A comprehensive investigation of organic active layer structures toward high performance near-infrared phototransistors

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ABSTRACT

Tin phthalocyanine (SnPc) is a kind of organic semiconductor material with excellent absorbing characteristic in near-infrared (NIR) region but rarely applied in photosensitive organic field-effect transistors (PhOFETs). Here, a series of SnPc based PhOFETs with different active layer structures were fabricated and characterized for the purpose of making a systematic investigation of organic active layer structure toward NIR phototransistors. Among the sample devices with different active layer structures, the tri-layer planar heterojunction structure of Device C exhibits high photoresponsivity of 2686.1 mA/W and the photosensitivity is up to 10^4. The tri-layer hybrid planar-bulk heterojunction configuration of Device D also possesses excellent overall performance, whose photoresponsivity reaches 1894.7 mA/W and photosensitivity is up to 5925. Meanwhile, the detectivity remains at the level of 10^{12} Jones. After a comprehensive investigation of different organic active layer structures, some useful design principles for NIR phototransistors are obtained. While the mobility of SnPc is relatively low, the photosensitive performance of the devices can be improved to various extent by applying planar and hybrid planar-bulk heterojunction configuration. Given the similar features of some organic NIR materials, we believe that the device design concepts we used for SnPc can be helpful to guiding and designing higher performance NIR phototransistors based on other organic materials.

1. Introduction

Recent developments in the field of organic electronic devices have led to a renewed interest in optical detecting, especially in near-infrared (NIR) region. NIR light can be applied broadly in industry, agriculture, transportation and other areas like medicine and military [1–4]. Photodetection in NIR region has been a hot topic and triggered intensive research into the manufacture of NIR sensitive devices [5–10]. It is becoming increasingly difficult to ignore the importance of organic NIR photodetectors because of their widespread applications in sensing and imaging [11,12]. Traditional inorganic counterparts have been widely applied but still with some limitations. For example, some NIR photodetectors based on narrow-bandgap semiconductors (such as InGaAs) must be cooled to utilize due to the abundant intrinsic thermal charge carriers, complicating the routine use of devices. Organic photodetectors have a number of advantages over their inorganic counterparts, such as low production cost, large-area fabrication, and superior mechanical flexibility [13–15]. Furthermore, there are a wide variety of

materials to choose from [16].

In order to be extensively adopted into various photosensitive devices and other applications, organic NIR sensitive materials are in need of some unique characteristic features, such as low energy band gap, good thermal and chemical stability, and high absorption coefficient in NIR region. A large amount of metal phthalocyanines (MPcs) have attracted great interest as an active component in modern organic electronic devices, like organic solar cells (OSCs), organic photodiodes (OPDs) and organic field-effect transistors (OFETs) [17–23]. Some of the representatives widely researched are zinc phthalocyanine (ZnPc), lead phthalocyanine (PbPc) and neodymium phthalocyanine (NdPc$_2$) [20,24,25], to name but a few. Among numerous NIR absorbing materials, tin phthalocyanine (SnPc), owing to its considerable near infrared absorbance characteristic and special photoelectric properties [26,27], is drawing intense attention in various photoelectric functional systems. To our knowledge, the previous reports on SnPc mainly focused on organic photovoltaic with planar or bulk heterojunction structures, which is more extensively applied in OSCs [27,28].

Photosensitive organic field-effect transistors (PhOFETs), as a particular type of OFETs, have emerged as a subject with intensive academic and commercial interest due to their integration of light detection and switch function in a single device [29,30]. Compared with OPDs, PhOFETs have the advantages of higher photo-to-dark current ratio and lower noise [31], which makes them the main research objects in our study. Generally speaking, light absorption characteristics, transport of channel carrier and the exciton dissociation efficiency are three critical aspects which dominate the performance of PhOFETs. One of the most significant current discussion on PhOFETs is how to fabricate devices that can work well in all the aspects mentioned above. Conventional single layer (SL) PhOFET devices cannot meet the conditions in most cases. To cope, some effective methods on design of the device configuration, like heterojunction structures and interfacial modification, are adopted. Some studies on NIR PhOFETs based on other kind of organic materials with different active layer structures have been reported. Binda et al. demonstrated phototransistors with GlySQ/PCBM bilayer planar heterojunction [32]. Song et al. displayed planar and bulk heterojunction structures of MEH-PPV and PbS QDs applied in transistors for NIR photo-detection, and photoresponsivity of 100 mA/W was obtained for the bulk heterojunction structure [33]. Besides, some PbPc based PhOFETs with different active layer structures were reported in our previous work [29,30]. Additionally, a small-scale study on SnPc-based heterojunction cell by Musubu Ichikawa et al. investigated the NIR photosensitive diode performance, proving that SnPc is suitable for NIR organic photodetectors and the detectivity of the device is 1.59×10^{11} Jones [34]. However, because of its much lower mobility, SnPc is rarely utilized for OFETs as an active layer, even exhibits no field-effect when the substrate temperature is not right [35].

In this work, we fabricated a set of SnPc-based NIR PhOFETs with different active layer structures by following some device design concepts and obtained high photoresponsivity of 2686.1 mA/W and 1894.7 mA/W for tri-layer planar heterojunction and tri-layer hybrid planar-bulk heterojunction configuration respectively, which are comparable or even higher than some reported NIR phototransistors with similar stack in literature [29,33]. In addition, a systematic investigation of SnPc-based PhOFETs with different active layer structures was made. There are some difficulties in integrating superior absorption with high mobility and exciton dissociation efficiency together into hybrid active layer structures for a phototransistor due to the suppression of the dimer absorption. However, we find that in Device D, this tri-layer hybrid planar-bulk heterojunction structure (pentacene/SnPc/SnPc:C$_{60}$) exhibited better performance compared to some other kind of hybrid planar-bulk heterojunction configuration in Devices E and F. Considering their unique and similar features of some MPcs (high absorption coefficient in NIR region & poor mobility), these device design principles can be useful to guide and design higher performance NIR phototransistors.

2. Experimental

2.1. Materials and device fabrication

All the organic materials were commercially obtained and used as received. Fig. 1a–f shows the schematic configuration of the PhOFETs with different active layer structures, and they are labeled with Device A-H, respectively. Bottom-gate top-contact geometry was used to fabricate the PhOFETs following the steps below: A heavily p-doped Si substrate with a resistivity of 0.03 Ω cm acts as the gate electrode with a 1000 nm thermally grown SiO$_2$ dielectric layer. The substrates were ultrasonically cleaned by acetone, ethanol, and deionized water, and were dried with high-pure N$_2$ gas blowing and baked in an oven with a temperature of 60 °C for 20 min. Then a monolayer of OTS was self-assembled by vacuum sublimation. As for the active layer fabrication of each device, different organic films were vacuum deposited using thermal evaporation technique under vacuum condition

(3.0×10^{-4} Pa). Au source/drain electrodes were vacuum deposited through a shadow mask which defined a channel length (L)/width (W) of 50 μm/3 mm.

2.2. Measurements and characterizations

All the measurements were performed immediately under room temperature condition after the devices were taken out of the thermal evaporation chamber. Data were collected by using an organic semiconductor characterization system. The output characteristics of the PhOFETs devices were measured under accumulation mode with drain voltage (V_d) from 5 to −50 V. The transfer characteristics were measured at saturation region ($V_d = -50$ V). For optical absorption measurements, thin film of pentacene (30 nm), C$_{60}$ (20 nm), pentacene (30 nm)/SnPc (20 nm)/C$_{60}$ (20 nm) and SnPc:C$_{60}$ (20 nm) were vacuum deposited on cleaned quartz substrates, respectively. TU-1901 spectrometer was used for the measurements of absorption spectra. For the measurements of photo effects, a NIR laser diode with a wavelength of 850 nm and a power density of 200 mW/cm^2 was used. The variation of optical power was realized by inserting neutral filters before the laser diode. In the next, temporal response was operated at a bias of $V_d = -50$ V, $V_g = -100$ V, with a square wave of NIR light ($\lambda = 850$ nm).

3. Results and discussion

Fig. 2 shows the absorption spectra of pentacene, SnPc, C$_{60}$, pentacene/SnPc/C$_{60}$ tri-layer planar heterojunction and SnPc:C$_{60}$ bulk heterojunction film. As can be seen from the spectra, the SnPc film exhibits excellent NIR absorption with an absorption peak at 878 nm and an appreciable absorption at 850 nm while C$_{60}$ film demonstrates no noticeable absorption in NIR region. The planar heterojunction film shows the narrow absorption band with an absorbance maximum at 890 nm. For the SnPc:C$_{60}$ bulk heterojunction film, a noticeable absorption peak around 742 nm is observed.

For a PhOFET, photoresponsivity (R) and photosensitivity (P) are two key parameters to evaluate the photosensitive performance, which can be expressed as

$$R = \frac{I_{\text{ph}}}{P_{\text{opt}}} = \frac{I_{\text{ph}}}{P_{\text{inc}}A} \tag{1}$$

$$P = \frac{I_{\text{ph}}}{|I_{\text{dark}}|} = \frac{|I_{\text{ill}} - I_{\text{dark}}|}{|I_{\text{dark}}|} \tag{2}$$

where P_{opt} is the incident power on the channel of the device, P_{inc} is the power of the incident light per unit area (i.e. illumination intensity), and A is the effective irradiated area of the device; I_{ph} is the drain-source photocurrent which equals to the difference between the current under illumination (I_{ill}) and in the dark (I_{dark}) at the same gate and drain voltages, characterizing a net enhancement of drain current induced by illumination. The value of detectivity (D^*) presents the minimum optical power to generate photocurrent, and the external quantum efficiency (EQE) represents the ability to provide photo-generated carriers per single incident photon, which can be defined as [21]:

$$D^* = \frac{RA^{1/2}}{(2qI_{\text{dark}})^{1/2}} \tag{3}$$

$$EQE = \frac{hc}{q\lambda} \tag{4}$$

Here, q is the elementary charge (1.602×10^{-19} C), h and c represents Planck's constant and velocity of light, respectively, and λ stands for the light wavelength.