



Tuning non-volatile memory characteristics via molecular doping of polymer semiconductors based on ambipolar organic field-effect transistors

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ABSTRACT

Expandability of organic electronics has stimulated ongoing research for the development of a variety of flexible and/or large-area optoelectronic applications. Among these electronic devices, organic non-volatile memories are emerging as suitable components for solid-state data storage because of their low-cost fabrication, large storage capacity, light weight, and conformable mechanical properties. To fully integrate organic memories with wearable and flexible/stretchable electronic systems, it is important to develop a device in which the properties such as threshold voltage and operating regime are controllable. This leads to improvement in the adaptability of the device to peripheral circuitry and encourages the development of multi-functional organic electronic components. Here, we investigate the tunable electrical properties of charge-trap (electret) memory devices based on organic field-effect transistors, obtained by the doping of an ambipolar polymer semiconductor. The electret memory devices using the doped semiconductor showed a remarkable enhancement in the charge-storage capacity, an excellent charge retention time of more than 10^7 s, and four-fold increase in charge carrier mobility. The improved memory characteristics associated with the controllable molecular doping could pave the way for the development of next-generation memory devices that are compatible with flexible and printed electronic technology.

1. Introduction

Organic non-volatile memories, made of polymers, are promising device components for flexible and printed electronics because of the applicability of simple and cost-effective solution processes on large-area substrates [1–3]. They can also retain the stored information in the absence of power even when the substrate is deformed by mechanical stress [4,5]. Among them, organic flash memories based on organic field-effect transistor (OFET) architecture have been proposed as a possible substitute for conventional silicon-based memory devices. It has been recently demonstrated that these memories are capable of downsizing the cell-size, achieving high data-storage density, fast switching time, and long-term reliability in soft electronic circuits [3,6,7]. Therefore, the development and process optimization of their component materials is of great importance for further enhancing their performances and functions. Although research efforts are mainly focused on the development and the engineering of charge-trap materials,

it is important to study organic semiconductors as well, whose properties are fundamentally related to operating speed, bias and reliability.

Semiconducting ambipolar polymers have been studied extensively over the last ten years [8–10]. In general, these materials have been synthesized with a structure containing a combination of electron rich and electron poor units in the polymer backbone, known as a push-pull structure. This configuration can be used to design low-bandgap (< 2 eV) polymers and modulate the energies of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) [11]. Ambipolar semiconductors show charge transporting properties of both holes and electrons with equal or only slightly different mobilities and threshold voltages [12]. Owing to their ambipolarity, they have a great potential for use in a variety of optoelectronic applications, such as OFETs, complementary-like circuitry, organic light-emitting transistors, light detectors, and organic solar cells [10,12–15]. Obviously, they can provide a much simpler production process with large-area and printing techniques for the fabrication of

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integrated logic circuits, without the individual patterning of each p- and n-type semiconductor regions [8]. Moreover, given the growing importance of reconfigurable electronics and neuromorphic applications, their polarity-reversible behavior has shown an artificial synaptic function in non-volatile memory devices [16]. Nevertheless, unbalanced ambipolarity of the organic semiconductors in OFET-type non-volatile memories often tends to cause an additional operating voltage and a low programmed/erased current state ratio during the reading operation [7,16]. These issues have limited fabrication of integrated circuits using ambipolar semiconductors and caused poor reliability and low energy efficiency in memory operations. Especially, Fermi level (E_F) alignment significantly influences the ambipolar charge transport and the charge-injection barrier height where charges tunnel from the semiconductor to the charge-trap sites.

An approach to manipulate memory operation based on ambipolar semiconductors is to control the concentration of free charge carriers. By increasing the number of free charge carriers, the E_F position shifts toward the corresponding band edges of the semiconductor [17]. The E_F is easily tunable by molecular doping of semiconductors, which is dependent upon the electron accepting or withdrawing properties of dopants. The E_F shift can provide an effective way for reducing the charge injection barriers at the electrode-semiconductor interface [17,18], and modulating the charge-carrier polarity in the channel region and the charge transfer barrier height between the semiconductor and the electret interfaces. Therefore, the threshold voltage (V_{Th}) shifts, which are related to the charge-trap density, and the ON/OFF current ratio in the OFET-based memories could be tuned by varying the doping concentration, independent of both charge trap layer and applied bias.

Here, we report that an efficient doping of organic semiconductors in OFET-based electret memory devices changes the polarity of charge carriers stored in the charge trapping layer and controls the V_{Th} shifts. The doping efficiency of the ambipolar semiconductor is confirmed by the modulation of the electrical properties of the transistor and memory devices, as well as by spectrometry characterization such as Ultraviolet photoelectron spectroscopy (UPS). P-doped organic semiconductor leads to limited ambipolar charge transport behavior, whilst it improves hole-trap density in the memory devices due to its favorable charge transfer barrier between E_F of active layer and trap states in charge storing (electret) layer. The polymer electret-based memory devices using the doped ambipolar semiconductors exhibited excellent endurance during memory operation, long-term charge retention, and a significant increase in the ON/OFF ratio and memory window through controlled V_{Th} .

2. Experimental

2.1. Device fabrication

Source and drain electrodes of Ni/Au (4 nm/14 nm) were patterned on Corning XG glass substrates by a conventional photolithographic process. Top-gate/bottom-contact (TG/BC) OFETs and electret memory devices were fabricated on the Au-patterned glass substrates, which

were ultrasonically cleaned in deionized water, acetone and isopropyl alcohol, and dried by nitrogen blow down. This was followed by ultraviolet-ozone treatment for 20 min. Poly[2,5-bis(2-decyltetradecyl)pyrrolo[3,4-c]pyrrole-1,4(2*H*,5*H*)-dione-*alt*-5,5'-di(thiophene-2-yl)-2,2'-(*E*)-2-(2-(thiophen-2-yl)vinyl)thiophene] (PDVT-10) was purchased from 1-material and used as received. PDVT-10 was dissolved in dichlorobenzene (3 mg mL⁻¹) and deposited by spin-coating (1500 rpm for 60 s) with ~15 nm thickness on the glass substrates, and then annealed at 250 °C for 30 min on a hotplate in a nitrogen-filled glove box to remove the residual solvent and to induce a favorable molecular ordering in the thin-film. To prepare the bi-layered dielectric films consisting of charge-trap (Poly(2-vinylnaphthalene); PVN) and charge-blocking (Poly(vinylidene fluoride-trifluoroethylene); P(VDF-TrFE)) layers, the polymers were dissolved in 2-butanone (with a concentration of 5 mg mL⁻¹) and acetonitrile (30–40 mg mL⁻¹), respectively. These solutions were spin-coated at 2000 rpm for 60 s with ~30 nm thick PVN and ~270 nm thick P(VDF-TrFE) layers, and thermal annealed at 80 °C for 1 h and at 60 °C for 15 min, respectively. The formed films onto each layer were obtained by a careful choice of the orthogonal solvents, which do not damage or dissolve the underlying layers during spin-coating. Finally, a 40-nm-thick aluminum gate electrode was thermally evaporated onto the dielectric film through a metal shadow mask.

2.2. Characterization

OFETs and non-volatile charge trap memory characteristics were measured using a Keithley 4200-SCS in a N₂ glovebox. The thickness of the dielectric films was measured using an XP-1 surface profiling equipment (Ambios Technology, Inc.). Ultraviolet photoelectron spectroscopy (UPS, AXIS-NOVA (KRATOS Inc.)) was used to determine the E_F of the semiconducting thin films with various doping ratios. The UPS spectra were measured using a monochromatic Al-K α photon source with an analyzer pass energy set to 5 eV for He I.

3. Results and discussion

Fig. 1a shows the schematic of an organic electret memory device (OEM) based on the TG/BC architecture, which offers partially intrinsic charge transport behavior of organic semiconductors due to its low contact resistance and protection the semiconductor layer from the ambient air by self-encapsulation [19,20]. In recent years, OEMs have been demonstrated following the development of various polymer electrets [21]. They have a device structure similar to those of conventional flash memories, in which the ON and OFF-states are defined by the trapping of charge carriers in a floating gate inside the dielectrics. Here, PVN, a representative electret material, acted as the charge trapping layer in the OEMs [4,7]. Charge carriers can be stored in the electret layer for long periods of time, and the stored charges induce a quasi-permanent V_{Th} shifts in the OEMs. PDVT-10, whose molecular structure is shown in Fig. 1b, was chosen as a polymer semiconductor, because it offers ambipolar charge-transport

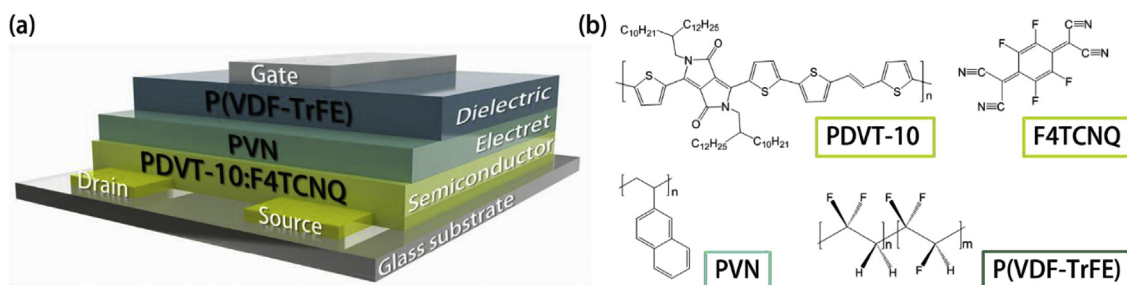


Fig. 1. (a) Illustration of the TG/BC OFET-type electret memory device structure on glass substrate and (b) chemical structures of PDVT-10 semiconducting polymer, F4TCNQ dopant, P(VDF-TrFE) polymer dielectric, and PVN polymer electret (counter-clockwise from top-left).

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