Multilayer organic based structures with enhanced hole transport

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Abstract. Multilayer Organic Based Devices (OBDs) were constructed by subsequent casting of organic films (from polymers, soluble in the same organic solvent). The problem with dissolution of the underlying layer was avoided by using electrophoretic deposition technique. Optimized conditions for electrophoretic deposition (EPD) of thin films with homogeneous and smooth surfaces, as confirmed by SEM, were found. The EPD, carried out at constant current, requires continuous increase of the voltage between the electrodes. In this way the decreased deposition rate caused by the decreased concentration of the material in the suspension and the increased thickness of the film deposited is compensated. The SEM images and the current voltage characteristics recorded, show that the hole transport polyvinylcarbazole (PVK) underlayer survive the treatment with the suspension used for the electrophoretic deposition of the active poly[2-methoxy-5-(3,7-dimethyloctyloxy)-1,4-phenylene vinylene] electroluminescent layer. The PVK hole transport layer increases the device current, as confirmed by the current-voltage measurements. The results obtained demonstrate the possibility of OBDs preparation for electroluminescent and photovoltaic applications.

1. Introduction
Organic Based Devices (OBDs) [1, 2] like solar cells, thin film transistors and light emitting diodes often suffer from poor charge carrier injection due to contact barrier formed between the metal (or ITO) electrode and the active semiconductor (conjugated polymer). This problem is usually solved by the deposition of an intermediate layer having a work function between the electrode work function and the energy of the corresponding transport band. Thus the contact barrier is overcome on intermediate steps - so called ‘ladder’ effect [3]. The preparation of multilayer structures by vacuum

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deposition techniques is relatively easy. Unfortunately, this method is not applicable to most of the conjugated polymers, due to their high molecular weight. Polymer layers are usually prepared by ‘wet’ deposition techniques like spin and deep coating, ink-jet printing, etc. The preparation of multilayer structures is almost impossible when the polymeric materials used are dissolved in the same solvent. In this paper we present a possible solution of this problem by using a combination of spin coating for casting of the polyvinylcarbazole (PVK) hole transport layer and a subsequent electrophoretic deposition of poly[2-methoxy-5-(3,7-dimethyloctyloxy)-1,4-phenylene vinylene] (MDMO-PPV) on the ITO|PVK structure.

2. Electrophoretic deposition technique

The phenomenon of electrophoresis has been known since the beginning of the 19th century and it has found applications during the last 40 years mainly in the traditional ceramic technology. A DC electric field is applied across a colloidal suspension of charged particles depositing a film of particles on the oppositely charged electrode. Electrophoretic deposition (EPD) is essentially a two-step process: electrophoretic transport and deposition. In the first step charged particles in a liquid are forced to move toward an electrode by applying an electric field across the solution. These charged particles may be generated by precipitating of the material mixing solvent and non-solvent.

In the second step the particles, deposited on the electrode surface, form a homogeneous film via coagulation.

A post-EPD processing step is usually applied, involving a suitable heat-treatment (firing or sintering) in order to densify the deposits and to decrease the porosity. The drying of the film, carried out in non-solvent vapors, is expected to yield polymer films with novel microscopic structures. In this case the stage of film formation is separated from the solidification process [4],[5]:

EPD requires stable suspension of charged particles in a way to respond to the applied electric field. This stability of the suspension can be realized in several ways [6]:

(i) Selective adsorption of ions onto the solid particle from the liquid;
(ii) Dissociation of ions from the solid phase into the liquid;
(iii) Adsorption of dipoles at the particle surface;
(iv) Electron transfer between the solid phase and the liquid phase due to differences in the work functions.

Examples for electrophoretic thin film deposition are reported in the literature, related to metals, polymers, carbides, oxides, borides and glasses [7].

Several successful attempts for depositing polymer materials like polymer photonic crystals [8] and polymeric donor-acceptor composites [9] have been reported. Polymer EPD can facilitate the formation of nanostructure in thin polymer films [10]. Additionally, EPD provides substantial control over the film thickness, marked enhancement of the deposition rate, and improved film composition homogeneity, compared to other wet casting-nanostructured thin film deposition methods [11]. Electrophoretic deposition is one of the most widely used coating methods capable of patterning.

Although the mechanism of the electrophoretic deposition is not clearly understand, EPD is already successfully used. However, a better understanding would reduce experimental work required to determine the optimal parameters of EPD.

Recently, considerable efforts are involved in the production of large area low-cost organic solar panels and cheap organic light emitting diodes. The EPD techniques suggest genuine solutions of most of the problems already mentioned. It could be expected that separating the stage of film formation from the solidification step in a mixture of solvent and non-solvent will allow the construction of a multilayer structure from films generally dissolved in the same solvent.

3. Experimental details

Toluene solution of MDMO-PPV (Aldrich) was heated at 70 °C for 20 min. After cooling down to RT the solution was filtered and non-solvent (acetonitrile) was added. The suspension obtained in this way was used for EPD immediately after preparation. After 15-20 min, due to coagulation of the
precipitated MDMO-PPV particles, the suspension becomes unusable. Both the solution concentration and the toluene/acetonitrile volume ratio were varied in order to optimize film quality. The EPD current was kept constant during the deposition of one sample by increasing the voltage applied between the electrodes. The current was varied from sample to sample in the range of 0.1 – 1 mA. The time for deposition of a single sample was 1 – 3 min.

The film thicknesses were measured by Taylor Hobson Talystep, Model 223-7. SEM images were taken from Philips 515 microscope.

Current-voltage (I-V) characteristics were measured in dark, in vacuum of 2.66 Pa with Keithley 617 electrometer. The preparation of samples for electrical measurements is presented on figure 1. On ITO glass (figure 1a) two strips each 3 mm wide, were formed by etching in acid solution (figure 1b). The sample was cleaned in deionized water, isopropyl alcohol and chloroform, and then dried in a stream of nitrogen. PVK was dissolved in toluene (70 g l⁻¹), stirred (magnetic stirrer) at 70 °C for 1 h. PVK films of approximately 500 nm thickness were casted by spin-coating at 500 rpm for 30 s. It was found that the quality of the deposited films strongly depends on the preparation conditions, e. g. rotation speed solution concentration and substrate temperature.

![Figure 1](image)

**Figure 1.** Consecutive stages (a ÷ f) of preparation of samples for electrical measurements: 1– commercially purchased ITO film deposited on glass substrate, 2 – spin-coated PVK on the ITO electrodes, 3 – cleared area on the glass substrate removing the PVK film by scratching, 4 – electrophoretically deposited MDMO-PPV film, 5 – vacuum deposited aluminium top electrodes; black circles present silver paste spots for connecting copper wires.

The films deposited cover both ITO strips on the sample uniformly (figure 1c). Then the PVK film was removed from the area outside the active region in a way to prepare ground for a contact formation (figure 1d). One of the ITO strips was connected to the voltage source and EPD of the MDMO-PPV film (thickness of 500 nm) was deposited selectively on it (figure 1e). Top aluminum electrode strips were deposited in vacuum of 1.33×10⁻³ Pa trough a mask in a way to cross perpendicularly both ITO electrodes (figure 1f). Finally Al and ITO electrodes were connected with copper wires by silver paste. In this way two types of samples were prepared on the same substrate – ITO|PVK|Al and ITO|PVK|MDMO-PPV|Al. For comparison ITO|MDMO-PPV|Al samples were prepared on separate substrates following the procedures presented on figure 1a, b, e, f. The electrode area is about 9 mm².

4. Results

4.1. Film morphology and structure

SEM study was carried out to estimate the influence of the suspension parameters on the film structure and morphology. 0.066 g l⁻¹ MDMO-PPV solution in toluene with acetonitrile (volume ratio 1:4) was used as starting material (suspension), further denoted as Suspension I. In this way the experimental conditions were kept close to the literature data [12] for a similar material (MEH-PPV). SEM morphology image of 500 nm thick MDMO-PPV film, deposited from Suspension I for 5 s at...

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current of 1 mA, is presented in figure 2. The presence of cavities of about 100 - 300 nm diameter and relatively wide smooth areas in between can be clearly seen. Cavities could result from the fast speed of the deposition, where the relatively big particles from the solution have no time to spill in a uniform film on the substrate surface.

![Figure 2](image1.png)  ![Figure 3](image2.png)

**Figure 2.** SEM image of 500 nm EPD film (sample tilted at 40°), deposited from Suspension I for 5 s at current of 1 mA.

**Figure 3.** SEM image of 500 nm EPD film (sample tilted at 40°), deposited from Suspension II for 150 s at current of 0.1 mA.

The general trend found shows that the film structure becomes smoother with increasing the amount of the solvent in the suspension. This result confirms the literature data, obtained for a similar material [13]. The best deposition conditions found are achieved at toluene/acetonitrile volume ratio 1:1. No film improvement was attained at further increase of the toluene concentration. This is why this ratio was kept constant but the MDMO-PPV concentration was decreased. The optimized conditions found, involve 0.033 g l⁻¹ MDMO-PPV solution in toluene mixed with acetonitrile (volume ratio 1:1), denoted further as Suspension II. Further decrease of MDMO-PPV concentration leads to strong increase of the suspension resistance even during the first few seconds of the deposition, resulting in unsuccessful film deposition process.

Uniform films were deposited from Suspension II for a time of 150 s at constant current of 0.1 mA. SEM image of 500 nm EPD film deposited from Suspension II for 150 s at current of 0.1 mA is presented on figure 3.

The films obtained in this way exhibit smooth surfaces without pinholes, suitable for electrical measurements.

4.2. **Electrical characteristics of the suspension**

During the EPD process the concentration of the material in the suspension decreases, the thickness of the film deposited on the electrode increases, leading to an increase of the electrophoretic cell resistance. The voltage changes, as a function of the time elapsed (at a constant current of 1 mA) during the deposition of MDMO-PPV from Suspension I, are presented on figure 4. At the beginning of the deposition the voltage increases almost linearly. This suggests a single process of decreasing the MDMO-PPV concentration during material deposition on the electrode.

The second nonlinear part of the curve could result from a simultaneous action of two processes - solution dilution and increased film thickness on the electrode. The second process could cause redistribution of the electric field between the increased film thickness and the suspension. This effect agrees with the theoretical considerations [6] for a deposition of wide-gap or insulator materials.
Figure 4. Dependence of the voltage applied on the time elapsed for the electrophoretic deposition of MDMO-PPV film from Suspension I; deposition current – 1 mA

In agreement with the literature data [13] the film deposition takes place at the anode, as the particles are negatively charged during the preparation of the toluene/acetonitrile suspension.

4.3. Current-voltage measurements

Current-voltage measurements (figure 5) on ITO|PVK|Al structure show that the toluene/acetonitrile (Suspension II) mixture used for MDMO-PPV EPD (see figure 1c) does not destroy the preliminarily deposited PVK film (figure 1c). This result shows that a combination of spin coating and electrophoretic deposition methods could be used for the preparation of multilayer structures, comprising thin films cast from materials, soluble in the same solvent.

The shape of the curve in forward direction shows a typical diode behavior [14]. The symmetry of the $I-V$ curve in both directions on the voltage scale should not be expected as the electrodes used have different work functions (ITO – 4.8 eV, Al – 4.17 eV). One possible reason for the symmetry observed could be due to the influence of high density dangling bonds, which could induce a broad distribution of localized states in the band gap [14]. Therefore the $I-V$ characteristic could be controlled by hopping of charge carriers on the localized states, rather than direct injection from the electrodes into the corresponding transport band.

Figure 5. I-V characteristic of ITO|PVK|Al structure measured in dark in vacuum of 2.66 Pa.

Figure 6. I-V characteristic of ITO|MDMO-PPV|Al (circles) and ITO|PVK|MDMO-PPV|Al (squares) samples measured in dark in vacuum of 2.66 Pa.
I-V characteristics, measured from ITO|MDMO-PPV|Al and ITO|PVK|MDMO-PPV|Al, are compared on figure 6. Both curves show typical diode behavior.

The introduced PVK film between the ITO electrode and the active MDMO-PPV semiconductor does not reduce the contact barrier but leads to an increase of the current. PVK has lower value of its HOMO orbital (-5.7 eV) comparing with that of MDMO-PPV (-5.2 eV) and should not reduce the contact barrier in ITO|PVK|MDMO-PPV|Al structure. Oppositely the higher conductivity of the PVK film, facilitate the hole transport from the ITO electrode to the MDMO-PPV semiconductor acting as a hole transport layer. This result proves that multilayer structures, consisting of films, deposited from materials, soluble in the same solvent, can be successfully used to increase the current in OBDs, like electroluminescent devices and solar cells.

I-V characteristics measured in the reverse direction in both cases looked similar. This points out that the electrical current flown trough the sample in both cases is most probably controlled by the high Al|MDMO-PPV contact barrier.

5. Conclusions
Optimized conditions for electrophoretic deposition of thin films with homogeneous and smooth surface (as evidenced by SEM) were found using 0.033 g l⁻¹ MDMO-PPV solution in toluene mixed with acetonitrile in volume ratio 1:1.

The EPD deposition was carried out at constant current, which required continuous increase of the voltage between the electrodes to compensate the decreased concentration of the material in the suspension and the increased thickness of the film deposited.

A combination of spin coating and electrophoretic deposition methods was used for the preparation of multilayer structures with thin films, deposited from materials, soluble in the same solvent.

The results obtained demonstrate the possibility for preparation of multilayer structures with improved electrical parameters in OBDs, like electroluminescent diodes and solar cells.

Acknowledgements
The authors would like to thank the National Science Fund of the Ministry of Education and Science, Bulgaria (grants DO 02-254 and BU-TH-205/2006) for the financial support of this study.

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