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Thickness-dependent internal quantum efficiency of narrow band-gap polymer-based solar cells



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ABSTRACT

Active layer thickness-dependent internal quantum efficiencies (IQE) of photocurrent within bulk heterojunction organic photovoltaic (OPV) devices were characterized. These active layers consisted of an electron-donating narrow band-gap polymer and an electron-accepting fullerene derivative. In order to calculate IQE spectra as a function of active layer thickness, incident photon-to-current conversion efficiency (IPCE) spectra and internal absorptance spectra of active layers with various thicknesses were estimated in these solar cell devices. The transfer matrix method (TMM) was used to calculate the internal absorptance spectra of active layers by using experimental optical constants of thin layers typical for these types of OPV devices including narrow band-gap polymer blend film. In addition, spatially resolved absorptance spectra were used to analyze obtained IPCE spectra as well as OPV device parameters (e.g., short circuit current density) at various active layer thicknesses. Finally, charge-carriercollecting probability as a function of active layer thickness was suggested with which the relationship between initial exciton generation and final power conversion efficiency can be more quantitatively described.

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1. Introduction

Recently, a polymer-based bulk-heterojunction (BHJ) solar cell exceeded 9% power conversion efficiency (PCE) [1]. However, this achievement already seems like "old news" due to the success of perovskite solar cells and their impressive PCE values compared with other novel solar cell designs [2]. Nevertheless, polymerbased organic photovoltaic (OPV) cells may have their own unique advantages compared with novel perovskite solar cells, or even traditional silicon-based solar cells. OPV cells, with their increasing importance as sustainable renewable energy sources [3,4], may establish their own market segment among these many diverse types of solar cells. Therefore, it is crucial to understand the precise operating mechanism for OPV cells, and other factors related to their PCEs to understand the operational limit for OPV cells.

Usually PCE can be expressed in terms of some basic solar cell properties such as photon absorption (photogeneration of excitons in the active layer), generation of charge carriers (CCs) from these

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http://dx.doi.org/10.1016/j.solmat.2015.07.002 0927-0248/© 2015 Elsevier B.V. All rights reserved. excitons, the subsequent transport of these CCs towards the counter electrodes before they are dissipated, and finally CC extraction across the interfaces formed between electrodes and various layers depends on the specific device structure. Hence, it is crucial to know how many photons can be captured in an active layer of a solar cell, at least at the initial stage, to understand and compare the performance of different types of solar cells. As next stage, the maximum ability of an active layer to capture a photon (internal absorption) is compared to the photocurrent generated by means of PCE or spectrally resolved IPCE to gain additional insight into how various types of solar cells perform. Another way to accomplish this comparison is to calculate the internal quantum efficiency (IQE) of the photocurrent (the ratio of the number of extracted electrons converted from the current to the number of photons absorbed in an active layer). Hence, an accurate quantity of excitons lost from either (1) excitons photogenerated in an active layer during CC generation, (2) transport to counter electrodes, and/or (3) extraction through interfaces can be estimated. An accurate ratio of the total number of electrons lost to the total number of electrons initially generated is a key factor for improving the PCE of polymer-based solar cells.

IQE can be calculated from ultraviolet-visible (UV-vis) absorption spectra and IPCE spectra. However, the complexity of the IQE calculation arises rapidly because the solar cell structure is based on a sandwiched thin film structure that has a typical thickness range from tens to hundreds of nanometers. Such a wide variation of thicknesses in conjunction with the presence of a highly reflective metallic top electrode will cause complicated internal reflections and significant interferences between waves propagated in the active layer. The active layer is where most CCs are generated and the incident light power extinguished. This is the reason why the internal absorptance in the active layer (O) in an actual device structure cannot be calculated using simple UVvis absorption spectra of a sample with a single active layer (e.g., on a glass substrate). In addition, there are plenty of complicated difficulties involved in estimating accurate optical constants for pristine and blended π -conjugated polymer films, as described by Klein et al. [5].

More than two decades ago, Pettersson et al. showed that the photocurrent action spectra of devices consisting of an active photoelectron-generating bilayer structure could be accurately calculated using the transfer matrix method (TMM) together with proper optical constants determined by spectroscopic ellipsometry [6]. With these results, the influences of the geometric structure on the efficiency of thin film devices can be quantitatively modeled. A few years later, Hoppe et al. showed Q spectra calculated by TMM, but for only BHJ OPV devices consisting of a poly(2methoxy-5-{3',7'-dimethyloctyloxy}-p-phenylene vinylene):1-(3methoxycarbonyl)propyl-1-phenyl[6,6]C₆₁ (MDMO-PPV:PCBM) blended active layer [7]. They reported calculated short circuit currents (I_{SC}) for various active layer thicknesses assuming an internal quantum efficiency of unity. Thus, their calculated I_{SC} values became a theoretical upper limit for the experimental values [8,9]. Other related studies for these BHI OPV systems have also been done. For example, Sievers et al. [10] used a π -conjugated polymer, poly(2-methoxy-5(2'-ethyl)hexoxy-phenylenevinylene) (MEH-PPV), and a fullerene derivative blend system; and Moulé et al. [11] and Monestier et al. [12] studied the poly (3hexylthiophene) (P3HT):PCBM system. Sievers et al. also compared the measured and calculated I_{SC} for a model improved by adding the exciton dissociation probability. Moulé et al. examined BHJ active layer blend ratios in combination with the thickness dependence of device performance. This latter work was done both experimentally and computationally. Yang et al. [13], to improve the PCE in OPV cells by structural modification of its layers in order to increase its photon capturing capability, extended these TMM-related studies. Dennler et al. [14] exploited the angle dependence of the PCE for OPVs. This work was followed by an intensity-dependent photocurrent generation study done by Moulé et al. [15].

Later, IQE-related studies were continued by Burkhard et al. [16,17], in which TMM tools were used to investigate the role of fullerene derivatives in OPV cells. At about the same time as Burkhard et al.'s work, Liu et al. [18] did a study on high IQEs in fullerene solar cells, and Betancur et al. [19] did a study comparing EQEs and IQEs. Meanwhile, Grancini et al. presented a study on hot exciton dissociation in polymer solar cells [20]. Grancini et al.'s work caused an important scientific discussion about hot exciton dissociation in which the complete understanding of photon energy-dependent IQE behavior is crucial. On this topic, Scharber et al. [21] noticed some important critiques of the IQE calculations reported by Grancini et al. and similar arguments given by Armin et al. [22]. Additional results were reported later using these similar methods [23,24].

Many experiments have been done to understand the complex situation within OPV devices. However, there are still some additional studies that could be done using experimental thickness-dependent IPCE data, e.g., to correlate further the thickness dependence of the IQE calculation. In addition, a novel narrow band-gap polymer, poly[4,8-bis](2-ethylhexyl)oxy]benzo [1,2-b:4,5-b']dithiophene-2,6-diyl][3-fluoro-2-[(2-ethylhexyl) carbonyl]thieno[3,4-b]-thiophenediyl] (PTB7), has not yet been characterized in this way although this material is one of the highest PCE donor material of a single BHJ layer device. Therefore, to gain a deeper insight into narrow band-gap device performance, we have decided to perform a wide range (66–320 nm) thickness-dependent device characterization with IPCE measurements to obtain a complete set of thickness dependent IQE spectra. For example, we will calculate the CC collection probability as a function of active layer thickness for OPV devices.

2. Experimental

2.1. Sample preparation

All chemicals were used as they were purchased without further purification. Pre-patterned indium tin oxide (ITO)-covered glass substrates (10 Ω /sq, 180-nm thickness from Samsung Corning) were ultrasonically cleaned for about 20 min in deionized water with < 2% detergent (Mucasol, Sigma Aldrich) followed by ultrasonic cleaning in deionized water, acetone, and isopropanol, consecutively, for about 20 min. Then the ITO substrates were treated with O₂ plasma for about 10 min. A poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate) (PEDT:PSS) (Clevios P VP AI 4083) layer of 50-nm thickness was spin-coated at 2700 rpm onto pre-treated ITO-covered glass substrates and then baked at 140 °C for over 10 min under ambient conditions.

PTB7 (1-Material Inc.) and [6,6]-phenyl-C₇₁-butyric acid methyl ester (PC71BM, Nano-C Inc.) were used as an electron donor and an electron acceptor, respectively. The chemical structures of PTB7 and PC71BM are shown in Ref. [1]. 2.16-wt% or 4.00-wt% chlorobenzene (CB) with 1,8-diiodooctane (DIO) co-solvent of 3 vol% solution of a donor/acceptor mixture (D:A) were stirred under a nitrogen atmosphere at 60 °C overnight. The blend ratio of PTB7:PC71BM was 1:1.5 by weight. The prepared D:A blend solution was filtered through a 0.45 µm syringe filter and spin-coated with different rpms onto the PEDT:PSS-covered ITO substrates. The thicknesses of the resulting BHJ photoactive layers were in the range 66-320 nm. The top electrode was prepared by thermally evaporating a combination of 0.3 nm lithium fluoride (LiF) and 120 nm aluminum (Al) layers under 10^{-6} mbar vacuum. Each device in this study was encapsulated with an engraved cover-glass using a commercial getter under N₂ atmosphere. The prepared device structure was glass(1.1 mm)/ITO (180 nm)/PEDOT:PSS(50 nm)/PTB7:PC71BM(66-320 nm)/LiF(0.3 nm)/ Al(120 nm) as schematically shown in Fig. 1.

The current-density versus voltage (J-V) characteristics of the OPV devices used in this study were measured by a Keithley 2410 source measure unit (SMU) under illumination by a Newport 94062A solar simulator in a clean room kept slightly below 25 °C. In order to maintain conventional standard test conditions (Air Mass 1.5 for the spectral irradiance distribution; 1000 W/m² for radiant intensity), the solar simulator was calibrated with a



Fig. 1. The structure of the device used in this study.

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