Realization of high detectivity organic ultraviolet photodetectors by modifying polymer active layer

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A B S T R A C T

Organic ultraviolet photodetectors (UV-PDs) consisting of a polymer active layer of poly (N-vinyl carbazole):[6,6]-phenyl-C71-butyric acid methyl ester were fabricated, and the properties of UV-PDs were systematically investigated by optimizing the thickness of active layer and temperature of thermal annealing. The result showed that, under an illumination of 350 nm ultraviolet light with an intensity of 0.6 mW/cm^2, the device exhibited a high detectivity of 1.07×10^{12} Jones, which is among the highest detectivity of the reported inverted UV-PDs. Through the UV–Vis absorption spectra and atomic force microscopy measurement, along with charge carrier mobility analysis, the high performance of UV-PDs was attributed to the improved UV absorption, preferred morphology and effective charge transport of polymer active layer.

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1. Introduction

Ultraviolet photodetectors (UV-PDs) have attracted increasing attention in the past few decades, due to their wide applications in many fields like solar astronomy, fire detection, biological sensing and so on [1–3]. Recently, owing to the potential in realizing flexible large-area devices, organic semiconducting materials with efficient ultraviolet light absorption and effective charge conduction emerged as the research highlight in UV-PDs, and significant progress has been achieved [4–6]. Moreover, to reduce the fabrication complexity, solution-processable polymers were utilized in UV-PDs lately. For example, Huang et al. achieved a high detectivity ($\sim 10^{15}$ Jones) of polymer UV-PDs by adding ZnO nanoparticles into poly(N-vinyl carbazole) (PVK) and poly(3-hexylthiophene-2,5-diyl) (P3HT) [7]; Wang et al. demonstrated a new type of polymer UV-PDs with a detectivity of 2.4×10^{11}

Jones based on phosphorescent material and [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) [8].

The performance of organic photodetectors (OPDs) including dark current, photoresponse relies on the employment of bulk heterojunction (BHJ), which are prepared by blending electron donor (p-type) and acceptor (n-type) materials. For polymer PDs, an important device performance parameter is the detectivity, which is dependent on both photocurrent and dark current. The spatial distribution of donors and acceptors in active layer greatly affects the photocurrent and dark current, and a BHJ with preferred morphology is described as an interpenetrating network for efficient charge transport and less recombination [9,10]. Also, the thickness of active layer is an important factor that influences the light absorption and exciton generation inside the active layer [11,12]. Hence, the modification of active layer has been demonstrated as an efficient way to improve the performance of polymer PDs. Currently, polymer PDs with detectivity more than 10^{10} Jones have been realized by optimizing the photoactive layer. For example, Keivanidis et al. found that dark

current of OPDs could be monitored by the morphology of photoactive layer [13]. Chung et al. has demonstrated PDs with high detectivity over 10^{10} Jones by enhancing photocurrent through optimizing the polymer/fullerene morphology [14]; Gong et al. has obtained polymer PDs with a detectivity greater than 10^{12} Jones by fabricating photoactive layer from solution with processing additive 1,8-diiodooctane [15]. However, in the case of UV-PDs, the influence of polymer active layer modification on organic UV-PDs has not yet been investigated in detail.

In this work, based on an active layer of PVK:[6,6]-phenyl-C71-butyric acid methyl ester (PC$_{71}$BM), the inverted organic UV-PDs with high detectivity were demonstrated. Firstly, the dependence of photocurrent, dark current and detectivity on the film thickness of PVK:PC$_{71}$BM layer was investigated. Then, the influence of annealing temperature on the morphology of polymer active layer was studied through atomic force microscope (AFM). Finally, by the optimization of these two factors, high detectivity polymer UV-PDs were obtained, and the detectivity variation of the device was discussed.

2. Experiment details

2.1. Device fabrication

Polymer UV-PDs with an inverted structure of ITO/ZnO$_x$/PVK:PC$_{71}$BM/MoO$_3$/Ag were fabricated. The ITO-coated glass substrates with a sheet resistance of 10 Ω/sq were consecutively cleaned in ultrasonic bath containing detergent, deionized water, acetone and isopropyl alcohol for 15 min each, and dried in an oven before UV/ozone treatment for 10 min. 0.5 M ZnO$_x$ precursor solution consisted of zinc acetate, ethanolamine, and 2-methoxyethanol solvent was spin-coated on top of the ITO-glass substrates [16]. After baking at 200 °C for 60 min in ambient, the polymer blend (PVK (99.9%, Riek metals) and PC$_{71}$BM (99.9%, Lumtec) (ratio = 1:0.8 by weight) dissolved in chlorobenzene with a concentration of 20 mg/ml) was spin-coated on the top of ZnO$_x$ thin film (25 nm). Thus, an active layer with different film thicknesses of 85 nm, 100 nm, 120 nm and 140 nm was formed by tuning the speed of spin-coating. In order to optimize the morphology of active layer, thermal annealing treatment was carried out. The active layer was annealed under various temperatures of room temperature (RT), 80 °C, 100 °C, and 130 °C for 10 min, respectively. Then, MoO$_3$ (30 nm) was vacuum deposited with an evaporation rate of 0.1 Å/s. At last, top electrode Ag (120 nm) was thermally deposited at a rate of ~1 Å/s under a pressure of 3×10^{-5} Torr through a shadow mask. Consequently, an effective device area of 2 mm^2 was formed.

Fig. 1 shows the chemical structures of PVK and PC$_{71}$BM, and the architecture of UV-PDs. In this device, ZnO$_x$ acted as an electron extraction layer as well as a hole blocking layer. Meanwhile, MoO$_3$ acted as a hole extraction layer. PVK and PC$_{71}$BM were used as donor and acceptor, respectively. After absorbing incident UV photons by the active layer of PVK:PC$_{71}$BM, charge transfer excitons are generated and dissociated into free charge carriers. Then,
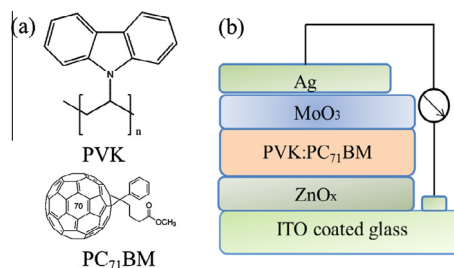

Fig. 1. (a) Chemical structures of PVK and PC$_{71}$BM; (b) device structure of polymer UV-PDs.

the holes and electrons are transported to the anode and cathode to form current, respectively.

2.2. Device characterization and film analysis

The 350 nm UV light source with a power of 0.6 mW/cm^2 was used to illuminate the UV-PDs through ITO side, and current density–voltage (J–V) characteristics in dark and under illumination were measured with Keithley 4200. UV–Vis absorption of PVK:PC$_{71}$BM polymer film was recorded with a UV–Vis spectrophotometer (SHIMAZU UV-1700). The morphology of active layer was employed by AFM (MFP-3D-BIO, Asylum Research), and the film preparation conditions were kept the same as device fabrication for comparison. All the measurements were performed at room temperature without device encapsulation.

3. Results and discussion

3.1. Film thickness optimization of polymer UV-PDs

UV-PDs consisting of the polymer active layers of 85 nm, 100 nm, 120 nm and 140 nm thick were fabricated to evaluate the influence of film thickness on device performance. The performance was evaluated by projected detectivity (D^*), which was used to estimate the signal-to-noise ratio of polymer UV-PDs. If we assumed that shot noise from the dark current is a major contribution to the noise [1], it can be expressed as Eq. (1)

$$D^* = (J_{\text{light}} - J_{\text{dark}}/P_{\text{in}})/(2qJ_{\text{dark}})^{1/2} \qquad (1)$$

where J_{light} and J_{dark} are the current density obtained under UV illumination and dark current density, respectively. P_{in} is the incident light intensity, and q is the electron charge. The value of photocurrent density (J_{ph}) was determined using the equation of $J_{\text{ph}} = J_{\text{light}} - J_{\text{dark}}$.

Table 1 summarizes the performance of polymer UV-PDs illuminated under 350 nm UV light at −1.5 V (J–V characteristics of UV-PDs are shown in Fig. A.1). As the thickness of active layer increased from 85 nm to 100 nm, the J_{ph} reached a maximum value of 1.15 mA/cm^2, with the highest detectivity of 5.72×10^{11} Jones. When the thickness of active layer was further increased, the J_{ph} decreased. In the BHJ devices, external quantum efficiency is a product of four individual efficiencies, i.e.