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Fabrication and characterisation of hybrid photodiodes based on PCPDTBT–ZnO active layers

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ABSTRACT

We report the fabrication and characterisation of an organic–inorganic hybrid photodiode (HPD) based on PCPDTBT and Zinc Oxide (ZnO) photoactive layers. The main benefit of using these materials is that multi spectral light sensing from the UV through to the Near Infrared is achieved, encompassing wavelengths ~350–870 nm. To our knowledge, this is one of the widest range responses reported for an inorganic–organic hybrid photodiode. The evaluation of the technology shows the devices exhibit one of the lowest levels of dark currents reported for a HPD, but some limitations exist due to a low on–off ratio and non-linearity of the responsivity at low incident power. The stability of devices made with PCPDTBT:ZnO active layers is compared to more commonly reported P3HT:ZnO devices in dark and it is shown that using PCPDTBT substantially improves lifetime.

1. Introduction

Organic or hybrid photodiodes (HPDs) using metal oxide acceptor materials could have a number of advantages over the inorganic technologies, including potentially low costs, solution processability and flexibility, which could enable photodiodes to be placed onto non-flat surfaces [1,2]. Previous reports of HPDs possess a reasonable on/off ratio of photocurrent during illumination when compared to the dark current (typically >2 orders of magnitudes) [3]. Another major advantage is that the absorption profile can be 'tuned' to absorb most visible wavelengths by altering the semiconductor inside the active layer within the active layer [4].

In recent years, Zinc Oxide (ZnO) has been widely studied due to its intrinsic properties suitable for optoelectronic applications such as in hybrid devices with organic semiconductors such as solar cells and photodiodes [5]. With a wide direct bandgap of ~3.4 eV at room temperature, ZnO has been regarded as an excellent semiconductor material for UV detection and possesses an absorption profile that compliments many organic semiconductors. ZnO can be easily deposited at room- or relatively low temperatures to form thin layers by standard techniques such as sputtering [6], atomic-layer deposition [7] and pulsed-laser deposition [8]. The electron mobility is generally limited by surface roughness and carrier scatterings at grain boundaries; however, the electron mobility in ZnO has been demonstrated to reach up to 110 cm^2/Vs, when using an elevated substrate temperature during the growth step [9]. In most cases where ZnO is deposited onto substrates at room temperature, the mobility is measured to be around 1–5 cm^2/Vs [10]. This value still remains much higher than many organic materials which are used as the acceptor material in organic photodiodes. ZnO has also been used widely for the development of hybrid photovoltaics or photodiodes (HPDs). In photovoltaics, performances up to 0.11% have been reported for 'planar' devices, where the ZnO is deposited as a flat, uniform surface and up to 0.76% for devices made with ZnO nanowires, which create an interdigitated interface with the organic layer [11]. In addition, up to 2.0% has been reported for devices using ZnO nano-particles/crystals in a bulk-heterojunction configuration with an donor material such as Poly(3-hexylthiophene-2,5-diyl) (P3HT) [11]. Most work on hybrid devices has focused on photovoltaics and utilised organic semiconductors such as polyfluorene [12], P3HT [11] or polyaniline [13]. Whilst the performance as photovoltaics is low, the potential as photo-diodes or detectors has not been fully investigated.

In this paper, the fabrication, development and characterisation of ZnO HPDs is reported using the polymer Poly[2,6-(4,4-

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bis-(2-ethylhexyl)-4*H*-cyclopenta [2,1-*b*;3,4-*b*′]dit hiophene)-*alt*-4,7(2,1,3-benzothiadiazole)] (PCPDTBT). Devices are shown to possess one of the lowest levels of dark current for a HPD, though the on–off ratio is limited due to the low photoresponse of the device. However, the main benefit of using these materials to make photodiodes is that multi spectral light sensing is possible from the UV through to the Near Infrared, encompassing wavelengths ~350–870 nm. To our knowledge, this is one of the widest response ranges reported for a hybrid-photodiode. It is also one of the first reports of using a low band gap co-polymer for a hybrid device. It is shown that using PCPDTBT ensures wide photoresponse, and also enhances air stability when compared to HPDs manufactured using more commonly used materials such as P3HT.

2. Experimental

The structure of the OPD device is shown in the inset of Fig. 1(a). OPD devices were initially prepared in a clean room environment using an 80 nm thick indium tin oxide (ITO) coated glass substrates (R_s = 16 Ω/square) that were first cleaned using deionised water, acetone and isopropanol in an ultrasonic cleaner, then treated in a UV-ozone reactor. For this work, a bilayer structure was used which is the simplest device geometry for a HPD. In this device architecture, a layer of ZnO is first deposited onto the electrode substrate, followed by the deposition of a donor organic semiconductor and finally by a top electrode.

A 25 nm layer of Zinc Oxide (ZnO) was deposited using sputtering (Edwards) at a rate of 1 Å/s and annealed at 250 °C. The donor material used was Poly[2,6-(4,4-bis-(2-ethylhexyl)-4*H*-cyclopenta [2,1-*b*;3,4-*b*′]dithiophene)-*alt*-4,7(2,1,3-benzothiadiazole)] (PCPDTBT), although in Section 4, Poly- (3-hexylthiophene- 2,5-diyl) (P3HT) was also used. These were prepared and mixed with chlorobenzene solvent with a concentration of 15 mg/mL, with thickness of 30 nm. Samples were transferred into a nitrogen atmosphere glovebox ([O_2], [H_2O] < 1 ppm), where the donor material was applied by spin-casting (1250 rpm for 60 s). Both the ZnO and donor material thickness was optimised. No annealing of the PCPDTBT was conducted, but P3HT was annealed at 140 °C. Finally, thermal evaporation of the cathode was undertaken through a shadow mask to define the device area. This consisted of a 10 nm layer of molybdenum trioxide (MoO_3) and 200 nm of silver (Ag). The corresponding energy band diagram of the device is shown in Fig. 1(b). The absorption profile of the PCPDTBT and ZnO is shown in Fig. 1(c).

The photoresponse studies were made with a Keithley 2600 source-measure unit (SMU) under the excitation of a Newport spectra solar simulator and a calibrated reference cell from Newport spectra. Responsivity measurements were made by illuminating the top surface of the OPD at normal incidence. The OPD response was measured in photoconductive mode, so an external reverse bias is applied via a Keithley 2600 SMU and the current was measured using either the SMU or a lock-in amplifier with an optically chopped input signal.

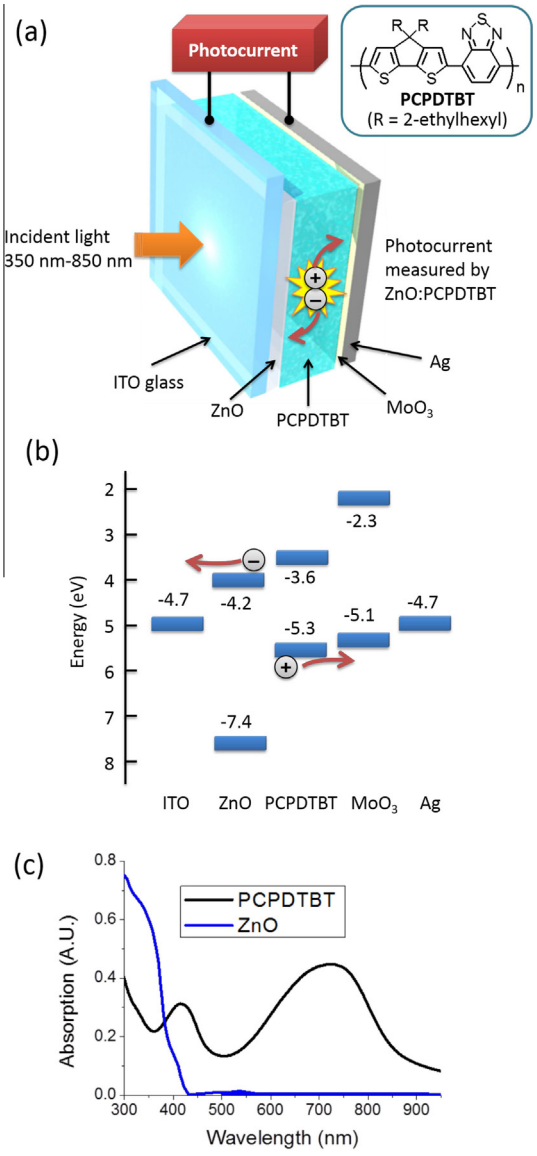

Fig. 1. (a) Schematic of the photodiode and (b) ideal flat band energy diagram for a PCPDTBT:ZnO photodiode (assuming ZnO E_V = −7.4 eV, E_C = −4.2 eV from [10]). Light is incident from the ITO side of the device. Other workfunction data is obtained from [14]. (c) Absorption profile of PCPDTBT and ZnO layers.

3. Photodiode characterisation

Fig. 2 shows the dark current and performance under 100 mW/cm^2 (AM1.5G) incident power for the fabricated PCPDPTBT:ZnO HPD. The solar cell performance under AM1.5G illumination is low, with a Power Conversion Efficiency (PCE) of 0.070%. This is to be expected owing to the planar interface, which usually leads to lower performances than devices based on ZnO nanocrystals or vertically aligned ZnO nanowires, because of the smaller interfacial area between the polymer and acceptor [11]. However, this does compare closely with the 'record' efficiency

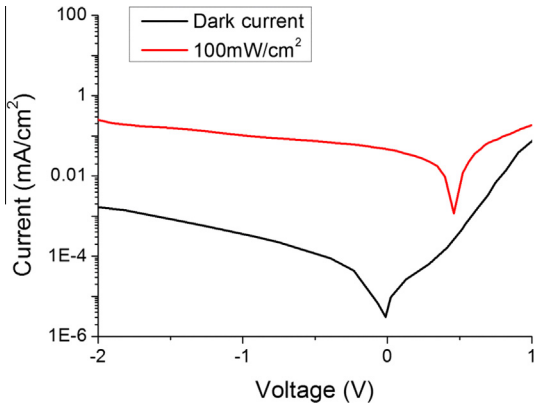

Fig. 2. Current–voltage characteristics of the PCPDTBT:ZnO photodiode under dark and with incident power of 100 mW/cm^2.