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# Solution-processed top-gate nonvolatile organic transistor memory devices with soluble fullerene-polymer composite as charge storage layers

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**Abstract**

**Top-gate organic transistor memory with solution-processed organic layers is presented. Soluble fullerene molecule of [6,6]-phenyl-$C_{61}$-butyric acid methyl ester is employed as an organic nano-floating gate electrode and dispersed in poly(methyl methacrylate) to form charge storage layers. Top-gate poly(3-hexyl thiophene)-based organic transistors with the charge storage layers exhibit writing and erasing characteristics with reversible threshold voltage shifts and nonvolatile memory behavior with retention time more than 1 h.**

## 1. Introduction

To realize flexible electronic devices, there is considerable interest in the development of nonvolatile memories based on organic field-effect transistors (OFETs) because of their low cost, light weight, and high flexibility. As well as flash memories in inorganic memories, OFETs with floating-gate electrodes are one of important class of rewritable organic memories, and the fabrication of OFET memories using metallic and semiconducting nanoparticles as nano-floating gates has been studied [1-3]. Recently, nano-floating gates made of semiconducting small molecules have attracted growing interest because of their high compatibility with various solution processes, such as spin coating and ink-jet printing, and a large variety of material selections [4,5]. However, solution-processing of floating-gate OFET memories is technologically difficult since it includes the solution deposition of a number of organic layers, and OFETs memories based on solution-processable organic materials have not been well developed. Moreover, most OFET memories have adopted top-contact configurations; however, it is desirable to employ bottom-contact configurations from the viewpoint of miniaturization of the source-drain electrodes of OFET memories. Especially, the use of top-gate/bottom-contact (TG/BC) configurations in solution-processed OFETs has been found to allow extracting high carrier mobility and high electrical stability without surface treatments of substrates [6,7], which is commonly used for high-performance bottom-gate OFETs.

In this study, we develop a TG/BC floating-gate OFET memory with good solution processability using soluble fullerene molecules dispersed in an insulating polymer as the charge storage layer. The device fabrication is simple, and all of organic layers are fabricated by the conventional spin-coating method. The nonvolatile memory operations in solution-processed OFET memory devices are investigated.

## 2. Experimental

Figure 1 shows the schematic structure of solution-processed TG/BC OFET memory device, together with chemical structures of organic materials. For the floating gate material, we used a soluble fullerene derivative of [6,6]-phenyl-$C_{61}$-butyric acid methyl ester (PCBM), which was dispersed in an insulating polymer of poly(methyl methacrylate) (PMMA) at low concentrations. The p-type polymer semiconductor of regioregular poly(3-hexyl thiophene) dissolved in anhydrous chlorobenzene was spin-coated on glass substrates having pre-fabricated Au source-drain electrodes on the surfaces. After thermal annealing of the P3HT layer, the PMMA:PCBM composite layer was deposited on the P3HT surface by spin coating using an orthogonal solvent for P3HT (*n*-butyl acetate), which prevents interfacial mixing among these layers [6,7]. Then, a fluoropolymer of CYTOP dissolved in a fluorinated solvent was spin-coated onto the composite film to form gate insulators. Finally, Al gate electrodes were defined on the CYTOP layer by shadow mask evaporation. The fabrication of organic layers and electrical measurements of the devices were carried out in a $N_2$-filled glove box.

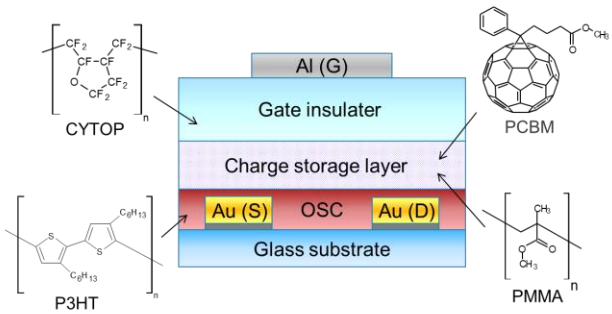


Fig. 1. Schematic structure of solution-processed TG/BC OFET memory device.

## 3. Results and discussion

Figures 2(a) and 2(b) show the transfer characteristics of the TG/BC P3HT FET with PMMA/CYTOP double layers (without PCBM) measured at the different ranges of gate voltage $V_G$ = 60 ~ −20 V and 20 ~ −60 V, respectively. Both transfer curves show negligible hysteresis between the forward and reverse sweeps of $V_G$, indicating that PMMA does not work as a storage layer for holes and electrons.

Figures 3(a) and 3(b) show the transfer characteristics of the top-gate P3HT FET with PMMA:PCBM (95:5) composite film measured as the positive and negative $V_G$ is increased by 10 V, respectively. The transfer curves show large positive shifts when the positive $V_G$ is applied, while the transfer curves are almost unchanged by the negative $V_G$ application. These results can be explained on the basis of the band diagram of the device shown in Fig. 4. The energy level of lowest unoccupied molecular orbital (LUMO) of PCBM is deeper than that of P3HT, and electrons injected to the LUMO of P3HT allow to transfer to PCBM for application of the positive $V_G$, which leads to the excess accumulation of holes in the P3HT layer and hence results in the positive shift of transfer curves. Also, PCBM has deeper highest occupied molecular orbital (HOMO) compared to that of P3HT, which results in a less influence of hole trapping into PCBM on hole transport through the HOMO of P3HT.

Figures 5(a) and 5(b) show the typical transfer characteristics after writing and erasing, and retention characteristics of top-gate P3HT FETs with PMMA:PCBM (97:3) composite films, respectively. The devices exhibit a threshold voltage shift ($\Delta V_{th}$) of ~18 V between writing and erasing and nonvolatile memory behavior with the retention time more than 3600 s (1 h), which is almost comparable to previously reported for other OFET memories with nanoparticles [1,3]. The observed small on/off current ratio is likely attributed to a relatively shallow HOMO level of P3HT and tuning of the energy levels of organic materials can lead to further improvement in retention characteristics.

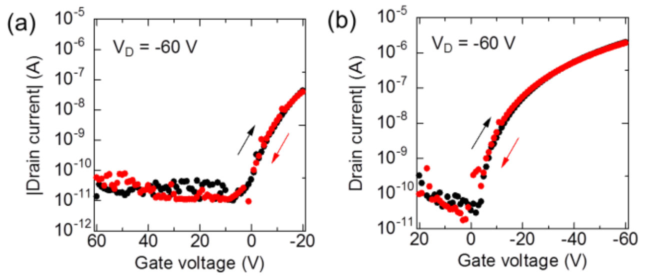


Fig. 2. Transfer characteristics of fabricated TG/BC P3HT FET memory with PMMA/CYTOP double layers measured at (a) $V_G$ = 60 ~ −20 V and (b) 20 ~ −60 V.

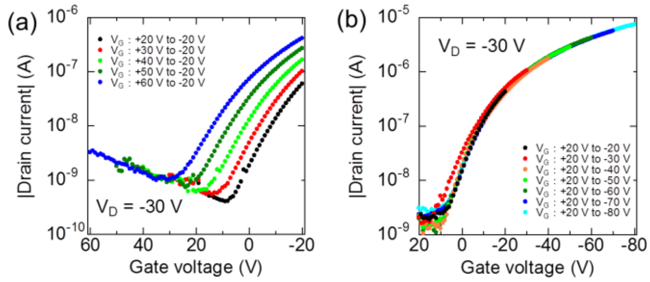


Fig. 3. Transfer characteristics of fabricated top-gate P3HT FET memory with PMMA:PCBM composite film measured for (a) positive and (b) negative $V_G$ applications.

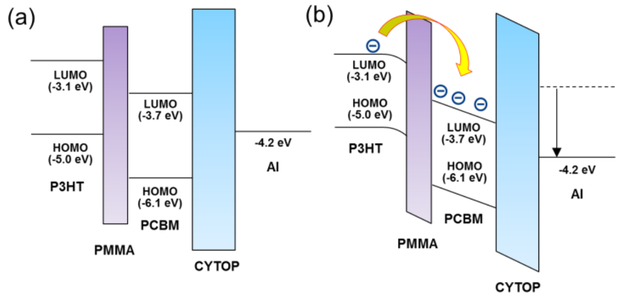


Fig. 4. Energy band diagrams of TG/BC P3HT FET memory with PMMA:PCBM composite film for (a) initial state and (b) $V_G > 0$.

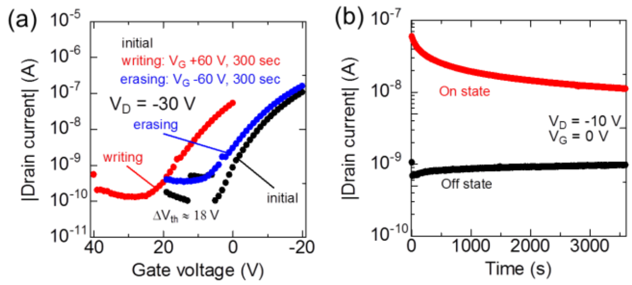


Fig. 5. (a) Writing and erasing, and (b) retention characteristics of top-gate P3HT OFET memory with PMMA:PCBM (97:3) composite film.

## 4. Conclusions

We have fabricated TG/BC floating-gate OFET memories using the spin-coating method and investigated memory characteristics of the devices. The results show that the solution-processed PMMA:PCBM composite film works as an electron storage layer resulting from the floating-gate function of PCBM molecules. The developed method can offer a way to fabricate the nonvolatile and rewritable OFET memories by simplified solution processes.


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