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Enhancement of Optical Memory Characteristics of Solution-Processed Organic Transistor Memories with Polymer-Small-Molecule Composite Charge Storage Layers

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ABSTRACT

The use of soluble polymer-small molecule composites to polymer-based top-gate organic transistors can facilitate the solution processing of nonvolatile organic memories. We found that the addition of soluble fullerene derivatives to PMMA:TIPS-pentacene composite films allows achieving a large threshold voltage shift of over 40 V by photo-assisted programming.

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 with multi-level data storage capacities and large-area organic image sensors with simple pixel configurations. However, the solution processing of floating-gate OFET memories is generally difficult because the solution process includes the fabrication of multiple organic layers without mixing with interfaces of soluble organic materials. In previous study, we have shown that the combination of polymer-based top-gate OFETs and vertical phase separation behavior in solution-processed polymer/small-molecule composite films enables to fabricate OFET memories with organic floating gates by simple solution processes [1]. We have found that the addition of a soluble fullerene 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(triiso propylsilylethynyl)pentacene (TIPS-PEN) enhances vertical phase separation in the composite film and improves the memory characteristics of floating-gate OFETs based on poly(3-hexylthiopehene) (P3HT) under light illumination [2].

In this paper, we report on the carrier transport and optical memory characteristics of solution-processed floating-gate OFET devices using poly[2,5-bis(3-tetra decylthiophen-2-yl)thieno[3,2-b]thienophene] (PBTTT) as the semiconductor layer. We observe that the decrease in the carrier mobility of the PBTTT FET memories using PMMA:TIPS-PEN composite films can be suppressed by the addition of PCBM to the composite films. Solution-processed floating-gate OFET memories containing [6,6]-diphenyl-C_{62}-bis(butyric acid methyl ester) (Bis-PCBM) exhibit a large threshold voltage shift (V_{th} shift) of over 40 V by programming under light illumination, which can be useful for the development of organic image sensing devices with good solution processability.

2. EXPERIMENTS

Figure 1 shows the device structure of a solution-processed top-gate OFET memory. The Au source and drain electrodes having thin Cr adhesion layers were defined on glass substrate by photolithography. After the surface of Au electrodes was modified with a self-assembled monolayer of pentafluorobenzenethiol (PFBT), the organic semiconductor layer was fabricated by spin-coating a 80 °C dichlorobenzene solution of PBTTT and subsequent thermal annealing at 180 °C. To fabricate the floating-gate structure on the PBTTT film, PMMA, TIPS-PEN, and PCBM (or Bis-PCBM) (weight ratio of 80:17:3) were dissolved in *n*-butyl acetate (an orthogonal solvent for PBTTT) and spin-coated on the PBTTT films. After annealing the composite film at 100 °C, a CYTOP gate insulator and Al gate electrodes were deposited by spin-coating and shadow mask evaporation, respectively. For comparison, we fabricated PBTTT FET devices with PMMA/CYTOP layers, PMMA:TIPS-PEN (80:20)/CYTOP layers, and PMMA:PCBM (97:3)/CYTOP layers.

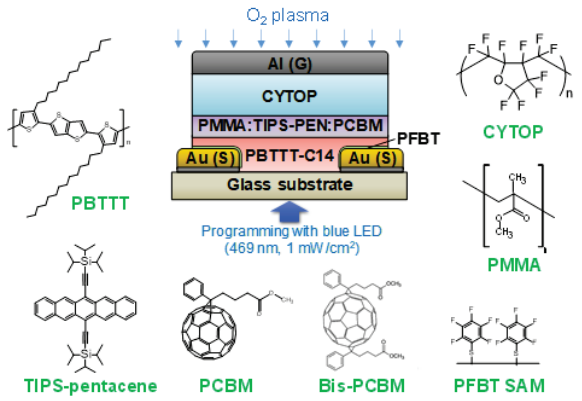

Fig. 1 Structure of a solution-processed top-gate PBTTT FET memory with the PMMA:TIPS-PEN:PCBM (or Bis-PCBM) (80:17:3) composite film.

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 with PMMA:PCBM composite films exhibit higher drain current. Such behavior can be explained by the difference in the HOMO levels of TIPS-PEN and PCBM [Fig. 2(b)]. Since the HOMO level of PBTTT is comparable to that of TIPS-PEN 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-PEN. Interestingly, we observe that the addition of PCBM to PMMA:TIPS-PEN composite films suppresses the decrease in the drain current of FET devices, indicating the improvement of the hole mobility of the PBTTT FET memories.

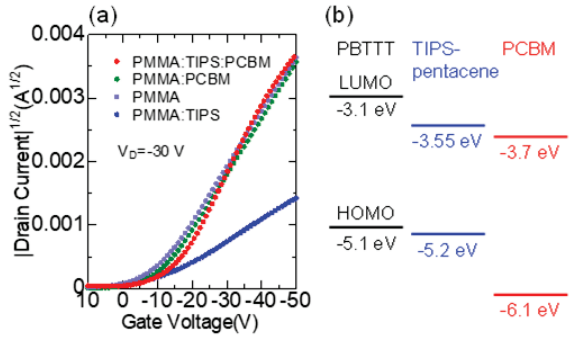

Fig. 2 (a) Transfer characteristics of PBTTT FET devices with different composite films. (b) Energy band diagram of organic semiconductor materials.

Figures 3(a) and (b) show the transfer characteristics of top-gate PBTTT FET memories with the PMMA:TIPS-PEN (80:20) and PMMA:TIPS-PEN: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 blue LED light (469 nm, 1 mW/cm^2) for programming, indicating that

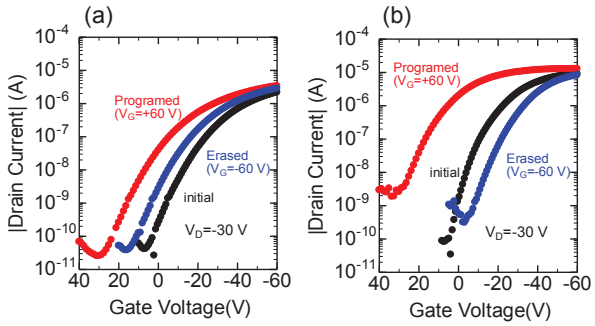

Fig. 3 Programming and erasing characteristics of PBTTT FET memories with (a) PMMA:TIPS-PEN (80:20) and (b) PMMA:TIPS-PEN:Bis-PCBM (80:17:3) composite films.

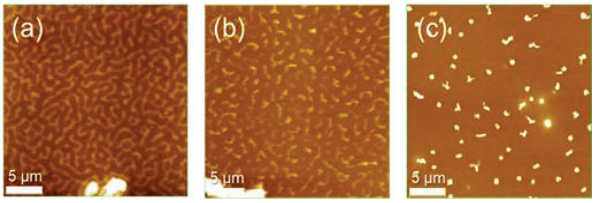

Fig. 4 AFM images of (a) PMMA:TIPS-PEN (80:20), (b) PMMA:TIPS-PEN:PCBM (80:17:3), and (c) PMMA:TIPS-PEN:Bis-PCBM (80:17:3) composite films formed on PBTTT films.

photogenerated electrons at the PBTTT film are stored at the LUMO level of TIPS-PEN floating gates. We observed that the amount of V_{th} shift after programming and erasing is significantly increased by the addition of PCBM or Bis-PCBM to PMMA:TIPS-PEN composite films. The devices with the PMMA:TIPS-PEN:PCBM composite films show a V_{th} shift of 33.7 V on average, while the V_{th} shift of the devices with the PMMA:TIPS-PEN:Bis-PCBM composite films increases to 40.9 V.

Figures 4(a), (b), and (c) show the atomic force microscope (AFM) images of the PMMA:TIPS-PEN (80:20), PMMA:TIPS-PEN:PCBM (80:17:3), and PMMA:TIPS-PEN:Bis-PCBM (80:17:3) composite films formed on PBTTT films, respectively. The obtained results suggest that the addition of soluble fullerenes enhances vertical phase separation and increases the number of TIPS-PEN molecules that work as the floating gates. Such behavior is likely to be due to the larger molecular weight of soluble fullerenes than TIPS-PEN, leading to the segregation of TIPS-PEN molecules toward the surface of composite films. The segregation is consistent with the improvement of hole mobility observed in the memory devices containing soluble fullerenes. We consider that a large change of film morphology by the addition of Bis-PCBM can be related to the difference in the degree of the intercalation of PCBM and Bis-PCBM in PBTTT films [3,4]. It has been reported that the larger size of Bis-PCBM than PCBM reduce the intercalation between the alkyl side chains of PBTTT molecules [4], which can contribute to the enhancement of vertical phase separation in PMMA:TIPS-PEN:Bis-PCBM composite films.

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