Solar Energy Materials & Solar Cells 128 (2014) 320–329

Contents lists available at ScienceDirect

Solar Energy Materials & Solar Cells

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

Implications of the device structure on the photo-stability of organic solar cells

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ARTICLE INFO

Article history:
Received 3 April 2014
Received in revised form
12 May 2014
Accepted 24 May 2014
Available online 14 June 2014

Keywords:
Organic solar cell
Bulk heterojunction
Schottky
Stability
Transient photocurrent
External quantum efficiency

ABSTRACT

Small molecule organic solar cells (OSCs) are systematically studied for their photo-stability in an inert N_2 environment. In this work, 28-day dark, light-stress and heat-stress experiments are conducted on OSCs with strongly varied mixing ratios. Comparisons are made between the emerging, high performance Schottky device structure and the more widely studied (standard) BHJ structure. In both structures, light stress experiments result in a 10–15% loss in power conversion efficiency. Simultaneous heat-stress experiments demonstrate that these variations are not related to thermally induced changes. Photo-induced losses in open circuit voltages are observed for both device structures and are attributed to organic-electrode degradation. However, variations in the other photovoltaic parameters are more strongly dependent on the active layer composition and associated device structure. Schottky OSCs are shown to be slightly more resilient to variations in short circuit current compared to standard BHJ OSCs, but they suffer from losses in fill factor. Microsecond transient photocurrent and external quantum efficiency measurements are employed to show that these fill factor losses are due to increased recombination, associated with increased trap density by the exciton-induced degradation of the C_{60} acceptor. This effect may be problematic for all Schottky OSCs due to their use of mixed layers with very high C_{60} content. The choice of device architecture is thus shown to alter degradation mechanisms, and so it can have implications on the overall OSC photo-stability.

1. Introduction

Organic solar cells (OSCs) have improved in efficiency immensely in the past decade, with competitive power conversion efficiency (PCE) values and accordingly a more recent focus on their potential commercial applications. In line with this focus, there has been an increasing research effort on the stability of OSCs, especially since OSCs must compete with entrenched silicon photovoltaic technologies that are known to have lifetimes in excess of 25 years [1]. To this end, there are now numerous studies on the ambient stability of OSCs that have shown moisture and oxygen to have deleterious effects on both the photo-active layers and the contact electrodes [2–7], including several reviews on this topic [1,8–10], and an extensive inter-laboratory OSC stability research effort [11–14]. The motivation for such studies arose naturally, since most OSCs are required to be tested in a dry, inert atmosphere (or otherwise encapsulated) in order to make good, reproducible electrical measurements. While a great deal of knowledge has been gleaned regarding the potential avenues toward ambient-induced degradation of OSCs, there yet remains many unknowns regarding OSC degradation mechanisms in inert environment, with generally fewer systematic studies completed in inert atmosphere [15–21]. Studying the intrinsic photo-stability and thermal stability of OSCs individually (i.e. in the absence of species that serve to chemically alter the photo-active species) is of particular interest, as it provides a more rigorous understanding of the physical processes involved in the decrease in PCE values under regular OSC operation. If specific materials or device configurations are found to be photo-unstable in an inert environment, it follows that they would degrade at least as fast or potentially faster under ambient test conditions. With a better understanding of how a particular OSC degrades, one may devise strategies that specifically target inadequacies, whether they are related to bolstering the stability of the constituent materials or employing alternative device architectures.

The OSC Schottky structure, which arises when a fullerene-rich photo-active layer is placed adjacent to a high work function anode [22], is an emergent device architecture with high efficiencies and open circuit voltages (V_{oc}). The finer working points of the Schottky device architecture have only recently begun to be investigated [23–27], while its stability in relation to more traditional device architectures remains largely untested. Given that the Schottky device architecture is responsible for some of the

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http://dx.doi.org/10.1016/j.solmat.2014.05.044
0927-0248/

highest efficiency single-cell vacuum-deposited small molecule OSCs [28–30], it behooves us to gain a better understanding of its photo-stability.

In this work, small molecule OSCs are studied for their photo-stability in an inert N_2 environment. By employing mixed bulk heterojunction (BHJ) layers with drastically different mixing ratios, from donor-rich to acceptor-rich, we are able to make comparisons between the traditional/standard BHJ OSC structure and the more recently developed Schottky OSC structure. The OSCs are tested over a period of four weeks, and their photovoltaic parameters are measured in parallel with their external quantum efficiency (EQE) spectra, UV/vis absorbance spectra and microsecond transient photocurrent behavior. This full suite of characterization techniques provides a more fundamental understanding of the intrinsic device photo-degradation behavior. The results show that thermal stresses at relevant temperatures (i.e. those that the OSCs typically reach during light-stress experiments) have little impact on device performance, regardless of the device architecture; however, light stress results in 10–15% losses in PCE after four weeks of continuous 1-sun intensity illumination. Schottky OSCs generally suffer from losses in fill factor (FF), but are slightly more resilient to variations in short circuit current (J_{sc}) compared to their standard (1:1 donor:acceptor) BHJ counter-parts. Transient photocurrent measurements indicate that the losses in FF are due to increased recombination effects within the devices after aging, suggested to be due to photo-induced degradation of C_{60}. Photo-induced losses in V_{oc} are associated with a slower transient photo-response, as observed in standard BHJ structure OSCs, and are posited to be due to degradation of the contacts and interfacial extraction layers. The results thus demonstrate that the choice of device architecture can have an impact on OSC degradation mechanisms and, as a consequence, can have implications on the ultimate OSC photo-stability.

2. Experimental

To fabricate the devices, patterned indium tin oxide (ITO) slides were first cleaned by successive sonication in acetone, Micro-90 surfactant and isopropyl alcohol. The slides were scrubbed with a cotton swab after the acetone and Micro-90 sonication steps. The slides were then placed in an oven at 100 °C for at least one hour, but no longer than one day before use. The substrates were then treated with O_2 plasma in a Trion RIE/ICP system at 20 mTorr pressure and 100 W ICP power (flow rate of O_2 kept at 20 sccm). 5 nm of MoO_3 (Sigma-Aldrich) was then deposited by thermal evaporation ($<5\times10^{-6}$ Torr base pressure) at a rate of 2 Å/s. The organic materials were subsequently deposited by thermal evaporation. The mixed layers were fabricated by the simultaneous co-deposition of C_{60} ($>99.9\%$, M.E.R. Corporation) and chloroindium phthalocyanine (ClInPc) donor material. ClInPc is a metal phthalocyanine (m-Pc) donor that has recently shown promise for its near-IR absorption and its potential to generate high V_{oc} OSCs [27,31,32]. Further, we have shown it to be a good candidate for efficient Schottky OSCs [20,25], making it an ideal donor for the present study. Its reasonably high performance in the Schottky architecture relates to the position of its highest occupied molecular orbital (HOMO), which is ideally situated to help generate photocurrent from C_{60} aggregates without drastically reducing the FF (e.g. due to trapped charges) [25,27]. ClInPc was obtained from the Xerox Research Centre of Canada, where it was also purified by train sublimation. Different mixing ratios were achieved by varying the deposition rates of ClInPc and C_{60}, and the sum total deposition rate of all materials was kept at 2 Å/s. The thicknesses of the deposited layers were monitored by quartz crystal microbalances in the deposition chamber that were calibrated with a Veeco Dektak 8 Stylus Profiler. 8 nm of bathocuproine (BCP, Luminescence Technology Corp, $>99\%$, sublimed-grade) was then deposited by thermal evaporation at 2 Å/s prior to the cathode. To finish the OSCs, 100 nm of Al was deposited by thermal evaporation at 3 Å/s. A final device area of 0.2 cm^2 was defined by the intersection of the Al electrode with the patterned ITO. All solar cells that were light-stressed and heat-stressed were fabricated on the same substrate and in the same deposition run in order to minimize deposition-to-deposition variation. In this manner, ClInPc:C_{60} OSCs with varying mixing ratios (3:1, 1:1, 1:3, and 1:7 donor:acceptor) can be fabricated in multiplicate with the same extraction layers/cathode on the same substrate. This greatly simplifies comparisons among devices and allows for easily identifying trends in performance with changes in mixing ratio and under different stability-stress conditions, as will be discussed at depth throughout this work.

Photovoltaic output parameters were measured with 1-sun AM1.5G radiation from an ABET Sun 3000 Class AAA Solar Simulator (ASTM E 927-10, IEC 60904-9 ED 2.0 and JIS C 8912 compliant) and a Keithley 2400 SourceMeter, as calibrated with a NREL-calibrated mono-crystalline silicon (KG5-window) reference cell. Light-stress, heat-stress and dark testing of the devices were done in inert N_2 atmosphere. UV/visible absorption measurements were performed in air with a Shimadzu UV-2501PC UV/vis Spectrophotometer. External quantum efficiency measurements were obtained in inert N_2 atmosphere with a set-up employing a Newport 260 Cornerstone Monochromator and a Stanford Research 830 Lock-in Amplifier, as controlled by custom software. Transient photocurrent measurements were performed with white LEDs, a Stanford Research Systems DG535 pulse generator (pulsed for 5 μs at 100 Hz) and a Tektronix TDS5054 oscilloscope. A custom MATLAB program was used to extract the transient photocurrent decay (falling) data and to calculate single/bi-exponential fits. Photo-stability tests were carried out with 100 mW/cm^2 white light, with the OSCs fan-cooled to maintain a steady temperature of 40 °C. Heat-stability tests were carried out in the dark, with the devices similarly maintained at 40 °C. Atomic Force Microscope (AFM) images were obtained in air using VEECO Dimension 3100 AFM in tapping mode.

3. Results and discussion

3.1. Initial ($t=0$) performance of standard BHJ and Schottky ClInPc:C_{60} OSCs

In this work we study the photo-stability of small molecule donor:acceptor OSCs, making use of ClInPc as a model donor compound and C_{60} as an acceptor material. The device structure and associated energy band diagram for the constituent materials used in the OSCs in this work are shown in Fig. 1 (A and B respectively). All devices studied in this work employ a 40 nm donor:acceptor mixed layer between a MoO_3 hole extraction layer (HEL) and a BCP electron extraction layer (EEL). MoO_3 and BCP are specifically chosen for this series of experiments, as they are known to be effective in creating small molecule OSCs with high photo-stability in an inert N_2 environment [20]. The use of a MoO_3 HEL also allows for the creation of a very high work function anode (up to 6.8 eV [22]), known to be necessary for the Schottky interface in fullerene-based Schottky structure OSCs. The 40 nm photo-active layer allows for reasonable power conversion efficiencies at most mixing ratios, by balancing photocurrent generation with charge transport. The composition of the mixed layer is varied from donor-rich to acceptor-rich, including 3:1, 1:1, 1:3 and 1:7 donor:acceptor mixing ratios. The comparison of a 1:1 donor: acceptor mixed layer to an acceptor-rich mixed layer (e.g. 1:3 or