The impact of controlled solvent exposure on the morphology, structure and function of bulk heterojunction solar cells

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The impact of controlled solvent exposure on the morphology, structure and function of bulk heterojunction solar cells

Raghavendra Hegde, Nathan Henry, Ben Whittle, Huidong Zang, Bin Hu, Jihua Chen, Kai Xiao, Mark Dadmun

Abstract

Films of poly(3-hexyl thiophene) (P3HT):[6,6]-phenyl C61-butyric acid methyl ester (PCBM) were controllably exposed to CS2 vapor in a column with a linear solvent vapor pressure gradient. Changes in the morphology of the P3HT:PCBM thin film were monitored and correlated to the ability of this thin film to act as the active layer in an organic solar cell. The results show that the crystallinity and crystal size of the P3HT increase initially with solvent vapor pressure and annealing time, but longer exposure to solvent decreases P3HT crystallinity and photovoltaic efficiency. Neutron reflectivity indicates that the PCBM segregates to the Si substrate in the as-cast thin film, but distributes throughout the film with solvent annealing. The changes in crystallinity and the depth profile of the P3HT:PCBM mixture differ from those induced by thermal annealing. The structural variation with solvent exposure is correlated to photovoltaic function, demonstrating that the solvent annealing provides a window of optimum efficiency, which depends on solvent exposure. Moreover, the control of depth profile and structure should be generally applicable to a broad range of polymer-nanoparticle mixtures and thus these results provide fundamental information that can be used to control the depth profile, morphology and function of thin film nanocomposites.

1. Introduction

Conjugated polymers are intriguing materials due to their potential use in organic electronics such as low cost, flexible solar cells, low-voltage field-effect transistors and organic optoelectronic devices such as modulators, optical filters, and polarization rotators. Due to their high absorption coefficient, they have become primary components in the active layer of organic solar cells (OSC), as thin layers can generate sufficiently high photocurrent to be practical. Organic solar cells are promising materials to convert sunlight into electricity, however in order to be economically competitive with inorganic photovoltaics, their power conversion efficiency must be improved. This improvement requires a more complete understanding of the correlation between active layer morphology and performance. This is because in the function of an OSC, the absorption of a photon forms a Franckel exciton, which has a large binding energy due to the low dielectric constant of the organic matrix. The exciton must, therefore, migrate to a donor–acceptor interface to dissociate, and then each phase must have a pathway to the electrodes to realize a photo-generated current [1]. Thus, the morphology of the OSC is critical in realizing an efficient photovoltaic cell.

The bulk heterojunction consisting of regioregular poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl C61-butyric acid methyl ester (PCBM) has become the archetypal OSC active layer in recent years, as power conversion efficiencies approaching 5% have been reported for the P3HT:PCBM active layer. In this system, the P3HT provides adequate hole mobility, the ability to self organize into a crystalline structure and a reasonable spectral overlap of its absorption spectrum with the solar emission spectrum. The improved solubility of PCBM appears to aid in the formation of desired morphology [2]. However, as-cast devices often exhibit poor photovoltaic efficiencies, and subsequent processing, such as casting from a mixed solvent, micro-wave annealing, thermal annealing, [3] and solvent vapor annealing (SVA) processes [4–11] are required to improve the photovoltaic efficiency.

Previous studies ascribe the increased efficiency in PCBM:P3HT with thermal annealing to an increase in P3HT crystallinity [12], which improves hole transport, as well as segregation of the PCBM to the device cathode [13]. It is reasoned that the increase in charge...

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carrier mobility with thermal annealing is due to an increase of the in-plane \( \pi-\pi \) stacking of P3HT, where charges can easily transport from one grain to another [14–19]. These previous studies clearly indicate that understanding and controlling the crystalline nature of the P3HT and the resultant morphology of the P3HT:PCBM mixture is essential to increase charge carrier mobility and charge collection, both of which improve the ultimate power conversion efficiency of the resultant solar cell.

Using thermal annealing to modify the morphology has limitations, in that it is difficult to achieve high heating or cooling rates since heat must transfer throughout the sample by thermal conduction [20]. Large scale phase separation and formation of structures which could be detrimental to the solar-cell performance have also been reported [21], as extended thermal annealing has been shown to create large crystals, from a few up to 100 \( \mu \)m [7].

On the other hand, solvent vapor annealing (SVA) provides an alternative method to control morphology. SVA is a versatile method where thin films are exposed to an atmosphere saturated with solvent vapors in which the solid film constituents are soluble. The solvent molecules diffuse into the deposited layer, the extent of which is dependent on and thus controllable by, extent of solubility and exposure time. The solvent imparts increased molecular mobility of the bulk heterojunction (BHJ) components, allowing the system to evolve towards a more thermodynamically stable morphology [22,23].

There have been few studies to monitor morphology and function changes in the active layer of OSC devices subjected to solvent annealing. Most of these solvent vapor annealing studies were conducted using a closed container with solvent [24–32]. There are many different techniques that can be applied to study the effect of solvent vapor on the morphology of conjugated polymers and nanomaterials. Liu et al. [25] investigated the change in the morphology of the P3HT/C_{60} blend exposed to the solvent vapor of chloroform or 1,2-dichlorobenzene (DCB). These investigators observed nanowires rich in C_{60} upon exposure to chloroform vapor and nanowires of P3HT with DCB vapor. Lu et al. [27] studied the influence of C_{60} solvent vapor exposure on a spin-coated poly(3-hexylthiophene) (P3HT) film. These authors reported a variation in P3HT crystal structure with C_{60} solvent evaporation rates. Slow C_{60} solvent evaporation provides sufficient time for the P3HT chains to stack, changing the morphology from the kinetically frozen form I to the more thermodynamically stable form II [27]. Kline et al. [18] reported enhanced P3HT:PCBM bulk-heterojunction photovoltaic efficiencies when subjected to a combination of 1,2-dichlorobenzene (DCB) vapor treatment and thermal annealing.

Thus, it is clear that the morphology changes and the power conversion efficiency (PCE) of bulk heterojunction OSC can improve with post fabrication annealing treatments. However, the thermodynamic driving forces that lead to these morphology changes during these annealing treatments are still not explicitly addressed in the literature. For instance, to our knowledge, there has been no study that documents the evolution of structure with solvent exposure for conjugated polymer/fullerene bulk heterojunctions. Recently, Lu et al. reported improved power conversion efficiency for P3HT/C_{60} composites by controlled solvent vapor treatment (C-SVT) [20].

In this manuscript, we report an examination of the impact of controlled solvent vapor treatment on the morphological evolution and function of P3HT:PCBM thin film bulk heterojunctions. In this study, the impact of C-SVT on the morphology, function, and crystallinity of P3HT:PCBM thin films are monitored. Varying the exposure time and vapor pressure using an in-house built apparatus controls solvent exposure, provides definite control of the extent of exposure to solvent vapor, providing a measure of control rarely implemented in solvent annealing procedures.

The morphology and structural changes in the solvent annealed BHJ thin films are investigated using grazing incidence wide-angle x-ray scattering (GIWAXS), neutron reflectivity (NR), and atomic force microscopy (AFM). Neutron reflectivity (NR) is a well suited technique to characterize the P3HT:PCBM thin film composite due to significant scattering length density contrast between the P3HT and PCBM [33]. The morphology changes that are induced by solvent annealing are compared to those observed by thermal annealing in an oven.

These studies provide novel information that details the morphology changes that occur in P3HT:PCBM thin films as a result of controlled solvent vapor exposure. Often neglected critical information that elucidates the variation in P3HT crystallinity during solvent annealing as well as changes in morphology driven by solvent induced molecular mobility in the thin film is presented. These structural studies are then correlated to the photovoltaic activity of the active layer to provide guidelines by which the active layer of conjugated polymer:fullerene bulk heterojunctions may be optimized with controlled solvent exposure.

## 2. Experimental

### 2.1. Materials and methods

All solvents were purchased from Aldrich and used as received. For the organic solar cell function studies, P3HT and PCBM were purchased from Reike Metals Inc., and Nano-C Inc., respectively. For all other studies, the poly(3-hexylthiophene) (P3HT) (\( M_n \approx 476,000 \) g/mol), and [6,6]-phenyl C_{61}-butyric acid methyl ester (PCBM) were purchased from Sigma-Aldrich.

Silicon wafers were used as substrates in these studies and cleaned in hot piranha (1:3 H_{2}SO_{4}:H_{2}O_{2} solutions) for 30 min followed by washing in abundant deionized (DI) water and dried using a stream of nitrogen gas. Thin films of 1 wt\% P3HT:PCBM (50:50 wt%) were prepared by spin coating from chlorobenzene onto Si substrates at 2500 rpm for 60 s. The resultant thin films were ~30 nm thick as measured by ellipsometry.

Solvent and thermal annealing conditions used in this study are listed in Tables 1 and 2, where the solvent is always carbon disulfide, C_{2}S_{2}. The schematic of the solvent annealing apparatus is shown in Fig. 1, where the total length of the vapor gradient i.e. distance from column opening to solvent surface is 100 cm. Three experimental variables can be controlled in this experiment.

### Table 1
Solvent annealed samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Vapor pressure (( p=L/L_0 ))</th>
<th>Rate-R (cm/sec)</th>
<th>Time (t)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As cast</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>SA_W_L50_5 s</td>
<td>0.5</td>
<td>50</td>
<td>5</td>
</tr>
<tr>
<td>SA_W_L50_30 s</td>
<td>0.5</td>
<td>50</td>
<td>30</td>
</tr>
<tr>
<td>SA_W_L90_5 s</td>
<td>0.9</td>
<td>50</td>
<td>3</td>
</tr>
<tr>
<td>SA_W_L90_30 s</td>
<td>0.9</td>
<td>50</td>
<td>30</td>
</tr>
<tr>
<td>SA_W_L90_120 s</td>
<td>0.9</td>
<td>50</td>
<td>120</td>
</tr>
</tbody>
</table>

### Table 2
Thermal annealed samples.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Temperature (°C)</th>
<th>Time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As cast</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>TA_w_150 C_5 min</td>
<td>150</td>
<td>5</td>
</tr>
<tr>
<td>TA_w_150 C_30 min</td>
<td>150</td>
<td>30</td>
</tr>
<tr>
<td>TA_w_150 C_60 min</td>
<td>150</td>
<td>60</td>
</tr>
</tbody>
</table>
solvent vapor pressure, treatment time, and rate of sample placement. The different solvent vapor pressure ($P$) was varied by changing the position of the BHJ thin film relative to the CS$_2$ solvent surface, where values of $L/L_0 = 0.50, 0.90$ are chosen as shown in Fig. 1a and b.

At $L/L_0 = 0.50$, the film is halfway down the solvent annealing column, whereas, at $L/L_0 = 0.90$, the sample is very close to the solvent surface. The rate of dropping the thin film sample from the top to the static level was instantaneous and kept constant at $100 \text{ cm/s}$. The treatment time ($t$) was varied by changing the idle time at a given height.

As reported in the literature [20], once solvent is added to the column, sufficient time must be allowed to create a stable vapor gradient in the column. In this study, the column was allowed four hours after addition of solvent to equilibrate. Additionally, care was taken to not disturb the solvent gradient in the column during annealing. After the solvent vapor treatment (or thermal annealing), samples were stored in an inert atmosphere in desiccators until further characterization was completed.

2.2. Neutron reflectivity

Neutron reflectivity was performed on the Liquids Reflectometer at the Spallation Neutron Source (SNS) at Oak Ridge National Laboratory. Specular neutron reflectivity was carried out on thin films coated onto 3 mm thick Si wafers. The neutron wavelength was varied from 2.5–5.0 Å and at several fixed angles of incidence ($0.15–1.40$), giving an effective $q$-range of $0.002–0.120 \text{ Å}^{-1}$.

2.2.1. Fitting of measured data

Unfortunately, it is not possible to directly extract structural information of the scattering sample from the reflectivity data. To circumvent this limitation, the reflectivity of a model scattering length density (SLD) depth profile is calculated and compared to the experimentally measured reflectivity. The reflectivity of the model depth profile is iteratively refined until the calculated and experimental reflectivity profiles match. With foreknowledge of the sample scattering characteristics and suitable constraints imposed to maintain a physically realistic system and conservation of mass, the fitting provides a result that accurately reflects the scattering structure of the sample. Conservation of mass is implemented in this fitting procedure by inclusion of a mass balance of the P3HT and PCBM in the model SLD depth profile.

The depth profile models of the composite P3HT:PCBM thin films were constructed using the Layers software provided by the Oak Ridge National Laboratory, which calculates the reflectivity of model depth profiles by dividing the sample into layers of variable SLD, thickness, and roughness. The $z$-axis resolution of neutron reflectivity can easily resolve the roughness for even relatively sharp interfaces by modeling interlayer roughness as a large number of narrow discrete steps in SLD and thus approximates a continuous transition, retaining model fidelity.

Models were constructed which set the SLD, thickness, and roughness within the confines of total thickness and SLD between the known SLD of P3HT and PCBM, which are $3.6 \times 10^{-6}$ and $7.0 \times 10^{-7} \text{ Å}^{-2}$ respectively as reported in the literature. [13,33,34,35,41] This model is then iteratively refined to optimize the accuracy of the fit between the real and model reflectivity while maintaining a realistic model. As a further check on the model, a mass balance of the model was maintained by constraining the sample total SLD to within 5% of the total SLD of the P3HT and PCBM incorporated into the films. A model is assumed to accurately reflect the scattering structure when the model reflectivity profile converges with the experimental profile, within the boundaries established, using $\chi^2$ statistics (Eq. (1)) with an acceptance threshold of $\chi^2 < 10$.

$$\chi^2 = \sum \frac{(R_{\text{calc}}-R_{\text{exp}})^2}{R_{\text{exp}}^2}. \quad (1)$$

The SLD profile is then analyzed to obtain the concentration profile of each component in the system. For instance, the PCBM concentration profile was determined from Eq. 2 [34,36]

$$\phi_{\text{PCBM}} = \frac{\rho(Z) - \rho_{\text{P3HT}}}{\rho_{\text{PCBM}} - \rho_{\text{P3HT}}}, \quad (2)$$

where $\phi(Z)_{\text{PCBM}}$ is the volume fraction of PCBM at depth $z$, $\rho(Z)$ is the experimental scattering length density at depth $z$, and $\rho_i$ is the scattering length density of each component.

2.3. Grazing incidence wide Angle x-ray scattering (GIWAXS)

X-ray diffraction from thin films was performed with a Phillips X’pert-Pro diffractometer in grazing-incidence geometry. The angle of incidence between the X-ray and the thin film surface ($\Omega$) was $0.3^\circ$ for all samples. The size of the polymer crystallites, $L$, was calculated from the resultant diffraction pattern using Scherrer’s equation, Eq. (3) [37]

$$L = \frac{0.9\lambda}{\beta \cos \theta}. \quad (3)$$

In this equation, $\lambda$ is the wavelength in Å and $\beta$ is the measured full width at half maximum (FWHM) of the P3HT (100) peak. The (100) peak was assumed to be Gaussian and Warren correction was applied to account for the instrumental broadening as per Eq. (4)

$$\beta = \sqrt{\beta_{\text{observed}} - \beta_{\text{instrumental}}}, \quad (4)$$

where, $\beta_{\text{observed}}$ is the observed FWHM and $\beta_{\text{instrumental}}$ is the instrumental broadening factor. The instrumental broadening factor was measured using a LaB$_6$ sample, where the line widths are determined in the 2$\theta$ range of 20–70$^\circ$ and extrapolated to 5$^\circ$. This analysis gives $\beta_{\text{instrumental}} = 0.2515$ at 5$^\circ$. The area of the (100) peak was determined using the peak-fitting module in Origin software where the background of the XRD scattering curve was determined and subtracted using the point method.

2.4. Atomic force microscopy (AFM)

AFM experiments were performed in tapping mode using a Digital Instruments scanning probe microscope to measure surface topography. The AFM tips were standard Veeco 0.01–0.025 $\Omega$-cm
Antimony(d) doped Si tips with a resonance of around 289–334 kHz and a spring constant \( k = 20–80 \) N/m with a cantilever thickness, \( t = 3.5–4.5 \) µm, length \( l = 110–140 \) µm and width \( w = 25–35 \) µm. Roughness and section analyses were performed on the height image. The average thin film roughness and PCBM crystal size reported from the AFM height image are the average of four annealing experiments and three height images at multiple places on the same sample.

2.5. ITO/PEDOT:P3HT:PCBM/Al solar cell assembly

A schematic of the organic solar cell (Fig. S1) is included in the Supplementary information. Chlorobenzene (anhydrous, 99.9%) was used to prepare blend solutions of P3HT and PCBM (1:0.8 weight ratio) and spin cast to form P3HT:PCBM thin films. In the fabrication of the solar cells, indium tin oxide (ITO) coated glass was first cleaned in an ultrasonic bath using detergent, deionized water, acetone, isopropanol, and chloroform for 10 min. Then, PEDOT:PSS (Baytron P 4083) was spin cast (film thickness \( \sim 40 \) nm) on the top of UV treated ITO glasses. After baking the PEDOT:PSS films in vacuum at 140 °C for 1 h, the photovoltaic P3HT:PCBM layer was spin coated at 800 rpm for 40 s. The film was then placed on a covered Petri dish and allowed to slowly dry. The active layer film thickness was measured by AFM to be \( \sim 120 \) nm. The active layer of P3HT:PCBM was also spun coated using Ortho-dichlorobenzene (ODCB) (anhydrous, 99.8%) as the solvent and subjected to the same annealing treatments as the samples that were characterized structurally (Table 1 and Table 2) and tested for photovoltaic activity.

3. Results and discussion

3.1. Solubility of PCBM and P3HT in CS2

The protocol for solvent annealing is to expose the mixture of P3HT and PCBM to the vapor of a solvent, carbon disulfide, CS2. Initially it was desired to choose a common, not selective, solvent. The relative solubility of P3HT and PCBM in CS2 is therefore an important parameter, as if it is selective to either component, the introduction of the solvent to the mixture could selectively segregate one component to the surface or selectively induce dissolution or precipitation.

To test the selectivity of CS2 for the two components, the solubility limits of P3HT and PCBM were determined in CS2 as well as chlorobenzene and dichlorobenzene using UV–vis spectroscopy. In this experiment, the absorbance of solutions at 650 nm is measured using UV–vis spectroscopy. The optical densities of the samples are then plotted as a function of PCBM concentration, and a deviation from linearity (i.e. the Beer–Lambert Law) is taken as the solubility limit. Table 3 shows the results of these experiments, indicating that CS2 is a common solvent for both components, but that both chlorobenzene and dichlorobenzene are selective solvents for P3HT.

3.2. Grazing incidence wide Angle x-ray scattering (GIWAXS)

GIWAXS is completed to monitor the change in crystallinity of the P3HT with solvent and thermal annealing. Diffraction patterns of the as-cast P3HT:PCBM samples indicate that the crystallinity of the thin film changes during storage at room temperature in an inert atmosphere, as shown in Fig. S2-a (see Supplementary information). The specular reflectivity of the as-cast samples also indicates a change in depth profile of the thin film during this room temperature storage, as shown in Fig. S2-b (see Supplementary information). Bertho et al. studied the effects of prolonged storage at elevated temperatures (annealing at 110 °C from 2 to 16 h) on both the morphology and the photovoltaic performance for MDMO-PPV:PCBM and P3HT:PCBM BHJs. They reported morphological changes which involved PCBM-cluster formation and crystallization of P3HT upon annealing[21]. The diffusion kinetics of PCBM in a P3HT matrix and morphology evolution at elevated temperature (140 °C) has also been reported, where the diffusion constant of PCBM within a P3HT matrix at 140 °C is reported to be 2.5 \times 10^{-14} \text{ m/s}[38]. These representative results demonstrate the quick evolution of structure with heating at elevated temperature, however similar studies at room temperature are less common.

The observed changes in the reflectivity profile can be interpreted to indicate the mobility of PCBM in the P3HT matrix even at room temperature. This mobility and morphology change at room temperature has not been previously reported in the literature and may occur because of the low glass transition temperature of P3HT (\( \sim 6 \) °C)[21]. These results emphasize the importance of developing a thermodynamically stable bulk heterojunction for long term use in organic solar cells, as at room temperature and in an inert atmosphere, the P3HT:PCBM thin film structure and morphology changes during prolonged storage.

GIWAXS scans (Fig. 2) show a single peak at 5.4°, which corresponds to the P3HT (100) crystal plane. There is no significant difference in the d-spacing of the as-cast and solvent annealed thin films. However, the area under the 100 peak and the sharpness of the peak varies among the samples, which indicates a transformation in crystallinity and crystal size (L) with solvent exposure.

The area of the P3HT (100) peak and crystal size (L) are plotted as a function of solvent annealing conditions in Fig. 3. At each vapor pressure level, the crystallinity increases with initial exposure time. At L/L0 = 0.50, increasing treatment time increases the area of the (100) peak (which indicates an increase in crystallinity) up to 30 s. However, annealing the thin film at higher vapor pressure (L/L0 = 0.90) increases crystallinity initially, but exposure of the sample to this nearly saturated vapor beyond 5 s results in decreased crystallinity. However, for all the solvent annealed samples, the crystal size L (Fig. 3) shows a continuous increase with solvent exposure. This set of data is interpreted to indicate that the initial exposure of the thin film to the solvent provides molecular mobility of the P3HT chains, allowing the polymer to crystallize. However, extended solvent vapor exposure results in

<table>
<thead>
<tr>
<th>Table 3</th>
<th>Solubility limit of PCBM and P3HT (wt%).</th>
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<tbody>
<tr>
<td></td>
<td>Chlorobenzene</td>
</tr>
<tr>
<td>P3HT (%)</td>
<td>13</td>
</tr>
<tr>
<td>PCBM (%)</td>
<td>7</td>
</tr>
</tbody>
</table>
the dissolution of crystals in the sample, where the smallest crystals are dissolved first, increasing the average crystal size in the sample but deceasing the total crystallinity.

GIWAXS scans of the thermally annealed samples are shown in Fig. 2b for comparison and show that the sharpness of the P3HT (100) peak increases with thermal annealing time. The area of this peak and the crystal size ($L$) of the thermally annealed samples are shown in Fig. 3c and d, indicating that the amount of crystallinity and the crystal size grow with thermal annealing reaching a plateau at longer times. It is interesting to note that the sizes of the crystals and the amount of crystallinity in the P3HT (as measured by the area of the 100 peak) are similar for the thermally annealed and solvent annealed samples, suggesting that the morphologies of the samples created by the two protocols have similar structural components.

In order to further understand the effect of solvent on the crystalline structure of the P3HT:PCBM sample, the thermally annealed samples were controllably exposed to solvent vapor. The thin film samples that were annealed at 150°C for 5 min and at 150°C for 60 min were solvent annealed at vapor pressure $L/L_{ref}=0.90$ for 5 and 120 s and the results are shown in Fig. S3a and b, respectively (see Supplementary information). In these samples, the area of the crystalline peak decreases with solvent exposure, consistent with the melting of crystals with this solvent exposure.

These controlled experiments provide valuable insight into the role of solvent vapor exposure on the morphology and crystallinity of
bulk heterojunctions. Clearly modest exposure to solvent vapor allows the solvent to plasticize the polymer, providing molecular mobility, which in turn results in an ordering of the polymer chain into a crystal. However, further solvent exposure can result in the loss of crystallinity, as excess solvent may dissolve crystal, particularly when exposing the thin film to a 'good' solvent for the polymer. However, this change in crystallinity may be beneficial or detrimental to the ultimate function of the active layer. It is envisaged that the P3HT crystals are the primary routes for hole transport. If the smaller crystals that are initially lost with solvent exposure are not part of an interconnected network, their dissolution could remove areas of charge traps and improve photovoltaic function. On the other hand, if they are the narrowest part of an interconnected network responsible for hole transport, their loss would dramatically lower the charge capture at the electrodes, decreasing photovoltaic efficiency of the device.

Similar results were observed for solvent and thermally annealed P3HT:PCBM (1:0.8) thin films that were spin-coated from ODCB. The change in crystallinity and crystal size $L$ of these samples are shown in Fig. 4. The as-cast P3HT:PCBM (1:0.8) thin films fabricated from ODCB attains a higher crystallinity than that of the samples formed from CB, presumably due to the slower drying of ODCB relative to CB. This comparison exemplifies the universality of the solvent annealing process, which can independently control crystallinity and crystal size in conjugated polymer:fullerene bulk heterojunctions by controlled exposure to solvent vapors.

To provide further control of the morphology with solvent vapor annealing, the influence of drying time after removal from ODCB was examined. The change in crystallinity and crystal size $L$ of these samples are shown in Fig. 4. The as-cast P3HT:PCBM (1:0.8) thin films fabricated from ODCB attains a higher crystallinity than that of the samples formed from CB, presumably due to the slower drying of ODCB relative to CB. This comparison exemplifies the universality of the solvent annealing process, which can independently control crystallinity and crystal size in conjugated polymer:fullerene bulk heterojunctions by controlled exposure to solvent vapors.

Fig. 6a indicates that the as-cast sample consists of a structure that is rich in PCBM at the Si surface, which is consistent with previously reported results [39–42]. This previous work reported that the depth profile of P3HT/PCBM thin-films cast from chlorobenzene consist of a low scattering length density (SLD) layer near the air surface that is depleted in PCBM and a PCBM rich layer next to the substrate. With solvent or thermal annealing, the surface depletion is suppressed, which is interpreted to indicate that the annealing processes facilitate the movement of PCBM to the film surface [13].

Representative measured and model specular neutron reflectivities of the solvent and thermally annealed samples are presented in Fig. 5, where the fitted SLD profiles are also plotted as a function of normalized film thickness in the insets. Fig. 5a shows the reflectivity of the as-cast P3HT:PCBM blend thin film, while Fig. 5b and c show the reflectivities of the samples after thermal annealing and solvent annealing, respectively.

The depth profiles of PCBM are extracted from these fits and are shown in Fig. 6. These fits indicate that the PCBM is segregated near the Si substrate in the as cast sample, which is consistent with previously reported results [39–42]. This previous work reported that the depth profile of P3HT/PCBM thin-films cast from chlorobenzene consist of a low scattering length density (SLD) layer near the air surface that is depleted in PCBM and a PCBM rich layer next to the substrate. With solvent or thermal annealing, the surface depletion is suppressed, which is interpreted to indicate that the annealing processes facilitate the movement of PCBM to the film surface [13].

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Fig. 4. GIWAXS results for P3HT:PCBM (1:0.8) thin film spin coated using ODCB solvent at 800 rpm. (a) area of P3HT (100) peak for solvent annealed samples, (b) crystal size ($L$) for the solvent annealed samples, (c) area of P3HT (100) peak for thermal annealed samples and (d) crystal size $L$ for the thermally annealed samples.

Fig. 5. Specular neutron reflectivity scans from ~300 Å P3HT:PCBM (50:50) blend thin films (a) as cast thin film, (b) thermally annealed at 150 °C for 60 min, (c) annealed at level 90 for 120 s. Insets show the SLD profile vs. normalized thickness of the model fit.
well as in interfacial excess peak of PCBM near the air surface. These results show that the PCBM selectively segregates to the air and silicon surface upon thermal annealing. As it is known that the surface energy of PCBM is higher (38.2 mJ/m$^2$) [26] than that of P3HT (26.3 mJ/m$^2$) [27], this surface segregation is ascribed to entropic forces. Therefore, the presence of the solvent during annealing provides a driving force for the PCBM to uniformly disperse throughout the thin film depth, a structure that is not found in thermally annealed samples. This exemplifies the importance of the solvent's ability to create a more homogeneous sample than thermal annealing, presumably due to the similar solvent quality of CS$_2$ for the P3HT and PCBM. The structures of samples that are similarly solvent annealed with selective solvents are currently being studied in our lab, where we expect annealing in a selective solvent will provide a method to further tune the depth profile of the nanocomposite thin film. The depth profile of electron acceptor (PCBM) near the air and substrate surface is important as it can impact the charge collection at the electrodes. For instance, a PCBM (acceptor) rich layer located at the air surface (near the cathode) and a P3HT (donor) rich layer located at the substrate (near the anode) should result in improved charge collection.

3.4. Atomic force microscopy (AFM)

AFM was also used to monitor the change in the surface structure of the BHJ thin films with solvent annealing. AFM height micrographs of the solvent annealed samples are shown in Fig. 7, where the phase contrast image indicates that the bright dots are PCBM, as PCBM appears brighter in the phase image due to its higher modulus. From these results, it is apparent that the number and size of the PCBM domains increases with annealing time and vapor pressure. Detailed AFM height micrographs for solvent annealed samples (at different vapor pressure) and thermally annealed samples (at different temperatures) are included in the supplementary information, Fig. S5–S9. The results of the AFM image analysis shows that the length and number of domains increases with an increase in vapor pressure and annealing time as plotted in Fig. 8. For the thermally annealed samples (see Supplementary information, Fig. S9), the PCBM aggregates to form crystals at 75 $^\circ$C and 125 $^\circ$C, while, the morphology of the sample annealed at 150 $^\circ$C is entirely different, presumably due to the formation of P3HT crystals at 150 $^\circ$C.

3.5. Effect of solvent annealing on the function of organic solar cells

The results reported above clearly document changes that occur in the P3HT:PCBM morphology, depth profile and crystallization as a result of controlled solvent vapor exposure. In order for this information to be most useful, these structural changes must be correlated to OSC photovoltaic function. With this in mind, nine identical solar cells were fabricated among which, five active layers cells were exposed to different solvent annealing conditions as shown in Table 1 and three active layers were subjected to thermal annealing in an oven as shown in Table 2. After solvent or thermal annealing of the active layer, an 80 nm thick aluminum electrode was evaporated at rate of 0.8 Â/s onto the active layer. The photovoltaic properties of these annealed active layers were then determined and are compared to that of
the as-cast active layer. These results are shown in Table 4 and Fig. 9. Results clearly indicate that the controlled exposure to solvent and thermal annealing of the active layer prior to cathode deposition dramatically improves solar cell efficiency relative to the as-cast devices. Samples annealed at $L/L_0 = 0.90$ for 5 s resulted in a 105% increase in efficiency over the as-cast device. This improved efficiency results from an increase in P3HT crystallinity as well as an increase in segregation of PCBM to the air interface, as evident from neutron reflectivity. Among the thermally annealed samples, the active layer annealed at 150 °C for 30 min results in a 110% increase in efficiency. However, it is interesting to note that for the solvent annealed samples at $L/L_0 = 0.90$, longer annealing time resulted in a decrease in PCE.

The structural characterization results indicate that the exposure of the sample to solvent vapor for longer time results in a more homogeneous depth profile and a decrease in P3HT crystallinity. In fact, comparing the P3HT crystallinity (GIWAXS results Fig. 3a) and cell efficiency results (Fig. 10b) clearly demonstrates that the cell efficiency is directly correlated to the P3HT crystallinity, where the decrease in P3HT crystallinity leads directly to lower cell efficiency at longer solvent exposure times.

**Fig. 7.** AFM height images (3 μm x 3 μm) of P3HT:PCBM thin film solvent annealed at different level $L/L_0$ of 0.50, 0.75 and 0.90 for 5, 30, 60, 120 and 180 s.

**Fig. 8.** Topology of the solvent annealed thin film samples observed from the AFM, number and length of 1D needle like PCBM crystals in a (3 μm x 3 μm) AFM height images.
The impact of controlled solvent exposure on the efficiency of a P3HT:PCBM device with the active layer spin coated using the best reported solvent ODCB was also tested. The results (Table 5 and Fig. 10) are consistent and similar to the results observed for the samples that were fabricated from CB solutions (Table 4 and Fig. 9).

The solar cell efficiency of P3HT:PCBM active layers with a 1:1 wt% ratio were also examined and the results are shown in Table 6 and Fig. S10,S11 (Supplementary figures), allowing a correlation of function to morphology and structure for the most well characterized samples. Compared to the (1:0.8) samples, the measured PCEs are significantly lower, which may be due to the quality of the P3HT and PCBM used. Regardless of this discrepancy, the qualitative changes that occur with solvent and thermal annealing are consistent with the changes that occur in the 1:08 samples. The PCE is high for the active layer that is annealed at $L/L_0 = 0.90$ at short times, and decreases with longer exposure to a nearly saturated solvent vapor. For all solvent annealed samples, the PCE results directly correlate to the P3HT crystallinity as shown in Figs. 9b and 10b, exemplifying the power of solvent annealing to exquisitely control the structure and crystallinity of P3HT in optimizing the power conversion efficiencies of organic solar cells.

The homogeneity of the depth profile of the sample is also important in device optimization, and these results clearly show that controlled solvent evaporation provides a controllable method to alter this depth profile. The neutron reflectivity results indicate controlled solvent exposure allows the PCBM to distribute throughout the film, but limits the formation of an excess of PCBM at the

**Table 4**

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<th></th>
<th>$V_{oc}$ (V)</th>
<th>$I_{sc}$ (mA/cm²)</th>
<th>FF (%)</th>
<th>Efficiency (%)</th>
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**Table 5**

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Fig. 9. (a) Current density vs. applied voltage curve for as cast and solvent annealed OSC samples, (b) Correlation between efficiency and area of (100) peak of P3HT.

Fig. 10. (a) Current density vs. applied voltage curve for solvent annealed samples, (b) Correlation between efficiency and area of (100) peak of P3HT.
surface. The ultimate depth profile and morphology depends on the amount of absorbed solvent, and its evaporation. For instance, at longer solvent annealing time, i.e. 120 s, the sample depth profile appears to be more homogeneous, as solvent dissolves P3HT crystals and provides more pathways for the PCBM to diffuse throughout the depth of the sample.

3.6. Discussion

The controlled exposure of the P3HT:PCBM to carbon disulfide vapor clearly alters the morphology and depth profile of the bulk heterojunction mixture, which in turn impacts its ability to act as an active layer in an organic photovoltaic device. Fig. 11 provides a schematic of one model of the change in morphology and depth profile with solvent annealing that is consistent with the results presented here. In this model, during spin coating, rapid evaporation of solvent results in a relatively uniform dispersion of P3HT:PCBM, where the system is far from its equilibrium state (Fig. 11a). With solvent vapor or thermal annealing, the molecules become more mobile, which results in ordering of P3HT and the exclusion of PCBM from these crystals.

During solvent vapor annealing, the thin film is swollen with the solvent [20], providing increased mobility for the PCBM molecules to diffuse away from the P3HT and, at 50% loading, the PCBM evolves towards thermodynamically favorable larger agglomerates and one dimensional needle like structures (Fig. 11b). The molecular mobility also allows the P3HT chains to crystallize, verified by the GIWAXS results. The increase in P3HT crystallization facilitates the phase separation of PCBM from the P3HT crystals (Fig. 11d). However, at longer solvent exposure, solvent clearly dissolves smaller and medium size P3HT crystals (Fig. 11c).

These results provide additional insight into previous work as well. For instance, Earlier studies have demonstrated that casting a BHJ layer from a solvent with a high boiling point can induce more crystallinity and improve cell performance [1]. This makes sense in that the slower evaporation of the solvent provides more time for the solvent to plasticize the polymer, and allow it to crystallize. In a more controlled experiment, Li et al. [26] studied the impact of the time taken for the solvent to dry after the spin-coating process (varied from 20–80 s) on the efficiency of the resultant P3HT:PCBM solar cells. In this work, the authors concluded the ordering of the \( \pi \)-conjugated structure of P3HT in the films is optimally developed when the time taken by the solvent to dry after the spin-coating is greater than 1 min. Our results are also consistent with previous work that demonstrated that P3HT crystallization is fastest when the amount of solvent is \( \sim 20\% \) [42]. At lower concentrations, the mobility of the polymer is hindered, while more solvent can inhibit ordering by minimizing interactions between chains.

In this solvent annealing process, the exposure to solvent is more controlled than a modification of the drying process after spin-coating, and provides a unique method to control and optimize the morphology, depth profile, and crystallinity of the conjugated polymer:fullerene mixture. The results presented here clearly demonstrate that judicious exposure to solvent can provide a method to independently alter the crystallization and crystal growth as well as the depth profile of the bulk heterojunction active layer. We expect that this process is broadly applicable to polymer:fullerene mixtures, and other polymer nanocomposites, offering a unique method to optimize the morphology and functionality of polymer nanocomposites.

### Table 6

<table>
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<tr>
<th>Sample</th>
<th>( V_{oc} ) (V)</th>
<th>( I_{sc} ) (mA/cm²)</th>
<th>( V_{max} ) (V)</th>
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<td>8.20</td>
<td>0.32</td>
<td>28.4</td>
<td>1.36</td>
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</table>

Fig. 11. Schematic of a model for the morphology evolution during solvent vapor annealing. (a) as cast P3HT:PCBM with relatively mixed state of P3HT:PCBM, (b) crystallization of P3HT which induces phase separation of PCBM, (c) Diffusion of PCBM in the layer at longer solvent exposure promoted by the dissolution of P3HT crystals and (d) 500 nm x 500 nm size AFM height image of solvent annealed thin film at \( I_{sc} \) ~ 0.5 for 5 s which shows long needle shaped domains of PCBM.

4. Conclusion

The modification of P3HT:PCBM thin films with controlled exposure to the vapor of a common solvent using a lab scale solvent annealing apparatus has been examined. The results indicate that exposure of this bulk heterojunction to CS\(_2\) alters the crystallinity and depth profile very effectively, presumably by inducing mobility of the components as the solvent plasticizes the mixture. Significant changes in the morphology of the thin films were observed quickly, i.e. at very short exposure time (\( \sim 5\) s). The as-cast P3HT:PCBM thin films appear to form a layered structure with a slight excess of PCBM segregated to the silicon substrate. Exposure to solvent vapor initially allows the crystallization of P3HT, which excludes PCBM molecules from the crystals, inducing phase separation. Simultaneously, PCBM molecules form large agglomerates. These morphological changes are correlated to photovoltaic efficiency, where this correlation clearly indicates that solar cell efficiency is governed by the extent of P3HT crystallinity and phase separation. Brief exposure (\( \sim 5\) s) to a nearly saturated solvent vapor results in higher P3HT crystallinity and nearly optimum photovoltaic efficiency, while longer solvent annealing times result in a decrease cell efficiency due to a decrease in P3HT crystallinity and large scale phase separation. Controlled solvent exposure provides a more controllable annealing process than thermal annealing, and takes less time than thermal annealing. For example, controlled solvent vapor exposure for just 5 s results in...
the improvement in solar cell efficiencies of 100–300%. Moreover, the fundamental information presented in this study should be generally applicable to a broad range of polymer nanocomposites and provide guidelines to control the morphology, function, and depth profile of the next generation of polymer nanocomposites.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.solmat.2012.07.014.

References

