from the HOMO of TTF to the LUMO of PCBM. Consequently, the HOMO of TTF and LUMO of PCBM become partially filled, and TTF and PCBM are charged positively and negatively, respectively. Therefore, carriers are generated, and the device exhibits a sharp increase in conductivity after the charge transfer.

In conclusion, electrically bistable devices utilizing organic materials with simplified structures have been demonstrated, using simple fabrication methods such as spin-coating and thermal evaporation. The predictable control-voltage values permit devices to be designed with required characteristics and the devices exhibit repeatable and non-volatile electrically bistable properties. Furthermore, the potential of stacking several memory layers on top of each other exists, thus drastically increasing their density, which is unlike the case for non-volatile memories based on inorganic materials. These results demonstrate a promising electrically bistable device for use in non-volatile memory applications.

![Graph showing typical frequency dependence of the device capacitance in both the ON and OFF states.](image)

Figure 4. Typical frequency dependence of the device capacitance in both the ON and OFF states.

![Graph showing log(I/V) versus V^1/2 for the device.](image)

(a) Log(I/V) versus V^1/2 fitting on/off current

(b) Log(I/V) versus V^1/2 fitting

Figure 5. Analysis of I-V characteristics for the device in the a) high-conductivity and b) low-conductivity states.
Experimental

The device fabrication procedure involved deposition of Al (0.2 nm in width and 75 nm in thickness) on thoroughly cleaned glass substrates by thermal evaporation under vacuum (below $6 \times 10^{-5}$ torr; 1 torr = 133 Pa) to form the bottom electrode. Before spin-coating the composite layer, the substrates were exposed to UV–ozone treatment for 15 min. Then, the polymer film was formed by spin-coating a 1.2-dichlorobenzene solution of 1.2 wt.-% polystyrene and 0.8 wt.-% TTF and PCBM. The film was thermally annealed at 80°C for 30 min. The thickness of the organic film was about 50 nm. The surface of the organic film was investigated by atomic force microscopy and surface scans. These showed a uniform surface with 5 Å root-mean-square roughness. Finally, 75 nm of Al was deposited as the top electrode, resulting in the Al/organic composite film/Al sandwich structure of the memory cells. The thickness of the organic layer and the metal electrodes were calibrated with a Dektak 3030 thickness profilometer. The active device area, which is defined as the overlap area of the bottom and top electrodes, was 0.04 mm². The current–voltage (I–V) characteristics of the devices were measured with a Hewlett Packard 4155B semiconductor analyzer. The capacitance measurements were carried out with an HP 4284 A Precision LCR Meter. The write–read–erase cycles were measured by a programmable Keithley 2400 source meter and recorded with a four-channel oscilloscope (Tektronix TDS 460A). All the electrical measurements were performed in a vacuum lower than $1 \times 10^{-5}$ torr at room temperature.

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