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## Non-destructive optical characterization of phase separation in bulk heterojunction organic photovoltaic cells

D. Georgiou<sup>a</sup>, A. Laskarakis<sup>a</sup>, M. Morana<sup>b</sup>, P.G. Karagiannidis<sup>a</sup>, S. Logothetidis<sup>a,\*</sup><sup>a</sup> Lab for Thin Films – Nanosystems and Nanometrology (LTFN), Department of Physics, Aristotle University of Thessaloniki, GR 54124 Thessaloniki, Greece<sup>b</sup> Konarka Austria, Altenbergerstrasse 69, 4040 Linz, Austria

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## ABSTRACT

The dithiophene donor–acceptor copolymers that are bridged either with carbon (C-PCPDTBT) or silicon atoms (Si-PCPDTBT) belong to a promising family of materials for use in photoactive layers for organic photovoltaic cells (OPVs). In this work, we implement the non-destructive Spectroscopic Ellipsometry technique in the near infrared to the far ultraviolet spectral region in combination with advanced theoretical modeling to investigate the vertical distribution of the C-PCPDTBT and Si-PCPDTBT polymer and fullerene ([6,6]-phenyl C71-butyric acid methyl ester – PC<sub>70</sub>BM) phases in the blend, as well as the effect of the polymer-to-fullerene ratio on the distribution mechanism. It was found that the C-PCPDTBT:PC<sub>70</sub>BM blends have donor-enriched top regions and acceptor-enriched bottom regions, whereas the donor and acceptor phases are more homogeneously intermixed in the Si-PCPDTBT:PC<sub>70</sub>BM blends. We suggest that the chemical incompatibility of the two phases as expressed by the difference in their surface energy, may be a key element in promoting the segregation of the lower surface phase to the top region of the photoactive layer. We found that the increase of the photoactive layer thickness reduces the polymer enrichment at the cathode, producing a more homogeneous phase distribution of donor and acceptor in the bulk that leads to the increase of the OPV efficiency.

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## 1. Introduction

During the last years, there have been enormous efforts for the fabrication of solution processable organic photovoltaic cells (OPVs) in which the photoactive film is a blend of a semiconducting polymer with a fullerene derivative, sandwiched between the anode and cathode electrodes [1–8]. The OPV power conversion efficiency can be increased by the implementation of low-band gap copolymers as electron donors into the bulk heterojunction (BHJ) photoactive layer [9–11]. That is since the extension of the light absorption to the infrared spectral range leads to the increase of the short circuit current ( $J_{sc}$ ) [12].

A promising low band-gap conjugated polymer that can be used as electron donor for OPVs is the poly[2,6-(4,4-bis-(2-ethylhexyl)-4H-cyclopenta [2,1-b;3,4-b']dithiophene)-alt4,7-(2,1,3benzothiadiazole)] (denoted as C-PCPDTBT). Blends of this polymer with a fullerene derivative [6,6]-phenyl C71-butyric acid methyl ester (PC<sub>70</sub>BM) have shown efficiencies over 5% whereas the use of a processing additive was found to be necessary to actively influence the nano-morphology and to increase the fill factor (FF) above 50% [12–19]. In addition, the Si-bridged copolymer poly[(4,40-bis(2-ethylhexyl)

dithieno[3,2-b:20,30-d]silole)-2,6-diylalt-(2,1,3-benzothiadiazole)-4,7-diyl] (Si-PCPDTBT) has been reported to show high hole mobilities and broad spectrum absorption, leading to OPVs with efficiency values of 5.2% when it is blended with PC<sub>70</sub>BM [12–15,17,20,21].

During the BHJ blend formation, the polymer and fullerene derivatives are distributed in the blend due to nano-scale phase separation. The driving force of this phase separation can be either the crystallization of one (at least) of the two components or the incompatibility between the two components and the solvent from a thermodynamic point of view [11,22]. The blend morphology controls the polymer:fullerene interfacial area that is required to be large in order to achieve an efficient charge separation at the donor–acceptor interfaces and the charge transport towards the anode and cathode electrodes [11,19,22]. Therefore, it is crucial to understand the distribution of the polymer and fullerene in the blend in order to control this phase distribution that will lead to the optimum charge separation and transport [11,12,20,23]. However, most analytical techniques cannot determine in a non-destructive manner the distribution of the polymer and fullerene components in the BHJ blend. Also, there is a need to assess the BHJ morphology during the thin film fabrication by printing using large scale roll-to-roll (r2r) processes [24].

In this work, we implement non-destructive optical characterization by Spectroscopic Ellipsometry (SE) in a wide spectral region from the near infrared to the far ultraviolet, in combination

\* Corresponding author. Tel.: +30 2310998174.

E-mail address: [logot@auth.gr](mailto:logot@auth.gr) (S. Logothetidis).

to advanced modeling procedures to investigate in detail the optical properties of BHJ blends of C- and Si-bridged dithiophene polymers with fullerene derivatives and the vertical distribution of the polymer and fullerene volume fractions in the BHJ blend. This methodology has been applied for other BHJ structures, such as for P3HT:PCBM and provided significant information on their blend morphology [11,22].

The C-PCPDTBT:PC<sub>70</sub>BM has been found to form donor-enriched top regions and acceptor-enriched bottom regions, whereas there is a better intermixing of the donor and acceptor in the Si-PCPDTBT:PC<sub>70</sub>BM blends. This can be attributed to the chemical incompatibility of the donor and acceptor phases as expressed by the difference in their surface energy, as well as to the used solvents (of different boiling points) for the fabrication of the blends of C- and Si-based dithiophenes. In addition, the increase of the blend thickness promotes the formation of a more homogeneous distribution of Si-PCPDTBT and PC<sub>70</sub>BM leading to a better transport for electrons, contributing to higher device efficiency values of the OPV cells.

## 2. Experimental details

The thin films of pristine polymers and fullerene derivatives were prepared by spin coating onto glass substrates. The prepared polymers were the pristine C-PCPDTBT with 0.8 wt% from chlorobenzene (CB) with thickness of ~70 nm, and the pristine Si-PCPDTBT with 1 wt% from ortho-dichlorobenzene (oDCB), with thickness of ~80 nm. The fullerene samples consist of the pristine PC<sub>70</sub>BM with 1 wt% from oDCB, and pristine PC<sub>60</sub>BM from CB. The C-PCPDTBT:PC<sub>70</sub>BM blends were prepared by using 1 wt% (for the ratio of 1:2.7) and 0.8 wt% (for the ratio of 1:1.5) from CB. The same preparation conditions were used for the Si-PCPDTBT:PC<sub>70</sub>BM blends, however oDCB has been used as the solvent. In this study, the use of a different solvent for the two polymers is justified by previous works [9,12–14,16,25–27] that indicated respectively CB and oDCB, in combination with the blend ratios and preparation recipes here adopted, as optimal choices in terms of conversion efficiency.

The test OPV devices were fabricated by gravure printing performed on a R&D coater, using a 20 cm wide PET web substrate and continuous printing in order to produce 10 longitudinal stripes. The solution was run on hot web and coating parameters were varied in order to achieve different film thickness 75, 125, and 200 nm. In order to dry the residual solvent, the samples were annealed for 5 min at 130 °C in air, and completed with evaporation of a patterned top LiF/Ag electrode and characterized under 1 sun illumination, according to standard procedures. Several runs and batches were produced by varying the main coating parameters (solution concentration, web speed and temperature) and with the target of reproducing the best results achieved in lab devices, normally prepared by doctor-blading and spin-coating.

The optical properties and the morphology of the pristine materials and their blends have been investigated by SE from the near infrared to the visible and far ultraviolet (NIR–vis–fUV) spectral region (0.7–6.5 eV) with steps of 20 meV at an angle of incidence of 70°. SE is a powerful technique for the robust and detailed investigation of the optical properties of nanomaterials for organic electronics applications [24,28–30]. The measurement principle of SE relies on the measurement of the polarization changes in a light beam of a known polarization state, caused by its reflection or transmission from a material structure [31–34]. This polarization change is represented as an amplitude ratio  $\Psi$  and a phase difference  $\Delta$  and is the measurement commonly written as  $\rho = \tan \Psi e^{i\Delta}$ , where  $\Psi$  and  $\Delta$  are the ellipsometric angles. The final optical properties are represented by the complex

refractive index  $\tilde{n}(\omega) = n(\omega) + ik(\omega)$  and the complex pseudo-dielectric function  $\tilde{\epsilon}(\omega) = \epsilon_1(\omega) + i\epsilon_2(\omega)$ , where  $\omega$  is the photon energy [31,33,34].

In order to take account the optical response of the intermediate layers (PEDOT:PSS and PEDOT:PSS/ITO) that were deposited onto glass or PET substrate, we have measured the PEDOT:PSS/glass and ITO/PET, PEDOT:PSS/ITO/PET and we have determined their optical response and their thickness. The thickness of the PEDOT:PSS layer onto glass was found to be 41 nm, while the thickness of PEDOT:PSS and ITO films were 43.7 nm and 100.5 nm, respectively.

The surface energy of the pristine materials were measured by contact angle (CA) technique, using water with a drop volume of 5  $\mu$ l and a surface tension of 72.8 mN/m. The surface free energy was calculated by the contact angle by the following expression [35]:

$$\cos \theta = -1 + 2 \frac{\sqrt{\gamma_{SV}} e^{-\beta(\gamma_{LV} - \gamma_{SV})^2}}{\gamma_{LV}} \quad (1)$$

where  $\theta$  is the contact angle,  $\gamma_{LV}$  is the liquid–air interface tension,  $\gamma_{SV}$  is the solid–air interface tension and  $\beta$  is an empirical constant equal to 0.0001247 (m<sup>2</sup>/mJ)<sup>2</sup>. For the investigation of the surface morphology, AFM measurements were performed with a SOLVER P47 Scanning Probe Microscope (NT-MDT). Tapping mode was utilized for better image acquisition using rectangular silicon cantilevers with 10 nm nominal tip curvature.

## 3. Results and discussion

### 3.1. Optical properties of pristine materials

The calculation of the optical properties of pristine polymer and fullerene materials has been initially performed in order to be used as reference for the analysis of the  $\langle \epsilon(\omega) \rangle$  of the BHJ blends. The measured and fitted  $\langle \epsilon(\omega) \rangle$  in the energy range 0.7–6.5 eV of the pristine C-PCPDTBT and Si-PCPDTBT films deposited onto glass substrates is shown in Fig. 1. The  $\langle \epsilon(\omega) \rangle$  has been analyzed by the use of a theoretical model consisting of air/(pristine material)/glass. The optical properties were modeled by the modified Tauc–Lorentz (TL) oscillator model, described by [36,37]

$$\left. \begin{aligned} \epsilon_2(\omega) &= \frac{A\omega_0 C(\omega - \omega_g)^2}{(\omega - \omega_g)^2 + C\omega^2} \frac{1}{\omega}, & \omega > \omega_g \\ \epsilon_2(\omega) &= 0, & \omega \leq \omega_g \end{aligned} \right\} \quad (2)$$

$$\epsilon_1(\omega) = \epsilon_\infty + \frac{2}{\pi} P \int_{\omega_g}^{\infty} \frac{\xi \epsilon_2(\xi)}{\xi^2 - \omega^2} d\xi \quad (3)$$

Although the expressions of  $\epsilon_1(\omega)$  and  $\epsilon_2(\omega)$  in the TL model are empirical, this model can describe the dielectric response and the optical properties of amorphous and crystalline films. The imaginary part  $\epsilon_2(\omega)$  is calculated by multiplying the Tauc joint density of states with  $\epsilon_2(\omega)$  obtained from the Lorentz oscillator model [31]. The real part  $\epsilon_1(\omega)$  is determined by the imaginary part  $\epsilon_2(\omega)$  by the Kramers–Kronig integration [31]. The TL model can determine the energy position of the fundamental gap  $\omega_g$ , the electronic transition energy  $\omega_0$ , the broadening  $C$  and the strength  $A$  of each oscillator. The energy  $\omega_0$  of TL model corresponds to the Penn gap where the strong absorption in a material takes place. The parameter  $\epsilon_\infty$  is a constant term that accounts for the electronic transitions at higher energies of the measured energy region [36].

Fig. 2 shows the bulk refractive index ( $n$ ) and extinction coefficient ( $k$ ) of the pristine polymers and fullerene derivatives (PC<sub>60</sub>BM and PC<sub>70</sub>BM) that has been reproduced from the best-fit results of the above analysis. Both polymers can harvest photons in the long wavelength range because of the wide and strong

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