

Using Self-Assemble-Monolayer on Nanopore Sidewalls to Fabricate Vertical Polymer Transistors with High Output Current

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1. Introduction

Improving carrier mobility in conjugated polymer is critical for the development of low-cost and high-performance organic photovoltaics (OPVs) and organic field-effect transistors (OFETs). Charge transport in conjugated polymers is anisotropic [1-3]. Field-effect hole mobility in regioregular poly(3-hexylthiophene) (RR P3HT), one of the most promising conjugated polymers, is higher than $0.1 \text{ cm}^2/\text{Vs}$ along the polymer backbone and the π - π orbital stacking and is lower than $2 \times 10^{-4} \text{ cm}^2/\text{Vs}$ along the insulating side chain [2,3]. Controlling chain orientation and improving molecule ordering are of great importance if we want to obtain high carrier mobility in the desired current flow direction. It is well known that P3HT molecules exhibit three possible orientation, they are edge-on, face-on and vertical orientations (Fig. 1a) [4]. For OPVs and organic vertical transistors, face-on or vertical orientations are preferred to improve the carrier transport in vertical direction.

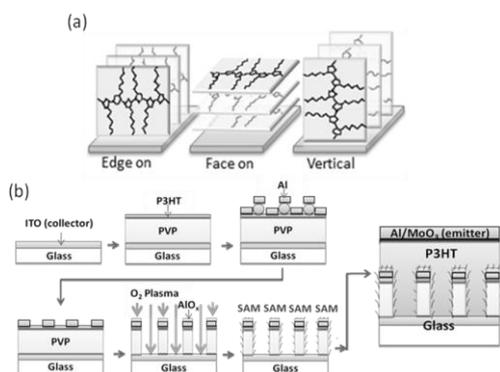


FIG. 1 (a) Schematic diagram of edge-on, face-on, and vertical orientation of P3HT molecules. (b) The process flow chart of vertical polymer transistors.

2. Method and Experiment

Methods

The vertical orientation is achieved based on the interaction between the sidewall and the polymer chains, treating self-assemble-monolayer (SAM) on the sidewalls may enhance the vertical chain alignment [4]. In this work, we present the experiment that use different SAM including HMDS (short alkyl chain), OTS-8 (medium alkyl chain), and OTS-18 (long alkyl chain) on sidewall of nanopores to improve the vertical hole mobility in P3HT.

Experiment

The process flow to prepare the nanopore template, to perform SAM treatment, and to fabricate the vertical transistor is shown in Fig. 1b. In this study, except conventional spin coating, we also use blade coating without spinning to deposit P3HT. The vertical transistor, named as the space-charge-limited transistor (SCLT), operates like a solid-state vacuum tube [5].

3. Results and Discussion

In SCLTs, the $J_C - V_{CE}$ plots of spin-coated P3HT EC diodes without and with OTS-18 treatment are compared in Fig. 2a. The P3HT thickness is around 450 nm. For spin-coated P3HT nanorod diode without SAM treatment (STD, spin coating), output current density is lower than $1 \text{ mA}/\text{cm}^2$ at $V_{CE} = -3 \text{ V}$. After using OTS-18 to treat the nanopore template, spin-coated P3HT diode delivers an output current density as $16.4 \text{ mA}/\text{cm}^2$ at $V_{CE} = -3 \text{ V}$. The $J_C - V_{CE}$ plots of blade-coated P3HT EC diodes without and with OTS-18 treatment are compared in Fig. 2b. The output currents of blade coated P3HT EC diodes are larger than those of spin coated P3HT EC diodes. With a P3HT thickness as 450 nm, the output current densities at $V_{CE} = -3 \text{ V}$ for STD (no SAM treatment) and OTS-18-treated blade-coated P3HT diodes are $6.8 \text{ mA}/\text{cm}^2$ and $31.6 \text{ mA}/\text{cm}^2$, respectively.

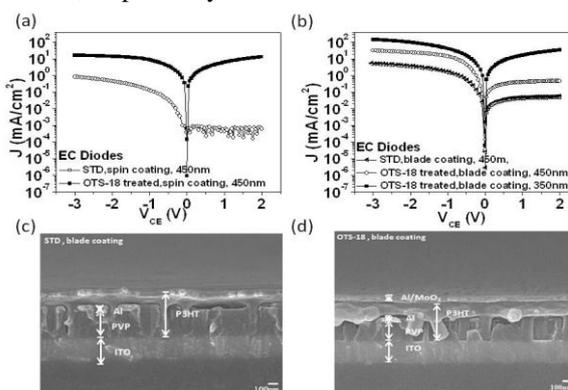


FIG. 2 (a) The $J_C - V_{CE}$ characteristics of spin-coated P3HT EC diodes without and with OTS-18 treatment; (b) The $J_C - V_{CE}$ characteristics of blade-coated P3HT EC diodes without and with OTS-18 treatment. SEM cross-section image of the blade-coated P3HT EC diode without OTS-18 treatment. (d) SEM cross-section image of the blade-coated P3HT EC diode with OTS-18 treatment.

Two reasons are proposed to explain the enhanced output current with OTS-18 treatment.

(1) The improved nanopore filling after SAM treatment. The cross sectional views of the blade-coated P3HT EC diodes without and with OTS-18 treatment are compared in Fig. 2c and Fig. 2d, respectively. Without treating OTS-18, some narrow spacing can be observed at sidewall areas. With treating OTS-18, the edges of the P3HT nanorods fit with the shape of the nanopores very well, indicating an almost completely pore filling and thus giving rise to a good contact between collector electrode and P3HT.

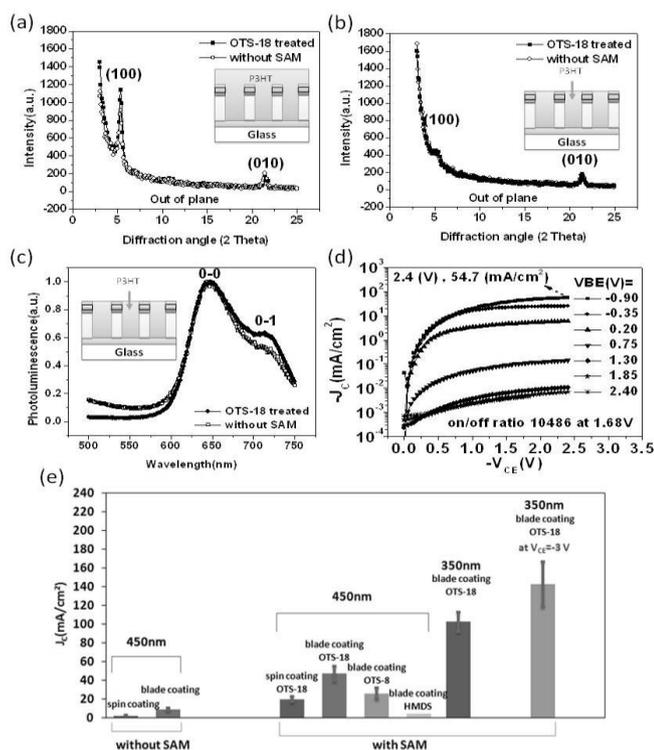


FIG. 3 GIXRD measurement graphs for (a) templates before removing P3HT above the porous templates; (b) templates after using oxygen plasma to etch away P3HT above the porous template. (c) The PL spectra after plasma etching. (d) The J_c - V_{CE} curves of blade-coated SCLT with OTS-18 treatment measured at different V_{BE} . (e) The average output current densities (J_c) measured at $V_{CE}=-2$ V and $V_{BE}=-0.9$ V of various SCLTs.

(2) The improved P3HT chain ordering or vertically aligned chain orientation after SAM treatment. The GIXRD spectra of blade-coated P3HT on STD template and on OTS-18-treated template are shown in Fig. 3a,b. Samples used in this analysis composed of P3HT inside nanopores and P3HT above nanopore structure are compared in the inset of Fig. 3a and Fig. 3b. Reflection of the (100) layer can be observed at $2\theta = 5.4^\circ$ for P3HT, indicating edge-on orientation. The face-on orientation, represented by the reflection of the (010) layer. By observing Fig. 3a and Fig. 3b, it is suggested that the OTS molecules on the top of aluminum grid help to align P3HT molecules with an edge-on orientation above the template. After etching away P3HT above the template, inside nanopores, almost no

edge-on orientation is observed. The face-on orientation is observed but is not dependent on OTS treatment. The vertical orientation is not detectable in out-of-plane GIXRD. In this study, we use photoluminescence (PL) spectroscopy to analyze the molecular packing of the rod-shaped P3HT. The PL spectra of blade-coated P3HT on STD and on OTS-treated templates after plasma etching are compared in Fig. 3c. The 0-0 to 0-1 peak intensity ratio, SR, is usually used as a probe for disorder [6,7]. The 0-0 peak is forbidden by symmetry in aggregates. When disorder occurs, the symmetry is broken to generate 0-0 emission. In Fig. 3c, SR becomes lower for P3HT molecules in OTS-treated nanopores, indicating an improved molecular ordering. In Fig. 3b, we hardly observe edge-on orientation for P3HT inside pores. OTS-18 treatment also not affects the face-on orientation. The only possible mechanism to explain the improved ordering for P3HT in OTS-18-treated pores observed in Fig. 3c is the SAM-enhanced vertical orientation.

Finally, the J_c - V_{CE} curves of blade-coated SCLT with OTS-18 treatment are shown in Fig. 3d, respectively. The on/off current ratio is around 10,000. Then we compare the SCLT characteristics when SCLTs are fabricated on STD (no SAM treatment) template and SAM-treated templates. Three different SAMs including OTS-18, OTS-8, and HMDS are used to fabricate SAM SCLT. Output current densities (J_c) measured at $V_{CE} = -2.0$ V and $V_{BE} = -0.9$ V of various SCLTs are plotted in Fig. 3e.

4. Conclusion

In summary, we present the first experimental results to reveal the importance of using self-assemble monolayer on the sidewall of vertical nanometer pores to increase the vertical conductivity of P3HT inside the nanometer pores. Finally, the SAM-treated vertical P3HT transistor delivers an output current as 50-110 mA/cm² (dependent on P3HT thickness) at 2 V with an on/off current ratio larger than 10,000. Considering the high output current, low operation voltage and high on/off ratio, SAM-SCLT is one of the best solution-processed organic transistors.

References

- [1] G. Gustafsson, O. Inganäs, S. Stafstrom, *Solid State Commun.* **76** (2004) 203.
- [2] H. Sirringhaus, P. J. Brown, R. H. Friend, M. M. Nielsen, K. Bechgaard, et al. *Nature* **401** (1999) 685.
- [3] H. Sirringhaus, R. J. Wilson, R. H. Friend, M. Inbasekaran, W. Wu, et al. *Appl. Phys. Lett.* **77** (2000) 406.
- [4] M. Aryal, K. Trivedi, W. C. Hu, *ACS Nano* **3** (2009) 3585.
- [5] Y. C. Chao, M. C. Ku, W. W. Tsai, H. W. Zan, H. F. Meng, et al. *Appl. Phys. Lett.* **97** (2010) 223307.
- [6] J. Clark, C. Silva, R. H. Friend, F. C. Spano, *Phys. Rev. Lett.* **98** (2007) 206406.
- [7] F. C. Spano, J. Clark, C. Silva, R. H. Friend, *Chem. Phys.* **130** (2009) 074904.