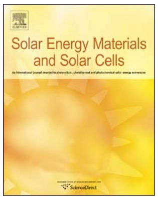
Solar Energy Materials & Solar Cells 160 (2017) 182–192

Contents lists available at ScienceDirect

Solar Energy Materials & Solar Cells

journal homepage: www.elsevier.com/locate/solmat



Novel organic photovoltaic polymer blends: A rapid, 3-dimensional morphology analysis using backscattered electron imaging in the scanning electron microscope

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ARTICLE INFO

Keywords:
Organic photovoltaics
Morphology
Backscattered electrons
Polymers
Scanning electron microscopy

ABSTRACT

Finding the optimal morphology of novel organic photovoltaic (OPV) polymer blends is a major obstacle slowing the development of more efficient OPV devices. With a focus on accelerating the systematic morphology optimisation process, we demonstrate a technique offering rapid high-resolution, 3-dimensional blend morphology analysis in the scanning electron microscope. This backscattered electron imaging technique is used to investigate the morphological features and length-scales defining the promising PffBT4T-2OD:PC70BM blend system and show how its photovoltaic performance is related to the nature of its phase separation. Low-voltage backscattered electron imaging can be used to probe for structure and domain stacking through the thickness of the film, as well as imaging surface morphology with highly competitive spatial resolution. For reference, we compare our results with equivalent images of the widely studied P3HT:PC60BM blend system. Our results also demonstrate that backscattered electron imaging offers significant advantages over conventional cross-sectional imaging techniques, and show that it enables a fast, systematic approach to control 3-dimensional active layer morphology in polymer:fullerene blends.

1. Introduction

Understanding the nature of phase separation in polymer blends is of great importance for obtaining the optimal performance from various blend systems [1]. Polymer blends have found a wide range of applications in the current energy landscape, having been recently used in novel electrolyte layers in batteries [2] or dye-sensitised solar cells [3,4], for example. However they are particularly prevalent in the field of organic photovoltaics (OPV), where control over the phase-separated morphology of the blend is a critical factor determining the photovoltaic power-conversion efficiency (PCE) [5–9]. One OPV material system that represents the current state-of-the-art is *poly[(5,6-difluoro-2,1,3-benzothiadiazol-4,7-diyl)-alt-(3,3′′′-di(2-octyldodecyl)-2,2′;5′,2″;5″,2′′′-quaterthiophen-5,5′′′-diyl)]*:[6,6]-*phenyl C71 butyric acid methyl ester* (PffBT4T-2OD:PC70BM). This material system has been reported to demonstrate a PCE of up to 10.5% [10]. In spite of its potential, this blend remains somewhat unexplored with no detailed model of its 3-dimensional morphology yet reported.

When fabricated into a photovoltaic device, the polymer component PffBT4T-2OD absorbs incident radiation (forming an exciton), and then acts as an electron donor to the fullerene component (e.g. PC70BM). The photogenerated electrons and holes are then extracted via the fullerene and PffBT4T-2OD phases, respectively [6]. In an efficient photovoltaic blend, there is generally intimate mixing between the polymer and fullerene, as the diffusion length of excitons in many conjugated polymers is limited to < 10 nm. Thus the formation of phase-separation on a similar length scale is generally believed to be essential for efficient exciton dissociation [5]. Additionally, it is

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Abbreviations: BSE, Backscattered electron; HeIM, Helium ion microscope

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http://dx.doi.org/10.1016/j.solmat.2016.10.029
Received 25 July 2016; Received in revised form 12 October 2016; Accepted 18 October 2016

necessary to extract dissociated charges from the device without problems relating to charge recombination. In an ideal blend morphology, continuous pathways should exist comprising individual electron- or hole-transporting phases to ensure efficient electron and hole extraction [11]. It is often proposed that phase-separated morphologies composed of columnar structures passing through the film thickness are highly suited to OPV application [12,13], as they combine optimal charge extraction characteristics with a large interface area.

Previous work with X-ray scattering has shown that optimised PffBT4T-2OD:PC70BM blend films are typically characterised by a ~300 nm thick film containing highly-crystalline polymer phases having length-scales of 30–40 nm [10,14]. The phase-separated domains were also shown to be highly pure, with little intermixing between the polymer and fullerene phases. Despite this, the detailed nature of the phase-separated blend morphology within this system was not determined. It is clear that building a detailed picture of the nanoscale structure within a PffBT4T-2OD:PC70BM blend will help in the design of new systems that reach even higher efficiencies [15].

Nanoscale phase-separation in polymer blend films can be revealed using high-resolution imaging techniques such as electron microscopy. Phasecontrast in these films is often low however, and thus the generation of unambiguous electron microscope images can be challenging [16]. Various techniques have been devised to overcome such issues, including the use of energy-filtered techniques in the scanning electron microscope (SEM) [17] or transmission electron microscope (TEM) [18,19] which employ energy-selective electron detection to boost the contrast between the blend components. Additionally, helium ion microscopy (HeIM) replaces the incident electron beam with a helium ion beam and can produce higher quality morphology images as a result [20]. Whilst such techniques are able to generate images with impressive lateral resolution, they require specialist equipment that is not widely available or, in the case of TEM-based methods, require complex and time-consuming preparation of electron transparent samples. This lack of easily accessible information has contributed to the morphology optimisation bottleneck that is hindering the advancement of new OPV systems – a situation well addressed in Ref. [15]. We have implemented low-voltage backscattered electron (BSE) imaging of OPV blends to enable rapid, 3-dimensional morphology characterisation in the SEM.

Previously, BSE imaging of polymer systems has been employed by 'staining' one polymer phase with a heavy metal compound to improve BSE contrast [21,22]. This technique typically uses high-energy primary beams, which can lead to poor surface sensitivity and a significant risk of sample damage. More recently, advancements in SEM technology and BSE detector performance have allowed the development of low-energy BSE methods, which have proven effective at combining high spatial-resolution with surface-sensitive material information [23]. This has been used to demonstrate material contrast on polymer films [25,26] using low-voltage BSE imaging without the necessity of staining. The rationale behind the technique is that contrast in BSE images mostly results from material variation, with the BSE signal strength defined by material properties such as atomic packing density or nuclear charge [27]. This is in contrast to conventional SEM imaging using secondary electrons (SE), where imaging contrast largely results from sample topography.

When using BSE to image a polymer blend sample, the interaction depth of the primary electron beam in the sample is an important factor to consider. BSE can theoretically be emitted from any depth up to the maximum interaction depth of the primary beam, although as a rough approximation they are most frequently emitted from the first half of this interaction depth [24,26]. The interaction depth of the primary beam is controlled by the landing energy, E_L, of the beam, with a higher E_L beam interacting up to a larger depth in the sample. As such, the emission depth of BSE can be controlled as a function of E_L. To most effectively probe a polymer film with BSE, E_L must be limited to ensure BSE are emitted from only the film and not the substrate beneath. In this work, we have limited E_L to 3 keV and below for this purpose. This is below energies used in previous polymer BSE imaging experiments [21,22].

For an OPV blend, BSE imaging can be used to probe the nature of the blend morphology over different depths through the film by changing E_L. By imaging with a very low energy, E_L=500 eV, BSE emissions are restricted to the top few nm of the sample, allowing the surface morphology to be probed. Likewise, by tuning E_L such that the BSE emission depth is roughly equal to the thickness of the film, we can probe for structures passing through the whole thickness of the film. When imaging morphology in this case, contrast in a BSE image is highly dependent on whether the BSE emission volume can be largely contained within domains of a single blend component (Fig. 1). If a given blend morphology is comprised of phase-separated structures that are highly aligned through the thickness of the film, it is possible to increase E_L whilst largely containing the BSE emission volume within domains of a single blend component. This results in an image that retains high contrast as a function of beam energy (Fig. 1a). However if BSEs are used to study morphologies with small length scales relative to the dimensions of the BSE emission volume, or disordered blend systems that are heterogeneous through the film thickness, at higher E_L the BSE emission volume at any given point will contain significant amounts of both blend components. In this case, BSE images will show very low phase contrast in the higher beam energy condition, as the BSE signal is averaged over both blend components (Fig. 1b). We can thus easily probe for morphologies showing columnar features or domain stacking ideal for OPV, based upon a BSE image at optimised E_L. We note that similar principles are used as the basis for multi-energy confocal microscopy, typically used to image biological samples deemed too fragile for TEM or focused ion-beam milling techniques [28,29]. However, to date these techniques have only been used at relatively low resolutions, or on stained samples.

Imaging a film using BSE at low E_L brings benefits in the form of reduced knock-on damage from the incident primary beam [30], however additional challenges occur as our BSE detector has inherently poor detection efficiency for low-energy electrons [23]. To overcome this issue, a large negative bias (−4 kV) can be applied to the sample stage in order to improve image quality. This has a three-fold effect [23]: (i) the primary electron beam is generated at higher energy and then decelerated to be incident on the sample with the desired 'landing energy' E_L, (ii) electrons emitted from the sample are accelerated and incident on the detector (mounted directly above the sample) with a

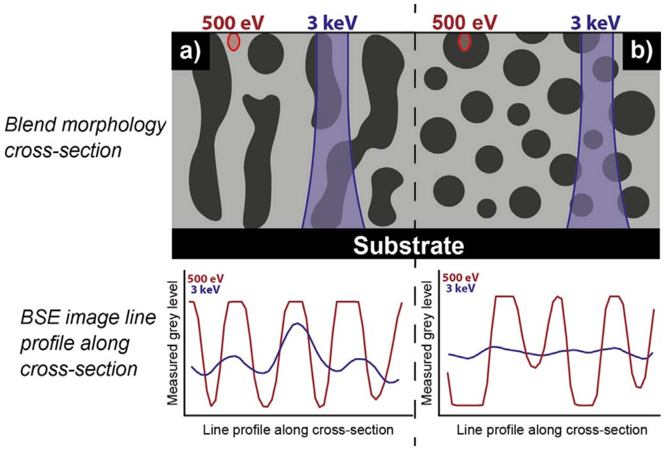

Fig. 1. Schematic of BSE imaging contrast when imaging different morphology types with E_L=500 eV and 3 keV. a) Represents an ordered morphology, with phases highly aligned through the thickness of the film. b) represents a more disordered morphology, with a small, randomly dispersed phase distribution. Red and blue shaded regions represent approximate BSE emission volumes at E_L=500 eV and 3 keV, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)