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Size-dependent behavior of polymer solar cells measured under partial illumination

Dong Gao, Dwight S. Seferos *

Department of Chemistry, University of Toronto, 80 St. George Street, Toronto, Ontario, Canada M5S 3H6

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ABSTRACT

We systemically investigate the size-dependent behavior of organic photovoltaics (OPVs) tested under partial illumination. An illumination mask was hypothesized to limit uncertainty associated with device size and illumination conditions when measurements are conducted on laboratory scales. Introducing the illumination mask into the measurement improves the accuracy of J_{SC}; however partial illumination will result in a decrease in V_{OC} and an increase in FF. This last observation is explained by diodes contributing both light and dark currents in the measurement. In addition to loss due to the energy required to separate bound excitons, these results suggest that non-optimized photo–dark current ratio could be another reason why measured V_{OC} is less than ideal V_{OC}.

1. Introduction

Organic photovoltaics (OPVs) have received increasing attention during the past two decades, due in part to their potential for lightweight low-cost devices, as well as the interesting physical processes that govern the operation of such devices [1–4]. A properly designed device layout and testing set-up are very important to obtain accurate results for device performance. Power conversion efficiency (PCE) is calculated from device area and incident light intensity. Accurate measurements of device area and light intensity are critical aspects of PCE measurements. There can be a great deal of uncertainty in device size from run to run, due to either shadow effects from metallization procedures or mismatch of layer-by-layer deposition [5]. Devices on laboratory scales are often smaller than 1 cm^2, and smaller than the light area that illuminates them. A further complication arises from error from the non-uniformity of incident light. For many lab scale solar simulators, a non-uniform light source such as an arc lamp is used, which will result in light intensity changes as the size and the position of testing sample are changed.

In addition to experimental uncertainty, size-dependent behavior of device performance has been reported and explained through different aspects. Series resistance scales with device area due to the intrinsic resistance of typical transparent electrodes. Resistive effects as a function of device area have been studied on small area devices [6], by using a sub-electrode structure [7,8] or by simulation [9]. Other studies have focused on edge effects (the special optical or electronic conditions that may exist at the device edge), which may also scale with size. For example, Cravino et al. concluded that additional current was generated and collected in the region that is outside the electrode pattern for a crossbar layout [10]. A high degree of optical scattering is present at the device edge, which is also a potential source of size-dependent behaviors [11]. In light of the many additive sources of experimental uncertainty, as well as size-dependent effects, we reasoned that using a well-defined illumination-restriction mask and testing under partial illumination conditions would lead to a more consistent device area and illumination intensity, and thus more consistent measurements. Herein, we describe the size-dependent behavior of OPVs using a 'light mask' (which is either of the same size or smaller than the device area) and contrast these measurements with those in which the device is fully illuminated.

2. Experimental details

Devices were fabricated on commercial indium tin oxide (ITO) substrates (Colorado Concept Coatings) that had a sheet resistance of $\sim 10\,\Omega/\square$. These substrates were cleaned in aqueous detergent, deionized (DI) water, acetone and methanol, and subsequently treated in a oxygen-plasma cleaner for 15 min to remove any residue and improve charge injection [12]. Next, poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS; Clevios P VP AI 4083) was spin-coated onto the substrates at 3000 rpm and annealed in air at 130 °C for 15 min. After

* Corresponding author. Tel./fax: +1 416 946 0285.
E-mail address: dseferos@chem.utoronto.ca (D.S. Seferos).

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annealing, substrates were transferred into a nitrogen-filled glove box, where a poly(3-hexylthiophene):[6,6]-phenyl C_{61} butyric acid methyl ester (P3HT:PCBM; 1:0.8 wt. ratio) blend was coated at 500 rpm and dried at room temperature for 24 h. Finally, a 1 nm LiF layer and a 100 nm Al anode were thermally deposited through shadow masks at $\sim 10^{-6}$ Torr. The size of LiF mask was larger than that of Al to avoid mismatch. Device areas, as defined by the area of circular Al anode, were varied from 0.07 to 0.50 cm^2. *I–V* characteristics were measured using a Keithley 2400 source meter under simulated AM 1.5G conditions with a power intensity of 100 mW/cm^2. The mismatch of simulator spectrum was calibrated using a Si diode with a KG-5 filter. EQE spectra were recorded and compared with a Si reference cell that is traceable to the National Institute of Stands and Technology. The areas of devices and masks were measured using an optical microscope. For restricted illumination measurements, a thin (0.2 mm) circular metal mask was placed in contact with the glass side of the device. The mask was dyed black to suppress light reflection.

3. Results and discussion

We will first describe devices ranging in size (0.07, 0.20 and 0.50 cm^2) that were measured under full illumination. Typical *J–V* curves and device output characteristics are given below (Fig. 1; Table 1). Statistic boxes for a total of 24 devices are given (Fig. 2). The devices used in our study operate with reasonably repeatable efficiency ($\sim$3%) for a polymer solar cell comprised of a P3HT:PCBM blend [3,13]. We chose a series of devices with repeatable performance for further discussion. In these experiments, we observe a large decline in the short circuit current (J_{SC}) for the largest device (0.50 cm^2), which we attributed to non-

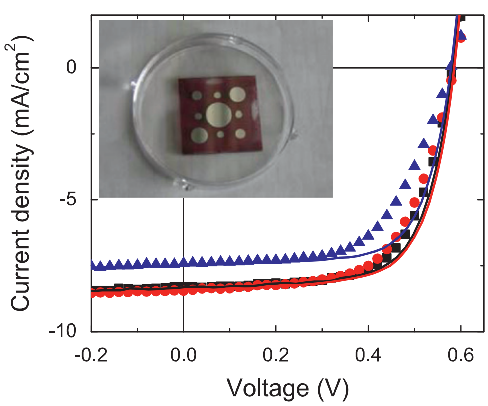

Fig. 1. *J–V* characteristics of fully illuminated OPV devices with 0.07 (black squares), 0.20 (red circles) or 0.50 cm^2 (blue triangles) area and *J–V* curves for ideal devices (black, red or blue line for 0.07, 0.20 or 0.50 cm^2 area, respectively) normalized for resistance. Inset: picture of devices with different sizes on the same substrate. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Table 1
Summary of fully illuminated device characteristics. All devices were fabricated on the same substrate.

Device area (cm^2)	R_s (Ω cm^2)	J_{SC} (mA cm^{-2})	V_{OC} (V)	FF (%)	PCE (%)	Illumination intensity (mW/cm^2)
0.07	2.86	8.20	0.58	65.92	3.14	100
0.20	6.27	8.45	0.58	62.00	3.04	
0.50	10.76	7.42	0.58	59.31	2.55	90

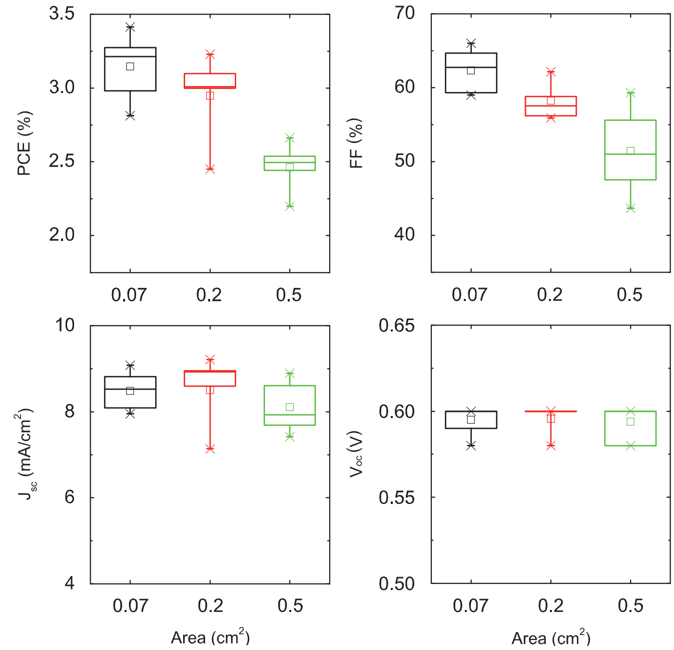

Fig. 2. Statistics for PCE, FF, J_{SC} and V_{OC} as functions of device area.

uniformity of the light intensity. To confirm this, light intensity within different areas was recalibrated by measuring the power output of light beam through light masks of the same size as those of these devices, as well as by testing the intensity at different positions from the center of the beam spot (Table S1). For devices equal to or less than 0.20 cm^2 in area, light intensity is 100 mW/cm^2 $\pm$ 2.5%, while intensity decreases to 90 mW/cm^2 for 0.50 cm^2 devices. These results show that recalibrating optical output power for a given device size is very important.

In fully illuminated devices, we also observe a significant decrease in fill factor (FF) when the device size is increased, while the open circuit potential (V_{OC}) is constant for all areas examined. The difference in light intensity noted above is not sufficient to account for this effect, and the discrepancy was further attributed to resistance. To investigate the influence of resistance, we determined series resistance (R_s) from device dark current under high bias. The distance between the two charge collecting probes, one on the edge of ITO substrate and the other on the center of Al electrode (d', Fig. 4 inset), is different for each device, and varies from 7.3 to 17.7 to 10.0 mm for 0.07, 0.20 and 0.50 cm^2 area devices, respectively. However this appears to be a very minor source of resistance since R_s declines linearly with device area, rather than probe position (Fig. 3a). The measured R_s was substituted into an equivalent circuit model of the OPV devices [14], where the total voltage of the equivalent diode (V_D) is defined as:

$$V_D = V - JR_s \quad (1)$$

and

$$J = J_0\left[\exp\left(\frac{V_D}{nk_BT}\right) - 1\right] + \frac{V_D}{R_P} - J_{ph} \quad (2)$$

After normalizing the measured *J–V* curves for voltage lost from R_s, *J–V*$_D$ characteristics for 'ideal' devices (equivalent to devices without series resistance tested under the experimental illumination conditions) show almost identical FF. Compared with the experimental J_{SC}, the ideal J_{SC} is almost unchanged, but the PCE is increased due to a larger FF. The PCE loss from FF is less than 5% for the small device (0.07 cm^2), but almost 15% when device area is 0.50 cm^2 (Fig. 3b). Power loss cannot be ignored