Organic Electronics 15 (2014) 2210–2217

Contents lists available at ScienceDirect

Organic Electronics

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

Performance enhancement of diindenoperylene-based organic photovoltaic cells by nanocolumn-arrays

Shuwen Yu [a], Andreas Opitz [a,*], Stefan Grob [b], Roland Resel [c], Martin Oehzelt [a,d], Wolfgang Brütting [b], Ingo Salzmann [a], Norbert Koch [a,d,*]

[a] Humboldt-Universität zu Berlin, Institut für Physik & IRIS Adlershof, Brook-Taylor Straße 6, 12489 Berlin, Germany
[b] Augsburg University, Institut für Physik, Universitätsstraße 1, 86135 Augsburg, Germany
[c] Graz University of Technology, Institute of Solid State Physics, Petersgasse 16, 8010 Graz, Austria
[d] Helmholtz-Zentrum für Materialien und Energie GmbH, Bereich Solarenergieforschung, Albert-Einstein-Straße 15, 12489 Berlin, Germany

ARTICLE INFO

Article history:
Received 9 April 2014
Received in revised form 1 June 2014
Accepted 20 June 2014
Available online 3 July 2014

Keywords:
Organic photovoltaic cells
Nanocolumns
Morphology
Structure

ABSTRACT

Crystalline and uniform nanocolumns of the organic semiconductor diindenoperylene (DIP) were fabricated by glancing-angle deposition and employed in organic photovoltaic cells (OPVCs) forming an interdigitated donor/acceptor heterojunction, with fullerene as electron acceptor. In comparison to reference bilayer devices the nanocolumn-based solar cells exhibit increased power conversion efficiency. Based on a comprehensive structural and morphological analysis, we identify three advantages of the interdigitated nanocolumn structures: (i) The active donor/acceptor interface area, crucial for exciton dissociation, is increased and the column diameter is in the range of the exciton diffusion length. (ii) The molecular orientation of DIP is such in the nanocolumns that light absorption is enhanced. (iii) The ubiquitous presence of vertical interfaces throughout nanocolumn-based devices is further beneficial to light absorption, as it fully compensates wavelength-dependent interference effects within the device structure. This work shows how the benefits of nanocolumns can go beyond simple interface area enlargement to improve the efficiency of OPVCs.

1. Introduction

Since the initial application of "sandwich" structure in organic photovoltaic cells (OPVCs) in the 1970s [1,2], the power conversion efficiency of OPVCs significantly increased only after introducing the donor/acceptor heterojunction concept [3], where layers of preferentially hole/electron conducting materials with an interface promoting exciton dissociation are employed. Today, high open circuit voltage (V_{oc}) and optimized light harvesting can be realized with a wide variety of organic semiconductors suitable for application in OPVCs [4–13]. However, the short diffusion length of photo-generated excitons in such materials (typically in the range of tens of nanometers [14,15]) significantly limits the fraction of excitons dissociated at the donor/acceptor interface, thus restricting the generation of mobile charges. To reconcile the exciton diffusion length with the average dimensions of organic heterojunctions, the concept of bulk heterojunction was introduced, which allows increasing the effective area of the donor/acceptor interface and, simultaneously, reducing the separation between individual donor and acceptor volumes [16–18]. While this approach turned out to be highly successful for polymer-based OPVCs processed from

* Corresponding authors. Address: Humboldt-Universität zu Berlin, Institut für Physik & IRIS Adlershof, Brook-Taylor Straße 6, 12489 Berlin, Germany (N. Koch).
E-mail addresses: Andreas.Opitz@hu-berlin.de (A. Opitz), Norbert.Koch@physik.hu-berlin.de (N. Koch).

http://dx.doi.org/10.1016/j.orgel.2014.06.023
1566-1199/

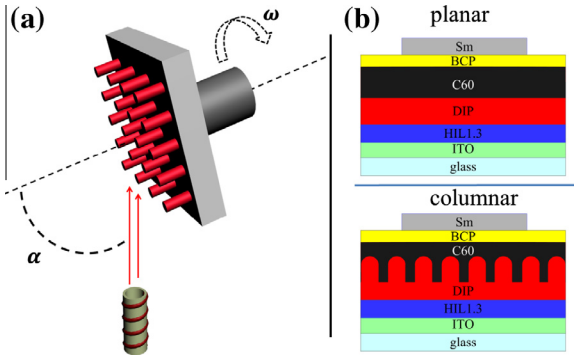

Fig. 1. (a) Experimental geometry of glancing-angle deposition (GLAD); α is the angle of the molecular flux with respect to the sample normal and ω the substrate rotation frequency. (b) Scheme of the OPVC structures used; top: conventional bilayer OPVC, bottom: OPVC with DIP-NCs.

solution [19] and molecular blend structure OPVCs typically from vacuum co-deposition [10,20,21], low charge-carrier mobility, exciton quenching, and morphological issues like dead-ends in the conduction pathway (i.e., individual, isolated phase grains without connection to the respective electrode) still limit the desired efficiency improvement of this approach [22–24]. Idealized structures to overcome these limitations are bulk heterojunction OPVCs comprising a crystalline, vertically interdigitated, and laterally structured configuration of separate donor/acceptor phases, with the aim to enable generated excitons to most likely reach an interface and the separated charges to be efficiently collected by the electrodes through individual donor/acceptor zones [25,26]. As demonstrated in previous studies, a preparation technique highly promising for realizing such structures is glancing angle deposition (GLAD) [27–30], as schematically illustrated in Fig. 1a, where high aspect-ratio nanocolumns (NCs) are established through shadowing effects [25,26,31,32].

Here, we compare OPVCs based on a conventional bilayer heterojunction of a donor/acceptor pair to devices with interdigitated heterojunctions comprising NC arrays. Diindenoperylene (DIP) was chosen as donor material to establish NC arrays via GLAD as it is an emerging material for OPVCs [13]. To accomplish the interdigitated donor/acceptor heterojunction, fullerene (C60) was employed as acceptor material by subsequent (vertical) physical vapor deposition in order to fill the voids between the NCs, as schematically illustrated in Fig. 1b. We show that the performance of NC-based devices is significantly improved compared to the bilayer reference OPVCs, which we relate to the increase in active interface area and enhanced absorption of the NC arrays, as well as reducing the influence of the "trade-off" between getting high light absorption with thick C60 films and obtaining good exciton dissociation efficiency, which requires a film thickness close to the exciton diffusion length.

2. Experimental

ITO coated glass substrates (Präzisions Glas & Optik, sheet resistance <20 Ω/sq, surface roughness (rms): 2 nm) were sonicated for 10 min in acetone and, subsequently, isopropanol. UV-ozone-treatment was applied to improve the wetting of the substrate by an aqueous suspension of the intrinsically conducting polymer poly(ethylene-dioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) (H.C. Starck GmbH, HIL 1.3), employed as substrate for OPVCs. PEDOT:PSS was spin-coated and subsequently annealed at 200 °C for 5 min under ambient conditions to desorb residual water. DIP was purified twice by gradient sublimation. NCs were grown by GLAD, the material sublimed from a resistively heated ceramic crucible with a deposition rate of ca. 0.1 nm/s (quartz crystal microbalance, base pressure $<5 \times 10^{-7}$ mbar) at room temperature. The incident angle of the molecular flux (α) with respect to the substrate surface normal was set to 84° (*c.f.* Fig. 1a) and

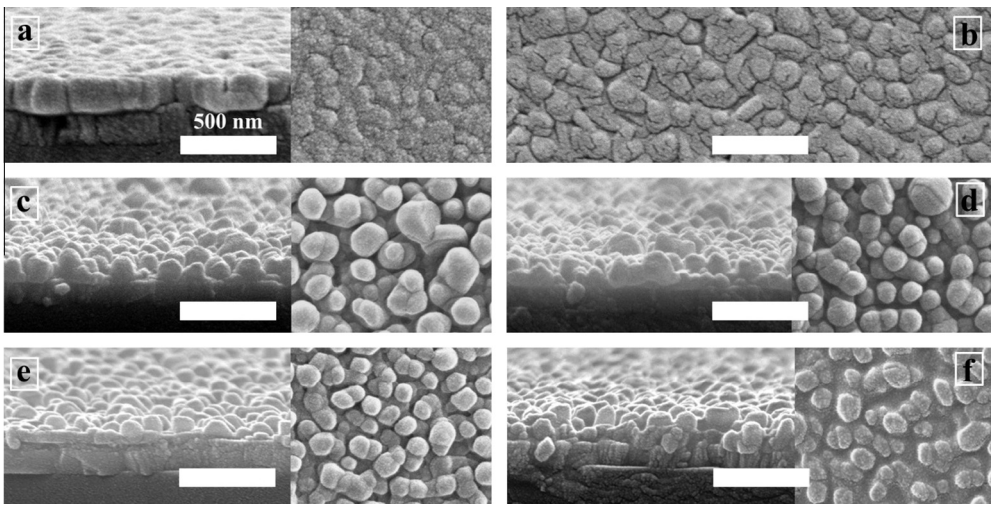

Fig. 2. SEM micrographs (cross section and top view) of DIP on bare ITO (left column) and PEDOT:PSS coated ITO (right column). (a and b) 50 nm vertically deposited DIP films, (c and d) 100 nm DIP-NCs, (e and f) 100 nm DIP-NCs on a vertically deposited 10 nm DIP underlayer.