



Gas expanded polymer process to anneal nanoparticle dispersion in thin films



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ABSTRACT

Organic photovoltaic (OPV) active layers made by spin-coating a solution comprising poly(3-hexylthiophene) (P3HT) and phenyl-C61-butyric acid methyl ester (PCBM) nanoparticles have been shown to adopt a non-uniform concentration profile across the thin film dimension. This inhomogeneous distribution can reduce the efficiency of the device. In the present work a new process, gas expanded polymer (GXP) annealing, is applied to P3HT/PCBM thin film blends, enabling the distribution of the PCBM nanoparticles to be manipulated by varying the GXP processing conditions. Films of 50 nm thickness (nominally) created by spin casting a blend of P3HT mixed with PCBM were annealed by oscillatory GXP and GXP at constant pressure using high pressure CO₂. An increase in P3HT crystallinity (detected by X-ray diffraction and UV–vis spectroscopy) along with a more uniform distribution of PCBM nanoparticles in the thickness dimension, as interpreted from neutron reflectivity measurements, were observed after oscillatory GXP annealing. In addition, static water contact angles suggest that the film/air interface is enriched in PCBM relative to the as-cast film. These results demonstrate that GXP annealing, which is commercially scalable, can be successfully used to create a uniform distribution of PCBM nanoparticles across the thickness dimension in a P3HT thin film.

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1. Introduction

Organic photovoltaic (OPV) devices convert solar energy into electrical energy. The potential advantages of OPVs over silicon-based devices include ease of processing and being light weight. Among the different active layer materials that have been investigated, blends of poly(3-hexylthiophene) (P3HT) and phenyl-C61-butyric acid methyl ester (PCBM) fullerenes are often used as a model system. OPVs based on the bulk heterojunction (BHJ) blend concept also exhibit modest power conversion efficiencies, reaching up to 10.6% for tandem arrangement [1]. Because the exciton generated upon photon adsorption has a very short lifetime, it is important to create BHJ domain sizes that match the short exciton diffusion length [2]. In terms of structure and performance, the “rivers and streams” structural model for nanoparticle dispersion proposed by Yin et al. [3] describes a theoretical optimal hierarchy. Yin et al. determined through small angle neutron scattering that three phases exist in the P3HT/PCBM

system: a pure crystalline P3HT phase, a PCBM-rich phase and an amorphous miscible phase of P3HT and PCBM [3]. According to this model, the amorphous P3HT/PCBM domain consists of a large number of donor/acceptor interfaces where the tightly bound excitons can dissociate. These charges then flow to the less dispersed “river” phases to transport to their respective electrode [3]. Along the axis from one electrode to the other, the depth profile of the PCBM should not preferentially collect at the anode [4], as a higher concentration of PCBM at the anode results in lower device efficiency [5,6]. Thus a mixed morphology along all axes combined with interconnected domains is desirable. The current spin coating process when used alone makes this complex structure difficult to control in a scalable, cost effective manner.

Prior work indicates that device efficiency and dispersion of nanoparticles can be improved in spin-cast nanocomposite films if they are subsequently exposed to thermal annealing [5,7,8] or solvent annealing [4,9–11]. Dang et al. have given a more exhaustive review of how thermal annealing and solvent annealing are known to affect both P3HT and PCBM morphology and the intimate dependence on P3HT regioregularity and molecular weight considerations [12]. In thermal annealing, heat treatment leads to improved P3HT crystallinity, which leads to an improvement in charge transport from grain

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to grain [13,14]. Thermal annealing also introduces the possibility of macrophase separation, which can reduce device performance [6,15]. Thermal annealing requires high heating and cooling rates for uniform heat transfer throughout the sample. Studies show that solvent vapor annealing improves the crystallinity of the polymer as well [6,16]. Solvent vapor annealing, however, is often not environmentally friendly due to the nature of organic solvents commonly used in connection with solvating P3HT. Thus, while both thermal and solvent annealing offer the advantage of improving P3HT crystallinity, the concomitant effect of coarsening the dispersion by occlusion of PCBM, often to the extent that nanoparticle aggregates occupy micron-scale domains, is deleterious.

Kiel et al. used neutron reflectivity to show that thermal annealing of P3HT/PCBM bulk heterojunctions at 170 °C led to the PCBM concentration being highest at the polymer/substrate interface both before and after annealing [17]. Germack et al. used near-edge X-ray absorption fine structure spectroscopy to arrive at similar results [18]. Chen et al., also using neutron reflectivity measurements, showed that PCBM selectively aggregates at the polymer/air interface when P3HT/PCBM bilayers are thermally annealed [5]. Parnell et al. also used neutron reflectivity to show that P3HT/PCBM films, when subjected to either solvent vapor or thermal annealing, showed an increase in concentration of PCBM at the polymer/air interface [4]. Thus, while either thermal or solvent vapor annealing are viable processes for changing the distribution of PCBM nanoparticles in a polymer film, neither method offers a process to limit the enhancement of PCBM at the anode where the holes are extracted.

In this work, gas expanded polymer (GXP) annealing is examined for the first time as an alternate method to control the distribution of PCBM nanoparticles in BHJ films. In particular, carbon dioxide (CO₂) is used as a high pressure gas or supercritical fluid to create a gas expanded P3HT/PCBM film. CO₂ is advantageous because it is a nontoxic and inexpensive fluid, and GXP processing using CO₂ is scalable; it is used in polymer synthesis and processing [19–21], where processes share a number of similarities to roll-to-roll printing and coating processes [22]. In addition, the solvating properties of the fluid can be quickly and easily controlled by changes in temperature and pressure. While there have been numerous works over the past two decades showing the effect of CO₂ swelling of liquids (termed gas expanded liquids or GXL) resulting in novel distributions of nanoparticles on surfaces [23], only a handful of works have shown the possibility of using CO₂ swelling of polymers to process polymer nanocomposites. For dodecanethiol-capped Ag and CdSe/ZnS nanoparticles dispersed in hexane, Anand et al. showed that it is possible to precipitate nanoparticles in a size selective fashion by controlling CO₂ vapor pressure [24–26]. A balance of van der Waals and steric interactions, as well as the physicochemical properties of the particles and of the solvent, were shown to mediate the deposition, which could be explained using Flory Huggins model and DLVO theory. Bhosale et al. have demonstrated that deposition and gas expanded liquid annealing produce a uniform monolayer of gold nanoparticles over wide areas when dispersed in CO₂-expanded hexane [27]. A critical range of CO₂ pressure was necessary to control the organization of the gold nanoparticle monolayer film. By oscillating CO₂ around a critical pressure, positional defects in the monolayer of decorated nanoparticles could be removed. While Bhosale's work demonstrated that oscillation of solvation power can anneal nanoparticle-containing thin films, by extension it holds promise for affecting PCBM dispersion in a P3HT/PCBM thin film. In fact, Amonoo et al. [28] used supercritical CO₂ to anneal a P3HT/PCBM thin film. While the processing did not include pressure oscillation or detailed morphological characterization through the thin dimension of the film, from energy filtered electron microscopy imaging and UV–vis spectroscopy they found

that morphological changes did occur and that the power conversion efficiency (PCE) of an OPV device could be improved beyond the gain imparted by thermal annealing: specifically, their devices displayed a PCE of 2.9% when annealed in supercritical CO₂ at 1500 psi and 50 °C versus 2.6% PCE for their thermally annealed system. The present paper reports more uniform dispersion of PCBM nanoparticles in a P3HT thin film detected through the thickness of the film. A CO₂ gas expanded polymer annealing process was used to affect the changes noted, and the solvating power was varied through pressure oscillations during processing versus constant pressure. The uniform concentration profile of PCBM achieved in this process has not been previously reported.

2. Materials and methods

2.1. Materials

[6,6]-Phenyl-C61-butyric acid methyl ester (PCBM, > 99.5%) and 91–94% regioregular poly (3-hexylthiophene) (P3HT), were purchased from Nano-C, Inc. and Rieke Metals, Inc., respectively, and used as received. Silicon wafers were used as substrates for neutron reflectivity measurements (3" diameter, P(100) University Wafer, donated by Hemlock Semiconductor) and glass substrates were used for X-ray diffraction, ultraviolet visible (UV/vis) spectroscopy and contact angle measurements. Chlorobenzene (99%+, Acros Organics) was used as received and high purity grade CO₂ (99.9%, Airgas, Inc.) was used.

2.2. Sample preparation

To fabricate thin films, P3HT and PCBM were co-dissolved in chlorobenzene (CB) at a total solids concentration of 10 mg/ml with P3HT and PCBM mixed in a mass ratio of 1:1. For neutron reflectivity studies, silicon wafers were cleaned by immersion in Piranha solution (a 3:1 (v/v) mixture of concentrated sulfuric acid and 30% (v/v) hydrogen peroxide) which was heated to 80 °C. *Caution:* Piranha solution should be handled with care, as it is a strong acid and oxidizer, reacting violently with organic compounds. After immersion for 30 min, the wafers were removed, rinsed with high purity water, and dried under dry nitrogen. The freshly cleaned wafer was then exposed to UV light (185–254 nm) for 5 min. All films were made by spin coating the P3HT/PCBM solution at 400 rpm for 4 min and then at 1000 rpm for 20 s. For X-ray diffraction, UV–vis and contact angle measurements, the P3HT/PCBM thin films were created by an identical spin coating procedure on clean glass slides. All glass slides were cleaned by sonicating the substrate sequentially for 15 min in soapy water, distilled water, acetone and then isopropanol. After sonication, the glass slides were dried with a stream of nitrogen gas. Material designations used in this paper for all the samples are shown in Table 1.

2.3. GXP annealing

A 2 L Anton Paar pressure vessel was installed in an Applied Separation Spe-ed™ oven with a temperature controller. This pressure vessel was coupled with two ISCO 500D syringe pumps for continuous CO₂ delivery. Two different protocols – oscillating and constant pressure exposures – were used to anneal P3HT/PCBM thin films. In each case, after sealing the sample in the vessel, it was flushed with CO₂ for 40 min in order to completely purge air from the system.

As shown in Figure 1, for the oscillation-annealed process, the pressure was first increased to a base pressure (e.g. 675 psi) by pumping CO₂ at a flow rate of 100 ml/min. Once this pressure was reached, oscillatory cycles were commenced by slowly pressurizing

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