Spray Deposition of Multilayer Polymer Structures for Optoelectronic Applications

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Spray deposition method was developed as a cost-efficient technique for fabrication of multilayer structures used in the organic based devices (OBD) like diodes, displays and solar cells. The active layers of OBDs were deposited using conventional airbrush. The temperature was varied for layer morphology optimization. The spray deposited at 70°C films showed smoother surface than the spin-coated ones, pinhole-free and uniform coatings were obtained. It was demonstrated that could be produced multilayer structure, containing layers from different organic materials, but all soluble in the same solvent. They remained separated without sublayer damaging. The performance of sprayed multilayer organic device was compared to that of the spin-coated. The structures prepared by spray showed better electrical performance and increasing of the current efficiency. [DOI: 10.1380/ejssnt.2009.859]

Keywords: Spray Deposition; Polymer Based Devices; Electroluminescent Materials; Thin Polymer Films; Current-Voltage Characteristics

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, because of chemical reaction on the substrate [5, 6], which pass under the influence of temperatures, most frequently higher than 300°C.

In this work is proposed 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 it could be governed 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 does not 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.

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 airbrush with outlet diameter of 0.2 mm, along with 4 atmospheres of air. The airbrush was stable fixed on stand, which guarantee repeatability of the spraying angle and distance to the substrate. It was 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 sprayings. 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(a) schematically shows the principle of spray deposition and Fig. 1(b) shows the heater control circuit. PVK films were fabricated on 2.5×2.5 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 was 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, Al cathode was deposited by vacuum thermal evaporation. 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

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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 DISCUSSIONS

First was 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 determined 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, was observed that droplets formed a ring in the monolayer, known as a coffee ring, along the initial contact line of the droplet [10]. That is why was 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 [9]. 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 was about 45°, 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.

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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 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 formation.

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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 [7].

With spraying technique a homogeneous, uniform PVK coating (Fig. 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 [8]. A coatings showed negligible gradient in the sheet resistance (average 16 $\Omega/\square$), which is caused by a gradient in the thickness. As it seems the thickness variation is not large and it could be considered that the film is uniform. Comparing the images from Fig. 2 to Fig. 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 it was 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. It seems that the substrate temperature of 70°C was the nearest to the volatile point of the used solvent in comparison with the cases, where 30°C or 150°C were adjusted. At 70°C the solvent was only partly evaporated near the vicinity above the substrate, because of the suitable thermal field created there at this temperature. In contrary to that, at 30°C all of the solvent remains and at 150°C the solvent was evaporated completely before the droplets reaches the substrate. As a result, at 70°C the substance remained on the surface was in semi-liquid form, which prevents wetting problems and solution flow or the other case–rough grainy formations, coming from a too dry polymer powder. For this reason, the obtained spray deposited layers are smooth. The solid particles at 70°C are formed immediately after the moment of reaching the substrate. The small amount of residual solvent could makes the polymer particles enough mobile over the surface to spread, interact and form homogeneous film. The solvent evaporation rate at this temperature, however, was optimum only for the sprayed droplets to migrate, spill on the surface and connect themselves into a smooth, non-porous film. At 70°C all of the solvent remains and at 150°C the solvent was evaporated completely before the droplets reaches the substrate. As a result, the obtained spray deposited layers are smooth. The small amount of residual solvent could makes the polymer particles enough mobile over the surface to spread, interact and form homogeneous film. The solvent evaporation rate at this temperature, however, was optimum only for the sprayed droplets to migrate, spill on the surface and connect themselves into a smooth, non-porous film. At 70°C all of the solvent remains and at 150°C the solvent was evaporated completely before the droplets reaches the substrate. As a result, the obtained spray deposited layers are smooth. The solid particles at 70°C are formed immediately after the moment of reaching the substrate. The small amount of residual solvent could makes the polymer particles enough mobile over the surface to spread, interact and form homogeneous film. The solvent evaporation rate at this temperature, however, was optimum only for the sprayed droplets to migrate, spill on the surface and connect themselves into a smooth, non-porous film. At 70°C all of the solvent remains and at 150°C the solvent was evaporated completely before the droplets reaches the substrate. As a result, the obtained spray deposited layers are smooth. The solid particles at 70°C are formed immediately after the moment of reaching the substrate. The small amount of residual solvent could makes the polymer particles enough mobile over the surface to spread, interact and form homogeneous film. The solvent evaporation rate at this temperature, however, was optimum only for the sprayed droplets to migrate, spill on the surface and connect themselves into a smooth, non-porous film.
FIG. 7: I-V characteristics of structures with sprayed and spin-coated polymers.

in the bottom polymer layer and the dissolving process starts to dominate over the solvent evaporation. Possibly thermal treatment of spin-coated films could remove the residual solvent only from the upper layer, which contacts with one of the electrode, but because the temperature is post-deposited applied, not in the moment of the multilayer formation process, mixing of the inner layers is occurred. In this case, no improvement of the device performance was achieved, even after spin-coated film annealing.

I-V curves of the devices with configuration of ITO/PVK/MEH-PPV/Al with sprayed and spinned polymer layers are shown on Fig. 7. It is clearly seen that the sprayed structures shows better performance. For voltage 6 V the current in spinned structure is $7 \times 10^{-8}$ A versus current in sprayed one, reaching about $2 \times 10^{-7}$ 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. The experiment with spray deposition was repeated to investigate the reproducibility of the process. Relatively small deviations (average $\pm 0.1 \mu$A) 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 does not allow more precise temperature control than average 3°C. Further work is necessary to optimize the temperature and composition control over the sub-layers within the active layer obtained with multiple pass spray coating technique.

IV. CONCLUSIONS

It was 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.

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