



Investigation of optical spacer layers from solution based precursors for polymer solar cells using X-ray reflectometry

Philip D. Andersen, Jakob C. Skårhøj, Jens W. Andreasen*, Frederik C. Krebs

Risø National Laboratory for Sustainable Energy, Technical University of Denmark, Frederiksborgvej 399, DK-4000 Roskilde, Denmark

ARTICLE INFO

Article history:

Received 10 July 2008

Received in revised form 6 October 2008

Accepted 17 November 2008

Available online 3 January 2009

Keywords:

Polymer solar cells

Plastic solar cells

Optical spacers

Titanium oxide

X-ray reflectometry

ABSTRACT

Optical spacer layers based on titaniumalkoxide precursor solutions were prepared by spin-coating on top of bulk heterojunction layers based on poly-3-hexylthiophene (P3HT) and phenyl-C₆₁-butyric acid methylester (PCBM). Models and experiment have shown that the performance of polymer solar cells can improve upon application of an optical spacer by shifting the maximum of the electrical field vector of the incident light into the active layer. This avoids the so called “dead zone” close to the reflective electrode. We demonstrate a simple linear model that can be used to predict the intensity variations of the electrical field vector of the incident light through a multilayer structure. Central to our study is the thickness of the optical layer and we find that it is critical to control the optical spacer thickness on the actual active layer employed. X-ray reflectometry allows for the simultaneous determination of the active layer thickness and of the optical spacer layer.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

Polymer solar cells [1–10] have gone through extensive developments in recent years where efficiencies in the 4–6% range [11–13] and long operational lifetimes under simulated sunlight [14–16] and under outside conditions [17] have been reported. Large area processing of polymer solar cells is also dawning and has been explored at the 0.1 m² level [18,19]. Polymer solar cells are generally multilayer structures and the normal device geometry comprises a transparent substrate, a transparent electrode (typically the anode), a hole barrier (typically PEDOT:PSS), the active layer, a hole blocking layer or spacer and finally the second electrode which is normally a reflective metal (typically the cathode).

The normal device is assembled in that order and this implies that the active layer is immediately adjacent to the reflective metal electrode. Since the magnitude of the electric field vector at the active layer–metal interface is principally zero, this implies that there is a “dead zone” where the magnitude of the electric field is low, extending well into the active layer. Since the absorption of the incident light scales directly with the square magnitude of the electric field vector and light absorption (harvesting) is a prerequisite for the formation of charge carriers, there has been a considerable amount of work addressing the optical effects in the polymer solar cell multilayer structures [20–32]. This has also inspired the “inverted” geometry where the reflective electrode is the anode and the cathode is the transparent electrode [33–36].

In this manuscript we outline the background for using optical spacers in the context of polymer solar cells and describe results derived from a simple 1-dimensional model assuming normal incidence of a monochromatic light source. Matlab™ was used for the simulations and the code is simple and available. We then address some important practical aspects of the formation of optical spacer layers derived from titanium alkoxide and show that X-ray reflectometry is a useful tool to assay the thickness of the optical spacer layer and the active layer.

2. Experimental

2.1. Modelling

Matlab™ was employed for simulating the electric field in the multilayer structure. The model takes as input the wavelength of the incident light, the amplitude at the substrate surface, interface positions in nanometres from the substrate and the complex refractive indexes for the layers. The number of layers can be chosen freely.

2.2. Preparation of films

Silicon wafers with a native oxide layer were used as substrates for the X-reflectometry studies. The active layer was prepared by spin-coating a 2.7 μm microfiltered solution of P3HT (20 mg mL⁻¹) and PCBM (20 mg mL⁻¹) in xylene at 800 rpm. The optical spacer solution was prepared according to the procedure described in [32]. Briefly, titanium(IV)isopropoxide, Ti(OCH(CH₃)₂)₄ (10 mL),

* Corresponding author. Tel.: +45 4677 4702; fax: +45 4677 4791.
E-mail address: jewa@riso.dtu.dk (J.W. Andreasen).

2-methoxyethanol, $\text{CH}_3\text{OCH}_2\text{CH}_2\text{OH}$ (50 mL) and ethanolamine, $\text{H}_2\text{NCH}_2\text{CH}_2\text{OH}$ (5 mL) were mixed in a three necked flask under argon and heated to 80 °C while stirring for 2 h and then to 120 °C for 1 h. The heating steps were repeated. The solution was cooled and immediately spin-coated onto the $\text{SiO}_2/\text{P3HT-PCBM}$ substrates at 1000, 2000, 3000 and 4000 rpm and dried in air for 1 h before heating to 150 °C for 10 min under argon. X-ray reflectometry was then carried out on the freshly prepared samples in the ambient atmosphere. The chemicals were purchased from Aldrich and used directly as received. The same precursor solution was spin-coated on glass substrates at 800, 1800, 2500 and 3200 rpm followed by the same drying and heating process used for the spacer layers deposited on the active layer. The thickness of these films was determined by profilometry.

2.3. Film characterization

The reflectometry experiments were carried out in a θ - θ (incidence–exit angle) geometry. The X-ray reflectometer is equipped with a Seifert sealed X-ray Cu tube operating at 40 kV, 20 mA. The emitted Cu K_α X-rays ($\lambda = 0.15418$ nm) are focused by multi-layer optics (Osmic) and collimated with slits. The reflected intensity is recorded with a Cyberstar scintillation point detector. Measurement of the reflectivity profile up to a scattering vector of $|\mathbf{q}| = 1.7 \text{ nm}^{-1}$ ($|\mathbf{q}| = 4\pi \sin \theta / \lambda$, where λ is the X-ray wavelength) was completed in 25 min. The data were normalized to the calculated Fresnel reflectivity for the substrate below the critical angle for total external reflection and fitted with a box model using the dynamical formalism of Parratt [37] implemented in a set of MATLAB[®] routines. The optimization was performed as a combination of a genetic algorithm and a constrained non-linear least squares minimization (the latter to ensure local convergence to the minimum). Thin boxes of intermediate density were included between the boxes corresponding to the major layers of the structure, and adequately represent diffuse or graded interfaces. In addition to the density profile, the effective footprint and a correction for absorption were fitted to the data. The reflectivity profile calculated from the fitted model was smeared using an empirical model for the instrumental resolution. The data points were weighted by an estimated relative error of 4% because the main source of uncertainty is systematic errors in the mechanical setup and not counting statistics.

The scattering length density for the substrate was constrained to vary within a few percent of the theoretical calculated values, assuming a mass density of 2.33 g cm^{-3} for Si and 2.20 g cm^{-3} for SiO_2 , whereas the active layer and spacer densities were allowed to vary by 50–100% with respect to nominal mass densities of 4.23 g cm^{-3} for TiO_2 (rutile) glass and 1.1 g cm^{-3} for the active layer, to allow for residual solvent, porosity and amorphous/semi-crystalline material.

We used our Grazing Incidence Wide Angle X-ray Scattering (GIWAXS) setup [38] to determine possible crystalline structure of the optical spacer layer.

The thickness of titanium oxide films on glass was determined by profilometry, using an atomic force microscope (PISA XE-150 Advanced Scanning Probe Microscope).

3. Results and discussion

3.1. Titanium oxide as an optical spacer

The benefits of using an optical spacer was demonstrated by Roman et al. [20] and employed a sublimed layer of C_{60} on top of the conjugated polymer. This original paper spawned a series of manuscripts that experimentally employed C_{60} as the optical spacer

layer and that theoretically addressed the problem of modeling the standing wave pattern that is obtained in the multilayer structure. The technique also spread to molecular organic photovoltaics where it is highly suited since these devices are prepared by sublimation of the organic n-type and p-type materials (typically a perylene and a phthalocyanine, respectively). For these systems the use of TiO_2 as the spacer layer appeared. TiO_2 is an excellent n-type conductor with a good energy level match of the conduction band to most organic materials and it also has excellent optical transparency in contrast to C_{60} that does absorb in the visible range giving light golden-brown coloured films. The first uses of TiO_2 as the optical spacer employed evaporation of a suitable titanium oxide precursor in a partial pressure of oxygen and this allowed for the preparation of the TiO_2 layer almost exclusively in the anatase form. The high-temperature treatment required to crystallize the layer (>450 °C) is however, not compatible with active layers consisting of an all-polymer bulk heterojunction. The most recent development has shown that a TiO_x spacer can be prepared from a precursor based on a titanium alkoxide in a suitably viscous alcoholic amine solution. After spin-coating the film a hydrolysis procedure in humid atmosphere followed by drying at 150 °C is important to obtain the correct optical spacer [32].

3.2. Optics and the matrix method

The propagation of electromagnetic waves are described by Maxwell's equations and from these the Eq. (1) for plane monochromatic waves can be derived

$$\vec{E}(y) = \bar{A} \exp[i(\omega t - Ky)] \quad (1)$$

where \vec{E} is the electric field vector of the light, \bar{A} is the amplitude, y is the distance, t is the time and, ω is the angular frequency. K is a function of the materials parameters of the medium in which the monochromatic wave is propagating and a function of the wavelength, λ , as shown in (2).

$$K = \frac{2\pi}{\lambda} (n - ik) \quad (2)$$

where n and k are, respectively, the real and imaginary part of the refractive index. By combining Eqs. (1) and (2) one obtains Eq. (3) that describes electric field vector in a material where there is both refraction and absorption.

$$\vec{E}(y) = \bar{A} \exp \left[i \left(\omega t - \frac{2\pi n}{\lambda} y \right) \right] \exp \left(- \frac{2\pi k}{\lambda} y \right) \quad (3)$$

Eq. (3) describes the optical field in a homogenous material. Any transition between different materials as in the case of a multilayer device such as a solar cell where the materials have different refractive indices will lead to refractive effects that depend on the refractive indices of the two materials and the angle of incidence. In the following we chose normal incidence which limit the refractive effect to pure reflection and transmission. As a further simplification, we limit our view to a single wavelength (550 nm) because of the practical challenge of finding n values for the full solar spectrum. The imaginary part of the refractive index represents the absorption in the material as the electromagnetic wave propagates through it. The absorption coefficient, α , is given in Eq. (4).

$$\alpha = \frac{4\pi}{\lambda} k \quad (4)$$

When light propagates through a material with α having a non-zero value the light energy is absorbed and the wave is reduced in intensity. The electric field thus, becomes an exponentially damped wave.

Download English Version:

<https://daneshyari.com/en/article/1496078>

Download Persian Version:

<https://daneshyari.com/article/1496078>

[Daneshyari.com](https://daneshyari.com)