Investigation of Spray Coating as a Deposition Technique for Fabrication of Multilayer Organic Structures

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Abstract - **Spray deposition method is developed as a cost-efficient technique for fabrication of multilayer structures used in the organic based devices (OBDs) like displays and solar cells. The deposition temperature is varied for layer morphology optimization. The films sprayed at 70 °C are smoother and more uniform than the spin-coated ones. A multilayer structures, consist of materials soluble in same solvent are produced without damaging. The sprayed multilayer structures showed increased current efficiency compared to the spin-coated.**

Keywords – **Spray deposition, Organic based devices, Electroluminescent materials, Thin polymer films.**

I. INTRODUCTION

Organic materials, especially polymers, have been used in organic electronics (OLEDs, solar cells etc.). In order to improve device performance new approaches are needed to grow thin films with high uniformity and accurate thickness control. Currently, polymer thin films are deposited via low-cost solution processes such as spin-coating, inkjet printing, and dip-coating [1, 2]. Although many novel processes like electrophoresis [3] have been investigated with the goals of high efficiency and low costs, the spin-coating remains the most widely used deposition technique. However, this process cannot be used in large area devices or in multilayer structures produced by materials soluble in only one solvent. Common defects, observed at centrifuged films are swirling pattern, streaks, pinholes and uncovered areas [4].

At the spray-coating, solution is sprayed, creating aerosols, which are directed toward the substrate, where the layer is deposited. This is the initial step of the spray pyrolysis method for preparing of inorganic films as a result of chemical reaction on the substrate [6]. Reaction pass, because of the high substrate temperatures of about 700-800 °C. In our work we propose modification of spray pyrolysis for polymer solution deposition, conformable with the specific of the used solid state materials and solvents. The solvent evaporates during spraying and the active polymer particles remain. Controlling the droplet size of the aerosol we could control the homogeneity of the polymer film. The organic semiconductors degrade at temperatures lower than 300 °C and the common suitable solvents have low boiling point (not exceeding 80 °C), so the process doesn't allow as high temperatures as at the classic pyrolysis.

The aim of this investigation is to obtain smooth, defect-free and uniform thin organic films with cheap, vacuum-free process for application in organic displays and solar cells. In such multilayer structures the film morphology is crucial for contact resistance reduction and increasing of the device current efficiency. We used polyvinylcarbazole (PVK), which is hole transporting and poly(2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylenevinylene) (MEH-PPV), which is electroluminescent. Both materials are dissolved in chloroform. The sample surfaces and cross-sections are investigated by Scanning Electron Microscopy (SEM). The structures prepared are compared to these deposited by spin-coating process. The difference of the device performance is established by current-voltage characteristic measurements.

II. EXPERIMENTAL

For the fabrication of PVK films, a solution of 10 mg of PVK (Sigma Aldrich) in 25 ml of chloroform was used for the spin-coating and the solution was diluted five times for the spray depositions. The diluted solutions was transferred to a handheld airbrush with outlet diameter of 0,2 mm, along with 4 atmospheres of air. We varied also the substrate temperature from 30 °C to 150 °C, the distance between substrate and the nozzle, the spray scanning time and the number of spray cycles. The temperature was kept with accuracy of ~ 6 °C by automatic regulating system consist of contact thermometer and circuit closer connected with the heater. Figure 1 (up) schematically shows the principle of spray deposition and (down) heater control circuit. PVK films were fabricated on 2.5x2.5 cm glass substrates for SEM. For the fabrication of bi-layer electroluminescent structure, indium tin oxide (ITO) glasses obtained by r.f. reactive sputtering were used as substrates. Onto the ITO anode we sprayed PVK film from chloroform solution (0,08 w%) at 70 °C, following by MEH-PPV spray deposition also from chloroform solution (0,08 w%) at 60 °C. Finally we deposited Al cathode by vacuum thermal evaporation.

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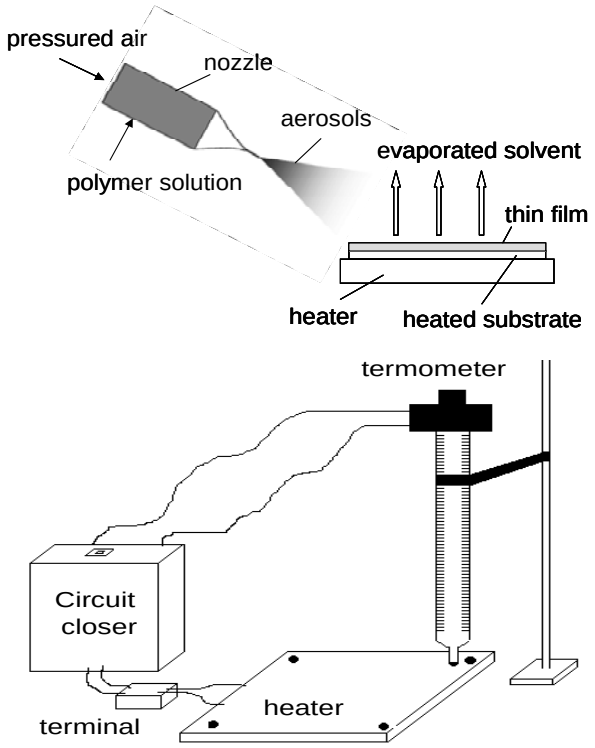

Figure 1. Experimental setup for polymer spray deposition (up); heater regulation circuit (down).

All polymer films thickness was measured from cross-section SEM images. At constant deposition conditions, the film thickness depends only on the number of sprayings. Alternative structure was prepared with spin-coated polymer layers. PVK-chloroform solution 5 mg/ml was centrifuged at 1100 rpm for 30 sec and MEH-PPV-chloroform solution 8 mg/ml was centrifuged at 1000 rpm for 30 sec. SEM images were made with JSM 5300 (JEOL) scanning microscope and the current-voltage characteristics was measured by precise TESLA BM 545 picoampermeter.

III. Results and Discussion

First we settled experimentally a most suitable distance from nozzle to the substrate at given air pressure. At distance bigger than 15 cm the resulting coating quality was not satisfying. As most of the solvent already evaporates during the flight stage, an almost dry powder hits the substrates and the film mobility was not sufficient to level out and form a homogeneous film. At distance smaller than 8 cm the wetting problems occurred and the solution streamed down. An optimum distance was determinate to be about 12 cm. This distance was affected by the boiling point of solvent.

For pressure above 4,5 atmospheres, during the drying time, we observed that droplets formed a ring in the monolayer, known as a coffee ring, along the initial contact line of the droplet [7]. That's why we choose to spray with optimum air pressure of 4 atmospheres.

Spray coating requires low concentration solutions. Thus satisfy the requirement to allow capillary effects to draw the material under the structures [8]. No difficulty is presented in placing sufficient material in a single pass. It could be expected, that diluting solution would reduce the grain size. The airbrush was moved across the substrate with intervals of a few seconds between each pass. The droplets then dry, before the following pass.

For all further shown experimental results the air pressure was kept at 4 atmospheres, the distance substrate-nozzle was 12 cm, the spraying angle - about 45 °C, the solution concentration was 0,08 w% in chloroform and the number of sprayings was 10. At these conditions a single pass with nozzle was measured to give about 40 nm thin film.

Figure 2 shows the results from spraying of PVK substrate temperature 30 °C, which is lower than chloroform boiling point (~ 50 °C). This structure could result from the slow solvent evaporation. The spray droplets formed too wet surface and additional thermal treatment is needed to remove the residual solvent. After post-deposition drying at 100 °C in air for 1 hour no improvement of the surface homogeneity was observed.

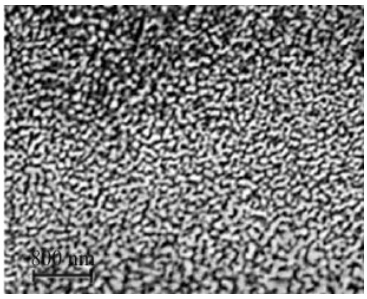

Figure 2. SEM of a PVK thin film produced with a concentration 0.08 w% in chloroform, deposited at 30 °C.

Figure 3 shows the PVK film prepared at 150 °C and the same other conditions. This film was formatted as a result from the too high evaporation rate and in consequence, the solution is already dried when it hits the substrate surface, because the heat field above the glass is too strongly. It is observed typical coating defect of peel appearance, coming from a mismatch of solvent. This is due to the stronger jam of the glass to the heater near the fixture point. The selective evaporation of the solvent leads to local disturbances of the surface tension known as the Marangoni effect [9].

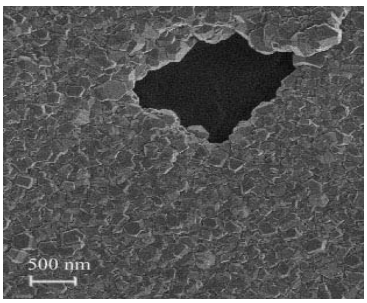

Figure 3. SEM of a PVK thin film produced with a concentration 0.08 w% in chloroform, deposited at 150 °C.

Even with a manual spraying technique, a homogeneous, transparent, uniform PVK coating (Figure 4) was obtained at 70 °C. The morphology of the produced coating was

similar to this found for dip coated sample made from the same precursor system [10]. Our coating showed a negligible gradient in the sheet resistance (average 16 Ω/□), which is caused by a gradient in the thickness. As it seems the thickness variation is not large and we could consider that the film is uniform.

Comparing the images from Figure 2 to Figure 4, it can be seen that the substrate temperature is an essential factor controlling the film structure and morphology. This could be used further for optimization of the deposition process. As we established a proper substrate temperature of 70 °C, in addition to the smooth surface, the solvent evaporates in the moment of the hitting with the substrate and remain only the polymer on it.

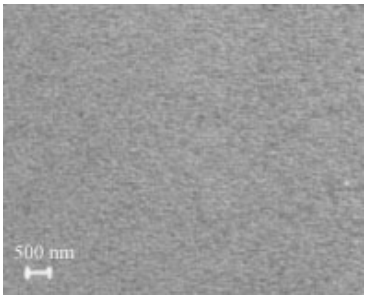

Figure 4. SEM of a PVK thin film produced with a concentration 0.08 w% in chloroform, deposited at 70 °C.

The solvent-free deposition allows to obtain a multilayer structure consists of different polymers, all dissolved in same solvent. A cross-section SEM of bi-layer structure PVK/MEH-PPV deposited from chloroform solution (Figure 5) shows separated undestroyed layers, in contrast to the spin-coated sample where the mixing of the layer interfaces occurred (Figure 6). This directly resulted on the electrical behavior of the structure, which is very sensitive to the film morphology.

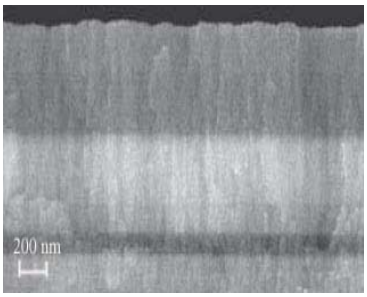

Figure 5. Cross - section SEM of sprayed bi-layer structure PVK/ MEH- PPV in chloroform, deposited at 70 °C and 60 °C respectively.

I-V curves of the devices with configuration of ITO/PVK/MEH-PPV/Al with sprayed and spinned polymer layers are shown on Figure 7. It is clearly seen that the sprayed structures shows better performance. For voltage 6 V the current in spinned structure is $7x10^{-8}$ A versus current in sprayed one, reaching about $2x10^{-7}$ A, which is evidence for increasing in the charge carrier injection efficiency. This is due to the increased contact area between the uniformed layers in the sample.

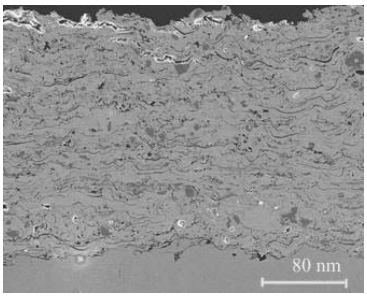

Figure 6. Cross - section SEM of spin-coated bi-layer structure PVK/MEH- PPV in chloroform.

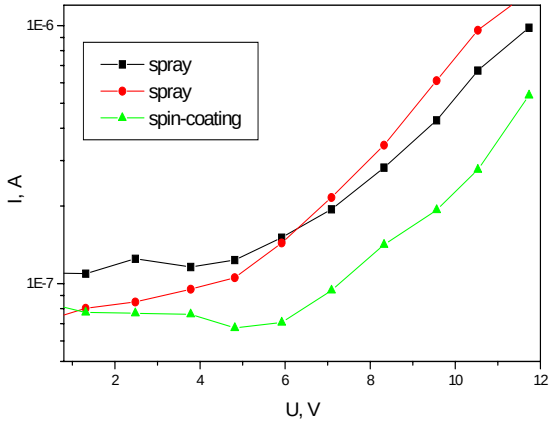

Figure 7. I-V characteristics of structures with sprayed and spin-coated polymers.

We repeated the experiment with spray deposition to investigate the reproducibility of the process. Relatively small deviations (average ± 0,1 μA) are observed, because the process passes in the air environment, not in argon filled glove box where contamination-free films could be deposited. Other reasons for the differences could come from the manual spray and inaccurately fixed spray angle, as well as the delaying time of the relay type temperature regulator, which doesn't allow more precise temperature control than average 3 °C. Further work is necessary to optimize the temperature and composition control over the sublayers within the active layer obtained with multiple pass spray coating technique.

IV. Conclusion

In conclusion, we successfully demonstrated the conventional spray painting method as a novel process for the fabrication of active layer of OBDs. The presented spray coating technique allows a fast and economic deposition on large area flat substrates. The spin-coating process tends to leave the top surface of the material with limited planarity, while at the spray coating method a high degree of planarization could be achieved. Furthermore, the spray deposition can be used to fabricate multilayer films from the same solvent in the solution. Improvement of the current efficiency in multilayer structure is achieved – approximately one order of magnitude higher values of the current. The results obtained from these investigations can be easily transferred to a system with better control of the

deposition parameters, such as automated and computer controlled spray coaters.

V. ACKNOWLEDGEMENTS

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