Aerosol flow homogenization in the spray polyphenylene vinylene thin film deposition

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Abstract. Two different spray deposition (SD) techniques – SD and homogenized SD (h-SD), were compared in the case of poly[2-methoxy-5-(3,7-dimethyloctyloxy)-1,4-phenylene vinylene] (MDMO-PPV) used as a model material. The h-SD setup includes a homogenizer (a chamber) for homogenization of the spray flow. The homogenizer allows droplet size control and spraying at a low air pressure. Films of about 1 µm thickness were prepared by SD and h-SD from a toluene solution with a concentration of 0.5 g l⁻¹. Optical micrograph images show that using h-SD results in obtaining uniform films without a distinguishable structure. Imaging by polarized light reveals the typical discs observed often in the spray deposition experiments. The spectral dependence of the photocurrent consists of two peaks. This property makes the structures with h-SD films more attractive for a photovoltaic application since this enhances the photovoltaic conversion in a wider visible light range. The I-V characteristics measured on samples with h-SD films show that exposure to white light increases the current by two orders of magnitude. One can thus conclude that the ITO|MDMO-PPV|Al structures with h-SD MDMO-PPV films behave as a photovoltaic cell.

1. Introduction
Organic semiconductor thin films are potential candidates for applications in microelectronic devices due to their easy processing and low cost [1]. Poly[2-methoxy-5-(3,7-dimethyloctyloxy)-1,4-phenylene vinylene] (MDMO-PPV) is a widely investigated organic semiconductor (HOMO and LUMO orbital positions at 5.4 and 3.2 eV, respectively, [2]) with a potential application as photoconductive or electroluminescent layers.

A variety of methods are being used to produce PPV films – spin-coating [3], electrophoretic deposition [4], Langmuir-Blodgett [5] and ink-jet printing [6].
Recently, spray-deposition (SD) through a conventional airbrush was introduced as an efficient large-area deposition technique [7, 8].

The SD method produces films on a large covered area at relatively low substrate temperatures (20 – 100 °C). The main problems impeding the wide usage of the spray deposition arises from the non-uniformity of the sprayed films. As a result, films with voids or considerably high grain size are usually produced.

In our previous experiments we found that MDMO-PPV films sprayed at room temperature of the substrate tend to cross-link in network fibers separated by voids [9]. This effect was reduced by increasing the substrate temperature during the spray deposition which decreases the void size and increases the covered part of the substrate [10]. In this paper, a way of increasing further the film uniformity is suggested by homogenizing the sprayed flow. Usually, the homogenizer consists of a heated chamber [11] where the solution is sprayed and heated in contact with the chamber walls. Our construction suggests a chamber of approximately 1 l volume where a more precise heating control is achieved by mixing directly the sprayed flow with hot air. The air is heated outside the chamber in an air convector to temperatures of 30 – 70 °C. SD using homogenization of the sprayed flow by mixing with hot air is denoted hereinafter as h-SD.

The paper presents a comparative study of the properties of SD and h-SD poly[2-methoxy-5-(3,7-dimethyl-octyloxy)-1,4-phenylene vinylene] (MDMO-PPV) films. The study seeks potential applications for these films in solar energy conversion technologies and other branches of organic electronics.

2. Experimental

A base solution (concentration of 1 g l\(^{-1}\)) was prepared by dissolving 20 mg MDMO-PPV (Sigma-Aldrich, catalogue number 546461) in 20 ml toluene (Sigma-Aldrich Toluene, catalogue number PLC22C11X). The solution was heated for 5 min at 60 °C, followed by ultrasonic treatment for 15 min and filtering by a filter of 0.35 µm hole size. A work solution without undissolved particles with a concentration of 0.5 g.l\(^{-1}\) was prepared by diluting 20 ml of the base solution by 20 ml toluene.

The aerosol flow was produced by a Paasche EZ-STARTER Single Action Airbrush Kit with a nozzle diameter of 0.5 mm. The parameters used for the SD process were: substrate temperature 30°C; distance from the spray nozzle to the substrate 10 cm; air pressure used for the formation of the sprayed flow 1 kPa; work solution amount 20 ml; deposition time 4 min; substrate motion velocity 1 mm/s.

The parameters used for h-SD process were: substrate temperature 30 °C; distance from the homogenizer’s outlet to the substrate 2 cm; air pressure for the formation of the sprayed flow 1 kPa; work solution amount 100 ml; deposition time 20 min; substrate motion velocity 1 mm/s.

Thin films for surface morphology characterization were spray deposited on microscope-grade glass. The substrates were cleaned with detergent and deionized water followed by a plasma treatment. Selected samples were studied by scanning electron microscope (SEM) Philips 515.

Selected films for photoelectrical characterization were deposited on Ossila substrates with preliminary prepared ITO electrodes after cleaning according to a standard procedure.

Aluminum electrodes were deposited in oil-free vacuum of 8×10\(^{-4}\) Pa.

The photoelectrical measurements were carried out in an oil-free vacuum of 2.2×10\(^{-5}\) Pa by a Keithley 6517A Electrometer. Monochromatic light was produced by an LSH502 LOT-Oriel halogen lamp and an MSH101 LOT-Oriel monochromator. The light power was controlled by adding grey filters and measured by a Gigahertz-Optik - X97 Irradiance Radiometer.

The photoelectrical measurements started by taking the spectral dependence of the photocurrent at zero applied voltage; the \(I-V\) characteristics were then measured in both directions of the voltage scale in dark and under exposure to a white light. Finally, the dependence of the photocurrent on the incident light power (irradiance) was measured.
3. Results and discussion

3.1. Sample characterization

Figure 1 presents an optical micrograph of a SD film deposited under the aforementioned conditions. It confirms that the SD film tends to cross-link in a network of fibers separated by voids. Comparing the color in the scratched line (in the middle of the picture), one can clearly see that voids (areas not covered by the material) have been formed. This observation is supported by electrical measurements of sandwich samples with SD films prepared under the same conditions; the measurements resulted in a short circuit between the electrodes.

A precise film surface characterization of the h-SD films was performed by SEM.

SEM images of a h-SD sample at two different magnifications are presented in figure 2. At the lower magnification of 10000 (figure 2a), spherical or disc-shaped particles of size of about 1 µm could be observed. They are probably related to the presence of dust or to non-dissolved MDMO-PPV particles. In figure 2b, a SEM image of the same film taken at magnification of 40000 is presented. Spheres or discs with a size of about 200 nm could still be observed and considered as being dust particles. The other, more uniform part of the film, could be related to the individual structure of the film. The SEM images of h-SD films confirmed that uniform and relatively smooth films free of pinholes have been obtained. These films are suitable for electrical measurements in a “sandwich” type samples.

3.2. Photoelectrical measurements

Figure 3 presents the spectral dependence of the photocurrent measured at zero voltage applied between the electrodes of structures with h-SD films. It consists of two peaks. The peak at 560 nm is known from photovoltaic structures with spin-coated and electrophoretically deposited MDMO-PPV films [12]. Another stronger and wider peak appears at 370 nm. The existence of these two peaks makes the structures with h-SD films more attractive for photovoltaic applications as it allows photovoltaic conversion in a wider visible light range. White light were used in the subsequent experiments on excitation of these two peaks.
The $I-V$ characteristics measured in dark and under white light illumination of a ITO|MDMO-PPV|Al structure with h-SD MDMO-PPV films of about 1 µm thickness are presented in figure 4. To estimate the electrical parameters of the samples, the data are plotted in a semilogarithmic scale (the negative values of the current are multiplied by $-1$).

The dark-current measurements (figure 4, curve a) resulted in non-linear and almost symmetrical characteristics with a contact barrier of about 0.3 V. These effects could be related to the bulk material properties, which seem to dominate in the thick MDMO-PPV film. An optimization of the spray parameters to obtain films of a lower thickness is, therefore, necessary. Despite the non-optimized conditions of forming a thick film where charge-carriers recombination is possible to occur, a photocurrent higher by two orders of magnitude (marked by the vertical line in figure 4) was obtained under illumination by white light. This result demonstrates the potential of the h-SD method for deposition of thin films for photovoltaic applications.

The dependence of the photocurrent on the incident light power (irradiance) for samples with h-SD MDMO-PPV films under illumination by white light is plotted in figure 5. It is seen that the photocurrent is proportional to $G^\gamma$, where $G$ is the photogeneration rate and $\gamma = 1.7$ is the slope of the graph presented.

To summarize, it could be pointed out that the spray deposition parameters have a considerable influence on the uniformity, coverage and grain size of the SD MDMO-PPV films. The homogenizer introduced allows one to control the droplet size by using low nozzle air pressure and achieve a very low air pressure by controlling the temperature and pressure of the additional flow that is mixed with the first one.

4. Conclusions

Thin films of thickness of about 1 µm were prepared by SD and h-SD from a solution with a concentration of 0.5 g.l$^{-1}$.

It was found that the homogenization of the sprayed aerosol flow by mixing it with hot air reduces the droplet size thus leading to deposition of more uniform films.

Optical micrograph images show that using h-SD results in forming uniform films without distinguishable structure.

The spectral dependence of the photocurrent consists of two peaks. This property makes the structures with h-SD films more attractive for photovoltaic applications as photovoltaic conversion takes place in a wider visible light region. The $I-V$ characteristics measured on samples with h-SD films show that exposure to white light increases the current by two orders of magnitude.
More experiments connected with the determination of the droplet size and size distribution should be carried out to achieve a full control over the process parameters. The application of the h-SD thin films in the development of organic electronics necessitates further studies on the mechanism and kinetics of the spray process, and on the structure and properties of the films.

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