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Analysis of improved photovoltaic properties of pentacene/C_{60} organic solar cells: Effects of exciton blocking layer thickness and thermal annealing

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Abstract

We report on the photovoltaic properties of organic solar cells based on pentacene and C_{60} thin films with a focus on their spectral responses and the effect of thermal annealing. Spectra of external quantum efficiency (EQE) are measured and analyzed with a one-dimensional exciton diffusion model dependent upon the complex optical functions of pentacene films, which are measured by spectroscopic ellipsometry. An improvement in EQE is observed when the thickness of the bathocuproine (BCP) layer is decreased from 12 nm to 6 nm. Detailed analysis of the EQE spectra indicates that large exciton diffusion lengths in the pentacene films are responsible for the overall high EQE values near wavelengths of 668 nm. Analysis also shows that improvement in the EQE of devices with the thinner BCP layer can be attributed to a net gain in optical field distribution and improvement in carrier collection efficiency. An improvement in open-circuit voltage (V_{OC}) is also achieved through a thermal annealing process, leading to a net increase in power conversion efficiency. Integration of the EQE spectrum with an AM1.5 G spectrum yields a predicted power conversion efficiency of 1.8 ± 0.2%. The increase in V_{OC} is attributed to a significant reduction in the diode reverse saturation current upon annealing.

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Keywords: Organic solar cells; Pentacene; Fullerene; Exciton; Spectral modeling; Annealing

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1. Introduction

Organic photovoltaic (OPV) cells are rapidly gaining attention due to their potential to be fabricated at low cost in thin, flexible, and light-weight forms. Recent developments of OPV cells with ~5% power conversion efficiencies are regarded as an important step towards the demonstration of their practical viability [1,2]. In general, power conversion efficiencies of PV cells are proportional to the

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product of a short-circuit current density J_{SC}, an open-circuit voltage V_{OC}, and a fill factor *FF*. Among them, J_{SC} represents the photocurrent density generated by a given PV cell and is directly related to a cell's light absorbing properties and quantum efficiencies associated with carrier generation and collection.

In most OPV cells, a relatively large exciton binding energy makes photo-generated excitons need to migrate to a donor/acceptor junction to dissociate into free carriers [3]. However, because of the limited exciton diffusion length L, or the characteristic distance over which excitons migrate before recombining, the thickness of a photoactive layer in multilayer-type organic solar cells is often limited to values typically of the order of L. Exciton diffusion lengths in common organic materials used in OPV, typically less than a few tens of nanometers, are often smaller than their optical penetration depths $1/\alpha$ in which α is the absorption coefficient. Such thin photoactive materials cannot absorb a large portion of the incoming photons and thus are subject to a small J_{SC}, limiting power conversion efficiencies. In this respect, the product of L and absorption coefficient α is regarded as a figure of merit for J_{SC} [4].

While the exciton diffusion length can depend on many different factors, one way to improve it may be to increase the molecular ordering in the organic films. In this case, however, the challenge is to retain ease of processing and scalability. Solution-processible columnar discotic liquid crystals were proposed in that respect [5], but it appears that more studies are needed to control their processing in device geometries. An alternative approach is to use polycrystalline thin films prepared by vacuum sublimation. Good examples of those can be found in films made of a linear oligoacene ($C_{4N+2}H_{2N+4}$), a molecule containing N-fused aromatic rings. In fact, polycrystalline thin films of pentacene ($N = 5$) and tetracene ($N = 4$) were employed as transport layers in organic field-effect transistors (OFET) in hopes of improving transport properties based on their relatively good molecular ordering. Hole mobilities as high as a few $\mathrm{cm^2/V\,s}$ (pentacene) [6,7] and $0.1\ \mathrm{cm^2/V\,s}$ (tetracene) [8,9] have been demonstrated.

Recently, pentacene [10–12] as well as tetracene [13] have been demonstrated also as promising p-type photoactive materials for organic solar cells. Using a C_{60} layer as an n-type transport layer to form a heterojunction with a pentacene layer, we have reported power conversion efficiency as high as 1.5% estimated for AM1.5 G illumination [10]. Relatively large exciton diffusion length of pentacene along with a high absorption in the visible spectrum was considered one of the key origins for efficient light harvesting. It is however noted that efficient solar cells are hardly achieved by optimization of a single parameter. For example, inefficient carrier collection can compromise the net photocurrent even though all the absorbed photons contribute to a carrier generation. Moreover, a balanced improvement in short-circuit current, open-circuit voltage, and fill factor is essential in practical applications as well as to further increase power conversion efficiencies.

Here, we report on the enhancement in the photovoltaic properties of pentacene/C_{60} OPV cells. We first present the optical constants (n, k) of pentacene thin films measured using spectroscopic ellipsometric techniques as a function of wavelength. Using those optical data, spectra of external quantum efficiency (EQE) of cells with different thicknesses of BCP layers are analyzed by an exciton diffusion model, which reveals the role of improved carrier collection efficiency, as well as the large pentacene exciton diffusion length, in achieving high EQE values. Finally, we present our study of the effect of a thermal annealing process that leads to a significant increase in open-circuit voltage with a detailed description of its effect on equivalent circuit parameters.

2. Experimental

PV devices and samples for ellipsometry, XRD, and AFM studies were fabricated by vacuum sublimation with a base pressure of approximately 10^{-7} Torr in a deposition chamber (SPECTROS, Kurt J. Lesker). Deposition rate for pentacene was continuously monitored by a quartz crystal balance and stabilized at ~ 0.3 Å/s during the deposition. Substrates were held at room temperature during the deposition. The general structure of the PV devices consisted of an ITO substrate, a thin-film heterojunction of pentacene and C_{60}, a thin layer of bathocuproine (BCP), and an Al or Ag top electrode. PV samples were fabricated without breaking vacuum unless noted otherwise. ITO-coated glass (15 Ω/sq.) was purchased from Colorado Concept Coatings, and a part of ITO used for PV device fabrication was etched before cleaning to later define a device area. Typical active area A of the devices was approximately $0.10\ \mathrm{cm^2}$ or larger. All the substrates were solvent-cleaned in an ultrasonic bath in the order of soapy water, deionized water, and ethanol, with nitrogen air blown between each cleaning step. Cleaned substrates were dried in a vacuum oven prior to deposition.

PV devices were tested in a nitrogen-filled glove box that is directly connected to the deposition chamber. The filtered output of a Xe lamp (ASB-XE-175EX, CVI) was used for broadband light illumination (350–900 nm), and a motorized monochromator coupled to the same light source was used for spectral measurements.

Ellipsometric measurement was done in ambient air using a J. A. Woollam M2000 variable angle spectroscopic ellipsometer (VASE). For this work, ellipsometric spectra were measured at angles of incidence of 50°, 55°, and 60° to ensure an accurate determination of the optical function of the material.

Atomic force microscopy (AFM) measurements were done in contact mode (PicoSpmII, Molecular Imaging) in an environmental chamber maintained at relative humidity of $\sim$30% at temperature of 297 K. The AFM cantilever was provided by MikroMasch. The cantilever's normal spring constant was 0.03 N/m, and the tip radius was about 10 nm. The static loadforce was $\sim$0.5 nN.