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Determination of diffusion lengths in organic semiconductors: Correlation with solar cell performances

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ABSTRACT

Organic semiconductors are promising candidates for future applications in solar energy conversion. Recent investigations of bulk heterojunction (BHJ) semiconductors have suggested a density of states and transport mechanisms by multiple trapping close to those observed in disordered inorganic thin films. That is why we have applied to BHJ thin films experiments that are currently used for disordered semiconductors. In addition to the steady state photoconductivity we have tested the ability of the steady state photocarrier grating (SSPG) technique to provide information on the minority carrier diffusion length. We found that SSPG can be applied to P3HT:PCBM thin films leading, for the best sample, to a diffusion length of the order of 125 nm. From the comparison of the transport parameters obtained on thin films with the performances of the devices integrating the latter, we conclude that SSPG is a very powerful tool for optimizing the BHJ thin film properties before their incorporation in solar devices.

1. Introduction

Organic bulk heterojunction (BHJ) semiconductors have received a growing attention in the last decade for they may constitute the basic absorbers of tomorrow solar cells. These absorber layers are made of a blend of phase-separated electron acceptors and donors and the transport of carriers occurs in these different domains with interaction of these carriers with the density of states (DOS). Determination of the DOS distribution and identification of the transport mechanisms still remain a matter of debate and several models have been proposed [1,2]. Most of these models rely on the study of the drift mobility measured by time-of-flight experiments and its behaviors with respect to applied field and temperature. Photoconductivity studies by R. A. Street et al. have widen the field of investigations by the measurement of spectral photoresponse [3] on solar cells based on P3HT:PCBM and PCDTBT:$PC_{70}BM$ absorbers [4]. In addition, transient photoconductivity and photovoltage techniques have been applied to the same materials and devices [5]. On the basis of their experimental results these authors have proposed a model for the DOS in BHJ. The DOS is based on the properties of both materials incorporated in the cell: the highest occupied molecular orbital (HOMO) being assimilated to the valence band of inorganic semiconductors and the lowest unoccupied molecular orbital (LUMO) being assimilated to the conduction band of inorganic semiconductors. Transient photoconductivity has revealed an exponential band tail followed by a flatter distribution of deep states. As underlined by R. A. Street, transient photoconductivity has been used to study low mobility transport inorganic materials as hydrogenated amorphous silicon (a-Si:H) [6]. Some procedure based on Laplace transform was even proposed to extract the DOS distribution from post-transit time of flight currents [7]. It is beyond doubt that a similarity exists between the behaviors observed in both types of materials (BHJ and a-Si:H) in which multiple trapping in localized states seems to control transport phenomena [3]. The review of transport phenomena in polymers by S. Baranovski is also in favor of this similarity [8]. That is why we wondered if other experiments could be applied to BHJ materials to gain more insight in the material properties and therefore could be a help in the optimization of solar devices. A

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rather large number of experiments have been dedicated to the study of transport parameters in semi-insulating and semiconducting thin film materials, most of them based on their photoconductivity property. Only the light excitation spatial and temporal 'shape' is varied from one experiment to the other. The aim of this communication is not to achieve a detailed review of all the techniques and the reader may have a look at the Refs. [9–13]. The simplest technique is the steady-state photoconductivity (SSPC) in which one measures the evolution of the film photoconductivity with temperature and/or a steady generation rate. From this experiment one can deduce the dark conductivity of the material and a mobility-lifetime product under illumination. The illumination of the film can also be spatially modulated by means of a light grating created by two interfering laser beams. The simplest experiment uses a steady grating as in the steady state photocarrier grating (SSPG) [10], from which one deduces the ambipolar diffusion length of the carriers.

In this communication we shall concentrate on the SSPC and SSPG techniques applied to P3HT:PCBM thin films and compare the parameters deduced from these experiments to the performances of solar devices containing the same layers as absorbers.

2. Experimental details

First, it has to be underlined that SSPC and SSPG techniques are applied to samples built in coplanar geometry. Films are deposited on top of an insulating substrate and two parallel electrodes are subsequently deposited on the thin film with a spacing of 1 mm. Problems of transport anisotropy can then be encountered for instance in the case of micro-crystalline silicon. Due to columnar growth of the crystallites, the transport parameters can be very different when measured alongside or perpendicularly to the substrate [14–16]. In the case of organic films, we could also expect transport anisotropy even alongside the substrate if the films were prepared with an alignment of the molecules in a preferential direction [17,18]. However, in the case of BHJ thin films prepared by spin coating, as it is the case here, the disorder of the intermixed phases should prevent the occurrence of transport anisotropy and we are quite confident that the transport parameters we deduced from our experiments, with current flowing parallel to the substrate, are the same that could be measured with current flowing perpendicularly to the substrate as in solar devices.

2.1. Samples preparation

The films for SSPG and bulk heterojunction active layers, 200 nm thick, were fabricated from a P3HT:$PC_{60}BM$ solution in anhydrous 1,2-dichlorobenzene (99%, from Sigma–Aldrich) (concentration in P3HT: 26 g/l) by spin coating. P3HT and $PC_{60}BM$ were purchased from Merck. One series was achieved with different ratios of P3HT and PCBM: 1:0.3, 1:0.6, and 1:1 respectively. These films were annealed 10 min at 140 °C under nitrogen atmosphere. In addition, a series of films with a ratio of 1:0.6 was deposited without annealing or with an annealing at 100 °C during 10 min under nitrogen atmosphere. For the coplanar samples, films were deposited on glass substrates, pre-cleaned by a UV-ozone treatment, and then covered with different types of metal to achieve parallel electrodes separated by 1 mm spacing: i) 150 nm of aluminum, ii) 10 nm of gold covered with 150 nm of silver and iii) 160 nm of silver alone. The ohmicity of the contacts was checked prior to the measurements with applied voltage up to 32 V. The measurements were performed with a voltage fixed at 20 V. The films were deposited at INES and studied at GEEPS. They were sent from INES in sealed nitrogen atmosphere to avoid any oxygen or water vapor contamination. At reception and during all the measurements at GEEPS, the films were kept under vacuum in a dynamically pumped cryostat ($<10^{-3}$ Pa) in order to avoid any contamination.

Organic solar cells were fabricated on pre-etched glass/ITO substrates with the structure: Glass/ITO/PEDOT: PSS/P3HT: PCBM active layer/Ca/Al. The substrate was pre-cleaned by a UV-ozone treatment for 30 min in air. Hole Transporting Layer (HTL) was spin-coated using PEDOT:PSS (Baytron-PH) annealed for 30 min at 180 °C in air. The active layer was prepared as for the SSPC and SSPG samples. Finally, a cathode of calcium and aluminum, 200 nm thick, was evaporated at 10^{-3} Pa through a shadow mask. This leads to solar cells with an active surface of 28 mm^2. The fill factor, short circuit current, open circuit voltage and power conversion efficiency were deduced from I(V) measurements. These measurements were carried out under nitrogen atmosphere using AM 1.5, 100 mW/cm^2 illumination, obtained by an Oriel SP94043A (Xe Lamp) Solar simulator. Characteristics and power conversion efficiencies were measured via a computer controlled Keithley SMU 2400 unit. A monocrystalline silicon solar cell, calibrated at the Fraunhofer Institut für Solare Energie Systeme (Freiburg, Germany), was used as a reference cell to confirm stabilization of the 100 mW/cm^2 illumination. The used apparatus was a standard system that is widely used and gives a relative error (mismatch factor) of around 5% on the estimated power conversion efficiency in the 300–1100 nm range in comparison with AM1.5G. The mismatch factors were measured using a spectrophotometer AECUSOFT, from Flashspec.

2.2. Characterisations

We have recently built a bench on which SSPC and SSPG measurements can be performed automatically [19] the sample being maintained under vacuum. The light illuminating the film is emitted by a He–Ne laser (633 nm). For both techniques, SSPC and SSPG, we have used a rather high flux of 3×10^{16} cm^2 s^{-1}. All the measurements presented here were done at room temperature.

With the SSPC technique we have investigated the ohmicity of the contacts and, when it was the case, we have deduced from these measurements the dark conductivity σ as well as the mobility-lifetime product $\mu\tau$ of the majority carriers. As far as organic polymers are concerned the notions of majority and minority carriers may be somewhat different from those used in inorganic semiconductors, particularly the doped ones. However, even in undoped inorganic semiconductors there is often one type of carrier that gives a major contribution to the current, dark or photocurrent, because either the carriers of this type are more numerous or more mobile or both. The same behavior is probably encountered in BHJ materials and in the following we shall call 'majority' carriers those which mostly contribute to the steady photocurrent, the 'minority' ones being the less mobile for instance.

The SSPG technique was first proposed by D. Ritter and coworkers [10]. It is one of the few experiments from which one can study the influence of the minority carriers on the transport of the majority ones and eventually deduce the diffusion length L_d of minority carriers. The SSPG basic idea is to split a laser beam of wavelength λ into two beams subsequently deflected to illuminate the sample in between the contact electrodes, the polarization of each beam being parallel to the electrodes, and each beam presenting an angle $\theta/2$ with the perpendicular to sample plane. Under these conditions an array of interferences is created in the sample with a grating period Λ given by the equation

$$\Lambda = \frac{\lambda}{2\sin(\theta/2)}. \quad (1)$$

One of the beams, the probe beam, is attenuated by a factor of