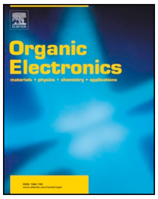
Organic Electronics 63 (2018) 200–206

Contents lists available at ScienceDirect

Organic Electronics

journal homepage: www.elsevier.com/locate/orgel



Air-stable and balanced split-gate organic transistors

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ARTICLE INFO

Keywords:
Ambipolar semiconductors
Multi-gate device
Air-stable
Air-exposure effects

ABSTRACT

Ambipolar organic electronics have been gaining interest as a simple alternative technology for implementing complementary-like circuits. Although practical applications require stable operation in the air, most previous studies on ambipolar organic electronics have reported results measured in high vacuum or N_2 atmosphere only. This is because ambipolar properties change to asymmetric p-type dominant or unipolar p-type characteristics when exposed to air. Little effort has been put into the fundamental investigation of the effects of the environmental atmosphere on ambipolar organic semiconductors. In this paper, we demonstrate ambipolar OTFTs with balanced p/n characteristics under ambient air using poly{[*N*,*N*′-bis(3-decylpentadecyl)-naphtho[2,3-*b*:6,7-*b*′]dithiophene-4,5,9,10-tetracarboxidiimide-2,7-diyl]-*alt*-5,5′-(2,2′-bithiophene)} (PNDTI-BT-DP). Based on the analysis using XPS, UPS, and electrical characterizations at various atmosphere, we concluded that the PNDTI-BT-DP has 0.45 eV higher than the target value for ambiplar charge injections with respect to Au contact electrode. The energy level of the PNDTI-BT-DP was up-shifted by 0.45 eV when the film was exposed to ambient air, which resulted in a change in the electrical properties. As a proof-of-concept application, we demonstrate the air-stable split-gate OTFTs that operate as either a unipolar p- or n-type device based on electrical control. Finally, we report results showing that the device characteristics for both p- or n-type operations were maintained after ~120 h of atmospheric exposure.

1. Introduction

Unlike conventional organic thin-film transistor (OTFT) technology [1–5], ambipolar OTFT technology allows a single device to have both p-type or n-type transistors [6–9]. Since most ambipolar organic semiconducting materials are solution-processable, both p- and n-type OTFTs can be simultaneously fabricated on the same substrate by simply coating ambipolar organic semiconductors. This process enables simple fabrication by reducing the complexity of the manufacturing processes, including separate p- and n-type deposition [10,11], patterning [12], and tailored annealing temperatures for specific p- or n-type material [13,14].

On the other hand, conventional ambipolar OTFTs suffer from a lack of air stability [6,15–20]. When operating in ambient air, degradation of electron transport typically occurs so that ambipolar conduction changes to p-type dominant or unipolar p-type conduction [21,22]. These phenomena result from oxygen or water effects, changing electrical characteristics of OTFTs. Recently, there were several studies that demonstrated ambipolar organic semiconductors operating in air [23–27]. However, these studies mostly focused on experimental demonstration without providing much insight into the underlying physical mechanisms. Therefore, to develop a systematic design methodology for air-stable ambipolar organic semiconductors, it is necessary to quantitatively analyze the dependence of the device characteristics depending on atmospheric oxygen effects.

For a comparative analysis between high vacuum and ambient conditions, we perform ultraviolet photoelectron spectroscopy (UPS), X-ray photoelectron spectroscopy (XPS), and electrical characterizations for OTFTs based on poly{[*N*,*N*′-bis(3-decylpentadecyl)-naphtho[2,3-*b*:6,7-*b*′]dithiophene-4,5,9,10-tetracarboxidiimide-2,7-diyl]-*alt*-5,5′-(2,2′-bithiophene)} (PNDTI-BT-DP). The device shows strong n-type characteristics in high vacuum but well-balanced ambipolar

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https://doi.org/10.1016/j.orgel.2018.09.022
Received 17 April 2018; Received in revised form 24 July 2018; Accepted 16 September 2018

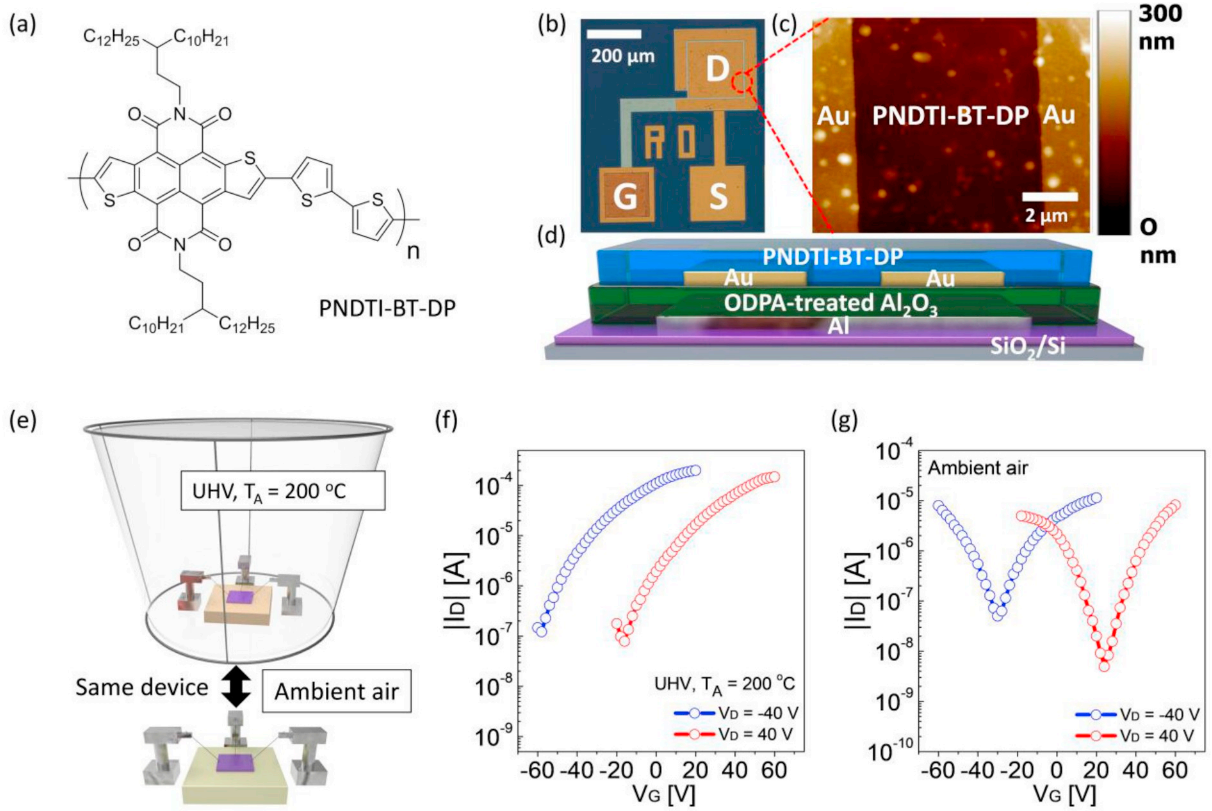

Fig. 1. (a) Chemical structure of PNDTI-BT-DP. (b) Optical microscopy image. (c) AFM topography. (d) Structure of a PNDTI-BT-DP OTFT. (e) Illustration of the measurement atmosphere. (f) Transfer characteristics of PNDTI-BT-DP OTFTs measured in high vacuum with annealing at $T_A = 200$ °C. (g) Transfer characteristics of PNDTI-BT-DP OTFTs measured in ambient air. $V_D = -40$ V (blue circle symbol), 40 V (red circle symbol). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

characteristics in ambient air. The analysis suggests that the HOMO/LUMO level of the ambipolar material was up-shifted by 0.45 eV when the device is exposed to ambient air, which resulted in a change in the electrical properties.

We also fabricate split-gate OTFTs, which utilize two gate electrodes to control the mode of charge transport [28–32]. Digital circuits typically require complementary operations to avoid waste of power due to static current. Unfortunately, ambipolar OTFT-based circuits suffer from static current because ambipolar devices are not turned off completely due to simultaneous hole and electron accumulation in a device. In the split-gate structure, the devices selectively operate in a unipolar p- or n-type mode depending on the applied voltage bias of the secondary gate electrode. This feature leads to a well-defined off-state region as well as a lower turn-on voltage. Note that the split-gate OTFTs need the two gate electrodes and accordingly two dielectric layers. Although the split-gate technology significantly improves the robustness of the circuits, all previous studies on split-gate OTFTs have reported measurement results in a high vacuum or N_2 atmosphere only. Several previous studies on split-gate OTFTs using unipolar p-type semiconductors reported their results in ambient air. However, the purpose of using the split-gate in the previous works was to reduce the contact resistance, which is different from making ambipolar OTFTs conditionally unipolar as described in this paper [33–35]. In this paper, we demonstrate for the first time air-stable split-gate OTFTs. The proposed device shows selective p- or n-type operation with a high on/off current ratio ($\sim 10^4$) after 120 h of air exposure. In addition, it is observed that the hole and electron conduction characteristics such as current, carrier mobility and turn-on voltages are well balanced over the entire measurement period.

2. Material and methods

2.1. Device fabrication

Bottom-gate/bottom-contact devices were fabricated using a SiO_2/Si substrate. All gate electrodes (200 nm) were deposited using an e-beam evaporator. Then, Al_2O_3 (200 nm) was deposited using the atomic layer deposition method. The contact electrodes (Au, 100 nm) were deposited using an e-beam evaporator. We conducted a self-assembled monolayer (SAM) treatment on Al_2O_3 using octadecylphosphonic acid (ODPA) in isopropyl alcohol (IPA). We spin-coated the PNDTI-BT-DP solution in 2 mg/0.5 ml (chlorobenzene) on top of ODPA-treated Al_2O_3 with the contact electrodes and subsequently dried the sample at 100 °C. The coated PNDTI-BT-DP was annealed at $T_A = 350$ °C for 1 h, which completed the sample fabrication. The channel length and channel width of the transistors of the PNDTI-BT-DP-based devices was L = 6 µm and W = 810 µm.

For PDPP3T and PDPP4T samples, we fabricated bottom-gate/top-contact devices using a SiO_2/Si substrate. We spin-coated the PDPP3T or PDPP4T solution in 8 mg/1 ml (1,2-dichlorobenzene) on top of ODTS-treated SiO_2. The coated films were annealed at $T_A = 150$ °C. The contact electrodes (Au, 100 nm) were deposited on top of the PDPP3T or PDPP4T films. The channel length and channel width of the transistors of the fabricated samples was L = 100 µm and W = 1500 µm.

For split-gate transistors, we deposited main gate electrodes (Al, 200 nm) using an e-beam evaporator. On top of the deposited 200 nm thick Al gate electrodes, we deposited Al_2O_3 (200 nm) using ALD. The control gate electrodes (Al, 100 nm) were deposited on top of the deposited 200 nm thick Al_2O_3 layer. Next, we deposited the contact electrodes (Au, 100 nm) and sequentially performed SAM treatment on