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High mobility ambipolar organic field-effect transistors with a nonplanar heterojunction structure

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ABSTRACT

Ambipolar organic field-effect transistors (OFETs) based on a bilayer structure of highly crystalline small molecules, n-type α,ω-diperfluorohexylquaterthiophene (DFH-4T) and p-type dinaphtho[2,3-*b*:2′,3′-*f*]thieno[3,2-*b*]thiophene (DNTT), are investigated. By employing DFH-4T/DNTT as the bottom/top layers and appropriate high work function (WF) electrodes in a bottom-gate, top-contact configuration, the superior ambipolar characteristics with matched electron and hole mobilities of 1–1.1 $cm^2 V^{-1} s^{-1}$ are achieved. Intriguingly, this high-performance device exhibits a unique feature of an extremely rough, nonplanar heterojunction in the DFH-4T/DNTT combination and a large electron injection barrier from the high WF electrodes to DFH-4T, suggesting some underlying mechanisms for the effective charge transport and injection. The electrical and structural analyses reveal that the crystal packing of the bottom DFH-4T layer supports the growth of a high-quality DNTT crystal network for high-mobility hole transport upon the nonplanar heterojunction, and also enables the formation of an enlarged organic/metal contact surface for efficient electron injection from the high WF electrodes, as the key attributes leading to an overall excellent ambipolar behavior. The effect of intrinsic charge accumulation at the heterojunction interface on the ambipolar conduction is also discussed. Furthermore, a complementary-like inverter constructed with two DFH-4T/DNTT ambipolar OFETs is demonstrated, which shows a gain of 30.

1. Introduction

The ambipolar organic field-effect transistors (OFETs) not only have fundamental interest in exploration of transport and recombination physics of opposite charge carriers, but also provide a great potential in complementary-like logic circuits applications with the advantages of simple fabrication, high noise margin, and low power dissipation [1–3]. Over the last two decades, there have been tremendous efforts on synthesis of n-type and low-bandgap organic semiconductors [4–8], device engineering [9–11], and scientific understanding of charge transport mechanisms [12,13] in development of ambipolar OFETs. To date many ambipolar materials have been proposed, but only a few can truly realize the high mobilities required for complementary circuit applications [7,14]. Alternatively, combination of highly conducting p- and n-type materials into bilayer or blend structures is a convenient and versatile strategy to realize ambipolar OFETs with high mobilities. For such heterojunction-based OFETs, the efficient injection of both holes and electrons can be achieved by choosing the materials with their respective HOMO and LUMO levels aligned with the work function of electrodes. This circumvents the need to use asymmetric electrodes for injection of different carrier types and simplifies the fabrication of complementary circuits. Control of the structural and electronic properties of heterojunctions has been shown as a key factor toward improving the ambipolar conduction [15,16]. Blend structures made by co-evaporated or soluble semiconductors usually form poor molecular packing and complex interpenetrating networks, resulting in inefficient charge accumulation and transport with much lower mobilities than for the pure materials. The highest mobilities reported for blend OFETs are in the order of 10^{-2}–10^{-1} $cm^2 V^{-1} s^{-1}$ [17]. In contrast, bilayer

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structures of sequentially deposited semiconductors allow fine control of film microstructures and physical separation of conductive channels for holes and electrons in different layers. The formation of the bottom layer has a direct impact on the quality of the heterojunction which determines the transport of a given carrier type in the top layer [18]. A uniform heterointerface between the two layers is commonly believed to be important for achieving ambipolar functionality. Through the appropriate material combinations and optimized deposition conditions, some bilayer OFETs have shown the ambipolar conduction with both electron and hole mobilities higher than 10^{-1} cm^2 V^{-1} s^{-1} [19]. The capability of well-defined charge transport and recombination routes in multi-layer structures has also been successfully applied to realize the light-emitting OFET with high quantum efficiencies [20].

In this paper, we report the high-mobility ambipolar OFETs composed of highly crystalline small molecules, n-type α,ω-diperfluorohexylquaterthiophene (DFH-4T) and p-type dinaphtho[2,3-*b*:2′,3′-*f*]thieno[3,2-*b*]thiophene (DNTT), in a bilayer structure (Fig. 1a). The combination of these two materials is interesting primarily due to their reported high mobilities [21,22]. However, to realize high performance ambipolar transistors the degrees of energy-level matching and structural compatibility between the two materials are the critical issues to be explored. As the energy diagram shown in Fig. 1b, the two materials have a relatively wide band-gap (~3 eV) and a large offset (~2.1 eV) between the HOMO level of DNTT and the LUMO level of DFH-4T. This raises a question whether the injection of electrons and holes can be equally efficient by using simple source/drain (S/D) contact geometries with one type of metal contact. Moreover, the microstructures and morphologies of DNTT and DFH-4T pristine films are shown to be very different, and thus is intriguing to investigate their heterojunction formation and its correlation with the ambipolar conductivities. Here we demonstrate that, by choosing appropriate deposition order of DFH-4T and DNTT and high work function (WF) metal electrodes, a well-balanced ambipolar OFET with electron and hole mobilities in the order of 1 cm^2 V^{-1} s^{-1} can be achieved. Interestingly, this high performance is based on an extremely rough, nonplanar heterojunction between DFH-4T (bottom) and DNTT (top) layers, suggesting that a flat, smooth interface is not a prerequisite for effective ambipolar transport in bilayer OFETs. From detailed analyses of electrical and structural properties of bilayer and single-component OFETs, we provide a clear insight of how the bottom DFH-4T layer affects the DNTT crystal growth and the organic/metal contact geometry, and thereby leads to the high-mobility hole transport upon the nonplanar heterojunction and an efficient charge injection from the high WF electrodes. We also characterize the degree of intrinsic charge accumulation induced by the heterojunction formation with planar diodes, and discuss this effect on the mobilities of bilayer OFETs. Finally, we integrate the high-mobility ambipolar transistors into a complementary-like inverter, achieving an output voltage gain as high as 30.

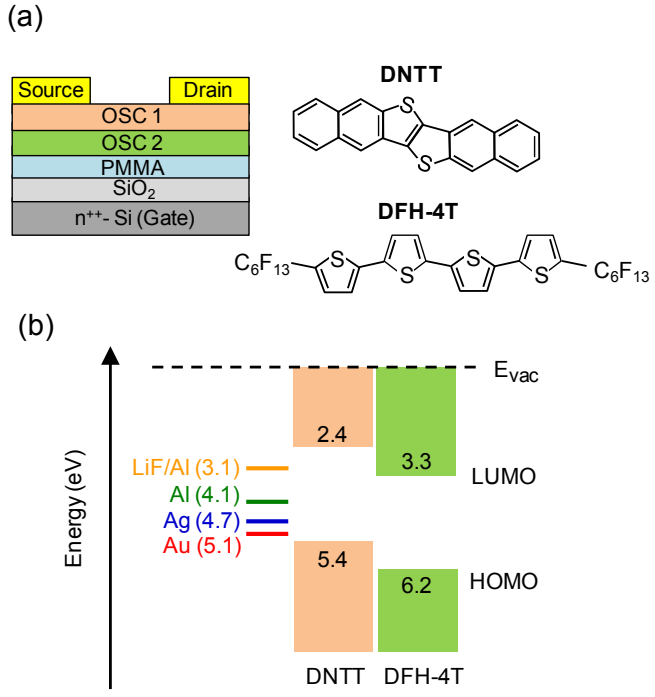

Fig. 1. (a) Schematic illustration of a bottom-gate, top-contact OFET with bilayer organic semiconductors (OSC) labeled as OSC2/OSC1 here. Also shown are the chemical structures of DNTT and DFH-4T. (b) Energy level diagram of DNTT, DFH-4T, and the used electrodes.

2. Device fabrication and characterization methods

The transistors for this study were fabricated in a bottom-gate, top-contact configuration (Fig. 1a). Heavily n-doped Si wafers with 300 nm thermally grown SiO_2 were used as device substrates. Prior to the deposition of organic semiconductors the cleaned Si/SiO_2 substrates were spin-coated with 200 nm thick poly(methyl methacrylate) (PMMA, Mw = 120 kg mol^{-1}) from 50 mg mL^{-1} solution in anhydrous n-butyl acetate and annealed at 130 °C for 12 h in a nitrogen glove box to remove residual solvent. The PMMA dielectric would facilitate the microstructural growth of organic semiconductors and provide a good dielectric with fewer −OH groups that could trap electrons. The organic semiconductors, DNTT and DFH-4T (purchased from Aldrich and Lumtec Co, respectively), were purified by thermal gradient sublimation before use. For both single-component and bilayer OFETs, DFH-4T and DNTT films (average thickness of ~30 nm) were deposited onto the substrate at 50 °C in high vacuum (<10^{-6} mbar) at a rate of 0.1 Å/s. Finally, the S/D electrodes were made by thermal evaporation of selected metals (~80 nm) and interlayers onto the organic films through a shadow mask. In this work four kinds of electrodes (Au, Ag, Al, and LiF/Al) were employed to modify the ambipolar charge injection. For LiF/Al electrodes a thin LiF interlayer (~1 nm) was incorporated between Al and organic semiconductors to improve the electron injection. The channel length (L) and width (W) of OFETs were 100 μm and 1500 μm, respectively. The DFH-4T metal-insulator-semiconductor (MIS) and metal-insulator-metal (MIM) diodes were also fabricated for capacitance–voltage (C–V) response measurements. In MIS diodes the DFH-4T and top electrodes were sequentially evaporated through a fixed shadow mask to eliminate the parasitic capacitance. The same shadow mask was also used to define the top contact of MIM diode without DFH-4T as a control sample. The planar diodes for intrinsic current measurements were prepared under the same conditions as the OFETs except that the glass substrate was used. Moreover, the complementary-like inverter was fabricated by combining two ambipolar OFETs with DFH-4T/DNTT as the bottom/top layers and Ag as the top electrodes.

The I–V characteristics of OFETs, planer diodes, and inverters were performed using an Agilent B1500A semiconductor parameter analyzer. The C–V measurements of DFH-4T MIS and MIM diodes were performed using a 4192A Hewlett Packard Impedance Analyzer. All the electrical measurements were carried out in the nitrogen glove box. Since the output voltage of impedance analyzer is limited between ±35 V, we fabricated the MIS and MIM diodes with the thinner dielectrics (70 nm SiO_2 and 100 nm PMMA) to obtain the dielectric capacitance (18.5 nF cm^{-2}) about three times