

EFFECT OF SPRAY DEPOSITION TIME ON OPTICAL AND MORPHOLOGICAL PROPERTIES OF P3HT:PCBM THIN FILMS

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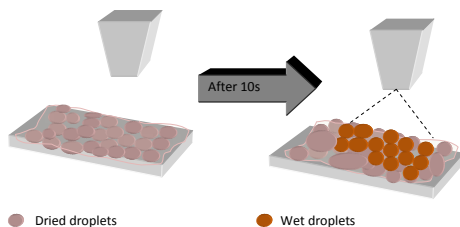
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Graphical abstract



Abstract

This paper investigated the effect of spray deposition time on optical and morphological properties of P3HT:PCBM thin films. The effects of spray deposition time on the optical and morphological properties of thin films were investigated using optical microscopy, UV-Vis spectrophotometry and atomic force microscopy (AFM). The AFM spectra show that the thin films prepared at 10s spray deposition time are more uniform while the 15s and 20s samples presented coffee ring shapes with inhomogeneous surface formation. The ridge-like features can be observed in the surface for all samples and become more pronounced with increasing spray deposition time. The root mean square (RMS) roughness of the samples increased with increasing spray deposition time. Based on the absorption results, it is concluded that higher spray coating times result in lower crystallinity of the thin film. The 10 s spray deposition time is the most suitable deposition time for producing thin films with good morphology and crystallinity for polymer solar cells (PSCs) with improved power conversion efficiency (PCE).

Keywords: Optical, morphological, thin films, spray coating, spray deposition time

Abstrak

Kertas kerja ini mengkaji kesan masa salutan semburan pada sifat optik dan morfologi filem nipis P3HT:PCBM. Kesan masa salutan semburan pada sifat-sifat optik dan morfologi filem nipis telah dikaji menggunakan mikroskop optik, UV-Vis spektrofotometri dan daya atom mikroskopi (AFM). Spektrum AFM menunjukkan bahawa filem nipis disediakan pada masa 10 saat salutan semburan adalah lebih seragam manakala sampel pada 15 dan 20 saat mempunyai bentuk cincin kopi dengan pembentukan permukaan tidak homogen. Ciri-ciri seperti rabung dapat dilihat di permukaan untuk semua sampel dan menjadi lebih ketara dengan peningkatan masa salutan semburan. Punca min kuasa dua (RMS) kekasaran sampel meningkat dengan peningkatan masa salutan semburan. Berdasarkan keputusan penyerapan, dapat disimpulkan bahawa masa salutan semburan tinggi menghasilkan penghabluran yang lebih rendah daripada filem nipis. Masa salutan semburan 10 saat adalah masa yang paling sesuai untuk menghasilkan filem nipis dengan morfologi dan penghabluran yang baik untuk sel-sel solar polimer (PSC) dengan kecekapan penukaran kuasa (PCE) yang lebih baik.

Kata kunci: Optik, morfologi, filem nipis, salutan semburan, masa salutan semburan

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1.0 INTRODUCTION

One of the major issues in commercializing polymer solar cells (PSC) is finding a roll-to-roll compatible, high yield and low cost production process [1]. Blade coating [2, 3], spin coating [4], spray coating [5-8], dip coating [1], screen printing, gravure printing and ink-jet printing are some of the methods used to fabricate the PSC. Spin coating is a standard method that has been used to produce uniform coatings of desired thickness; however, material wastage of more than 90% becomes prohibitive as the film-coated area becomes larger. Ink-jet printing is a promising cost-efficient process for PSC fabrication due to its efficient materials usage and precise patterning with resolutions of 20–30 μm , superior to spin coating and other conventional methods [9, 10]. However, ink-jet printing is not easily adapted to mass volume manufacture due to its complexity and low volume throughput [11].

Blade coating and slot-die coating are suitable for high volume commercialization of PSC, as these methods are fast, high volume, and have a low roll-to-roll cost of production. Power conversion efficiency (PCE) of more than 6% can be achieved in blade coating process due to the ability of the donor and acceptor to quickly self-assemble into the desired ordered and interpenetrating morphology in the absence of centrifugal force. However, the wet film formation is relatively low compared to spin coating, and aggregate or crystallite formation at high concentration often occurs [12]. The dip coating process is commonly used for conventional dyeing and can provide easy and fast deposition of polymer films over a large area [1]. The dip coating process is fast and only requires a single pass in contrast to the spray coating and inkjet printing processes, and the resultant films are pinhole free [1, 13]. The downside is a slow natural drying step that is unsuitable for high volume production.

Spray coating techniques have great potential for large scale production since these methods are not limited by substrate size or low utilization of polymers, and may be a promising replacement for conventional spin coating methods [14]. Spray coating can utilize a wide variety of fluids with various rheologies, making the production of fully spray coated PSC devices a possibility. However, the control of film thickness and roughness is an issue [15], and most current research focuses on optimizing the morphology of the active layer by using high boiling point solvents [16], additives, solvent mixtures, post spray thermal annealing [15, 16], additional spray coatings, and optimizing the spray coating parameters. Spray coating is a well-established method used in the graphic arts, painting and coating industries [6, 7], and is already being used for PSC fabrication [15, 17, 18]. The parameters of the spray deposition technique that affect the desired morphology and performance of the fabricated solar cells include nozzle to substrate distance, spraying

duration, carrier gas pressure, and substrate temperature.

In this work, poly (3-hexylthiophene) (P3HT) and phenyl- C_{61} -butyric acid methyl ester (PCBM) were used to study the effects of spray deposition time on the morphology and optical properties of the active layer. The impacts of spray deposition time on the film formation, surface topography, morphology and optical properties of spray coated thin films were specifically investigated. Since spray coating technique using an air brush is considered a new technique for fabricating thin films, systematic study on certain parameter is crucial for understanding the mechanism behind the film formation. The effects of spray deposition time on the optical and morphological properties of thin films were investigated using optical microscopy, UV-Vis spectrophotometry and atomic force microscopy (AFM). The subsequent findings provide insight into developing PSCs with optimized morphology.

2.0 EXPERIMENTAL

Poly (3-hexylthiophene) (P3HT) and phenyl- C_{61} -butyric acid methyl ester (PCBM) from Sigma Aldrich were used as received. P3HT and PCBM were used as the electron donating unit and electron acceptor unit, respectively. The thin films fabrication method has been described elsewhere [19]. P3HT and PCBM were dissolved in 2 ml toluene in a 1:1 weight ratio. The choice of toluene as the solvent is due to the fact that it can help preventing the coffee ring effects in the spray coated thin films [19, 20]. The solutions were stirred overnight at room temperature using a magnetic stirrer at 500rpm. The thin films were prepared by spray coating pre-cleaned glass or quartz substrates with the polymer solutions. Substrate to nozzle distance and air pressure were set at 7 cm and 1 bar, respectively. The spray deposition times were varied from 10 s, 15 s and 20 s. This range has been set based on the previous study by [21-23]. The thickness of the thin films was in the range of 200–300 nm, as measured using a surface profiler. The UV-Vis absorption spectra of the polymer films were taken with a UV-Vis spectrophotometer (Shimadzu UV-3101-PC). The topographical properties of the polymer films were obtained using atomic force microscopy (AFM) in tapping mode. The macro-morphology of the thin films was measured using optical microscope (Dino-Lite AM7013MZT).

3.0 RESULTS AND DISCUSSION

3.1 Macro-morphology of the Spray-Coated P3HT: PCBM films

Figure 1 shows the effects of spraying duration on the final thin film. The spraying duration were varied from 10s to 20s. The coffee ring-shaped can be observed clearly

in 15s and 20s samples suggesting that the drying time for each droplet is lower than the interval time between the first and second droplets. The coffee ring-shaped is the formation of ring-shaped structure attributed to the drying coalescent droplets. This coffee ring effect can be a major problem in industrial applications where a uniform deposition of particles is required. This makes each droplet does not manage to combine hence leaves boundary. As the spraying duration was increased from 10 to 20s (Figure 1 a)-c)), the thin film surface formation is become more inhomogeneous. For 10s thin films (Figure 1 a)), the thin film formation is more uniform somehow the coffee ring shape is still prominent.

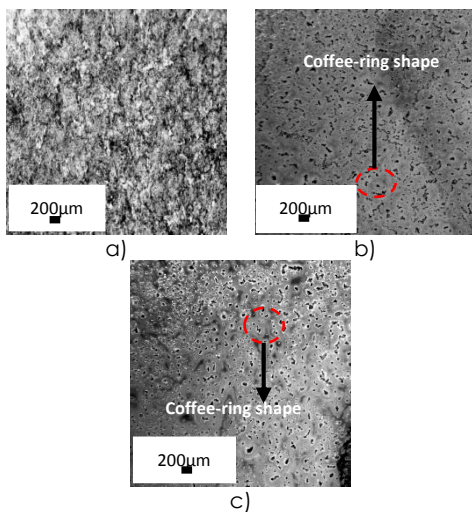


Figure 1 Optical images of spray coated P3HT:PCBM layers on top of glass substrate at a) 10s b) 15s and c) 20s spraying deposition time

The surface images of the thin films were further analysed using ImageJ software to get the better view of the droplets formation. From the edges-view (Figure 2), it can be observed that the 10s samples had nanometer edge of the droplet which each of them seem connected to each other. While 15s and 20s thin films had numerous pinholes with the thick edge of the droplet. Each droplet is also not connected to each other with poor surface coverage. Both 15s and 20s samples demonstrated a ring-like deposits which due to the capillary flow such that continuous deposition partially dissolved the previous droplets and replenishes the liquid solution for resolidification at the pinned contact line [24].

It should be noted that the film morphology is affected by many factors such as flux of the droplets, ambient condition, and also the characteristics of the solution (e.g. vapor pressure, boiling point, and surface tension: 28.52 dyn/cm at 25°C) [8]. Toluene, a low boiling point solvent (b.p~111°C) with a low vapor pressure of 28.4 mmHg at room temperature is a volatile solvent. Hoth *et al.* [6] explained the importance of the solvents selection for spray coating process. Too low drying rate of the liquid droplets will immediately pushed sideward by the pressure gas of the airbrush, producing a non-uniform

wetting. On the other hand, organic solvents with too high evaporation rates, at a certain nozzle to substrate distance inhibited the formation of film deposition due to dry droplets prior reaching the substrate.

A non-uniform wetting is observable for 15s and 20s samples. Giroto *et al.* [15] reported that the estimated drying time for the spray-coated droplets is in the microsecond range, suggesting insufficient time for complete dissolution of the underlayer. In general, the evaporation of droplets is controlled by stationary diffusion of the liquid molecules in the gas phase, thus the drying time of the droplets (t_{drying}) is proportional to the inverse of the droplet radius, r ($t_{drying} \propto r^2$). Ju *et al.* [25] classified the deposited film morphology into three categories which is particle mode, wet mode and thin-film mode. Both of 15s and 20s samples demonstrated a wet mode mainly due to the excessive solution from the continuous spray duration for 15s and 20s.

As can be observed in Figure 2 b) and c), the droplets are deposited on top of another and significant increment of the droplet's base radius demonstrating a decreased contact angle between the solution and previously deposited material [15]. These results in increment of the surface roughness of the thin films were discussed in the next subsections.

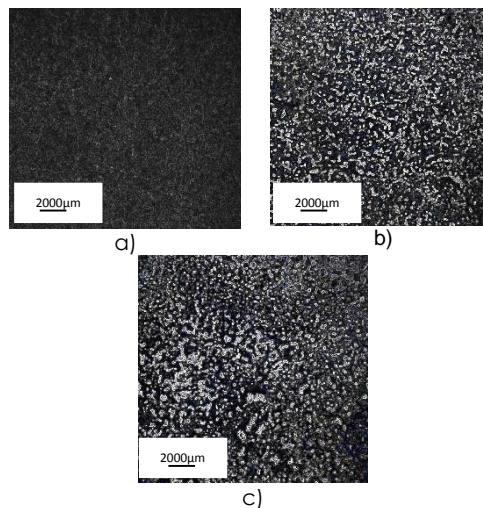


Figure 2 Edges-view images of spray coated P3HT:PCBM layers on top of glass substrate at a) 10s b) 15s and c) 20s spraying duration. Edges of the droplets can be seen clearly in 15 and 20s samples while the edges for 10s samples is in smaller scales

3.2 Nano-Morphology of the Spray Coated P3HT:PCBM Films

The morphology of the active layer has a critical influence on the charge separation and transport within the donor and acceptor networks. To observe the topographical properties of the active layers, AFM has been performed on the P3HT:PCBM spray coated film. The phase image produced by a tapping mode AFM reflects the difference in mechanical energy dissipated from the vibrating tips into the underlying samples. Thus, the phase-separated domains of the P3HT and PCBM

can be gained from the appearance of a binary phase in a BHJ material. Figure 3 shows topographical images for P3HT:PCBM spray coated from a toluene based solution at different spray durations.

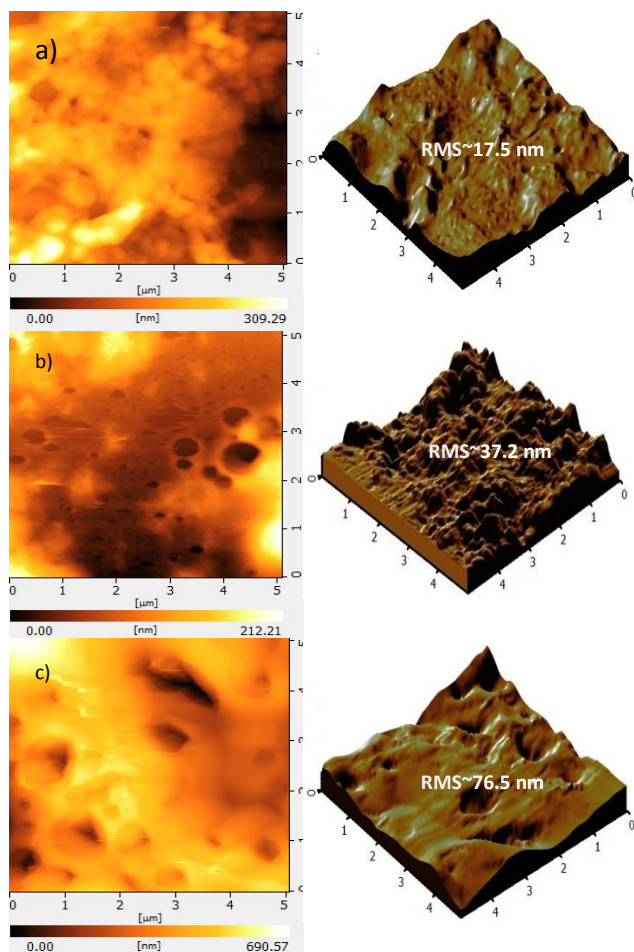


Figure 3 Surface topography of P3HT:PCBM film at different spray deposition times a) 10s b) 15s and c) 20s

Ridge-like features can be observed on the surface of all samples, but become more pronounced with longer spray durations. Figure 3a shows a uniform phase, with discernible domains of P3HT and PCBM. The individual domains with size $\sim 100\text{--}500\text{nm}$ can be seen clearly and the nanoscale phase separation between the binary phase is noticeable throughout the entire area of observation. When spraying duration was extended to 15 s and 20 s, the domains become less discernible, but the size of each dark and bright region domain is increased, suggesting that domain overgrowth is occurring.

The solvent evaporation rate has a major effect on the surface roughness of organic thin film, with faster evaporation rates inducing finer phase separation and amorphous morphology [15, 25–27]. As shown in Figure 3, the root mean square (RMS) roughness of the samples was increasing with the spraying duration. The 20s sample had a high height variation $0\text{--}690.57\text{nm}$, which is unfavourable, as it results in a lower fill factor [28]. It

should be emphasized that, non-uniform surface roughness will affect the interfaces of the photoactive layer and have a direct impact on the performance of the spray coated device [29]. Higher surface roughness may result in a more efficient charge collection at the interface due to the higher contact area between the polymer film and the metal cathode [30].

The increased surface roughness might also enhance internal reflection and improve light collection, thus increasing device efficiency. Yet, Li *et al.* [31] observed that surface roughness plays only a minor role in device efficiency enhancement. Lee *et al.* [5] suggested that surface roughness is not a good indicator for estimating the final device performance, particularly for spray coating devices. Nevertheless, most researchers concluded that the variation in film thickness and roughness will cause charge recombination due to the limited charge mobility, or percolated pathways, in conjugated polymers, resulting in poor device performance [17, 26, 28].

Fukuda *et al.* [26] found that by the addition of DMSO $\sim 2.9\text{mmHg}$ as a second organic solvent, the RMS roughness decreased in proportion with the concentration of DMSO added. Evidently, the sprayed particles do not evaporate as easily as the concentration of DMSO increases, spreading the wet droplets in a perpendicular direction against the glass substrate, and thus reducing the surface roughness. In this room temperature experiments with toluene as the sole solvent, and vapour pressure at approximately 2.7mmHg , we had wet droplets for spray deposition times in excess of 15 s with proportional increases in surface roughness.

This result contradicts with Fukuda *et al.* [26] and can be explained diagrammatically in Figure 4. When a liquid drop orthogonally impacts a solid substrate, the drop may deposit into a thin disk, disintegrate into secondary droplets, or possibly rebound [32]. At 10 s spray duration, the droplets spread on the surface at impact and subsequently cure through evaporation of the solvent, resulting in a thin dry film. With times in excess of 10 s, solutions sprayed enter into the space of previously deposited droplets, as shown in Figure 4. Upon contact, the solution droplets immediately dissolves a small part of the underlying material, filling up the gap between them, and starts to connect to form a larger droplet. Since toluene is a volatile solvent, complete dissolution of the underlayer is unachievable due to insufficient time. Therefore, spraying the solution for more than 10 s will produce droplets that are deposited on top of one another with a high probability, resulting in higher surface roughness and wet droplets.

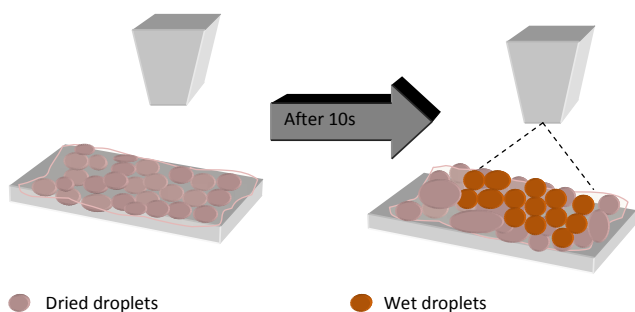


Figure 4 Schematic representation of surface film formation at 10s and above 10s deposition times

3.3 Absorption Properties

Figure 5 shows the absorption profiles for P3HT:PCBM at different spray deposition times. The 15s samples have the same absorption profiles as the 10s samples. Both samples show four features in absorption: peaks at 510nm, and two vibronic shoulders at 550nm and 610nm for P3HT and 330nm for PCBM. 10s films have the most prominent vibronic features indicating strong interchain-interlayer among the P3HT chains as well as good polymer ordering in the blend films [5]. However, the shape of P3HT peaks change significantly for the 20s spray deposition time. The peaks at 510nm and vibronic shoulders at 550nm diminish significantly. Reduced PCBM film coverage may explain the absorption loss, as PCBM appears to be bound in the crystallites [6]. Steirer *et al.* [6] found that the crystalline structures have higher optical densities than the surrounding film, and will result in absorption loss.

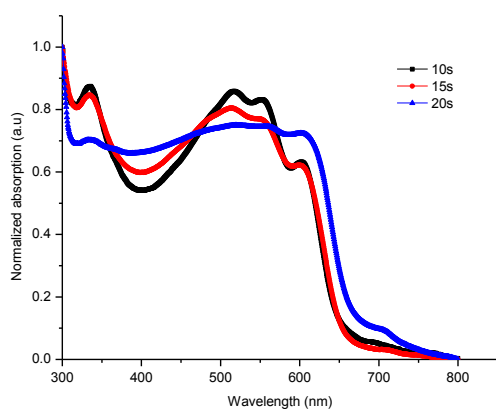


Figure 5 Schematic representation of surface film formation at 10s and above 10s deposition times

The reduced vibronic shoulders for the 20s samples at 550nm reflects lower crystallinity and poor interchain interactions among the P3HT molecules. This was due either to higher height variation (from AFM results) or rapid drying during atomization and deposition of the active layer. Below 400nm, the light absorption is dominated by PCBM (its peak at 330nm) or

semiconducting nanoparticles (with increasing absorption toward lower wavelengths) [33]. According to Mie's theory, the higher absorption at this wavelength is a hint to greater agglomeration, as larger agglomerate sizes would lead to increased absorption [33].

4.0 CONCLUSION

P3HT:PCBM thin films have been successfully fabricated using a simple spray deposition method. By varying the spray coating time, different morphologies and absorption properties can be observed. The 15s and 20s samples presented coffee ring shapes with inhomogeneous surface formation. This is due to the capillary flow associated with continuous deposition partially dissolving the previous droplets and having more liquid solution for re-solidification at the pinned contact line. The 10s thin films are more uniform. The ridge-like features can be observed in the surface for all samples and become more pronounced with increasing spray duration. The RMS roughness of the samples increased with increasing spray duration. Based on the absorption results, it is concluded that higher spray coating times result in lower crystallinity of the thin film. The 10 s spray deposition time is the most suitable deposition time for producing thin films with good morphology and crystallinity for PSCs with improved power conversion efficiency (PCE).

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