Organic Electronics 14 (2013) 2932–2939

Contents lists available at ScienceDirect

Organic Electronics

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

Electrical characterization of organic solar cell contact degradation resulting from ambient exposure

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ARTICLE INFO

Article history:
Received 30 May 2013
Received in revised form 8 August 2013
Accepted 9 August 2013
Available online 5 September 2013

Keywords:
Organic solar cell
Ambient degradation
Contact resistance
PEDOT:PSS

ABSTRACT

The electrical and photocurrent characteristics resulting from low light ambient degradation of organic bulk heterojunction solar cells are reported. The degradation is associated with the contacts and the active layer shows no evidence of any change in properties. Ambient exposure induces an exponential current–voltage characteristic in the contact region. An empirical model for the cell current–voltage characteristics shows how the cell properties may be corrected to recover the characteristics of the active layer. Modeling compares the effects of ohmic and exponential contact resistance on the solar cell response of a typical cell.

1. Introduction

So many organic semiconductor materials are being designed and synthesized in the attempt to improve organic bulk heterojunction (BHJ) solar cells [1,2], that it is difficult to perform a full characterization of all the materials and combinations. They are often evaluated on the basis of a single measurement of the cell response at 1-sun equivalent illumination [3–5]. It is therefore important that the measurement accurately reflects the true performance of the active BHJ layer and is not adversely affected by an extrinsic problem such as contact resistance. Contact resistance is well known to affect the cell performance [6], and ambient exposure is found to degrade cell properties [7–21]. The ambient degradation effects vary greatly from material to material and depend on the how the cell is encapsulated.

Exposure to the ambient is often related to the contacts rather than the active layer and the combination of exposure and light add photo-oxidation to the possible degradation effects [7–10]. The poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS) layer used in many organic solar cells is known to be particularly sensitive to atmospheric exposure. Kawano et al., showed that water adsorption by PEDOT:PSS degraded cells but dry air does not and they found that the effects was an increased resistance associated with the PEDOT contact [11]. Norrman et al. found that the relative importance of oxygen and water on cell degradation was different for normal or inverted devices, and also showed a large uptake of O_2 in P3HT and PCBM with the combination of exposure and illumination [12]. Girtan and Rusu report reduced degradation for exposed cells containing a PEDOT:PSS layer when the ITO layer was omitted, indicating that the degradation effect is at the ITO/PEDOT interface [13]. De Jong et al. also found that the ITO/PEDOT:PSS interface is not stable under air exposure, and that the cause is enhanced indium diffusion into the PEDOT layer, proposing that an H_2O reaction with PSS etches the ITO [14]. Somewhat in contrast, Lloyd et al. found that the dominant exposure effect was with the electron metal contact [15]. They reported that Ag is less stable then Ca/Al, and that the inclusion of the PEDOT:PSS layer had no effect on the degradation. Seeland et al. found that unsealed P3HT:PCBM cells with Al electrodes, exposed to light or in the dark ambient, showed strong degradation,

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http://dx.doi.org/10.1016/j.orgel.2013.08.007

primarily characterized by a large decrease in the short circuit current and a smaller decrease in the fill factor. The effect was attributed to oxidation of the Al contact and showed up as dark spots in electroluminescence [16]. Supporting the poor stability of PEDOT:PSS, Sun et al. reported that replacing this layer with MoO_x greatly improves the cell stability to air exposure [17]; the MoO_x hole contact layer is now commonly used [18,19]. Reese et al. found that the combination of air exposure and prolonged illumination oxidizes the fullerene in the active layer resulting in an electron trap that reduces the mobility, giving another pathway to ambient degradation [20]. They found that the blend of P3HT and PCBM is more stable to exposure than P3HT alone, and that the effect of light and exposure is to bleach the excitonic absorption bands. Lilliedal et al. studied roll-to-roll BHJ cells printed in ambient and found evidence of contact degradation that was reversed by strong illumination, apparently associated with the use of ZnO contacts [21]. Reese et al. describe further studies of the effects of light and dark ambient, showing that the P3HT:PCBM active layer is stable and degradation originates with the metal/organic interface [22].

Most of these studies do not provide a detailed electrical characterization of the degraded devices, either reporting the reduction of total cell efficiency or separate measurements of open circuit voltage (V_{oc}), short circuit current density (J_{sc}) and fill factor (FF) [7–22]. The purpose of this paper is to provide a more detailed electrical characterization of organic cells degraded by air exposure, so that the effects can be recognized and quantified from the electrical characteristics. The cells used here contain a PEDOT:PSS hole contact layer and therefore contact degradation is anticipated upon exposure to air. We develop an empirical electrical model for the effects that allows the degradation to be analyzed, to separate the contact effect from the intrinsic cell properties. We actually find that contact degradation is the only effect of atmospheric exposure and the active layer shows no observable degradation in the particular material system studied. A previous publication analyzes the effects of an ohmic series resistance on the electrical properties of the cell and shows how the cell current–voltage characteristics $J(V)$ can be corrected to give the internal performance of the active BHJ layer [23]. The present data show that air exposure creates highly resistive contacts, but that the contact is highly non-ohmic, and we discuss the correction for this case.

2. Materials and methods

The active layer of the BHJ solar cells comprises the donor poly(3-hexylthiophene-*co*-3-(2-ethylhexyl)thiophene) and the acceptor phenyl-C_{61}-butyric acid methyl ester; ($P3HT_{75}$-*co*-EHT_{25}:PCBM). The devices have a standard device architecture of glass/ITO/PEDOT:PSS/Active layer blend/Al, and details of their preparation are described elsewhere [24]. One device without any encapsulation and another device with glass encapsulation were used for this study. The encapsulation was performed using light/UV-curing adhesive with high barrier function against water vapor (DELO-KATIOBOND LP655). The devices were degraded by leaving them exposed to air and light in a lab in which ordinary fluorescent room lights were on most days but there was no exposure to sunlight or other strong illumination. The room light brightness was less than 100 $\mu W/cm^2$ and so the total daytime light exposure is equivalent to less than 1 min of sunlight. The samples were measured periodically and exposure was continued for a total of 97 days. The measured characteristics were the dark and illuminated current–voltage characteristics, the steady state photocurrent at different white light intensities from a halogen light source and the photocurrent spectral response measured at short circuit. The photocurrent measurements were made using a lock-in technique that automatically subtracts the dark current and the spectral response measurement technique is described elsewhere [25]. The illuminated current–voltage $J(V)$ characteristics were obtained by adding the photocurrent and dark current, and we confirmed that the result was identical to the direct measurement of the $J(V)$ steady state characteristics.

3. Measurement results

Fig. 1 shows the change in the forward dark current characteristics for the unencapsulated $P3HT_{75}$-*co*-EHT_{25}:-PCBM cell during 3 months of ambient exposure. The initial dark current is typical of an organic solar cell with a shunt resistance dominating below about 0.5 V, an exponential diode region up to about 0.8 V with ideality factor of 2, and a series resistance at higher voltage. The data labeled 'stored' was measured after the sample had been in a nitrogen storage container for about 1 month. The door

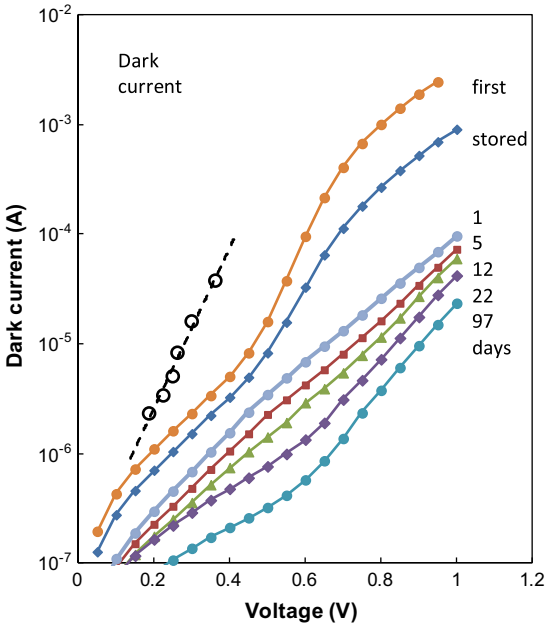

Fig. 1. Plot of the voltage dependence of the forward bias dark current for the unencapsulated organic solar cell after various stages of exposure to the ambient, extending for 97 days. Open circles and dashed line shows the voltage difference between the first and 5 day data.