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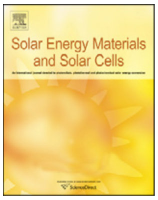

MoO_3/CuI hybrid buffer layer for the optimization of organic solar cells based on a donor–acceptor triphenylamine

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ABSTRACT

We investigate the effect of anode buffer layers (ABLs) on the performances of multi-layer heterojunction solar cells with thienylenevinylene–triphenylamine with peripheral dicyanovinylene groups (TDCV–TPA) as donor material and fullerene C_{60} as acceptor. The deposition of a CuI layer between the ITO anode and the electron donor significantly improves the short-circuit current density (J_{sc}) and fill factor (*FF*) but reduces the open-circuit voltage (V_{oc}). On the other hand, a MoO_3 buffer layer increases the V_{oc} but leads to limited J_{sc} and *FF* values, thus reducing power conversion efficiency (*PCE*). In this context, we show that the use of a hybrid anode buffer layer MoO_3/CuI leads to a considerable improvement of the cells performances and a *PCE* of 2.50% has been achieved. These results are discussed on the basis of the dual function of MoO_3 and CuI. While both of them reduce the hole injection barrier, CuI improves the conductivity of the organic film through an improvement of molecular order while MoO_3 prevents leakage current through the diode. Finally the results of a cursory study of the ageing process provide further support to this interpretation of the effects of the various buffer layers.

1. Introduction

The continuous progress of the performances of the organic photovoltaic cells (OPV cells) demonstrates that OPV cells are a potential avenue to low weight and flexible next generation solar cells [1–5].

Active materials based on small molecules are the focus of increasing interest for the fabrication of organic solar cells. In fact compared to polydisperse polymers, small molecules allow the development of reproducible synthesis purification and process. A high level of purity is critical not only for the efficiency of the solar cells but also for lifetime of the device.

The fabrication of OPV cells by vacuum deposition presents the advantage of simple fabrication of multilayer devices and straightforward control of the layers thickness [6]. A classical planar heterojunction OPV cell involves a bilayer of donor and acceptor material sandwiched between transparent and metal electrodes. The light absorbing layer is generally the electron donor (D) like for example copper phthalocyanine (CuPc) associated with an electron acceptor (A), such as fullerene C_{60} [7].

It is well known that carrier exchange at the interfaces between the electrodes and the organic materials exerts a determining influence on device performance. The energy level of the highest occupied molecular orbital of the electron donor should match the work function of the anode [8]. Rates of charge collection of the electrodes must be large and electron- and/or hole-selective. Charge selectivity is often achieved using buffer layers (BLs), interposed between the electrodes and the organic materials. Usually the anode is an indium tin oxide film (ITO) and the cathode is an aluminum film. The insertion of an exciton blocking layer (EBL) between the A and Al layers has been shown to significantly improve the performances of OPV cells [9]. Bathocuproine (BCP) is often used as EBL, as aluminum tris(8-hydroxyquinoline) (Alq_3) EBL is known to improve the lifetime of OPV cells [10,11].

An anode buffer layer (ABL) can be inserted between the D layer and the ITO anode. Often PEDOT:PSS (poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate)) is used as ABL; however it has been shown that reactions take place at the interface

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between the active layer and the PEDOT:PSS, which shorten the lifetime of the OPV cells [12]. Other ABLs were proposed. For instance, we have shown already that thin films of gold and/or MoO_3 are highly efficient ABL [13–16].

A huge amount of work has been devoted to the reduction of the barrier at the anode/electron donor interface [8,13–18]. On the other hand, the effects of the surface energy of the anode on the structure and morphology of the organic films have been scarcely considered [19,20]. However, the charge-carrier mobility in organic semiconductors based on π-conjugated molecules strongly depends on the molecular order in the films [21]. In this context, the use of an ABL that could simultaneously ensure the interfacial band matching and contribute to improving the molecular order in the absorbing layer could be of great interest.

It has been shown recently that CuI can be used to control the molecular orientation of metal phthalocyanine (MPc) in MPc/C_{60} OPV cells [19,22,23]. In this work we extend the study to the effect of CuI to the performances of multi-layer OPV cells based on tris(dicyanovinyl–triphenylamine) (TDCV–TPA) as donor and C_{60} as acceptor (Scheme 1).

Previous work has shown that whereas TDCV–TPA is a promising donor in OPV cells with PEDOT:PSS [24] or MoO_3 [25] as ABL, the *FF* and J_{sc} values of the cells remain limited.

We show here that the use of a CuI ABL significantly improves *FF* and J_{sc} but to the detriment of V_{oc}. However, we show that the use of a hybrid double anode buffer layer (DABL) can counterbalance this detrimental effect and lead to high *FF* and J_{sc} values while maintaining V_{oc}, thus resulting in a significant increase of conversion efficiency.

2. Experimental

TDCV–TPA was used as donor in multi-layer heterojunction solar cells of the type ITO/ABL/TDCV–TPA/C_{60}/Alq_3/Al. The ABL was either MoO_3 [14] or CuI or a combination of the two. The standard substrate dimensions were 25 mm × 25 mm. After masking a broad band of 25 mm × 20 mm, the ITO was etched using Zn+HCl [26]. Before thin films deposition, the ITO-coated glass substrate was scrubbed with soap, rinsed with distilled water, and dried. After introduction in the vacuum chamber (10^{-4} Pa), the ABL, CuPc, C_{60}, Alq_3 and aluminum layers were deposited onto the substrate by sublimation. The thickness of the CuI layer was varied from 1 to 4 nm, while the MoO_3 layer was 4 nm thick [13]. The already optimized thickness of the TDCV–TPA layer was 20 nm [25], that of C_{60} was 40 nm and that of Alq_3 9 nm. The effective area of each cell was 0.1 cm^2. The thin films thicknesses were estimated *in situ* using a quartz monitor. After EBL deposition, the aluminum top electrodes were thermally evaporated, through a mask of 1×10 mm^2 active area.

Generally, without protecting layer the performances of the solar cells are known to decline rapidly. In order to limit instability an encapsulating layer of amorphous selenium (Se-a), was thermally evaporated before exposing the devices to atmospheric conditions. A selenium protective coating (P_{Se}) has been proved to efficiently protect the devices against oxygen and water [27], for at least a few hours in air, depending on its thickness [28]. The longer lifetime of the devices thus obtained allows a more precise analysis of the effects of ABL. Following the protocol proposed in Ref. [29], the procedure used to study the ageing process of our OPV cells corresponds to the intermediate level labeled "Level 2". The operational lifetimes have been measured under AM1.5, in air and at room temperature. Between every measure, samples were stored in air and in the light of day. Cells were in open circuit conditions. It should be noted that, at least, six diodes are realized by the cycle of deposit and three cycles of deposits have been used for the ageing study.

The final cell architecture was glass/ITO (100 nm)/ABL/TDCV–TPA (20 nm)/C_{60} (40 nm)/BCP (9 nm)/Al (100 nm)/Se (100 nm).

Different techniques have been used to characterize the ITO/ABL and ITO/ABL/TDCV–TPA structures. The films structure was analyzed by X-ray diffraction (XRD) with a Siemens D5000 diffractometer using $K\alpha$ radiation from Cu ($\lambda_{K\alpha}$=0.15406 nm). Optical measurements were carried out at room temperature using a Carry spectrometer. The film optical density was measured at wavelengths of 1–0.30 μm.

The morphology of the different structures used as anode was analyzed by scanning electron microscopy (SEM) with a JEOL 7600F at the "Center de Micro-caractérisation de l'Université de Nantes". AFM images on different sites of the film were taken *ex-situ* in ambient conditions. All measurements have been performed in tapping mode (Nanowizard III, JPK Instruments). Classical cantilevers were used (Type PPP-NCHR-50, Nanosensor). The average force constant and resonance were approximately 14 N/m and 320 kHz, respectively. The cantilever was excited at its resonance frequency.

The characteristics of the photovoltaic cells were measured using a calibrated solar simulator (Oriel 300W) at 100 mW/cm^2 light intensity adjusted with a reference cell (0.5 cm^2 CIGS solar cell, calibrated at NREL, USA). Measurements were performed in ambient atmosphere. All devices were illuminated through TCO electrodes.

The effects of the ABL on the TDCV–TPA film conductivity were investigated using the *J–V* characteristics of hole-only devices with MoO_3 or CuI ABL. These devices were grown using high work-function electrode buffer layers. Hole-only devices were fabricated by replacing C_{60} and Alq_3 EBL by the high work function MoO_3, which is well known as hole injector (collector) and for electron blocking layer [30,31]. Hole-only devices have been made with the ITO substrate used in OPV cells. After ABL deposition a 20 nm TDCV–TPA film was deposited. The organic film was covered with 7 nm of MoO_3 and aluminum was used as top electrode.

A Kruss G40 Contact Angle Measuring System G40 was used to estimate the surface energy of anode surfaces through the sessile drop method. A drop of liquid with known surface tension (water, formamide, ethylene glycol and glycerol) is put on the anode surface and according to the Owens, Wendt, Rabel and Kaelble method, the surface tension, split up into a polar and a disperse fraction, can be deduced from the accurate measure of the angle between the substrate surface and a line tangential to the circumference of the drop [32].

The work function of the anode was measured using a Kelvin Probe instrument (KPTechnology Model SKP5050). All measurements were made at ambient conditions at *ca* 23 °C. The vibrating probe consists of a stainless steel tip of 10 mm diameter having a work function of 4.947 eV. The tip was calibrated against a gold surface before and after each measurement. The calibration value varied by approximately 20–30 meV before and after each measurement, thus keeping the measurement error within ± 30 meV.

The sampled surface is illuminated by a Hg–Zn–Cd discharge lamp giving a peak wavelength at 253 nm (4.947 eV), short enough to be absorbed by the ITO. Non-scanning mode is used to measure the work function with about 500 repetitions for a single point. Work function of the sample is given by adding the measured work function (W_F) with the correction factor (4.947 eV). The Kelvin method measures the difference of electrostatic potential (CPD) between the tip and the surface of the sample which are brought into contact, as a result of the Fermi energies equalization. The vibrating capacitor consists of the surface of the sample under test, reference surface of the electrode and the insulating medium (here air) between them. The CPD is evaluated