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Spray deposition of thin organic films♣

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Thin organic films were deposited by a low temperature spray technique (substrate temperature 40-130°C). Poly(N-vinylcarbazole) and poly[2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylene vinylene] solutions, in chloroform and a chloroform-toluene mixture with concentrations of 0.004-0.1 weight percentages were prepared. The films obtained were investigated by optical micrography, SEM and UV-VIS spectroscopy. By varying the deposition conditions (e.g. solution concentration, substrate temperature, type of the solvent, air pressure) the film structure and morphology could be changed dramatically – from separate aggregates, to polymer networks, to films with pinholes of different diameters, and to stacked disks and grains.

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1. Introduction

Recently, there has been an increasing interest in solution based processes for thin film deposition. The main advantages of these techniques are simplicity of the process and its applicability to substrates of any size [1]. It is quite difficult to prepare a separated coating or layer-by-layer deposited films with a spin-coating method. This impedes the production of multilayer structures, as the sublayers could be dissolved or damaged by the solvent of the next layer deposited. One of the possible options is the selection of proper solvents, so that alternating stack layers are deposited from polar and non-polar solvents. This approach is not always applicable, because it limits the range of the used polymer materials. With a spin-coating technique, there are only two parameters (the polymer solution viscosity and the spinning speed), strongly influencing the layer formation. However, this method has the disadvantage of defects related to poor coverage, striation and layer thickness variation caused by the centrifugal forces [2]. This leads to the production of irregular organic films, which deteriorates the optoelectronic device performance, because of the bad contact at the electrode/organic interface. The spray deposition technique [3] could be used to overcome some of these disadvantages. The most important processes are the aerosol generation and transport, solvent evaporation, droplet impact with consecutive spreading, and precursor decomposition [4]. The deposition temperature is involved in all these processes, except in the aerosol generation. Consequently, the substrate surface temperature is the main parameter that determines the film morphology and properties [5]. The other spray process parameters, which define the film quality, are: the initial concentration of the solution, the flow rate of the pressured air, the angle of pulverization, the time of spraying, the time intervals between consecutive sprayings and the nozzle-substrate distance. The film thickness is controlled by the number of sprayings [6]. According to the above mentioned parameters and the nature of deposited material and substrate, a desired film thickness can be obtained.

In this work, spray deposition parameters for films obtained from poly(N-vinylcarbazole) – PVK and poly[2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylene vinylene] - MEH-PPV solutions, in chloroform and a chloroform-toluene mixture were optimized.

2. Experimental

PVK and MEH-PPV materials (Sigma Aldrich) were dissolved in volatile solvents at varying concentrations

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♣ Paper presented at the International School on Condensed Matter Physics, Varna, Bulgaria, September 2008 from 0.004 to 0.1 weight percentage (w%). The organic films were then deposited by the spray technique. A schematic drawing of the spray deposition setup is presented in Fig. 1. All the samples were prepared on glass substrates, preliminarily cleaned using isopropyl alcohol. The deposition was carried out in a chamber, where a heater, which determines the substrate temperature, was provided. The surface temperature was controlled with a "K type" thermocouple. The temperature was varied in intervals below the melting point of the material. Some of the experiments were carried out at room temperature to check the solvent influence on the film homogenization. Solutions with various concentrations were prepared. The influence of different solvents was estimated.

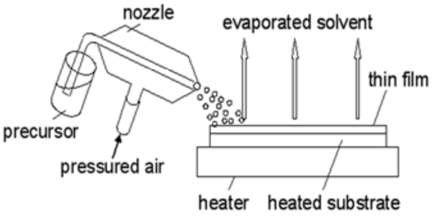

Fig. 1. Schematic drawing of the spray deposition setup.

Different working conditions during the polymer thin film deposition were chosen. Some of the parameters were varied, aiming at process optimization and good layer quality. By controlling the substrate temperature and the solution spraying cycles, the evaporation rate could be changed. Some of the deposited layers were post-treated in air at different temperatures. The distance between the nozzle and the samples was kept at 15 cm. The pauses between two consequent sprays were 5 seconds. Samples with different numbers of spraying cycles, according to the desired thickness, were made. 20 sprayings lead to a film thickness of about 400 nm. The thicknesses were measured by a Talystep thickness prophilometer. The films were preliminarily examined by optical micrography. Some representative samples for more detail information were imaged by SEM. UV-VIS spectroscopy was carried out to investigate the layer transmittance.

3. Results and discussion

A PVK film with a thickness of about 400 nm was sprayed on a glass substrate at a temperature of 50°C, from a solution with a concentration of 0.03 w% in chloroform. The air pressure was 3 mbar. Optical micrography showed holes with sizes of about 10 μm and smooth areas in between (Fig. 2.).

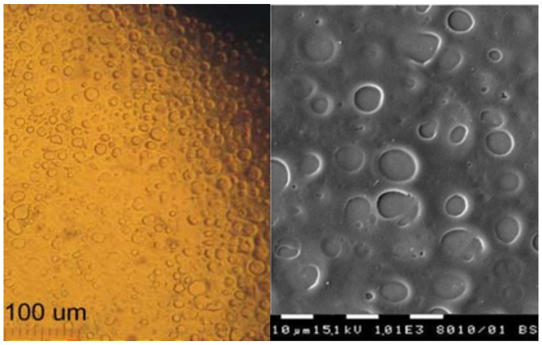

Fig. 2. Optical micrography (left) and SEM (right) of a PVK thin film produced with a concentration 0.03 w% in chloroform, deposited at 50°C.

These effects could be connected with the inhomogeneity of the sprayed flow, containing drops with different sizes. The small drops spill on the substrate surface, forming a uniform liquid film. The holes are formed from the hits of the bigger drops in the surface. As a result of this process, high edges are raised over the film surface which are clearly seen in the SEM image as bright rings around the holes.

To reduce this effect, and to remove the residual solvent, post-deposition thermal treatment was applied. However, after treatment at 130°C (the boiling point of chloroform is 62°C, and the PVK melting point 300°C) in air for 1h 30 min, the holes remained almost without changes in size and distribution.

To remove the effect of the hole formation, the air pressure for further experiments was reduced to 2.2 mbar. Evaporation on a hot substrate (140°C), keeping the solvent concentration the same, was applied (Fig. 3). The other conditions were not changed. The film thickness was about 400 nm. The images show that a grain structure was obtained. Grains with almost equal sizes are uniformly distributed over the whole film surface. The size of each grain is about 2 μm. This structure could result from the fast solvent evaporation, as the spray droplets had no time to migrate and spill onto the surface.

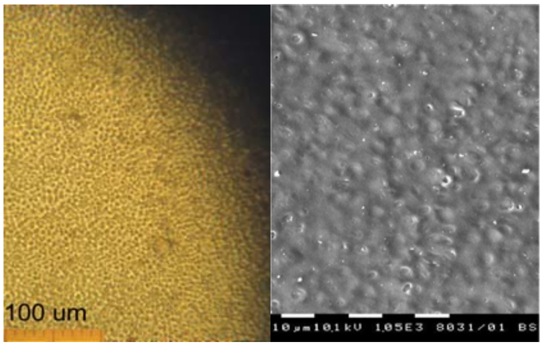

Fig. 3. Optical micrography (left) and SEM (right) of a PVK thin film produced with a concentration of 0.03 w% in chloroform, deposited at 140°C.

Comparing the images in Fig. 3 and Fig. 2, it can be seen that the substrate temperature is an essential factor controlling the film structure and morphology. This could be used further for optimisation of the deposition process.

It could be expected that diluting the solution would reduce the grain size more. Depositing a film from a PVK solution with a concentration of 0.004 w% in chloroform lead to a dramatic change in the structure (Fig. 4).

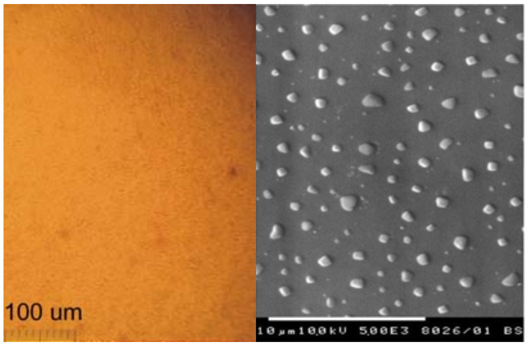

Fig. 4. Optical micrography (left) and SEM (right) of a PVK thin film produced with a concentration of 0.004 w% in chloroform, deposited at 140°C.

By optical micrography, no apparent structure is observed. However, the SEM picture shows aggregate formation. Between the aggregates, the glass surface is not covered. The aggregates could be connected with the lack of material after the solvent evaporation, which is not sufficient to form a uniform film, and to the surface tension of the substrate.

In an attempt to increase the time for solvent evaporation and improve the PVK film structure, a mixture of chloroform (boiling point 62°C) and toluene (boiling point 110°C) in the ratio 1:1 was prepared. The solution concentration was again 0.03 w%, and the glass substrate was heated to 140°C. The film obtained was about 400 nm thick. The results are shown in Fig. 5.

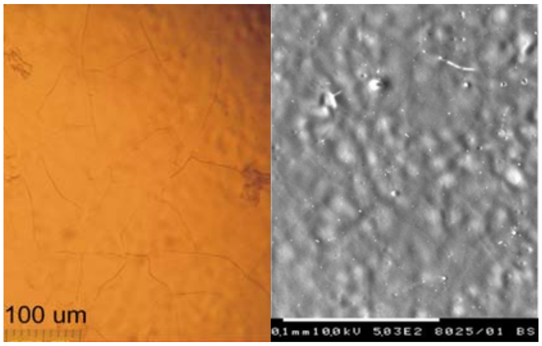

Fig. 5. Optical micrography (left) and SEM (right) of a PVK thin film produced with a concentration of 0.03 w% in chloroform:toluene 1:1, deposited at 140°C.

There is a heaping of polymer aggregates in the form of a dense layer containing shallow hollows. This structure could be connected with the increased time for the solvent evaporation. The film is cracked, which is due to the slowly evaporated toluene. It could be expected that decreasing the substrate temperature would prevent cracking, increasing the uniformity and smoothness of the films.

Comparing the images in Figs. 3. and 5. it can be seen that preparing a mixture of two or more solvents with different boiling points could be an effective tool for controlling the film growth, and consequently the film structure and morphology.

Finally, MEH-PPV films were deposited from a solution with a concentration 0.01 w% in chloroform onto a glass substrate, at room temperature. Optical micrography images showed that a wide-meshed network structure is obtained (Fig. 6).

Optical micrography and SEM showed that increasing of the concentration of the solution by one order of magnitude leads to the formation of a film with uniform distributed holes (Fig. 7.). The film thickness was about 600 nm.

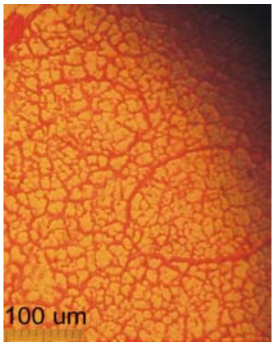

Fig. 6. Optical micrography of MEH-PPV, prepared with a concentration of 0.01 w% in chloroform, deposited at room temperature.

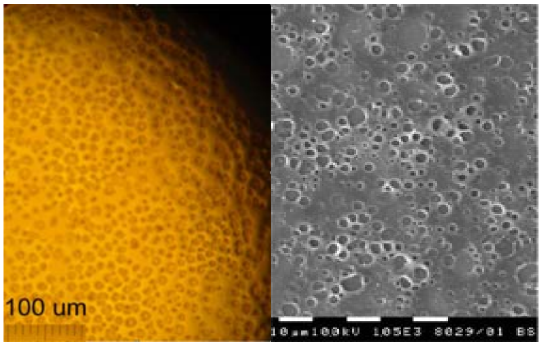

Fig. 7. Optical micrography (left) and SEM (right) of MEH-PPV, prepared with a concentration of 0.1 w% in chloroform, deposited at room temperature.

The optical transmittances in UV-VIS region of 300 nm thin PVK films, prepared with a concentration of 0.03 w% in chloroform, at 50°C and 140°C, are shown in Fig. 8.

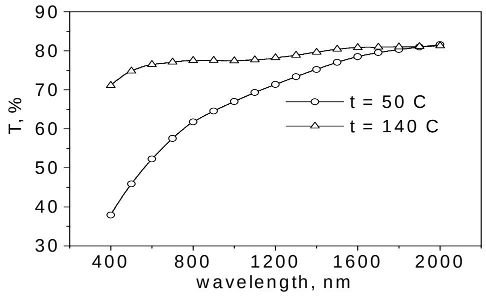

Fig. 8. UV-VIS spectra of 300 nm PVK thin films prepared with a concentration of 0.03 w% in chloroform, and deposited at temperatures of 50°C and 140 °C.

As can be seen from the SEM, at the lower temperature the film surface is irregular, strewn with hollows having different sizes. These objects scatter and absorb the light stream and the film transmittance in the visible range is strongly reduced. Additionally, some drop is expected in this range, because of Rayleigh scattering from molecules with similar sizes. Increasing the temperature leads to a reduction in the film roughness. This appears in the spectrum as an increase in the average transmittance in the visible region, from 50 % to about 75 %.

4. Conclusions

By varying the deposition conditions, the film structure and morphology could be changed dramatically – from separate aggregates, to polymer networks, to films with pinholes of different diameters, and to stacked disks and grains. Crucial parameters are the solvent concentration and substrate temperature. The type of the solvent and the air pressure also play an important role.

Acknowledgements

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