Pentacene/fullerene (C$_{60}$) heterojunction solar cells: Device performance and degradation mechanisms

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We demonstrate power conversion efficiencies of 1.5% from molecular photovoltaic devices based on bilayer pentacene/fullerene heterojunctions under 1 sun AM1.5G simulated irradiation. Importantly, we demonstrate the independence of the device performance on active area in the range 0.05–0.65 cm^2, a critical consideration for future scaling up to manufacture. A degradation study under constant solar illumination shows two parallel mechanisms for degradation; a photooxidation resulting in a drop of the generated photocurrent, and a UV annealing effect reducing the fill factor, both of which can be eliminated by careful choice of analysis conditions.

1. Introduction

Organic semiconductors remain the focus of intense research for photovoltaic (PV) applications due to their potential for low cost, facile manufacture. Heterojunction molecular devices have traditionally been based on phthalocyanine donor layers (in particular CuPc) in conjunction with fullerene (C$_{60}$) acceptor layers, however the low exciton diffusion lengths have led to the requirement of blends to achieve respectable device efficiencies [1,2]. More recently, pentacene has also emerged as a promising candidate to replace phthalocyanines due to its significantly higher exciton diffusion length and charge mobility [3,4]. Whilst devices based on pentacene blends have exhibited

efficiencies up to 2%, the relative improvement in performance over bilayer devices is less significant than that seen for comparable devices using phthalocyanines as the donor material [5]. The use of the more easily produced bilayers in complex device structures such as tandem cells should therefore provide less of a penalty to overall performance when using pentacene as the donor material. The need to protect devices based on pentacene/C$_{60}$ from degradation is well known [6], however the precise mechanisms of degradation are rarely studied and a more detailed understanding is required to design suitable encapsulation methods [7].

In this paper we demonstrate efficient pentacene/C$_{60}$ bilayer solar cells optimised for active layer thickness. The power conversion efficiency (η_{p}) of the best devices reaches 1.5% under true simulated 100 mW cm^{-2} AM1.5G irradiation, comparable to that reported by other groups [3,4,8]. The device performance was found to be independent of

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device active area for the range 0.05–0.65 cm^2 which provides optimism for future scaling up of similar devices. A study of the degradation of the devices was performed under various measurement conditions, and showed the presence of two distinct mechanisms; a photooxidation resulting in rapid loss of photocurrent, and a UV annealing effect leading to poor electrode contact and the appearance of a kink in the *J–V* curves. Analysis under vacuum conditions with UV-filtered light led to stable performance over 70 min under constant illumination.

2. Experimental details

All devices were grown by vacuum deposition in a Kurt J. Lesker Spectros system with base pressure of around 8×10^{-8} mbar. Indium tin-oxide (ITO) coated glass substrates were supplied by Psiotec with a sheet resistance of 15 $\Omega/\square$, and were solvent cleaned before use. Pentacene (Aldrich, 94%) and bathocuproine (BCP, Aldrich, 98%) were twice purified by thermal gradient sublimation before use, whilst C$_{60}$ (MER Corp, 99.5%) was used as received. Devices for the comparison of varying pentacene thickness were prepared from fresh source material for each growth as this gave optimised performance. Devices for active area and degradation analysis were grown from used source material which gave lower, but reproducible performance. Layer thicknesses of the organic thin films were measured during growth on a quartz crystal microbalance (QCM). The QCM reading was previously calibrated to real layer thicknesses from atomic force microscope (AFM) step-edge measurements in tapping mode on a Digital Instruments Nanoscope IIIa microscope. Al electrodes were deposited in situ to a thickness of 100 nm through a shadow mask to form an active area of 8 mm × 2 mm (0.16 cm^2) except where otherwise stated. *J–V* curves were measured by a computer-controlled Keithley 2400 sourcemeter, with 1 sun (100 mW cm^{-2}) AM1.5G illumination provided by a Sciencetech solar simulator with intensity monitored by a calibrated photodiode. External quantum efficiency (EQE) measurements were also recorded via the Keithley sourcemeter, with monochromatic light provided by a Bentham tungsten lamp/monochromator combination.

3. Results and discussion

Fig. 1 shows *J–V* curves under 1 sun AM1.5G illumination and the trend in device parameters for a series of planar heterojunction devices based on an ITO/pentacene/ 40 nm C$_{60}$/10 nm BCP/Al structure grown with varying thicknesses, d_D, of pentacene. The pentacene was grown at a rate of 0.1 nm/s with no substrate heating. A 40 nm C$_{60}$ layer was used as it matches the reported exciton diffusion length, but was also found to be the optimum thickness [9].

Peak performance is observed for a device with $d_D = 43$ nm, with $J_{SC} = 6.7$ mA cm^{-2}, $V_{OC} = 0.41$ V and fill factor (FF) = 0.54 leading to $\eta_p = 1.5\%$. The J_{SC} value shows a significant improvement over devices we have reported previously containing CuPc as their donor layer, and this can be attributed to the improved exciton transport and
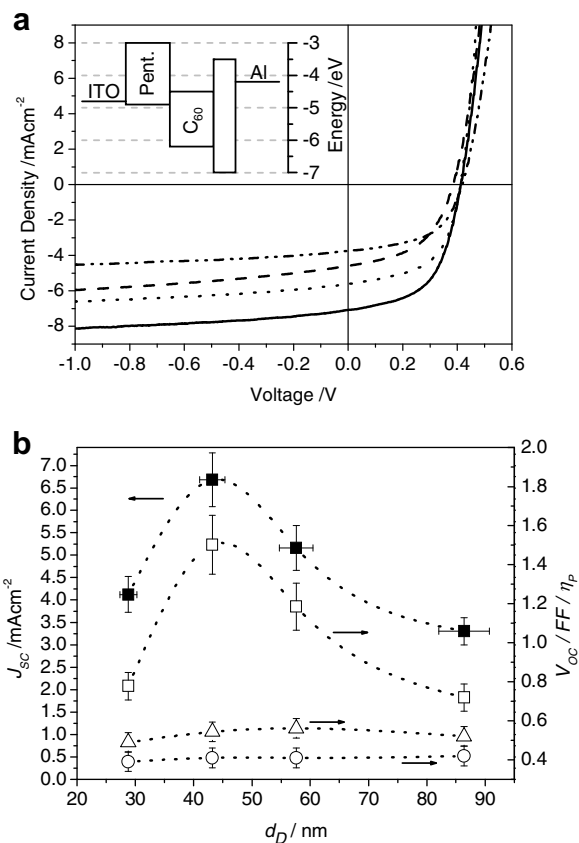

Fig. 1. (a) *J–V* characteristics of planar heterojunction devices of structure ITO/ d_D pentacene/40 nm C$_{60}$/10 nm BCP/Al with $d_D = 29$ nm (dashed line), 43 nm (solid line), 58 nm (dotted line) and 86 nm (dash-dotted line) and (inset) a schematic energy level diagram for the device. (b) A plot of J_{SC} (filled squares), V_{OC} (open circles), *FF* (open triangles) and η_p (open squares) as a function of d_D.

dissociation, higher charge mobility and improved extraction due to better matching of the donor HOMO energy level to the ITO electrode [1]. At lower pentacene thickness a loss in J_{SC} reduces performance (e.g. $d_D = 29$ nm; $J_{SC} = 4.1$ mA cm^{-2}, $\eta_p = 0.8\%$) consistent with a thinner active layer reducing exciton formation, whilst a similar effect is observed at higher than optimum thickness (e.g. $d_D = 58$ nm; $J_{SC} = 5.2$ mA cm^{-2}, $\eta_p = 1.2\%$) due to increased numbers of undissociated excitons. The *FF* is consistently between 0.50 and 0.55 across the full range of thicknesses. V_{OC} is seen to remain fairly constant regardless of device thickness, and this is to be expected in similar devices with no obvious source of internal field drop. It is interesting to note that V_{OC} is almost 0.1 V lower than in comparable CuPc/C$_{60}$ heterojunctions, an effect due to the decreased interface gap (donor HOMO – acceptor LUMO difference) from 0.5 to 0.4 eV, which is considered responsible for V_{OC} in organic PV devices [10].

The optimum pentacene thickness of ∼43 nm is approximately consistent with that found by Yoo et al. in a similar device structure [8], although Mayer et al. report devices with a lower optimum thickness of $d_D = 20$ nm [11]. The