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Effect of the Addition of Soluble Fullerene Derivatives to the Charge Storage Layers of Solution-Processed Optical Organic Transistor Memories

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Abstract

The effect of the addition of soluble fullerene derivatives to polymer insulator/small-molecule semiconductor composite charge storage layers on the performances of solution-processed organic transistor memories has been investigated. It is found that the addition of soluble fullerene derivatives allows to improve hole transport properties and achieve a large threshold voltage shift of over 35 V by programming under light illumination. The obtained performances can be useful to develop printable organic image sensing devices capable of multi-level data.

1. Introduction

Exploring the optical memory functions of organic field-effect transistors (OFETs) with floating-gate structures are attracting for developing flexible and printable memories capable of storing multi-level data including continuously-varying optical signals. This feature can be applied to organic image sensing devices. In recent years, organic memories using top-gate/bottom-contact (TG/BC) OFETs [1] have attracted growing interest because of their good compatibility with various coating and printing technologies. In previous studies, we have found that the combination of polymer-based TG/BC OFETs and vertical phase separation that appeared in insulating polymer/small-molecule semiconductor composite films enable to fabricate OFET memories with organic floating gates by spin-coating processes [2]. We have shown that the addition of a small amount of a soluble fullerene derivative of [6,6]-phenyl-C_{61}-butyric acid methyl ester (PCBM) to the composite film consisting of poly(methyl methacrylate) (PMMA) and 6,13-bis(triisopropylsilylethynyl)pentacene (TIPS-pentacene) facilitate to enhance the memory characteristics of OFET memories based on poly(3-hexylthiopehene) (P3HT) under light illumination [3].

In this study, we investigate the effect of the addition of soluble fullerene derivatives on the optical memory characteristics of solution-processed TG/BC OFET memories based on poly[2,5-bis(3-tetradecylthiophen-2-yl)thieno[3,2-b] thienophene] (PBTTT) to enhance memory functions.

2. Experimental

Figure 1 shows the device structure of solution-processed TG/BC OFET memories developed in this study. Au source and drain electrodes with thin Cr adhesion layers were defined on glass substrates by photolithography. After the substrates were cleaned in an ultrasonic bath with acetone and isopropanol and by a UV/O_3 cleaner, the surface of Au source-drain electrodes was modified with a hole injecting self-assembled monolayer of pentafluorobenzenethiol (PFBT). After the warm dichlorobenzene solution of regio-regular PBTTT was spin-coated onto the substrates, the fabricated thin films were annealed in vacuum at 180 °C for 5 min. To fabricate the floating-gate structure on the PBTTT films, PMMA and TIPS-pentacene were mixed with a small amount of PCBM or [6,6]-diphenyl-C_{62}-bis(butyric acid methyl ester) (Bis-PCBM) in a weight ratio of 80:17:3. These mixtures were dissolved in *n*-butyl acetate (an orthogonal solvent for PBTTT) and spin-coated on the PBTTT films, and the resulting films were dried at 100 °C for 10 min under a N_2 atmosphere. Then, CYTOP was spin-coated as the gate insulator. After Al gate electrodes were fabricated on the CYTOP film via shadow mask evaporation, the organic layers outside the active areas of the devices were removed by O_2 plasma etching using the Al gate electrodes as etching masks to isolate the memory devices. Finally, the fabricated memory devices were heated to 60 °C under vacuum for over 1 h to remove dopants such as oxygen and water from the PBTTT films. For comparison, we fabricated PBTTT FET devices with PMMA/CYTOP layers, PMMA:TIPS-pentacene (80:20)/CYTOP layers, and PMMA:PCBM (97:3)/ CYTOP layers in the same manner.

The memory characteristics were investigated in the dark and under blue LED light (center wavelength: 469 nm), which were exposed onto the backsides of the devices.

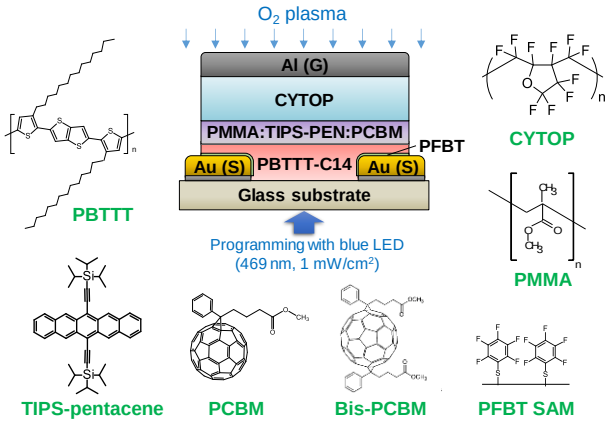

Fig. 1. Device structure of a solution-processed top-gate/bottom-contact PBTTT FET memory with the PMMA:TIPS-pentacene:PCBM (or Bis-PCBM) (80:17:3) composite film and the chemical structure of organic materials.

3. Results and discussion

Figure 2(a) shows the transfer characteristics of PBTTT FETs having PMMA insulators containing different small-molecule semiconductors. The drain current of FET devices is decreased when TIPS-pentacene molecules are added to PMMA insulators, while the devices PMMA:PCBM composite films exhibit higher drain current. Such behavior can be attributed to the difference in the HOMO levels of TIPS-pentacene and PCBM [Fig. 2(b)]. Since the HOMO level of PBTTT is comparable to that of TIPS-pentacene and much smaller than that of PCBM, hole transport in the PBTTT layer can be only affected by trapping of holes into the HOMO level of TIPS-pentacene. However, we observe that the addition of PCBM to PMMA:TIPS-pentacene composite films suppresses the decrease in the drain current of FET devices. The results strongly suggest that the addition of PCBM causes a large change in the phase-separated structure of the PMMA:TIPS-pentacene composite film. We consider that PCBM molecules tend to segregate to the bottom of composite films because of a larger molecular weight of PCBM than TIPS-pentacene. The addition of PCBM can enhance the segregation of TIPS-pentacene molecules toward the surface of composite films and hence reduce hole trapping into TIPS-pentacene molecules.

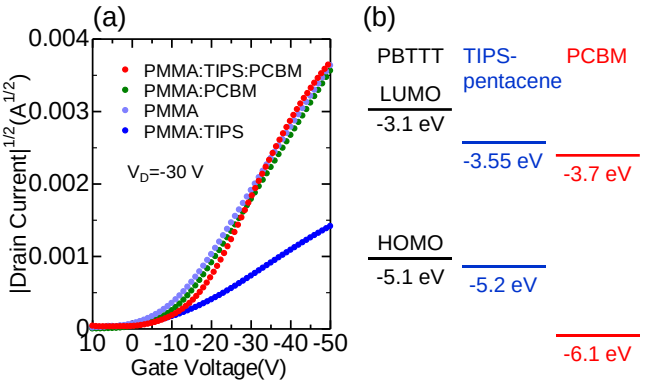

Fig. 2. (a) Transfer characteristics of PBTTT FET devices with different composite films. (b) Energy band diagram of organic semiconductor materials.

Figures 3(a) and (b) show the transfer characteristics of TG/BC PBTTT FET memories with the PMMA:TIPS-pentacene (80:20) and PMMA:TIPS-pentacene:Bis-PCBM (80:17:3) composite films before and after programming and erasing, respectively. The transfer curves shift to the positive direction from the initial states when a positive gate voltage (V_G) of 60 V is applied under light illumination for programming, indicating that photogenerated electrons at the PBTTT film are stored at the LUMO level of TIPS-pentacene floating gates. We found that the shift of threshold voltage (V_{th} shift) after programming and erasing is significantly increased by the addition of a small amount of PCBM or Bis-PCBM to PMMA:TIPS-pentacene composite films. The devices with the PMMA:TIPS-pentacene:PCBM composite films show a V_{th} shift of approximately 35 V [4], while the amount of V_{th} shift of the devices with the PMMA:TIPS-pentacene:Bis-PCBM composite films increases over 40 V.

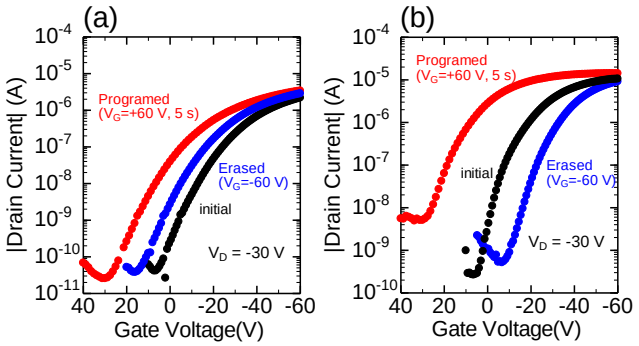

Fig. 3. (a) Programming and erasing characteristics of PBTTT FET memories with (a) PMMA:TIPS-pentacene (80:20) and (b) PMMA:TIPS-pentacene:Bis-PCBM (80:17:3) composite films.

Figures 4(a), (b), and (c) show the atomic force microscope (AFM) images of the PMMA:TIPS-pentacene (80:20), PMMA:TIPS-pentacene:PCBM (80:17:3), and PMMA:TIPS-pentacene:Bis-PCBM (80:17:3) composite films fabricated on PBTTT films, respectively. The obtained results suggest that the addition of Bis-PCBM enhances the vertical phase separation of PMMA and TIPS-pentacene and increases the number of TIPS-pentacene molecules that work as the floating gates. A mechanism of the enhanced phase separation is unclear at present. However, the intercalation of small molecules between the alkyl side chains of PBTTT molecules is possibly related to the observed behavior. It has been reported that the larger size of Bis-PCBM than that of PCBM reduce the intercalation of the alkyl side chains of PBTTT molecules [5], which can contribute to the increase in the number of TIPS-pentacene floating gates by the addition of Bis-PCBM to PMMA:TIPS-pentacene composite films.

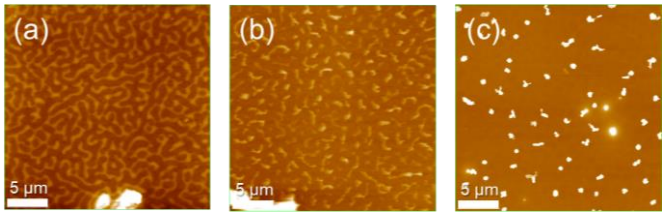

Fig. 4. AFM images of PMMA:TIPS-pentacene (80:20), PMMA:TIPS-pentacene:PCBM (80:17:3), and PMMA:TIPS-pentacene:Bis-PCBM (80:17:3) composite films formed on PBTTT films.

Acknowledgements

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