Solar Energy Materials & Solar Cells 99 (2012) 204–212

Contents lists available at SciVerse ScienceDirect

Solar Energy Materials & Solar Cells

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

Random vs regularized OPV: Limits of performance gain of organic bulk heterojunction solar cells by morphology engineering

Biswajit Ray*, Muhammad A. Alam

School of Electrical and Computer Engineering, Purdue University, West Lafayette, IN 47906, USA

ARTICLE INFO

Article history:
Received 18 September 2011
Received in revised form
22 November 2011
Accepted 24 November 2011
Available online 4 January 2012

Keywords:
Organic bulk heterojunction solar cell
Solution processing
Planar heterojunction
Optimum morphology

ABSTRACT

Inexpensive solution processing of bulk heterojunction (BHJ) type organic photovoltaic (OPV) cells offers an attractive option for the low cost solar energy conversion. Solution processing creates a disordered morphology consisting of two organic semiconductors, intermixed randomly within the light-absorbing layer of the cell. In this paper, we use a detailed three-dimensional process-device co-modeling framework to show that in spite of the inherent structural randomness of the morphology, *the efficiency of solution-processed BHJ cells is nearly optimal – close to those of the perfectly ordered structures*. In addition, we show that the morphological randomness by itself does not increase the performance variability of large-area cells. Both the results indicate that the inexpensive solution processing of BHJ cells imposes no inherent limitation on the performance/variability and the ultimate efficiency of such solution-processed films should compare favorably to the other ordered OPV cells fabricated by more expensive techniques. Finally, we explore the theoretical optimum morphology for BHJ cells and find that fill factor is the only parameter through which efficiency can be enhanced by morphology engineering. We conclude by exploring the performance gains/limits of organic solar cells with the improvement in transport parameters.

Published by Elsevier B.V.

1. Introduction and background

Since the invention of planar heterojunction (PHJ) based organic solar cells [1], the efficiency of organic photovoltaic (OPV) technology has improved continuously, and currently it exceeds 8% for bulk heterojunction (BHJ) OPV[2]. The PHJ cells consist of a simple two layer stacked structure of donor (D) and acceptor (A) type organic semiconductors (Fig. 1a). The innovation of such stacked structure (or heterojunction) facilitated the efficient dissociation of photo-generated excitons at the planar D–A interface. However, the short circuit current density (J_{SC}) of PHJ cell is low, primarily because most of the photo-generated excitons self-recombine before being harvested by the D/A heterointerface. In fact, only those excitons generated within a diffusion length ($L_{ex} \sim 10$ nm) from the planar HJ can contribute to photo-current (see Fig. 1a). This problem of poor exciton collection (or low J_{SC}) was later solved by the bulk heterojunction (BHJ) morphology [3], where the junction between the donor and acceptor materials is distributed randomly throughout the volume of the cell, see Fig. 1b. Regardless the point of photo-excitation, this distributed D/A junction can harvest excitons efficiently, and hence BHJ–OPV cells have high J_{SC}. Unfortunately, the BHJ–OPV suffers from higher recombination [4] of the photo-generated carriers at the increased donor/acceptor interfacial area. Thus, even though BHJ solar cells have achieved close to 100% internal quantum efficiency for J_{SC} [5], the interfacial recombination loss reduces its open circuit voltage (V_{oc}) and the fill factor (*FF*) significantly.

Many groups [6–10] have explored in great detail the transport and recombination of excitons, electrons and holes in BHJ solar cells by numerical simulations. These studies confirm that the performance of the BHJ–OPV is strongly correlated with the underlying morphology. However, a statistical analysis of the performance of BHJ cells as a function of the degree of randomness of its morphology has not been reported in the literature. Thus, despite many recent reports of performance gains of ordered heterojunction OPV (OHJ-OPV, see Fig. 1c) cells fabricated by various top–down approaches (e.g., nano-imprint, templating, etc.) [11–13], it is fair to ask if one could achieve similar performance gain by optimizing the inexpensive solution based fabrication process [14–17]. Indeed, there is no convincing theoretical/numerical argument to show that the intrinsic random morphology of BHJ–OPV must necessarily lead to inferior performance compared to OHJ–OPV created by sophisticated fabrication methods. There is also very little discussion regarding the performance variability of the solution-processed BHJ cells

* Corresponding author.
E-mail addresses: biswajit.025@gmail.com (B. Ray), alam@purdue.edu (M.A. Alam).

0927-0248/$ - see front matter Published by Elsevier B.V.
doi:10.1016/j.solmat.2011.11.042

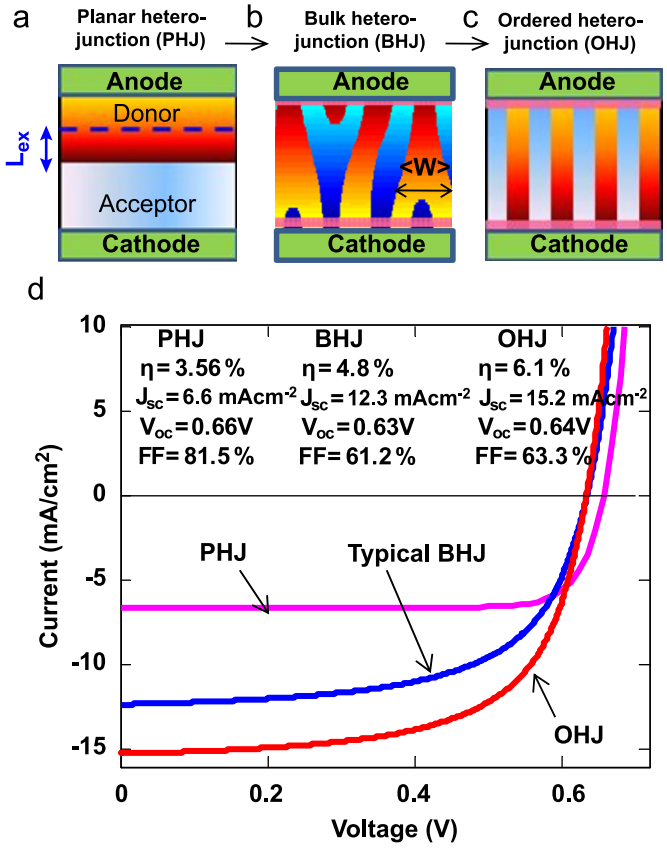

Fig. 1. Structures of various organic solar cells. (a) Planar heterojunction (PHJ), (b) Bulk heterojunction (BHJ), and (c) ordered heterojunction (OHJ) OPV cell in the chronological order of development. (d) Comparison of typical *J–V* characteristics for various OPV geometries.

originating from the inherent structural randomness and the implications of such variability for large-area modules. A systematic understanding and statistical analysis of such variability are important to predict/improve the panel efficiency of series-connected cells [18]. Finally, even though there are several recent works on the optimum geometry for OPVs [19–21], it remains unclear if such structures provide significant efficiency gain over that of random BJH-OPV (for comparable transport/recombination parameters). In the absence of such explicit comparison, it is difficult to predict the circumstances for which engineering ordered morphology may be appropriate.

In this paper, we address the above mentioned issues through a computational framework (based on transport simulation of excitons, electrons and holes) which connects the morphology of an OPV to its efficiency. We have four major conclusions: (1) We find that the regularization of BHJ morphology does not improve the OPV efficiency significantly. Instead, we show that efficiency of random BHJ cells, fabricated by inexpensive solution-based processing (with optimum mixing ratio and anneal duration), is close to that of the perfectly ordered structures. (2) We also demonstrate that even though the morphology of BHJ cells is inherently random, this *intrinsic* structural randomness does not affect the performance of large-area cells. However, precise control of various process parameters related to *extrinsic* variability remains a significant concern. (3) Next, we show that instead of the fully ordered structure (Fig.1c), a fin-like geometry (Fig. 4a), whose dimensions have been optimized for a given combination of material parameters, offers the highest efficiency. (4) Finally, we explain how the transport parameters affect OPV efficiency, and we find the limits of efficiency enhancement by improving the transport parameters like mobility, exciton diffusion length, etc.

The paper is organized as follows: We first describe the process and device modeling approach used in this analysis. Then we present a detailed comparison between the performance of ordered and random BHJ cells. Next we discuss the performance variability of BHJ cells due to its morphological randomness. Finally, we formulate the design rules for the optimal morphology and discuss the performance gain/limit with the improvement of various transport parameters like exciton diffusion length, charge carrier mobility, etc.

2. Process device co-modeling of BH–OPV

In order to explore the effect of bulk heterojunction morphology on the device performance, we first simulate the random BHJ morphology by the phase field approach. Specifically, we use the Flory–Huggins free-energy formulation within the Cahn–Hilliard transport model [22] to describe the spinodal decomposition of the respective donor–acceptor organic semiconductors. The details of the process model equations and the model parameters [23,24] are summarized in Tables 1 and 2. More sophisticated phase-field models and kinetic Monte Carlo approaches [8] have also been used by many groups to describe the finer features of the morphology. Since our goal is to explore the generic impact of morphology on efficiency of OPV cell, a simpler description of phase segregation based on the Cahn–Hilliard model, analogous to those used in Ref. [6,7], is adopted. Once the morphology is simulated, it is characterized by an average domain size [25], *W*, as shown in Fig. 2a. Unlike the BHJ morphology, the planar heterojunction (PHJ) and the ordered heterojunction (OHJ) structures are simulated not from a process model, but with fixed geometrical dimensions associated with the top–down fabrication process.

The transport of carriers (excitons, electrons, and holes) on the simulated morphology is modeled by the drift–diffusion formalism (see Eqs. (3–10) in Table 1). Optical absorption is considered only in the donor material, as is typical for P3HT:PCBM based system [26]. However, the key conclusions will not change if both donor and acceptor absorb photons. The absorption profile is assumed uniform with an effective exciton generation rate in the donor material (details on absorption profile are described in [26,27]). We then solve the steady state exciton diffusion equation in the distributed donor regions. We assume that the efficiency of exciton dissociation at the donor–acceptor hetero-interface is very high and is independent of field at the interface [28,29], so that the exciton concentration at the D–A boundary can be set to zero regardless the operating conditions. In recent years, the model for exciton transport has been generalized to include hopping transport and more complex dissociation dynamics [30], but we adopt a simpler semi-classical approach for this first discussion regarding the efficiency/variability of BHJ–OPV due to the randomness in the morphology.

The solution of exciton transport equation gives the exciton dissociation flux at the D–A interface, which we use as the charge carrier generation term in the electron and hole continuity equations [6,7]. The recombination term in the continuity equations is implemented to reflect a bi-molecular recombination process at the D/A interface [31]. Even though there is a debate in the literature regarding the dominant recombination mechanism at the hetero-interface [32], the key conclusions in the paper do not depend sensitively on the details of the recombination mechanism. Since the D–A interface is the only region where free carriers can be generated from excitons and the free