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Photolithographic patterning of organic photodetectors with a non-fluorinated photoresist system

Pawel E. Malinowski [a,*], Atsushi Nakamura [b], Dimitri Janssen [b], Yoshitaka Kamochi [c], Ichiro Koyama [c], Yu Iwai [c], Anna Stefaniuk [a], Ewelina Wilenska [a], Caterin Salas Redondo [a], David Cheyns [a], Soeren Steudel [a], Paul Heremans [a]

[a] Imec, Kapeldreef 75, B-3001 Leuven, Belgium
[b] FUJIFILM Electronic Materials (EUROPE) N.V., Zwijndrecht, Belgium
[c] FUJIFILM Corporation, Shizuoka, Japan

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ABSTRACT

We report on the fabrication of organic photodetectors (OPD) based on isolated islands of P3HT:PCBM. Pattern transfer to the active material was done with photolithography based on non-fluorinated solvents and the excessive organic semiconductor was removed with oxygen plasma reactive ion etching. The photoresist system used was found to be benign to the P3HT:PCBM layer as confirmed by absorption, thickness and roughness measurements. Current–voltage characteristics and external quantum efficiency (EQE) remained unchanged after the patterning process. It was demonstrated that it is possible to photolithographically pattern isolated islands with 200 μm edge length with the same dark current density ($<10^{-5}$ A/cm^2 at −2 V bias voltage) and photocurrent density ($>5 \times 10^{-3}$ A/cm^2 at −2 V). Furthermore, concerning the solar cell performance, the patterned, small-area devices showed power conversion efficiency of 2.1% and fill-factor of 60%. Dark current was observed to depend on the size of the remaining semiconductor island, which was demonstrated on OPDs with diameter of 50 μm. The presented results show the feasibility of fabrication of isolated devices based on organic semiconductors patterned with non-fluorinated photolithography.

1. Introduction

Devices based on organic semiconductors steadily gain maturity, with the advancements in organic photovoltaics (OPV) [1], organic photodetectors (OPD) [2] and organic thin-film transistors (OTFT) [3] and with organic light-emitting diodes (OLED) [4] leading the way to industrialization. With better materials, processes and system integration solutions, one of the bottlenecks of the organic technology is the limit of the currently available pattern transfer techniques. The most common technology – shadow masking – can provide features in the range of 30 μm, but it requires rather cumbersome hardware maintenance and cannot be easily upscaled to large substrate sizes. Widely investigated additive techniques such as ink-jet printing offer similar resolution, however, are not well suited for more complex layer stacks. There are also several other emerging processes, such as self-assembly [5] or laser transfer [6]. Similarly to the inorganic semiconductor industry, the most promising technique to reproducibly achieve pattern resolution below 10 μm on large wafer sizes seems to be photolithography. However, the lithography process in organic semiconductors is not straightforward as most of the standard solvents used within photoresists as well as for development and strip dissolve

* Corresponding author.
E-mail address: malinows@imec.be (P.E. Malinowski).

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or severely damage the organic active layers. To avoid degradation, frozen CO_2 photoresists [7] and hydrofluoroether-based photoresists [8] were described in literature. Even though the devices reported look very promising, non-standard chemistry and process conditions pose questions about upscalability and cost-effectiveness of these technologies, related to issues such as high costs of disposal of halogenated waste. In this work, patterning of organic photodetectors is demonstrated with non-fluroinated photolithographic products based on solvents already used in the microelectronic and flat panel display (FPD) industry that are also neutral to the organic active layers. Patterned devices are used to study the dark current mechanisms in OPDs.

2. Experimental

In the experiments, all devices are fabricated on top of commercial 3×3 cm^2 glass substrates with pre-patterned, 140 nm thick indium-tin-oxide (ITO) bottom electrodes (TFD, Thin Film Display). After detergent-water-solvent cleaning, the samples undergo deposition of a cross-linkable edge-cover layer (ECL). Two cross-linkable ECL materials were used in the experiments: one semi-transparent (Fujifilm SC100) and the other one opaque (Fujifilm SKS-A202D). The edge-cover is designed to act as an interlayer dielectric and defines the active area of the photodetector by limiting the contact area of the ITO (Fig. 1a and c). Next, 10 nm of MoO_3 is thermally evaporated as a hole injection/collection layer (HIL) [9]. The active layer is a 1:1 donor–acceptor blend of poly(3-hexylthiophene) (P3HT, Rieke) and [6,6]-phenyl-C_{60} butyric acid methyl ester (PCBM, Nano-C) with 20 mg/ml concentration in orthodichlorobenzene (ODCB). It is spin-coated at 600 RPM in a nitrogen glovebox. A favorable blend morphology is achieved by a 10′ slow-drying step in saturated atmosphere and a 10′ hot-plate bake at 130 °C, resulting in an approximately 150 nm thick active layer. At this step, the active layer is patterned with photolithography (Fig. 1b and d) using the OS-R1001 photoresist system from Fujifilm. The island shapes are defined to determine parts of the active OPD area that should remain (Fig. 1b). After that, oxygen plasma reactive ion etching is used to remove the exposed active layer until the MoO_3 HIL, which acts as an etch-stop layer. The etch time is optimized so that after removing the exposed polymer, a layer of photoresist still protects the defined P3HT:PCBM island. When the organic semiconductor is removed, the remaining photoresist is stripped. The top contact (20 nm Ca/120 nm Ag, deposited using thermal evaporation) is defined by a shadow mask to form the cathode with a maximum area of 0.13 cm^2, with 12 discrete cross-bar devices on each glass substrate. For the measurements, current–voltage characteristics (dark and under illumination) were obtained using Keithley 2602 SourceMeter and Abet Sun 2000 solar simulator (1 sun AM1.5G spectrum). All photocurrent measurements were performed in nitrogen, under bottom illumination, with the light entering from the anode side.

3. Results and discussion

First, reference P3HT:PCBM-based devices were fabricated using different openings in the edge-cover layer and no patterning. Looking at the OPV performance, the power conversion efficiency was lower once an ECL was used Table 1), mostly due to decreased short-circuit current (J_{SC}) and partly due to lower fill-factor (FF). This might be related to a slight change of active layer thickness inside the ECL openings and geometrical effects limiting photocurrent extraction. For the dark current, it was observed that for the ECL opening areas between 12 mm^2 and 0.04 mm^2, the dark current density increases with the decrease of the area (Fig. 2), suggesting dominance of the perimeter leakage current over the bulk leakage current. At the same time, there is a clear bias voltage dependence. Photocurrent, on the other hand, remains constant for all

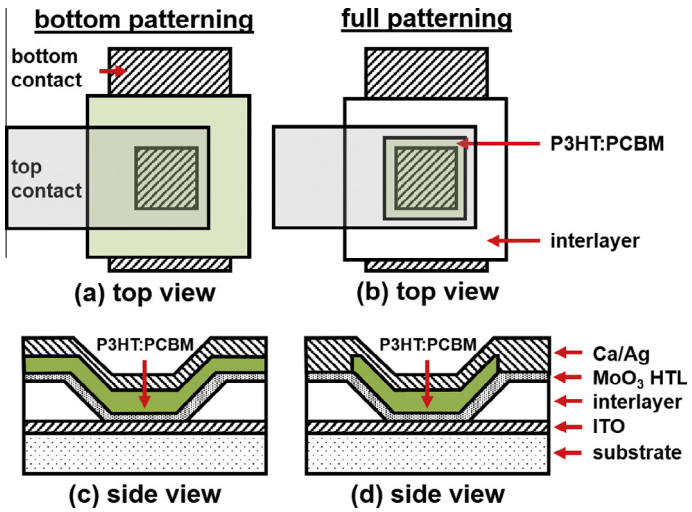

Fig. 1. Schematic structure of a patterned P3HT:PCBM photodetector: (a) top view of a single cross-bar structured device; (b) top view of a single OPD island; (c) side view of an OPD with an edge-cover layer; and (b) side view of a fully patterned OPD.