Thin Solid Films 592 (2015) 94–98

Contents lists available at ScienceDirect

Thin Solid Films

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

Integration of near infrared and visible organic photodiodes on a complementary metal–oxide–semiconductor compatible backplane

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ARTICLE INFO

Article history:
Received 13 February 2015
Received in revised form 17 August 2015
Accepted 20 August 2015
Available online 22 August 2015

Keywords:
Organic photodiode
Photodetector
Sensors
Complementary metal–organic–semiconductor

ABSTRACT

This paper reports about the integration of polymer-based bulk heterojunction organic photo diodes (OPDs) onto complementary metal–oxide–semiconductor (CMOS) compatible electrode materials. The fabrication and performance of four absorber systems in indium tin oxide-free OPDs for sensing applications have been studied. These are based on the following polymer–fullerene blends: Poly(3-hexylthiophene-2,5-diyl):[6,6]Phenyl C_{61} Butyric Acid Methyl Ester and Poly(3-hexylthiophene-2,5 diyl):Di[1,4] methanonaphthaleno [1,2:2′,3′;56,60:2″,3″][5,6]fullerene-C60-Ih, 1′,1″,4′,4″-tetrahydro-, indene-C60 bisadduct to detect light in the visible range and Poly[[4,8-bis[(2-ethylhexyl)oxy]benzo[1,2-b:4,5-b′]dithiophene-2,6-diyl][3-fluoro-2-[(2-ethylhexyl)carbonyl]thieno[3,4-b]thiophenediyl]]:[6,6]Phenyl C71 Butyric Acid Methyl Ester and Poly[2,1,3-benzothiadiazole-4,7-diyl[4,4-bis(2-ethylhexyl)-4H-cyclopenta[2,1-b:3,4-b′] dithiophene-2,6-diyl]]:[6,6]Phenyl C71 Butyric Acid Methyl Ester to detect a wide range of visible and near infrared. Devices were built in top absorption geometry, where the light passes through a transparent cathode towards the absorption layer. The fraction of absorbed photons in the transparent calcium/silver cathode, the titanium nitride/aluminum anode and in the absorption layer Poly(3-hexylthiophene-2,5-diyl):[6,6]Phenyl C_{61} Butyric Acid Methyl Ester has been simulated for comparison to the experimental results. We found that the spectral sensitivity of the device mainly depends on the absorption blend layer itself, proving that the OPDs on CMOS profit from the advantageous properties of organic absorbers, covering a very broad spectral absorption.

1. Introduction

Photo detectors are applied in many fields such as industrial process monitoring, health care and life science for optical sensing. They are used for wearable user interfaces in defense [1] and civil applications [2] as well as in astronomy [3], data transmission [4–6], or presence detection [7]. The most common detectors are based on inorganic semiconductors with appropriate materials for light detection. Amorphous silicon [8], InGaAs, GaN, and CdS are commonly used as components in passive and active matrix detector devices [6,9]. These inorganic semiconductors provide high performance in terms of spectral photoresponse and efficiency [6,10], but show some technological drawbacks. They need expensive process lines, including high temperature, vacuum deposition and photolithography processes. In combination with non-standard complementary metal–oxide–semiconductor (CMOS) materials, the device integration becomes very expensive [9]. In contrast to inorganic semiconductors, the field of organic semiconductors opens up promising possibilities in terms of low-cost fabrication and processing. On the one hand, the integration on flexible substrates has a high potential regarding weight and low cost, especially as large area organic photodiodes (OPDs) [11]. On the other hand, the combination of CMOS backplanes and organic materials that are deposited on top of a silicon wafer allows a fill factor of up to 100% while offering a reduction of process complexity and cost [12]. A key feature of organic semiconductors is the broad spectral response, reaching from the near ultraviolet (NUV) over the visible (VIS) to the near infrared (NIR) wavelength range, depending on the chosen absorption material [13]. The sensibility in the NUV region is important for the future generation of high energy radiation sensors that use scintillation layers [14]. The most common organic photodetectors are based on a solution process with bulk heterojunction (BHJ) absorption layer systems. Usually, they are built on indium tin oxide (ITO) as transparent electrode on glass substrates as so-called bottom absorbers. The light enters the device through the ITO anode and is transferred to the absorption layer, typically a blend of Poly(3-hexylthiophene-2,5-diyl (P3HT) and [6,6]Phenyl C_{61} Butyric Acid Methyl Ester (PCBM) or their derivatives. The drawbacks of ITO are its parasitic absorption of blue light, a rather high sheet resistance which induces a high series resistance, and most importantly: the cost of indium [1].

In this paper, we demonstrate ITO-free BHJ photodetectors with different absorption layers and conduct optical simulation to explain the

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http://dx.doi.org/10.1016/j.tsf.2015.08.034
0040-6090/

experimental results of a P3HT:$PC_{60}BM$ device in detail. For fabrication, we make use of silicon substrates with pre-deposited electrical contacts (anode) based on an Al-alloy with a titanium nitride (TiN) cover layer. Both materials are available in standard CMOS foundries and are therefore a good interface to enable OPD-integration on CMOS–wafer. The Al-alloy connects the anode of OPD to the gate electrode of CMOS. The TiN prevents the oxidization of the Al-alloy in air and additionally separates the aluminum from strongly acidic [Poly-[3,4-ethylendioxythiophen]]:[polystyrene] (PEDOT:PSS) layer. The PEDOT:PSS works as transport layer in the OPD device. On top of the TiN/Al-electrode and transport layer, four kinds of absorption systems are applied and characterized. One BHJ photodetector is based on the polymer fullerene blend Poly(3-hexylthiophene-2,5-diyl):[6,6]Phenyl C_{61} Butyric Acid Methyl Ester (P3HT:$PC_{60}BM$) and another on Poly(3-hexylthiophene-2,5 diyl):Di[1,4] methanonaphthaleno [1,2:2′,3′;56,60:2″,3″] [5,6]fullerene-C60-Ih, 1′,1″,4′,4″-tetrahydro-, ICBA (P3HT:ICBA). A third absorption layer is composed of Poly[2,1,3-benzothiadiazole-4,7-diyl[4,4-bis(2-ethylhexyl)-4H-cyclopenta[2,1-b:3,4-b′] dithiophene-2,6-diyl]]:[6,6]Phenyl C71 Butyric Acid Methyl Ester (PCPDTBT:$PC_{70}BM$) for detection of NIR while the last system consists of Poly[[4,8-bis[(2-ethylhexyl)oxy]benzo[1,2-b:4,5-b′]dithiophene-2,6-diyl][3-fluoro-2-[(2-ethylhexyl) carbonyl] thieno[3,4-b]thiophenediyl]]:[6,6]Phenyl C71 Butyric Acid Methyl Ester (PTB7:$PC_{70}BM$) to increase the sensitivity in the visible range. The third and fourth system feature an additional additive, 1.8-diiodooctane (DIO) to improve the internal quantum efficiency, the charge separation, and transport [15–18]. All OPDs are built in top absorption geometry where the light passes through a semitransparent Ca/Ag cathode towards the absorption layer. The OPDs have been characterized by current density–voltage-characteristics (J–V) under dark and light (illuminated) conditions with a reverse bias of −2 V. Afterwards, we determined the incident photon-electron conversion efficiency (IPCE) for every device and determined the optical properties (reflectance, transmittance) of the anode and cathode layers separately. For the case of P3HT:$PC_{60}BM$ as a commonly discussed reference material, we compare the measured IPCE to simulation results and discuss the optical properties with respect to the device sensitivity.

2. Experimental details

The anode was deposited onto a silicon oxide isolation layer on the silicon substrate and has an active pixel area with a size of 22.14 mm^2. It consists of 80 nm Al-alloy and is capped by a 10 nm TiN layer. The TiN layer is a special part of process to manufacture the anode and cover and protect the anode against oxidation at the atmosphere. The sheet resistance of TiN is $<10\ \Omega/sq$ and shows a layer roughness of 0.7 nm. This is equivalent to standard ITO for OPD anodes with a sheet resistance of 30 Ω/sq and a layer roughness of 1.3 nm [19]. The work function of TiN is around 4.2 eV [20] and exhibits a small difference for the injection barrier of Al-alloy/TiN anode to the organic materials. All anode layers were formed by sputter deposition and are structured via photolithography. At first, we manually cleaned the substrates in an aqueous solution containing detergent, followed by rinsing with de-ionized water. Afterwards the substrates are sonicated sequentially for 15 min twice in acetone and isopropanol and dried in an oven at 383.15 K for 2 h and finally treated by a high vacuum argon plasma for 10 min. The transport layer was spin-coated from a filtered PEDOT:PSS suspension (Clevios P VP AL 4083) at 1250 rpm for 120 s and baked on a hotplate at 413.15 K for 10 min under ambient condition. Before drying on the hotplate, we removed the PEDOT:PSS from the outer contact surfaces of the electrodes. As an absorption layer, the material systems shown in Table 1 have been spin-coated using the given process parameters. All materials were dissolved in chlorobenzene and filtered (0.45 μm Polytetrafluoroethylene filter). The DIO was purchased from Alfa Aesar, the P3HT was supplied by Rieke (AL4002). The $PC_{60}BM$ and the $PC_{70}BM$ were provided by NANO-C and the ICBA, PCPDTBT and PTB7 were delivered by 1-Material. As cathode, thin layers of Ca (2 nm) and Ag (10 nm) were thermally evaporated on top of the device at a pressure of 2×10^{-4} Pa. Fig. 1 shows the cross section of the devices architecture. All devices were encapsulated by a cavity cover glass with an UV-cured adhesive. The OPDs containing P3HT:$PC_{60}BM$ and P3HT:ICBA were annealed at 413.15 K for 10 min after encapsulation. The whole process of spin coating has been done under clean room conditions and the encapsulation was carried out in a glove box in nitrogen atmosphere. The fabrication of the organic and cathode layers and the process flow are described in [21–23]. The J–V behavior was measured with a Newport solar simulator (Oriel 2 sun) and the IPCE was measured with a system, Model QEX7, from PV measurement Inc. Details of the characterization have been published elsewhere [24–26]. For optical simulation we are using the absorption module of a semiconducting thin film optics simulation software "SETFOS", version 3.3. SETFOS used transfer matrix approach to calculate the optical properties of a multilayer structure and the absorption profile is derived by considering the complex refractive index of each layer, where n is the refractive index and k is the extinction coefficient [27]. We extract the optical constants such as there refractive index and extinction coefficient for P3HT:$PC_{60}BM$ blend film by analysis of data obtained from variable-angle spectroscopic ellipsometry (VASE) with an analyzer (NIR–VIS–UV VASE, J.A. Woollam Co., Inc.) [28]. The principle of characterization in detail has been published elsewhere [28].

3. Results & discussion

The results of IPCE measurements are shown in Fig. 2 which demonstrates the different spectral responses of each OPD. The highest IPCE is observed for the material blend PTB7:$PC_{70}BM$ which has a peak in the red at 665 nm and in the near-UV at 340 nm, reaching 40% and 27% IPCE, respectively. Compared to PTB7:$PC_{70}BM$ at 340 nm, P3HT:$PCB_{60}BM$ shows 7% less IPCE, P3HT:ICBA exhibits 10% less and PCPDTBT:$PC_{70}BM$ has 16% less IPCE. Compared to bottom absorption OPDs fabricated by us, these results are expected as we found the maximum of absorption with PTB7:$PC_{70}BM$ and the minimum of absorption with PCPDTBT:$PC_{70}BM$, see Fig. 3. PCPDTBT:$PC_{70}BM$ shows the broadest range of spectral response in comparison to the other systems. This blend still reaches 13% of IPCE in the NIR at 800 nm. All four OPDs show a pronounced absorption peak between 340 nm and 360 nm. To understand the micro-optical behavior including loss channels of our OPD devices with opaque anode (TiN/Al) and semitransparent cathode (Ag), we calculated the fractions of absorbed photons inside the anode, cathode and the active layer of the P3HT:$PC_{60}BM$ device. The optical constants of P3HT:$PC_{60}BM$ with a blend ratio of 1:0.7 which we used in the optical simulation are shown in Fig. 4a). In the upper part of Fig. 4, the extinction coefficient shows one broad absorption peak

Table 1
Summary of the applied blend layer absorption systems and the corresponding fabrication parameters.

Material	Ratio wt.%	Coating rpm/times	Thickness nm	Drying min
P3HT:$PC_{60}BM$	1:0.7/2.0 wt.%	1000 rpm/45 s	~80 nm	140 °C/15 min (air)
P3HT:ICBA	1:0.7/2.0 wt.%	650 rpm/60 s	~87 nm	140 °C/15 min (air)
PCPDTBT:$PC_{70}BM$	1:2.0/3.0 wt.%	2350 rpm/45 s	~75 nm	80 °C/15 min (overnight in UHV)
PTB7:$PC_{70}BM$	1:1.5/2.25 wt.%	1750 rpm/45 s	~70 nm	8 h (overnight in UHV)