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Insights on the morphology of polymer donor:acceptor blends by optical metrology

A. Laskarakis

Lab for Thin Films - Nanobiomaterials - Nanosystems & Nanometrology (LTFN), Department of Physics, Aristotle University of Thessaloniki, 54124 Thessaloniki, Greece

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A B S T R A C T

One of the main challenges that need to be addressed to successfully implement polymer donor:acceptor blends as photoactive layers in Organic Electronic (OE) devices (e.g. Organic Photovoltaics - OPV) is the understanding of the effect of the processing and printing parameters on their morphology and the distribution of the donor and acceptor components in the photoactive layer. In this work, we present a comprehensive optical metrology methodology for the determination of the morphology of well-established polymer blends that include poly(3-hexylthiophene (P3HT) donors and phenyl-C61-butyric acid methyl ester ($PC_{60}BM$) and phenyl-C71-butyric acid methyl ester ($PC_{71}BM$) acceptors, which are used as photoactive layers for OPVs. Also, we determine the distribution of the donor and acceptor phases in the blend by analysis of the measured pseudodielectric function $\langle\varepsilon(\omega)\rangle$ by the use of effective medium theory modelling in combination with an exponential gradient model that approximates the modification of the refractive index in the different parts of the blend. This methodology emphasizes the capabilities and potential of optical metrology to be used as a quality control tool in large scale manufacturing for OE devices.

1. Introduction

Organic Electronic (OE) devices have the potential to revolutionize generation of electricity (organic photovoltaics – OPVs from conversion of photons to electric charges), information systems and lighting panels (organic light emitting diodes – OLEDs), electronic circuits and sensors (organic thin film transistors – OTFTs) solar fuel (H_2) production from H_2O reduction (photoelectrochemical cells – PECs) [1–12]. Their unique key advantages include cost-efficient and low temperature fabrication process by large area roll-to-roll (r2r) printing on flexible substrates (as plastic, paper, flexible glass), low weight, conformability for adaptation to complex surfaces, semitransparency, and recyclability [13–15]. These advantages will enable the cost-effective manufacturing of flexible OE devices for high-volume commercial applications in automotive, transport, buildings, wearables, smart packaging, to name but a few [3,11,16].

Each OE device consist of a multilayer stack of soluble nanolayers such as π-conjugated organic semiconductor blends as the active layer (e.g. photoactive in OPVs or light emitting in OLEDs), transparent electrodes and barrier layers (inorganic, polymer, hybrid) that can be printed on flexible polymer substrates as PolyEthylene Terephthalate – PET [17–23].

Nevertheless, despite the significant advances in achieving high power conversion efficiency (PCE) in OPVs that reach above 13% in small scale devices [24,25], it is crucial to optimize all the manufacturing process steps (printing, treatment, curing, scribing, encapsulation) and to fabricate high quality nanolayers with tunable and reproducible structure, and physical (e.g. optical, electronic) properties, thickness, and surface/interface nanostructure.

That is since any fluctuations in the layers nano-structure and thickness can result to OPV devices with non-reproducible functionality. The processing and printing parameters of the large scale roll-to-roll (r2r) manufacturing processes, such as rolling speed, the annealing temperature, material viscosity, printing speed are strongly affecting the structural and uniformity and thickness of the printed films. Therefore, it is essential to implement non-destructive analytical techniques to the manufacturing technologies, to optimize the process and to ensure the reproducibility of the printed OE nanomaterials and device architecture in terms of thickness, structure and quality.

A large variety of analytical methods has been implemented for the characterization of the optical and structural properties of polymer blends for OE devices, which include X-ray techniques (as X-ray Reflectivity and Grazing Incidence X-ray Diffraction-GIXRD) [26–31], X-ray Photoelectron Spectroscopy (XPS) [32,33] Transmission Electron Microscopy (TEM) [34–36], Near-Edge X-ray Absorption Fine Structure Spectroscopy (NEXAFS) [35,37], neutron reflectivity [30,38], secondary ion mass spectroscopy (SIMS) [33,39,40], optical absorption spectroscopy [26,29–31,33,41], and Electron Energy Loss Spectroscopy

E-mail address: alask@auth.gr.

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(EELS) [42–44].

These methods can provide powerful insights and detailed information on the morphology of the polymer blends, the phase segregation of the different components (polymer donors, electron acceptors) inside the blend along the lateral and vertical directions of the sample surface. For example, TEM, SIMS, and NEXAFS can provide accurate information on the three-dimensional structure of the bulk of the photoactive layer, neutron reflectivity has been used for the study of the stratification of the structure of blend films, whereas optical absorption spectroscopy can provide valuable insights on the thickness and optical properties of the polymer blends. The investigation of the chemical structure of the photoactive layer and the chemical composition at the interfaces with the contacts, electrical techniques such as capacitance-voltage (C-V) methods have been successfully used [34,45–48].

The above mentioned techniques can provide complementary and detailed information, nevertheless, each one is associated with specific limitations that makes their integration to pilot and production lines a challenging task. That is attributed to their: a) destructive character (chemical treatment, use of radiation, annealing, microtome processing, etc.), b) high measurement times (from some seconds to hours), c) limitation to manual and ex-situ measurements due to the complexity in instrumentation.

Robust optical metrology techniques such as Spectroscopic Ellipsometry (SE) have proved to be an important tool for the understanding the distribution of the electron donors and acceptors inside the structure of the photoactive blend for OPV devices [28,45,47,49–56]. These methods have a significant potential to be used as an in-line metrology tool for the quality control of large scale production processes. This is due to their non-destructive operation, high measurement speed ($<$ 50 ms for SE working the Vis-fUV spectral region), capability to model the optical properties, composition, morphology and thickness of complex multilayer structures in combination to flexibility in adaptation to pilot and production lines. In this work, we present a comprehensive methodology for the investigation of the optical properties, homogeneity, thickness, surface roughness and quality of organic semiconductors, which include poly(3-hexylthiophene (P3HT), phenyl-C61-butyric acid methyl ester ($PC_{60}BM$) and [6,6]-Phenyl-C71-butyric acid methyl ester ($PC_{71}BM$), in pristine form and blended in bulk heterojunction (BHJ) structures by Spectroscopic Ellipsometry (SE). Also, we investigate the effect of the thermal treatment of donor:acceptor blends on their optical response. Finally, we investigate the vertical distribution of the P3HT electron donor and PCBM acceptor volume fractions at the top and bottom parts of the photoactive blend. The current work extends from the above works dealing with the investigation of the optical properties by SE in a wide spectral region from the near infrared - visible - far ultraviolet (NIR-Vis-fUV) spectral region (0.7–6.5 eV), whereas it has been applied for both spin-coated and printed photoactive blends.

2. Experimental details

The thin films of pristine P3HT electron donors and PCBM fullerene derivatives were prepared by spin coating on glass substrates in a nitrogen-filled glove box. The prepared polymers were the pristine P3HT with 0.8 wt% from chlorobenzene (CB). The pristine PCBM fullerene samples include $PC_{71}BM$ with 1 wt% from Ortho-Dichlorobenzene (oDCB), and pristine $PC_{60}BM$ from chlorobenzene (CB). The spin-coated active blends consist of a highly regioregular P3HT from Rieke Metals (Sepiolid, P200, molecular weight, M_n = 10–30 kDa, poly-dispersity index, PDI = 1.7–2.2, regioregularity > 95%) and $PC_{60}BM$ from Solenne BV. The blend solution (1:0.8 *w/w*) has been prepared with a total concentration of 21.6 mg/ml in $CHCl_3$.

Prior to the deposition of the P3HT:$PC_{60}BM$ blends, a thin film of poly(3,4-ethylenedioxythiophene) polystyrene sulfonate PEDOT:PSS (PVPAI4083, Heraeus) has been deposited by spin coating on the ITO/glass substrate (20 Ω/sq). The PEDOT:PSS dispersion has been filtered using a 0.45 μm filter. The PEDOT:PSS/ITO/glass samples were annealed on a hot plate at 140 °C for 10 min to remove any residual H_2O left. The P3HT:$PC_{60}BM$ blends were spin coated on the glass/ITO/PEDOT:PSS at 700 rpm for 20 s, forming thin films with thickness of ~200 nm.

The printed P3HT:$PC_{60}BM$ active layers were prepared by r2r gravure printing on PEDOT:PSS film stripes, printed on commercially supplied PET flexible substrates (thickness: 125 μm). The r2r printing process has been performed by a lab scale r2r system from RK Print Coat Instruments Ltd. [57]. The ratio of the P3HT:$PC_{60}BM$ blend was 1:0.8. After the gravure printing of the P3HT:$PC_{60}BM$ layer, the wet film passed through the drying units in order to evaporate the solvent.

The optical properties and the morphology of the studied organic semiconductors were investigated by a Horiba Spectroscopic Ellipsometer (SE) in the near infrared - visible - far ultraviolet (NIR-Vis-fUV) spectral region (0.7–6.5 eV). The operation 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 under study [52,58]. This polarization change of the reflected light is represented as an amplitude ratio Psi (Ψ) and a phase difference Delta (Δ), and the measured quantity by SE is the complex reflectance ratio ρ given by the relation: [58–60]

$$\rho = \tan(\Psi)\cdot e^{i\Delta} \tag{1}$$

Although some information on the optical properties can be deduced directly from the SE measurements, quantitative data can only be obtained by numerical fit of specific optical models to the measured SE spectra. This procedure includes the formulation of a theoretical model (which approximates the film architecture and structure of the studied material), and the fitting of the measured $\langle\tilde{\varepsilon}(\omega)\rangle$ to this model by using the desired parameters, as variables in the numerical analysis. The quality of the numerical analysis fit is determined by the calculation of the root mean square error parameter, which calculates the error value between the measured and theoretical Ψ and Δ values [52,61,62].

In this work, we have used the Tauc-Lorentz (TL) model. In this model the imaginary part $\varepsilon_2(\omega)$ of the dielectric function is determined by multiplying the Tauc joint density of states by $\varepsilon_2(\omega)$ obtained from the Lorentz oscillator model. The TL model determines the fundamental gap ω_g, the electronic transition energy ω_0, the broadening C and the strength A of each oscillator [24,30–32,58,63,64]. This model is described by the following expressions: [64,65]

$$\varepsilon_2(\omega) = \frac{A\omega_0 C(\omega-\omega_g)^2}{(\omega^2-\omega_0^2)^2 + C^2\omega^2}\frac{1}{\omega}, \quad \omega > \omega_g$$
$$\varepsilon_2(\omega) = 0, \quad \omega \le \omega_g, \tag{2}$$

whereas the $\varepsilon_1(\omega)$ is determined by the $\varepsilon_2(\omega)$ through the Kramers–Kronig integration: [65]

$$\varepsilon_1(\omega) = \varepsilon_1(\infty) + \frac{2}{\pi}P\int_{\omega_g}^{\infty}\frac{\xi\varepsilon_2(\xi)}{\xi^2-\omega^2}d\xi \tag{3}$$

3. Results and discussion

3.1. Optical properties of pristine organic semiconductors

Fig. 1 shows the experimentally measured ⟨ε(ω)⟩ as a function of the photon energy ω of representative pristine P3HT samples; without annealing, and annealed for 3 min to different temperatures to 85 °C, 145 °C and 160 °C. The effect of the annealing process is profound on the measured $\langle\tilde{\varepsilon}(\omega)\rangle$ due to the changes of the crystalline ordering of P3HT in the film, which is reflected to the higher intensity of the optical absorptions in the $\langle\tilde{\varepsilon}(\omega)\rangle$ spectra, which is shown in Fig. 1.

For the extraction of quantitative information from the measured $\langle\tilde{\varepsilon}(\omega)\rangle$ spectra shown in Fig. 1, we have analyzed the $\langle\tilde{\varepsilon}(\omega)\rangle$ by the use of a theoretical model that consists of consisting of a multilayer stack of

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