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Full Length Article

Ambipolar organic transistors with high on/off ratio by introducing a modified layer of gate insulator

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ABSTRACT

Oxotitanium phthalocyanine (TiOPc)-based organic thin-film transistors (OTFTs) were fabricated by introducing *para*-sexiphenyl (*p*-6P) thin-film as the modified layer of gate insulator. The typical ambipolar transport behavior may be observed in ambient, which exhibited a balanced charge transport with a hole mobility of 8×10^{-2} and an electron mobility of 3×10^{-2} cm^2/V.s. More importantly, the on/off ratio for both *n*- and *p*-type accumulation-mode has reached 10^4 and simultaneously exhibited good air-stability. Furthermore, capacitance-voltage characteristics were presented in order to further clarify the operation procedures of two kinds of charge-carriers. The excellent ambipolar transport behavior is attributed to the surface modification properties of *p*-6P for better electron transport and highly ordered thin-film morphology of TiOPc. These results demonstrate that the surface characteristics of insulator play a crucial role in realizing ambipolar devices.

1. Introduction

In recent years, ambipolar organic thin-film transistor (OTFT) has received more attention because it possesses technical advantages including low power dissipation, high signal to noise and simple circuit design [1,2], exhibiting potential applications in flexible complementary logic circuits. In practical operation, most organic semiconducting materials only exhibit unipolar transport properties either electron or hole in a single device. It is still a challenge to realize high-performance ambipolar OTFT. Up to now, three approaches have been reported to achieve ambipolar charge transport. The first approach is to use organic *p*-*n* heterojunction as the active layer of OTFT, which electron and hole can be operated in *p*-type and *n*-type layer, respectively usually called organic heterojunction mode [3–5]. The second is to co-deposit two materials with different conducting type to the channel region of OTFT [6–8]. The third approach is the most attractive, which is the use of single ambipolar organic material as the active layer of OTFT [9,10]. This method is the best choice due to its simple fabricating process, however, it is also very difficult to achieve balanced electron and hole transport because of the scarce of ambipolar organic materials. In term of ambipolar OTFT, a challenge in device performance is that often exhibited poor on/off current ratio when comparing with these conventional unipolar devices that limited its practical application especially for complementary circuits. Therefore, the development of new path to realize ambipolar with high current modulation is very important in the community of organic electronics. In the previous studies, intrinsic organic semiconducting thin-film may operate either electron or hole simultaneously that is considered as the candidate of ambipolar materials [11]. The main factors impeding ambipolar transport in intrinsic organic semiconductor are charge-trap sites on substrate, injection barriers, and doping effects by chemical impurities, oxygen and moisture in atmosphere [12–14]. Therefore, it is actually very difficult to achieve ambipolar transport for most organic semiconductors.

OTFT is a good device platform to detect the ambipolar properties of intrinsic semiconductor because the conducting channel just locates at several organic monolayers neighbored the gate insulator. Thereby, the quality of neighbored several monolayers thin-film will determine the charge transport capability and polarity governed by the properties of substrate. As an example, the introduction of self-assembly monolayer (SAM) as the modified layer of insulator in OTFT has been proposed as an effective path to realize the ambipolar transport [15]. Oxotitanium phthalocyanine (TiOPc) is a classic intrinsic molecular semiconductor that has been widely employed in photoreceptor. The pioneer work about TiOPc disclosed that TiOPc can be operated either *p*- or *n*-channel OTFT depending on the amount of exposed oxygen. Thereby, its nature is

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appropriate for the studies of charge transport in intrinsic molecular semiconductor. However, TiOPc-based OTFTs usually exhibit single hole-accumulation mode in air because oxygen often acts as doping molecules that changes the intrinsic electric characteristics of TiOPc [16]. In previous studies, the ambipolar transport concerning to TiOPc only can be realized by preparing organic heterojunctions such as: TiOPc/CuPc or TiOPc/C60 pairs in invert ambient [17,18]. To date, the ambipolar transport characteristics measured in air have still not been observed. Oxygen doping is considered as a reasonable explanation for the absence of electron transport.

In the present work, an ambipolar OTFT with air stability based on TiOPc thin-film was demonstrated by employing *p*-6P as the modified layer of gate insulator. Para-sexiphenyl (*p*-6P) molecule has been widely used as an epitaxial substrate to grow highly ordered metal phthalocyanine thin-film and it exhibits typical *p*-type transport behavior in ambient [19]. Especially, it was used to fabricate ambipolar OTFT by forming pn heterojunction with perylene diimide derivatives (*n*-type) [20]. One hand, *p*-6P is commonly used as an epitaxial substrate to optimize the thin-film morphology of TiOPc. On the other hand, it acts as the modified layer to screen electron-traps brought by OTS particles by intermolecular aggregating. In the case, the ambipolar charge transport has been realized in a single device. Electrons and holes were accumulated to form conducting channels and transported at different gate and drain biases, which were confirmed by current-voltage (IV) and capacitance-voltage (CV) measurements. Besides, the AFM images of TiOPc on *p*-6P showed a morphological optimization compared with that of TiOPc thin-film on bare SiO_2 substrate. All results imply TiOPc can transport both electron and hole by introducing suitable modified layer.

2. Experiment

Top-contact OTFTs were fabricated using heavily doped *n*-type silicon wafer serving as the gate electrode and a layer of silicon dioxide layer with 300 nm (Ci = 10 nF/cm^2) by thermal oxidation as gate insulator. All wafers were treated by octadecyltrichlorosilane (OTS) solution as previously described [15]. The corresponding device configuration is shown in Fig. 1(a). TiOPc was purchased from Sigma–Aldrich without further purification before used, and *p*-6P was synthesized according to the described method [21]. Two organic materials were continuously deposited on the substrate at a rate of approximate 1 Å/s under a background pressure of 10^{-4} Pa, and the substrate temperature was kept at 180 °C. Then, the wafers were rapidly transferred to a vacuum chamber to define the source and drain contacts by thermally evaporating Au through a mask shadow with a background pressure of 10^{-4} Pa. The width and length of the device channel was defined as 3800 and 180 μm, respectively. Electrical characteristics of OTFTs were performed by a semiconductor parameter analyzer (Agilent technology 4155C) in ambient. The atomic force microscopy (AFM) images were obtained by SPI 4000 with tapping mode. X-ray diffraction (XRD) was measured by D/Max-2200 with Cu Kα source (k = 1.541 Å).

3. Results and discussion

The output curves of TiOPc-based thin-film transistor are shown in Fig. 1(b,c), which exhibit typical ambipolar transport behavior by applying various gate and drain biases. The *p*- and *n*-type current can be well modulated by gate electric field that means both electrons and holes may be effectively accumulated at the interface to form conducting channel. The linear and saturation regions can be clearly observed from these output curves. Note that a current reverse phenomenon between electron and hole usual appeared in typical ambipolar OTFT has not been observed in our devices. Usually ambipolar OTFTs show diffusive current at lower gate bias and higher drain bias in the output curves. In the present cases, such behavior has not appeared that is probably due to the ambipolar transport in our devices only come from a single layer thin-film (TiOPc) and the intrinsic properties of TiOPc. Only pure electron- or hole- accumulation mode was achieved similar with typical

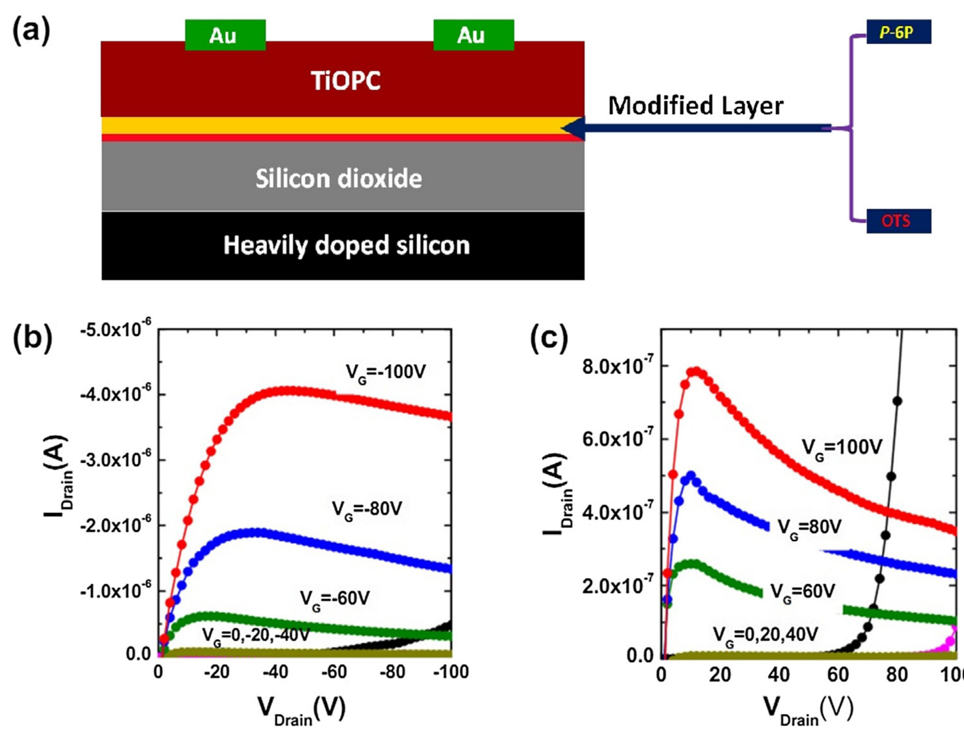

Fig. 1. (a) Schematic diagram of the structure of a top-contact OTFT the *p*-6P modified layer; (b) The output curves of *p*-channel TiOPc-based OTFT; (c) The output curves of *n*-channel TiOPc OTFT.