Organic Electronics 15 (2014) 2742–2748

Contents lists available at ScienceDirect

Organic Electronics

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

Modeling the structure–property relations in pillar-structured organic donor/acceptor solar cells

Teng Zhang [a,b], Erik Birgersson [a,*], Joachim Luther [a]

[a] Solar Energy Research Institute of Singapore, National University of Singapore, Engineering Drive 1, S117574 Singapore, Singapore
[b] Department of Chemical and Biomolecular Engineering, National University of Singapore, 117576 Singapore, Singapore

ARTICLE INFO

Article history:
Received 3 March 2014
Received in revised form 24 May 2014
Accepted 16 July 2014
Available online 7 August 2014

Keywords:
Organic solar cells
Heterojunction
Morphology
Drift–diffusion
Optimization
Recombination

ABSTRACT

Recently, organic solar cells with ordered morphologies in the form of vertical, interpenetrating donor- and acceptor-pillars have been demonstrated with various fabrication techniques. In order to find the optimal shape and size of these pillar structures, the conventional computational method requires simulating and comparing across different pillar designs; this may be time consuming since the pillar designs could have a large number of variations. In this paper, we establish a theoretical and computational framework that allows for efficient optimization of pillar-type morphologies. We first capture the effects of two key morphological parameters – the specific donor/acceptor interfacial area and the donor/acceptor volume ratio – with closed-form structure–property relations. We then illustrate through three-dimensional device modeling that the photovoltaic behavior of these pillar-structured cells is essentially determined by these two morphological parameters. The cross-sectional pattern of the pillar structures, on the other hand, has no major influence on the cell performance. Finally, we demonstrate a fast procedure to generate a power-density map that can aid in designing the optimal pillar structures.

1. Introduction

The performance of organic solar cells based on large molecules is heavily dependent on the nanoscale morphology of their photoactive layers [1–4]. Due to the strong exciton binding energy and the short exciton diffusion length exhibited in organic semiconductors suitable for photovoltaic conversion, most OSCs adopt the bulk heterojunction (BHJ) morphology to ensure efficient exciton dissociation and free charge carrier generation [5,6]. In the photoactive layer of an organic BHJ solar cell, the electron-donating material is intimately mixed with the electron-accepting material to form large, dispersed donor/acceptor (D/A) interfaces where excitons dissociate efficiently into free charge carriers. The nanoscale intermixing between the donor and acceptor materials, however, usually leads to convoluted percolation pathways for charge carrier transport, thereby impeding the extraction of free electrons and holes from the solar cell via the contacts. The compromise between the competing needs for charge carrier generation and extraction in disordered D/A morphologies represents a key performance-limiting factor for organic BHJ solar cells [7].

A certain degree of control over the disordered D/A morphology is possible through tuning of the device fabrication conditions, such as the thermal annealing temperature [8,9], the choice [11] and the evaporation rate [10,12] of solvents, and the use of processing additives [13]. Ho et al. demonstrated that well-connected interpenetrating D/A networks with high internal quantum efficiencies can be achieved thorough the use of phase-directing agents [14] and a molecular nanotemplating method based on acceptor-doping into a crosslinked donor network [15].

* Corresponding author.

http://dx.doi.org/10.1016/j.orgel.2014.07.036
1566-1199/

Recently, more precise control over the D/A morphology has been achieved for a variety of donor and acceptor materials through novel fabrication techniques such as oblique/glancing angle deposition [16,17], nanoimprint lithography [18,19], and template-assisted synthesis [20–22]. These methods allow for fabrication of ordered morphologies in the form of vertical, interdigitated donor- and acceptor-pillars with different cross-sectional patterns, as illustrated in Fig. 1. Such pillar structures satisfy the morphological requirements for both efficient free charge carrier generation and extraction as they provide short and direct pathways for free charge carrier transport while still maintaining feature sizes as small as 20 nm [16] to ensure efficient exciton collection at D/A interfaces. It was recently proposed that pillar-type morphologies which have inter-diffused D/A interfaces could theoretically outperform the corresponding pillar-structures with smooth interfaces [23]. The interdiffusion across the interfaces effectively increases the interfacial area thereby enhances the exciton collection efficiency. In this paper, we shall limit the discussions to the conventional pillar-structures which have smooth D/A interfaces.

Besides experiments, numerous modeling studies [24,25,27,26,28–30] have also suggested that donor and acceptor pillars perpendicular to the electrodes with a feature size of around 10 nm may represent an ideal photoactive layer morphology for organic BHJ solar cells. While recent characterization studies suggest the existence of both pure and intermixed phases in the photo-active layer [31–34], the existing continuum-level models adopt a simplified two-phase picture so as to keep the governing formulation and physical parameters tractable. These two-phase models captures the D/A morphology in the form of pure and contiguous donor and acceptor phases with smooth interfaces in-between. The governing equations of two-phase models describe the drift and diffusion of charge carriers in the donor and acceptor phases as well as charge carrier generation and recombination processes at D/A interfaces. In order to find the optimal pillar structure, the existing computational method involves implementing the two-phase device model for certain periodic pillar structures, such as an array of interpenetrating fins (see Fig. 1)a, and subsequently changing their dimensions systematically until a maximum model-predicted efficiency is found [29]. While this approach is able to capture the morphological effects of certain pillar-structure designs through the computational domain geometry, it does not provide a set of general structure–property relations that applies to all pillar-type D/A morphologies. As a result, separate modeling studies are required for pillars structures with different cross-sectional patterns. Even when limited to the study of one particular design of pillar-structure, the repeated implementations and computations of the 3D two-phase device models required for studying structures with varying dimensions are time consuming.

The structure–property relations in organic solar cells have been explored with several computational techniques, including dynamic Monte Carlo simulations [35], two-phase device modeling [28], and a graph-based approach [36]. In particular, Alam et al. [28] suggests through two-phase modeling that the efficiency of disordered morphologies is close to that of ordered, pillar-structured morphologies. They have also demonstrated optimized dimensions of an ordered fin-type structure for a given set material properties. These computational studies, however, do not establish explicit relations between morphological characteristics and the effective properties of the D/A blend, but rather explore such relations numerically based on a simulations over a number of representative morphologies. In this context, we establish an efficient computational framework that captures the inherent relations between the morphological features and the photovoltaic properties of the pillar-structured organic solar cells in the form of simple mathematical expressions. Our method is based on the previously

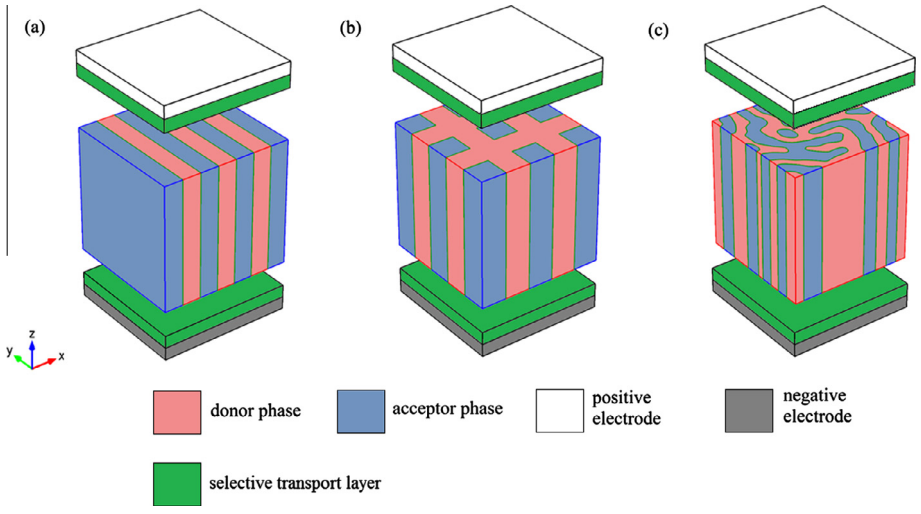

Fig. 1. Schematics of pillar-structured donor/acceptor solar cells: (a) fin-shaped interpenetrating pillars; (b) square-shaped interpenetrating pillars; (c) randomly-shaped interpenetrating donor- and acceptor-pillars. All donor and acceptor pillars are assumed to be perpendicular to the electrode contacts.