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Trap-Minimized Printed Thin-Film Transistors based on Layered Organic Semiconductors

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ABSTRACT

Herein, we present our recent studies to develop all-printed thin-film transistors (TFTs) that exhibit both high-performance and sharp-switching operations. Our key concept is to take advantage of self-organizing characteristics of highly layered-crystalline organic semiconductors (OSCs) in manufacturing uniform channel layers interfaced with highly lyophobic gate-dielectric surfaces, eventually providing trap-minimized all-printed TFTs.

1 Introduction

Organic electronic materials have a unique advantage over the other semiconducting materials in that they can be processed in solution under ambient conditions. This feature has been investigated to develop various print-production technologies for the scale-up production of electronic/photonic devices under the concept of “printed electronics” technologies.

In this paper, we report our recent studies to develop all-printed organic TFTs that exhibit both high-performance and sharp-switching operations. We first demonstrate that a class of unsymmetrical rod-like organic molecules composed of extended π-electron skeletons (π-cores) linked with relatively long alkyl chains affords excellent OSCs that present exceptionally high layered crystallinity. Many compounds form layered herringbone (LHB) packing motif which is optimal for obtaining two-dimensional semiconductive carrier transport layers. We present and discuss the design and development of this type of solution-processable OSCs [1−12].

Achieving sharp on/off switching at low voltages has been a crucial challenge in printed organic TFTs. It is necessary to reduce carrier traps that are usually generated at semiconductor/gate dielectric interfaces. A use of gate dielectric layers that have very low surface energy should be effective to eliminate interfacial carrier traps, although it becomes quite difficult to produce uniform channel layers on such highly lyophobic gate dielectric surfaces. Recently, we successfully developed “extended meniscus-guided (EMG)” coating technique that allows to manufacture fairly uniform channel OSC layers on the surfaces of highest lyophobic amorphous perfluoropolymer, Cytop, by fully taking advantage of the high layered crystallinity of the OSCs [13]. We demonstrate that the trap-minimized printed TFTs are obtainable by using the unique solution process.

2 Highly Layered-Crystalline OSCs

Fused-ring π-cores based on thienoacenes are the fundamental building block for organic electronics applications. They feature extended π-electronic states over the π-cores, which causes strong intermolecular π–π interactions, thus allowing efficient charge transport. An essential requirement of OSCs for their use in organic TFTs is to involve the high layered crystallinity, because self-organizing architecture such as two-dimensional LHB packing is optimal for achieving ideal semiconductor/gate dielectric interfaces.

Figure 1 presents the unsymmetrical rod-like organic molecules, developed so far [1−7]. Following common and unique features are observed in the compounds: 1) substitution of extended π-cores by alkyl chains (-C_nH_{2n+1}) longer than n = 4~6 is effective to establish unidirectional molecular orientations in the each herringbone (HB) layer (Fig. 2a); 2) unsymmetrical substitution is more favorable than symmetrical one for enhancing the layered crystallinity, because the former forms bilayer-type molecular packing composed of head-to-head alignment of the respective unidirectional HB layers; 3) the other-sided substitution with phenyl ring also contributes to enhance the layered crystallinity by the HB-type arrangement of benzene rings; and 4) density functional theory calculations for the intermolecular interaction energies demonstrate that the crystal stability is more enhanced by the layer formation of longer alkyl chains (Fig. 2b).

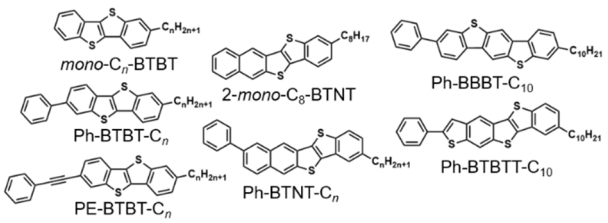

Fig. 1 Molecular structures of developed OSCs [1-8].

The formation of unidirectional HB layer is effective to achieve efficient charge transport, providing OSCs with high intrinsic mobilities ranging between 5~20 cm^2 V^{-1} s^{-1} [9,10]. The layered crystallinity also allows self-organized growth of precursor OSC layers at air-liquid interfaces in the solution process, which affords unique advan tage of OSCs [11]. Furthermore, it is possible to manufacture OSC layers with single-molecular-bilayer thickness over a wide area, by utilizing mixture of OSC molecules with different chain lengths [12].

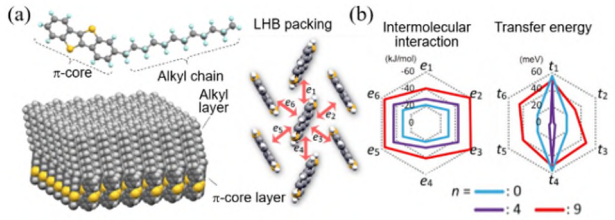

Fig. 2 LHB packing of typical OSCs [1,2].

3 Realizing Sharp-Switching Printed TFTs

A scheme of the EMG coating technique is presented in Fig. 3a [13]. This technique is composed of simple two steps; first, a lyophilic U-shaped metal film is manufactured on the highly lyophobic Cytop surface, and then the OSC solution is swept unidirectionally from the bottom of the U-shape by a conventional blade coating. By the technique, we successfully manufactured highly uniform crystalline OSC thin films covering a wide area of the Cytop surface. The metal films (either printed or vacuum deposited) used in the technique can also be utilized as source/drain electrodes in bottom-gate-bottom-contact (BGBC)-type TFTs.

In the technique, the U-shaped metal film pattern is designed to work both for initiating the OSC film growth and for keeping the meniscus extended on the Cytop surface. By in-situ microscope observations of the film growth, we found that the growing edge of the OSC film is located within the extended meniscus, where the interfacial OSC film, covering through over the air-liquid-solid contact line (Fig. 3b), is responsible for keeping the meniscus extension, eventually leading to the successive film growth. The outer metal film area at the both ends of the contact line also works to prevent the solution meniscus from shrinking against the surface tension on the Cytop surface.

Typical transfer characteristic is shown in Fig. 4a for the BGBC-type printed TFT based on printed Ph-BTNT-C_n single crystal thin film as channel and evaporated Au films as source/drain electrodes. The carrier mobility reached as high as 4.9 (linear regime) and 5.5 cm^2 V^{-1} s^{-1} (saturation regime). Low-voltage operation below 2 V was achieved, along with small turn-on voltage (V_{on}) around 0

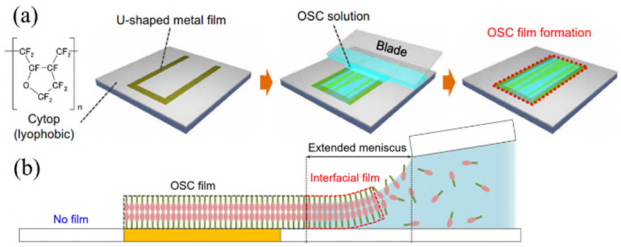

Fig. 3 Scheme of the EMG coating technique [13].

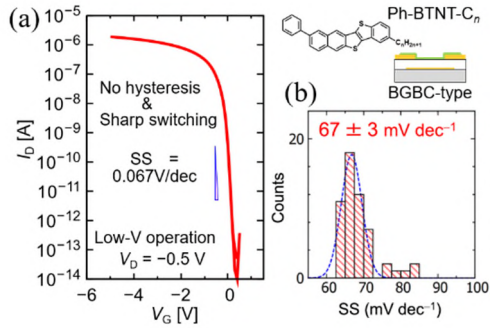

Fig. 4 Transfer characteristics and SS values of printed Ph-BTNT-C_n TFT [13].

V and negligible hysteresis. All the transfer curves exhibited very sharp on/off switching with the subthreshold swing (SS) value at 67 mV dec^{-1} in average, as shown in Fig. 4b. This value is close to the theoretical limit of the SS value (59.6 mV dec-1 at 300 K).

We also manufactured all-printed TFTs with use of ultrafine conductive silver patterns as source/drain and gate electrodes as obtained by the surface photoreactive nanometal printing (SuPR-NaP) technique [14,15]. The Cytop layer works not only as gate dielectric layer, but also as base layer in the SuPR-NaP technique. The obtained devices exhibited sufficiently sharp on/off switching with SS value at about 170 mV dec^{-1}.

4 Conclusion

We have shown that the integrated developments of highly layered-crystalline OSC materials and their thin-film processing allow us to realize high-performance and sharp-switching printed organic TFTs. Considering of unexplored rich combinations between π-cores and substituents, further designability is possible for developing OSCs that show higher performance and functionality for the printed electronics applications. For this goal, we think it is necessary to develop and utilize computer-based designing of highly layered crystalline OSC materials, for accelerating the further developments of all-printed organic TFTs.

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