Thiophene and Selenophene Donor-Acceptor Polyimides as Polymer Electrets for Nonvolatile Transistor Memory Devices

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Introduction

The configuration of OFET memory devices is a conventional transistor with an additional polymer electret between a semiconductor layer and dielectric layer. Polymer electrets are dielectric materials with a long-term charge storing ability or electrostatic polarization, including ferroelectric polymers[1], polymer composites[2], and non-conjugated polymer. Donor-acceptor polymers can enhance the charge storages through the induced intramolecular charge transfer (ICT) from the donor to acceptor moiety under an applied electric field. However, such class of polymers has not been explored as polymer electret for OFET memory devices. We report the memory behavior of *n*-type *N,N'*-bis(2-phenylethyl)-perylene-3,4:9,10-tetracarboxylic diimide (BPE-PTCDI) based OFET memory devices using polyimide electrets. The polyimide electrets, PI(APSP-6FDA) and PI(APST-6FDA), are consisted of electron-donating 2,5-Bis(4-aminophenylenesulfanyl)selenophene (APSP) or 2,5-Bis(4-aminophenylenesulfanyl)thiophene (APST) and electron-accepting 4,4'-(hexafluoroisopropylidene)diphthalic anhydride (6FDA). For comparison, poly (4,4'-oxydianiline-4,4'-hexafluoroisopropylidenediphthalic anhydride) (PI(ODA-6FDA)) is also used as a polymer electret. The BPE-PTCDI OFET memory device enables the reversible trapping of hole carriers in gate dielectrics. The selenophene and thiophene moieties in PIs are expected to enhance the electron-donating ability.

Results and Discussion

Figure 1 shows the optical absorption spectra of three PIs in solid state films on quartz substrates. The absorption peak maximum wavelengths of PI(APSP-6FDA), PI(APST-6FDA), and PI(ODA-6FDA) are observed at 288 nm (4.31 eV), 299 nm (4.15 eV) and 224 nm (5.54 eV), respectively. They are attributed to the π-π* transition of selenophene (HOMO→LUMO4) (4.38 eV), thiophene (HOMO→LUMO5) (4.68 eV) and oxydianiline (HOMO→LUMO5) (5.55 eV) according to the theoretical analysis. The memory characteristics of PI(APSP-6FDA), PI(APST-6FDA), and PI(ODA-6FDA) were examined through OFET memory devices with a bottom-gate/top-contact configuration using *n*-type BPE-PTCDI as a charge transport layer, as shown in **Figure 2**. The order on the mobility of the BPE-PTCDI devices with different polymer electrets is PI(APSP-6FDA) ($(3.6\pm0.07)\times10^{-3}$ $cm^2V^{-1}s^{-1}$) > PI(APST-6FDA) ($(2.4\pm0.06)\times10^{-3}$ $cm^2V^{-1}s^{-1}$) > PI(ODA-6FDA) ($(1.8\pm0.11)\times10^{-3}$ $cm^2V^{-1}s^{-1}$). It is consistent with the grain size of BPE-PTCDI on the three PIs. The grain size on the PI(APSP-6FDA), PI(APST-6FDA) and PI(ODA-6FDA) surfaces are 205, 136, and 73 nm, respectively. (**Figure 3)**The drain current of **Figure 4** was measured with V_d= 100V. When applied a negative gate bias (V_g = -80 V, V_d= 0 V for 1s), the entire transfer curves of PI(APSP-6FDA), PI(APST-6FDA) and PI(ODA-6FDA) are substantially shifted in the negative direction with threshold voltages (V_{Th}) of -42, -21, and -5 V, respectively. The memory windows between writing and erasing process are 63, 42, and 8 V for PI(APSP-6FDA), PI(APST-6FDA) and PI(ODA-6FDA), respectively, which are probably related to the electron-donating characteristics of the PIs. The strong electron-donating moieties, selenophene and thiophene moieties are able to provide a higher probability to enhance charge transfer than oxydianiline moieties. Furthermore, due to the heavy-atom effect, the selenophene moiety is the stronger donor than thiophene moiety, leading to the more stabilized charge-transferred states in PI(APSP-6FDA). The retention time of the ON and OFF states of the device at a gate voltage of 0 V are maintained for 10^4 s with a high on/off current ratio of around 10^3. (**Figure 5**) The write-read-erase-read (WRER) cycles can be operated over 100 cycles.

Conclusions

We have successfully synthesized two new donor-acceptor PIs, PI(APSP-6FDA) and PI(APST-6FDA), as polymer electrets for BPE-PTCDI-based OFET memory devices. The BPE-PTCDI OFET memory device based on the PI(APSP-6FDA) electret exhibited the highest field-effect mobility and the largest memory window compared to the others because the strong electron-donating led to the efficient charge transfer form BPE-PTCDI to PI(APSP-6FDA), and resulted in largest shifts of threshold voltages. Moreover, PI(APSP-6FDA) or PI (APST-6FDA) transferred the charges from BPE-PTCDI to electrets easier than the oxydianiline moiety of PI(ODA-6FDA). Furthermore, due to the heavy-atom effect, the selenophene moiety is the stronger donor than thiophene moiety, leading to the more stabilized charge-transferred states in PI(APSP-6FDA). The present study suggested that the donor-acceptor polyimide electrets could have potential applications for high performance nonvolatile OFET memory devices.

Reference

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2. Leong, W. L.; Lee, P. S.; Lohani, A.; Lam, Y. M.; Chen, T.; Zhang, S.; Dodabalapur, A.; G. Mhaisalkar, S. *Adv. Mater.* **20**, 2325(2008).

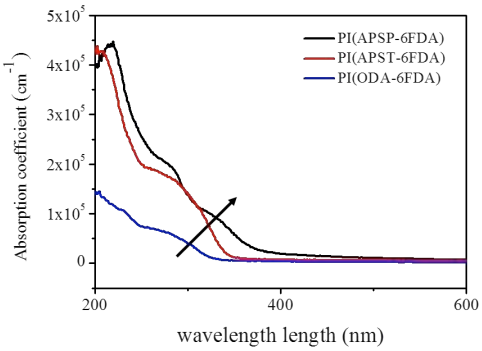

Figure 1. UV-vis absorption spectra of PIs

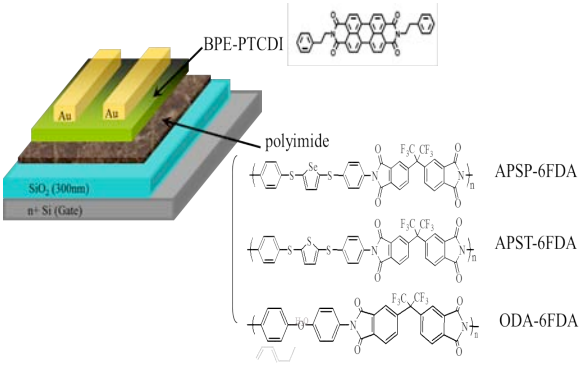

Figure 2. Schematic structure of the BPE-PTCDI thin film based OFET memory device.

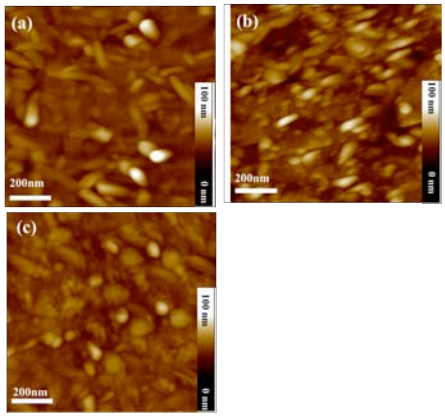

Figure 3. AFM topographic images of pentacene on different polymer surface: (a) PI(APSP-6FDA), (b) PI(APST-6FDA) and (c) PI(ODA-6FDA) on 1 μm x 1 μm area.

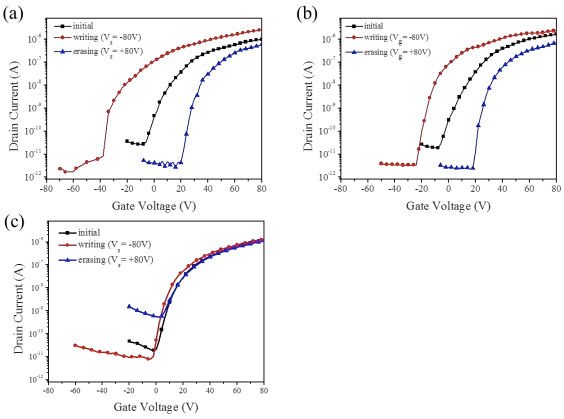

Figure 4. Shifts in transfer curves for BPE-PTCDI OFET memory device with (a)PI(APSP-6FDA), (b) PI(APST-6FDA) and (c) PI(ODA-6FDA) as polymer electrets.

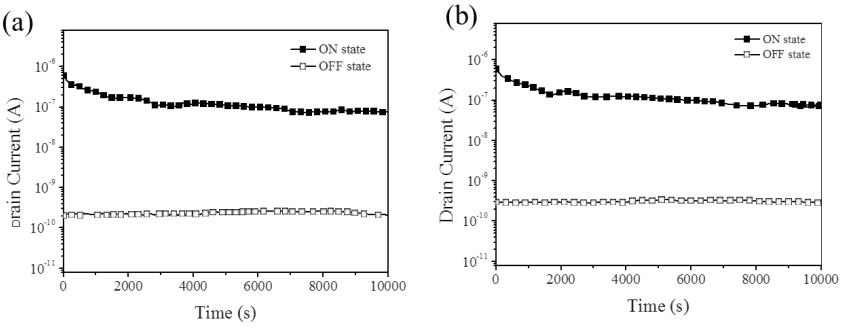

Figure 5. Retention time testing of the OFET memory devices based on BPE-PTCDI thin film with (a) PI(APSP-6FDA) and (b) PI(APST-6FDA) as electrets.