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Technical paper

Effect of Spraying Parameters on the Morphology of Spray-Coated Active Layers for Organic Solar Cells

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Abstract

Over the past decade, organic solar cells (OSCs) have demonstrated their great potential for the low-cost mass production of renewable energy. However, the conventional active layer deposition technique (spin-coating) is not suitable for mass production due to its incompatibility with the roll-to-roll process. Spray-coating is a promising candidate for in-line production of OSCs but parameters such as distance between the spray nozzle and substrate, applied pressure and number of sprays should be optimized to produce adequate film thickness and morphology. Here, we verified how these processing parameters influence the thin film properties and observed that film thickness increases with decreasing nozzle-substrate distance, increasing number of sprays or applied pressure. The processing parameters were adjusted to produce spray-coated films with similar properties to the spin-coated ones thus confirming that spray-coating could replace spin-coating for mass production of OSC devices.

Keywords: *active layer; organic solar cells; P3HT; spray-coating; surface morphology.*

1. Introduction

Due to increasing worldwide energy consumption, the demand for low-cost and large area photovoltaic modules production has been growing over the past decades. In fact, renewable energy can be produced at a low-cost through novel technologies such as organic solar cells (OSCs) which have a great potential for mass production using the roll-to-roll process. However, the conventional organic solution deposition method (spin-coating) is mostly suitable for lab-scale device fabrication. In fact, spin-coating not only generates a large amount of active material and solvent wastes but is also limited in terms of covered area and difficulties often arise when scaling-up the OSC fabrication process by spin-coating. Consequently, recent studies have been focusing on developing and investigating alternative deposition processes adequate for mass production of large-scale modules. Among others, spray-coating, [1-5] slot-die coating,[6] gravure printing [7] and inkjet printing [8] have shown particularly encouraging results. When it comes to spray-coating, the coated solution properties (viscosity and used solvent) as well as the process parameters (spray nozzle-substrate distance, number of sprays, pressure and spray speed rate) can greatly influence the quality of the produced films and consequently, the OSC device performances.[9] While OSC efficiencies and stability play an essential role for the potential commercialization of these new type of photovoltaic devices, a particular attention should also be given to reducing the use of chlorinated solvents which is harmful for both the human health and the environment.[10] Previous attempts to apply spray-coating to solar cell fabrication clearly demonstrate that similar performances to spin-coated films can be achieved while considerably decreasing the amount of wasted material. [11] Furthermore, past studies emphasize that the solvents used for the polymer layer deposition and the spraying time affect the surface morphology and thickness of the spray coated films.[1-3] Spray-coated films typically have a rougher surface as compared to the spin-coated ones.[4] Device performances may also be affected by blend ratio of donor acceptor materials and solution flow rates.[5] To further investigate the effect of spray parameters to the film thickness and morphology, in this study we spray-coated a poly(3-hexylthiophene-2,5-diyl) (P3HT): (6,6)-phenyl-C61-butyric acid methyl ester ($PC_{61}BM$) solution by controlling the distance between the spray nozzle to the substrate, the applied pressure and the number of sprays. We compared the resulting morphologies with spin-coated film used as a reference and demonstrated that thin active layers which could be applied to OSC fabrication can be achieved by controlling the spray-coating parameters.

2. Procedure and Experimental

Glass substrates were cleaned using a standard cleaning procedure in acetone, deionized water and isopropanol. The substrates are then exposed to isopropanol vapor (heated at 200°C for 3 min) to ensure that no residual solvent traces can be found on the substrate surfaces. The P3HT and $PC_{61}BM$ were purchased from Rieke Materials and Luminescent Technology, respectively. The P3HT:PC61BM solution was prepared in 25:20 mg/ml in chlorobenzene. After stirring for 4 hours at room temperature, the solution was spin-coated at 350 rpm for 10 s followed by a planarization step at 700 rpm for 50 s on top of clean glass substrates. Spray-coated films are produced using an airbrush where the compressed air flow through a venturi that creates suction and allows the solution to flow from an interconnected solution feed under atmospheric pressure. High air velocity then atomizes the solution to create small solution droplets. The solution that passed through the nozzle produced conical shape as shown in Figure 1 (a). In our vertical spray-coating design (or set-up) (Figure 1 (b)), the nozzle-substrate distance, the number of sprays and the spray pressure can be individually controlled. Spraying distance and spraying times were respectively set to 5, 8 and 10 cm, and 8, 12 and 16 times. The films were sprayed at an applied pressure of either 0.1 or 0.2 MPa. The experiments were carried out by fixing two of the processing parameters and studying the influence of the third one on the quality of the produced thin films. The thickness of the films was obtained by using Dektak profilometer and the surface morphologies were characterized by Scanning Electron (SEM) and Atomic Force Microscopy (AFM).

3. Results and Discussion

All the data obtained from the experiments are analysed and discussed according to the effect of spray parameters to the film thicknesses and the surface characterization of the films.

3.1. Influence of Spray Parameters on P3HT:PC61BM Film Thicknesses

The P3HT:PC$_{61}$BM film thicknesses are analysed based on the spray parameters such as the distance of substrate to the spraying nozzle, number of spraying cycles and different pressure applied.

3.1.1. Spraying Nozzle to Substrate Distance

Table 1 summarizes the thicknesses of P3HT:PC61BM films obtained by spray-coating 8 times at a pressure of 0.1 MPa. The film thickness is measured using Dektak profilometer. The average thickness of spin-coated and spray-coated P3HT:PC$_{61}$BM films are recorded in the Table 1. In this study, different spray conditions are conducted to see how it affects the deposited film thickness.

Table 1: Effect of Spray Distance to the Film Thickness

Deposition method	Deposition parameter	Average thickness (nm)
Spin coated	350 rpm followed by 700 rpm	703.39
Spray coated	5 cm, 0.1 MPa, 8×	1022.21
	8 cm, 0.1 MPa, 8×	924.24
	10 cm, 0.1 MPa, 8×	747.66

In both Table 1 and Figure 2, we can clearly observe a trend with the film thickness decreasing with increasing spraying distance. For P3HT: PC$_{61}$BM, the films thickness decreased from 1022.21 nm to 747.66 nm when sprayed at 5 cm and 10 cm, respectively. These results reflect that film thickness decreases with increasing spray distance This trend can be easily understood when taking into account geometrical aspects of the spray-coating process. When the spray nozzle is positioned further away from the substrate, the solution spreads over a larger radius as compared to shorter nozzle-substrate distances. These results suggest that upscaling of the spray-coating process could be easily achieved by simply increasing the nozzle-substrate distance or moving the nozzle along the x-y plan when larger substrates are used. Note that a smaller distribution of the film thicknesses is achieved at a nozzle-substrate distance of 8 cm under the given experimental parameters (pressure of 0.1 MPa, 8 spraying cycles).

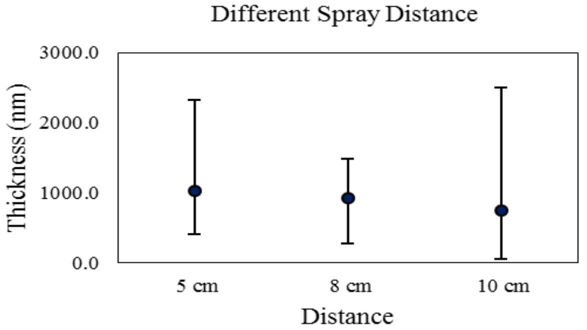

Fig. 2: Thickness of P3HT: PC$_{61}$BM films sprayed at various nozzle-substrate distances at a pressure of 0.1 MPa with 8 spraying cycles.

3.1.2. Number of Spraying Cycles

On the other hand, Table 2 and Figure 3 shows that, when the number of repeated spraying steps are increased from 8 to 16 times, the P3HT: PC61BM film thickness increased from 747.66 nm up to 1511.44 nm. As expected, the film thickness increases with the number of repeated spraying cycles. In fact, the average thickness of films obtained with 8, 12 and 16 repeating cycles displays a quasi-linear increase in film thickness. Note that the small variations in this trend (thicker film obtained for a large number of repeated cycle) may be due to the fact that, as demonstrated in Figure 1, under these spraying conditions, a large variability of the thickness can be observed. Nonetheless, these results clearly emphasize that the number of spray is one of the important parameters to control the thickness of films deposited using the spray-coating technique.

Table 2: Effect of Number of Spray Cycle to the Film Thickness

Deposition method	Deposition parameter	Average thickness (nm)
Spin coated	350 rpm followed by 700 rpm	703.39
Spray coated	8× 0.1 MPa, 10 cm	747.66
	12× 0.1 MPa, 10 cm	1006.93
	16× 0.1 MPa, 10 cm	1511.44

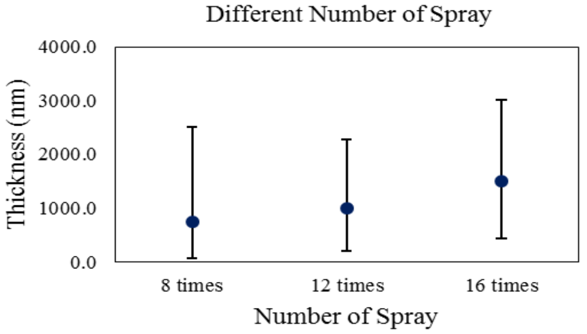

Fig. 3: Thickness of P3HT: PC$_{61}$BM films sprayed at various number of repeated spraying cycles at a pressure of 0.1 MPa and a spraying distance of 10 cm.

3.1.3. Different Pressure Applied

Last but not least, the spraying pressure seems to play a key role in the formation of high quality thin films by spray-coating. Consequently, we investigated the effect of increasing pressure from 0.1 to 0.2 MPa on the thin film thickness and its variability, when the distance and number of spray are fixed at 10 cm and 8 times, respectively. Figure 4(a) and Table 3 indicate that the film thickness increases about 104 nm when sprayed at higher pressure.

Table 3: Effect of Spray Pressure to the Film Thickness

Deposition method	Deposition parameter	Average thickness (nm)
Spin coated	350 rpm followed by 700 rpm	703.39
Spray coated	0.1 MPa, 10 cm, 8×	747.66
	0.2 MPa, 10 cm, 8×	852.10

This further confirms that sprayed film thickness can also be controlled using spraying pressure and that thicker films can be formed at higher pressure. Additionally, the data in Figure 4(a) clearly emphasizes that a higher applied pressure will lead to more homogeneous films with relatively small thickness variation over the sprayed area on the substrate. Once again, this may be a key parameter when it comes to the fabrication of large-scale devices and/or continuous process over large areas in which reproducibility is of major importance.

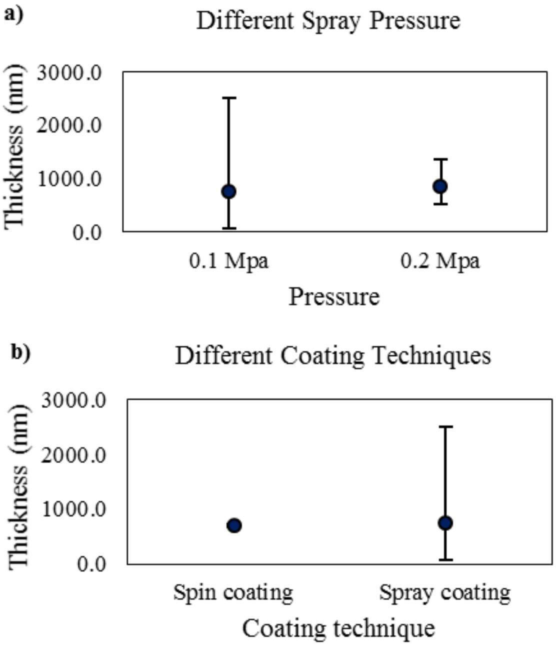

Fig. 4: (a) Thickness of films sprayed at different pressure with fixed distance and number of spray, and (b) thickness of films deposited using different coating techniques.

Recent studies on new polymer materials for OSC fabrication suggest that high efficiencies may be achieved using active layers with thicknesses of 300 nm and above. [12] However, achieving thick active layers by spin-coating can sometimes be problematic due to the limited solubility of active materials in organic and aqueous solvents. In fact, P3HT and PC61BM are commonly deposited using chlorinated solvents such as chlorobenzene and the concentration used in this work is relatively close to the solubility limit of P3HT. Here, we optimized the spin-coating speeds (300 rpm followed by a planarization step at 700 rpm) to deposit the P3HT:PC61BM blend solution to form thick and relatively homogeneous films. Under these conditions, homogeneous P3HT:PC61BM films with a thickness of approximately 700 nm can be produced (Figure 4(b)). On the other hand, preparing spray-coated films with similar thicknesses is relatively easy and was achieved by spray-coating P3HT:PC61BM films at a pressure of 0.1 MPa, a distance of 10 cm for 8 repeating cycles. Figure 4(b) show thickness variation in spray-coated films as compared to the spin-coated ones, which is consistent with previous study. [2] This aspect could be further improved by controlling the solution concentration and applied pressure, which is outside of the scope of this study. Also, it is worth mentioning that to produce similar active layer thickness in our experiments, approximately 150 and 135 microliter of solution per substrate were used for both spin-coating and spray-coating respectively. With further optimization of the spray-coating set-up, the materials waste could be further reduced, especially when larger substrates are used. These arguments clearly suggest that spray-coating is a complimentary deposition process adapted for large-scale and in-line production of high quality active layers for OSC devices.

3.2. Surface Characterization of P3HT:PC$_{61}$BM Film

While the thickness variation may strongly favour spin-coating over spray-coating, a particular attention should be given to the microscale morphologies of the films to assess whether the spray-coated films could be used as active layers in OSCs. We consequently compared the surface morphology of samples with similar thicknesses by using SEM and AFM. Note that both spin-coated and spray-coated films were obtained without using filters to remove large crystals as this would also reduce the viscosity of the solutions. In fact, in the SEM images of the spin-coated films displayed in Figure 5(a) we can observe the formation of large crystal-like structures which result from the high concentration of P3HT used and spin-coating at relatively low speeds. Low spin-coating speeds results in the process being mainly controlled thermodynamically (slow-evaporation process) unlike the kinetic control usually achieved by high speed spin-coating (700 rpm and over). The slow solvent evaporation consequently leads to the formation of large P3HT crystals which are disadvantageous for high efficiency OSC fabrication. This result contradicts most studies which report that spin-coated films exhibit smooth surface but it is worth noticing that most of these studies are done with relatively high spin-coating speeds.

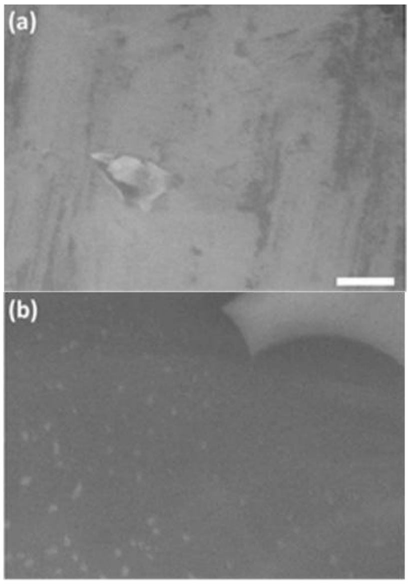

Fig. 5: SEM images (25 x 35 mm2) of (a) spin-coated and (b) spray-coated films. The images were taken at 1350× magnification, 15 kV and the scale bar corresponds to 5 µm.

On the other hand, the SEM image of spray-coated active layers (Figure 5(b)) suggests that relatively smooth surfaces are obtained with the appearance of small crystals along with larger structures (upper right part of Figure 5(b)). These larger structures may be due to either dewetting of the top surface of spray-coated films or to drying patterns resulting from the micro-droplets formed during the spray-coating process. To further understand the origins of the spray-coated thin film morphology and compare it with that of spin-coated films, we measured AFM images of the two types of sample (Figure 6). Under these spin-coating conditions, the spin-coated films not only exhibit the formation of some large scale P3HT crystallites (Figure 5(a)) but also a large number of hole-like structures (Figure 6(a)) which may be related to the slow-drying process as discussed above. These inhomogeneities (approximately 50 nm depth) may generate some variations in the electric field applied to the active layers if used in OSC device architectures and should, consequently, be avoided.

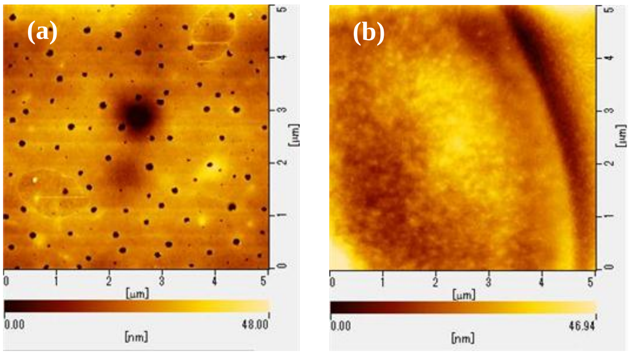

Fig. 6: AFM images of thick (a) spin coated and (b) spray coated films.

The AFM topology images of the spray-coated films confirm that a micro-droplet-like structure can be observed on the surface of the thin active layers (Figure 6(b)). Similarly, to the hole-like structure observed in spin-coated films, this droplet-like structure can be detrimental for efficient OSC fabrication. However, as it is due to drying patterns, it may be easily removed by applying higher pressures (formation of smaller droplets which dry faster) or by increasing the nozzle-substrate distance. More importantly, both the surfaces on the droplet-like structure and around it displays a very low surface roughness as compared to spin-coated films which suggest that spray-coating may be a more adequate process for the formation of homogeneous thick active layers for OSC fabrication.

4. Conclusion

Based on our results, we can conclude that the spray parameters such as distance between the spray nozzle to the substrate, pressure applied and number of spraying cycles play important roles in spray-coating technique. In fact, these parameters not only control the deposit film thickness but also the film homogeneity. Furthermore, unlike spin-coating, thick active layers can be easily achieved with spray-coating which may be of major importance when it comes to fabricating high efficiency devices with newly developed materials. We are able to produce spray-coated films with the desired thickness which is comparable to that of maximum thickness achieved using the spin-coating technique. The surface morphology of the spray-coated film indicates that spray-coating technique is suitable technique to replace spin-coating technique in mass production of high efficiency OSCs.

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