A critical look at organic photovoltaic fabrication methodology: Defining performance enhancement parameters relative to active area

L.J. Rozanski, Chris T.G. Smith, Keyur K. Gandhi, Michail J. Beliatis, G. Dinesha M.R. Dabera, K.D.G. Imalka Jayawardena, A.A. Damitha T. Adikaari [1], Michael J. Kearney, S. Ravi P. Silva *

Advanced Technology Institute, University of Surrey, Guildford, Surrey GU2 7XH, United Kingdom

ABSTRACT

With the ever-increasing focus on obtaining higher device power conversion efficiencies (PCEs) for organic photovoltaics (OPV), there is a need to ensure samples are measured accurately. Reproducible results are required to compare data across different research institutions and countries and translate these improvements to real-world production. In order to report accurate results, and additionally find the best-practice methodology for obtaining and reporting these, we show that careful analysis of large data sets can identify the best fabrication methodology. We demonstrate which OPV outputs are most affected by different fabrication or measurement methods, and identify that masking effects can result in artificially-boosted PCEs by increasing fill factor and current densities, requiring care when selecting which mask to use. For example, our best performing devices ($> 6\%$ efficiency) show that the smallest mask areas have not produced a surfeit of the highest performers, with only 11% of the top performing devices measured using a 0.032 cm^2 mask area, while 44% used the largest mask (0.64 cm^2). This trend holds true for efficiencies going down to 5%, showing that effective fabrication conditions are reproducible with increasing mask areas, and can be translated to even larger device areas. Finally, we emphasise the necessity for reporting the best PCE along with the average value in order to implement changes in real-world production.

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1. Introduction

As organic photovoltaics (OPV) move towards record power conversion efficiencies (PCEs), translating these novel technologies to real-world products is becoming not just a reality, but a critical component for renewable energy [1]. Currently, a well-studied polymer, poly[[9-(1-octylnonyl)-9H-carbazole-2,7-diyl]-2,5-thiophenediyl-2,1,3-benzothiadiazole-4,7-diyl-2,5-thiophenediyl] (PCDTBT), has gained considerable interest for achieving up to 7.5% PCE when combined with [6,6]-phenyl-C70-butyric acid methyl ester ($PC_{70}BM$) [2]. Recent literature has focused not only on increasing PCEs, but also on providing proof of concept with larger-area modules [3–5]. However, it has been difficult to replicate the high efficiencies seen in small, research laboratory-scale OPV cells when scaling up to large areas. This is due to a host of factors, but has been primarily been identified as being to be due to the high sheet resistance of the transparent electrode at larger areas [6,7].

Considering the variety of new materials being produced, and the potential to modify both active layers and interfacial layers, determining the optimal device 'recipe' requires a full analysis of thoroughly tested (and reproducible) results. Producing a reliable and well-understood reference device is essential when examining new materials and for determining if new materials or device structural changes produce consistent and effective results. Reproducibility is desirable for many groups, ours included, as our history of utilizing novel inorganic nanomaterials [8–10] in OPV have resulted in enhanced outputs [11]. As we are keen to ensure these results can be translated to larger area devices (essential for shifting new technology into products), reproducibility of fabricated devices will also help streamline new material trials. Prior to scaling up to larger areas, accurate measurements are necessary, preferably on a minimum active area under controlled conditions. Examining the reproducibility of results across a large number of different device batches to determine where errors can be eliminated is also vital. The importance of these twin drivers becomes clear when examining the recent OPV meta-analysis provided by Jørgenson et al., where reported PCEs remained consistent across larger areas ($> 1\ cm^2$) [12]; however, the authors noted

* Corresponding author. Tel.: +44 1483 689825.
  E-mail address: s.silva@surrey.ac.uk (S.R.P. Silva).
  [1] Author's present address: Department of Energy & Climate Change, 3 Whitehall Place, London SW1A 2AW, United Kingdom.

significant variation occurring with single layer OPV below 0.5 cm^2 active areas. Additionally, while this paper focuses on a simple donor-acceptor OPV device structures, variation across devices will increase considerably when using additives [13]. Large-scale analyses such as presented here can help isolate the most promising additives.

As has been demonstrated by multiple research groups [14–18], a set standard of measurement conditions needs to be implemented to ensure the most accurate results are reported. Ultimately, the standard for reporting high PCEs requires certification by internationally recognized agencies such as NREL or Fraunhofer ISE. While this requirement is accepted as standard, it is not a feasible option for most university laboratories as a means of confirming their day-to-day results while trying to improve known systems. Furthermore, a continuing, in-depth analysis of data, produced over the course of a project, can identify problems in the manufacturing process or find errors in measurement/reporting accuracy. Additionally, a large-scale analysis of multiple samples can isolate the most promising methodology from the natural variation occurring across research laboratories. Researchers following a standard recipe and 'tweaking' it to optimize results would give rise to local minima. The parameters not affecting the final results (such as small variations in film thickness from different spin speeds) can also be identified as areas where further research is unnecessary. Herein we show the importance of such an analysis that can be applied to larger area OPV, which require higher-throughput fabrication methods such as printing.

There should also be consideration of the OPV active area under examination, as larger areas are needed for translation to the marketplace. Numerous groups have reported decreasing solar cell efficiencies with increasing active area; which we believe is primarily the result of increased indium tin oxide (ITO) electrode sheet resistance [19–23]. Even with the awareness that small OPV active areas can artificially boost PCE through excess current collection [24,25], some recent papers fail to state their active area dimensions when reporting high PCEs. Fewer still report the reproducibility and/or variation, although the trend is now shifting towards presenting data in this manner [26–31]. With the increasing demand for good results, focus has shifted to generating ever higher PCE numbers, or 'hero devices' which are hard to reproduce in competitor laboratories [12]. As a result, it is impossible to ascertain if a reported improvement occurs for one out of ten devices or one out of a thousand, knowledge vital for real-world production. Moreover, it is crucial to understand which methodology produces reproducible results for new devices and materials, as well as ensuring these improvements translate to larger modules. This is why a shift towards larger OPV active areas, along with sharing details across research institutions [32] will move research towards more reliable, largely consistent results, analyzed using a fixed methodology.

We have undertaken an analysis of multiple reference OPV samples, with slight variations in their recipe, across three years and numerous researchers, to examine reproducibility and ensure we are reporting the best standard results. Initially this paper focuses on the effects of masking area, relative to the full device area, and then moves onto determining which fabrication methods produce reliable, enhanced results. The fabrication recipe analysis was performed for: Pedot-PSS annealing temperature variation, layer thickness changes, active layer solvent ratio, and masking area effects. Combinations of the above were examined in a complex matrix and analyzed against the history of process steps. For this paper, 133 single active area substrate devices were measured, with masking areas varied from 0.032 cm^2 to 0.64 cm^2. This was done so that the best fabrication parameters can be scaled towards a full 1 cm^2 active area, providing accurate measurements for industry standards.

2. Experimental

2.1. OPV device structure and materials

OPV devices were fabricated on 15 Ω/sq. ITO on glass substrates (0.7 × 15 × 15 mm, Luminescence Technology Corp.) with the ITO patterned in a centered 9 × 15 mm strip, sonicated in acetone and isopropanol, followed by an oxygen plasma treatment (5 min, 100 W, 20 sscm O$_2$, Emitect K1050X plasma cleaner) prior to film deposition. The vertical layer configuration was: ITO/PEDOT-PSS/PCDTBT:PC$_{70}$BM/BCP/Aluminum. Poly[3,4-ethylenedioxythiophene] poly[styrenesulfonate], (PEDOT-PSS, Clevios P VP AI 4083, Heraeus) was filtered (0.45 μm), and the 40 nm film was annealed for 10 min between 160 °C and 200 °C. Poly[[9-(1-octylnonyl)-9H-carbazole-2,7-diyl]-2,5-thiophenediyl-2,1,3-benzothiadiazole-4,7-diyl-2,5-thiophenediyl] (PCDTBT, Solaris Chem Inc.), and [6,6]-Phenyl C70 butyric acid methyl ester (PC$_{70}$BM, Solenne BV), both used without modification. 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP or bathocuproine, Luminescence Technology Corporation) was evaporated through a shadow mask (4–16 nm thickness), followed by 75 nm of aluminum to complete the reference device. PCDTBT was used in a 7 mg/mL concentration to the PC$_{70}$BM (1:4 ratio) with varying solvent ratios of dichlorobenzene to chlorobenzene (from 1:0 to 3:1). All fabrication steps after PEDOT-PSS application were performed in a glovebox.

2.2. Measurement and masking

A precision calliper was used to measure the openings of completely opaque metal masks with the following areas: 0.032 cm^2, 0.123 cm^2, 0.283 cm^2, 0.385 cm^2, and 0.64 cm^2. Devices were measured in air, without encapsulation, using a four-point probe configuration, with the aluminum electrode and ITO electrode overlap of 0.90 cm^2 centered on the 15 × 15 mm^2 square substrate to minimize excess charge collection [24,18]. The holder is designed such that no light can penetrate around the edges of the mask or substrate once both are in place, and designed so that the device is at the same height as the reference silicon cell. The calibrated silicon reference cell (ReRa Systems), was 20 × 18 mm^2 in area, and careful placement (within the marked areas) of the device holder was used to ensure reproducible measurements. An Abet Technologies 10500 solar simulator (class AAB) at AM 1.5G, 1-Sun was utilized for J–V measurements, while a Bentham Instruments PVE 300 with 1-Sun white light bias was used for external quantum efficiency (EQE) measurements.

3. Results and discussion

3.1. Masking effects

We analyzed a series of OPV devices with different masked areas to determine the effects of masking on device outputs. Fig. 1A shows the vertical device structure, and Fig. 1B shows the energy levels for the device materials. In Fig. 1C, we demonstrate a trend for OPV outputs relative to mask area. Here, a larger active area (0.90 cm^2) is measured with a series of masks with decreasing area (0.64 cm^2, 0.385 cm^2, 0.283 cm^2, 0.123 cm^2, 0.032 cm^2). For this device, as the illuminated mask area decreases relative to the full electrode area, there is a trend of slightly increasing J_{sc}, from 11.21 mA/cm^2 (0.64 cm^2 mask), up to 12.59 mA/cm^2 (0.032 cm^2 mask). The J–V outputs for each area are shown in Supplementary Table 1. Across multiple samples, this trend of increasing J_{sc} with decreasing mask area holds, and has been explained as increased light scattering effects or film inhomogeneity within the mask [14]. More importantly, there was a steady