JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS Vol. 12, No. 9, September 2010, p. 1952 - 1956

Influence of the electrophoretic suspension on the underlayers in organic based devices

D. MLADENOVA[a,b], D. DIMOV[a], D. KARASHANOVA[a], S. BOYADZHIEV[b], T. DOBREVA[c],
D. BUDUROVA[d], V. SINIGERSKY[d], I. ZHIVKOV[a]
[a] *Central Laboratory of Photoprocesses "Acad. J. Malinowski", Bulgarian Academy of Sciences, Acad. G. Bonchev Str. bl. 109, 1113 Sofia, Bulgaria*
[b] *Department of Microelectronics, Technical University of Sofia, Kl. Ochridski Blvd. 8, 1756 Sofia, Bulgaria*
[c] *Central laboratory of Physico-chemical Mechanics, Bulgarian Academy of Sciences, Acad. G. Bonchev Str. bl. 1, 1113 Sofia, Bulgaria*
[d] *Institute of Polymers, Bulgarian Academy of Sciences, Acad. G. Bonchev Str. bl. 103A, 1113 Sofia, Bulgaria*

Influence of the electrophoretic suspension on the previously deposited film in multilayer Organic Based Devices (OBDs) in a case when both polymers are soluble in the same organic solvent was investigated. The problem with dissolution of the underlying layer was avoided by using electrophoretic deposition technique. The OBD consists of ITO bottom electrode, spin coated polyvinylcarbazole (PVK) film, electrophoretically deposited (EPD) poly[2-methoxy-5-(3,7-dimethyloctyloxy)-1,4-phenylene vinylene] (MDMO-PPV) film and aluminum top electrode. The EPD deposition, carried out at a 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 are compensated. A comparison of AFM images of untreated and treated in the electrophoretic suspension films shows that the treatment causes an appearance of holes surrounded by high edged rings, raised over the film surface. The current voltage (*I-V*) characteristics recorded from ITO|PVK|Al structures with treated in the electrophoretic suspension PVK films show that the holes formed in the film did not leads to a short connection between the electrodes, probably due to the sharp walls of the raised rings around the holes. *I-V* characteristics measured on diode structures show that the introduced PVK hole transport layer increases the device current. The processes need more optimization to get an application level of electroluminescent and photovoltaic OBDs preparation.

(Received August 2, 2010; accepted September 15, 2010)

Keywords: Thin films, Organic based devices, Polyvinylcarbazole, Poly(p-phenylene vinylene)

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 overcame on intermediate steps - so called 'ladder' effect [3]. The preparation of multilayer structures by vacuum 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 electrode|PVK sample.

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 past 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].

The advantages of EPD are [5]:
(i) High deposition rates;
(ii) Coatings can be prepared in any possible shape;
(iii) Dense and uniform films;
(iv) Film thickness can be controlled by varying deposition conditions;
(v) Simple and easy to scale up process.

EPD requires stable suspension of charged particles able 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 polimer materials like polymer photonic crystals [8] and polymeric donor-acceptor composites [9] have been reported. Polymer EPD incorporates the separate phenomena of colloid formation in suspension (solidification), colloid propulsion to the deposition sites (electrophoresis), and colloid aggregation and adhesion onto a substrate (deposition) [10]. These combined processes can facilitate the formation of nanostructure in thin polymer films. 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]. Unlike other wet casting techniques that cannot readily produce polymer films of good quality, applying EPD processes, film with combined low surface roughness, long-range thickness, homogeneity, and distinct nanostructure can be prepared.

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

PVK was dissolved in toluene (base solution of 50 g.l^{-1}), stirred (magnetic stirrer) at 80 °C for 4 h. The solution was cooled down to 42 °C. The substrate was heated to 55 °C then PVK films of approximately 300 nm thickness were cast by spin-coating at 500 rpm for 40 s. It was found that the quality of the deposited films strongly depends on the substrate temperature.

Toluene solution of MDMO-PPV (Aldrich) (0.033 g.l^{-1}) was heated at 70 °C for 20 min. After cooling down to RT the solution was filtered and non-solvent (acetonitrile) was added (volume ratio 1:1). The suspension obtained was used for EPD immediately after preparation. After 15-20 min, due to coagulation of the precipitated MDMO-PPV particles, the suspension becomes unusable. The EPD current was kept constant at 0.2 mA for 200 s during the deposition of the sample by increasing the voltage applied between the electrodes.

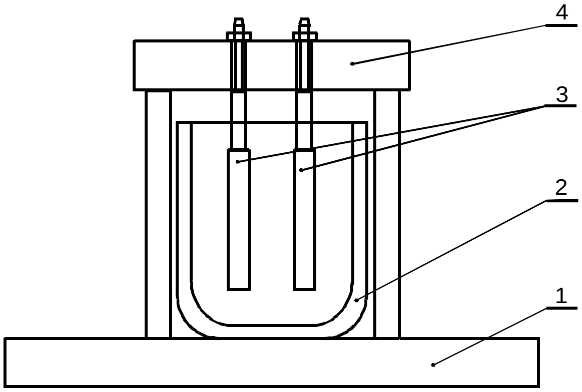

Fig. 1. Schematic draw of the electrophoretic cell: 1 - PVC base, 2 - glass vessel of the electrophoretic cell, 3 - electrodes, 4 - electrode holder.

All film thicknesses were measured by Taylor Hobson Talystep, Model 223-7.

Surface morphology images were taken by AFM (Ambios Technology Corporation) in tapping mode (frequency of 300 KHz, amplitude 20-30 nm) at a scanning rate of 0.5 Hz.

Current-voltage (*I-V*) characteristics were measured in dark, in vacuum of 2.66 Pa with Keithly 617 electrometer.

The preparation of multilayer samples for electrical measurements is presented on Fig. 2. On ITO glass two strips (1) each of 3 mm wide, were formed by etching (Fig. 2a). The sample was cleaned in deionized water, isopropyl alcohol and chloroform, then dried in a stream of nitrogen.

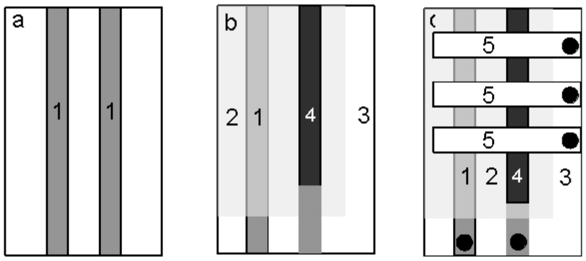

Fig. 2. Preparation of samples for electrical measurements: 1- 3 mm ITO strips formed by etching, 2 – spin-coated PVK on the ITO electrodes 3 – cleared area on the glass substrate removing the PVK film by scratching, 4 – electrophoretically deposited MDMO-PPV film, 5 - vacuum deposited aluminum top electrodes; black circles present silver paste spots for connecting copper wires.

The PVK films deposited cover both ITO strips on the sample uniformly (Fig. 2b) (2). Then the PVK material was removed from the area outside the active region in a way to prepare ground for a contact formation (Fig. 2b) (3). 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 (Fig. 2b) (4). 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 (Fig. 2c) (5). 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. The electrode area of all samples is about 9 mm^2.

3. Results and discussion

Film morphology and structure

AFM study was carried out to estimate the influence of the suspension parameters on the film structure and morphology. The image of 300 nm thick PVK film deposited from solution 50 g.l^{-1} by spin-coating at 500 rpm for 40 s is presented on Fig. 3. The image shows a relatively smooth surface. A calculations from the corresponding hystogram (not presented on the picture) of the most frequently presented peaks results in a film roughness of 23 nm.

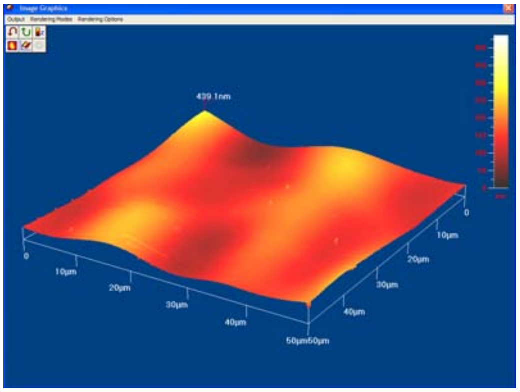

Fig. 3. AFM image of 300 nm thick PVK film deposited from solution 50 g.l^{-1} by spin-coating at 500 rpm for 40 s

A part of the same sample was treated for 200 s in the electrophoretic suspension used for a preparation of the next layer. It is seen on the AFM image (Fig. 4) taken at the same conditions as for Fig. 3 that the treatment of the film causes an appearance of holes surrounded by high edged rings raised over the film surface. Relatively wide smooth areas between the holes could be observed.

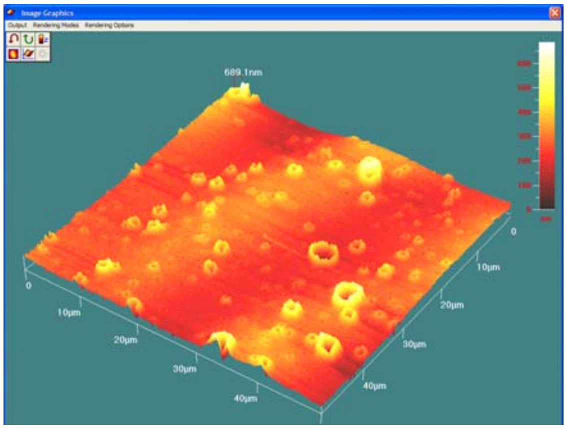

Fig. 4. AFM image of 300 nm thick PVK film deposited from solution 50 g.l^{-1} by spin-coating at 500 rpm for 40 s and subsequently treated in the electrophoretic suspension for 200 s

TEM investigation of untreated and treated in the electrophoretic suspension for 200 s films was carried out. TEM image of 50 nm thick PVK film deposited from solution 9 g.l^{-1} by spin-coating at 50 rpm for 200 s is presented on Fig. 5. The image shows an uniform film structure with small grain size of about 0.5 – 1 nm. A diffraction pattern that observed from the same sample did not show any remarkable rings and reflections, so the film structure could be considered as amprphous.

Fig. 5. TEM image of 50 nm PVK film deposited from solution 9 g.l^{-1} by spin-coating at 500 rpm for 40 s.

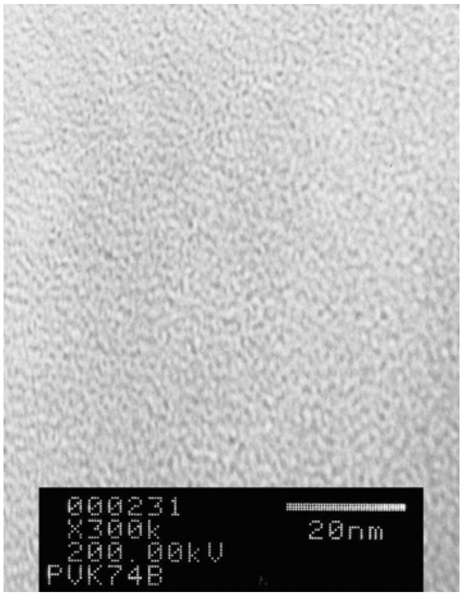

Fig. 6. TEM image of 50 nm PVK film deposited from solution 9.l^{-1} by spin-coating at 500 rpm for 40 s then treated in the electrophoretic suspension for 200 s

A part of the same sample was treated in the electrophoretic suspension for 200 s. The image taken from the smooth areas between the holes (see Fig. 4) show that the film structure does not change apparently.

Current voltage measurements

Dark current-voltage measurements (Fig. 7) on ITO|PVK|Al structure with PVK film thickness of 300 nm after treatment in the electrophoretic suspension was carried out in vacuum of 2.66 Pa.

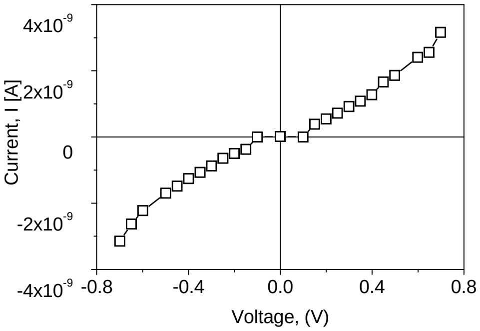

Fig. 7. I-V characteristic of ITO|PVK|Al structure with PVK film thickness of 300 nm after treatment in the electrophoretic suspension measured in vacuum of 2.66 Pa

It could be seen that the pinholes resulted in the film under the influence of the electrophoretic suspension did not leads to a short connection between the electrodes, probably due to the sharp walls of the raised rings around the holes. The values of the current measured are typical for a wide-gap semiconductor as PVK.

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 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 [13]. 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.

I-V characteristics, measured from ITO|MDMO-PPV|Al and ITO|PVK|MDMO-PPV|Al, are compared on Fig. 8. Both curves show typical diode behavior.

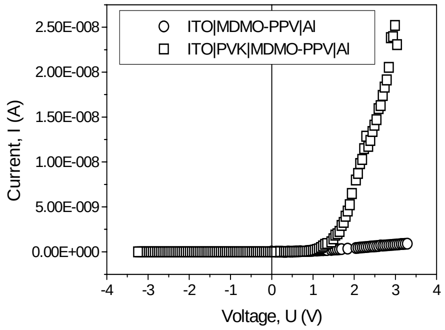

Fig. 8. I-V characteristic of ITO|MDMO-PPV|Al (circles) and ITO|PVK|MDMO-PPV|Al (squares) samples measured in dark in vacuum of 2.66 Pa.

The introduced PVK film between the ITO electrode and the active MDMO-PPV semiconductor does not remarkable 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, could 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, containing 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.

4. Conclusions

Influence of the electrophoretic suspension on the previously deposited film in Multilayer OBDs in a case when both polymers are soluble in the same organic solvent was investigated. Thin PVK films with roughness bellow 30 nm was obtained by spin-coating technique. Treatment of the film for 200 s in the electrophoretic suspension causes an appearance of holes surrounded by high edged rings raised over the film surface. The *I-V* characteristics measured from structures with treated in the EPD suspension PVK films show that the holes formed in the film did not leads to a short connection between the electrodes. *I-V* characteristics, measured from ITO|MDMO-PPV|Al show typical diode behavior. An introduction of PVK film as anode buffer layer leads to an increase of the current.

Acknowledgements

The authors would like to thank the Open Laboratory for Experiments of Micro- and Nanocomposites and 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.

References

[1] F. Garnier, Acc. Chem. Res., **32**(3), 209 (1999).
[2] H. Peisert, M. Knupfer, T. Schwieger, G. G. Fuentes, D. Olligs, J. Fink, Th. Schmidt, J. Appl. Phys., **93**, 9683 (2003).
[3] S. Lee, Y. Wang, X. Hou, C. Tang, Appl. Phys. Lett., **74**, 670 (1999).
[4] K. Landfester, R. Montenegro, U. Scherf, R. Gqnter, C. Asawapirom. S. Patil, D. Neher, T. Kietzke, Adv. Mater., **14**, 651 (2002).
[5] A. Boccaccini, I. Zhitomirsky, Curr. Opin. Solid State Mater. Sci., **6**, 251 (2002).
[6] P. Sarkar, P. Nicholson, J. Am. Ceram. Soc., **79**(8), 1987 (1996).
[7] Vu Quoc Trung, Thesis (2006).
[8] N. V. Dziomkina, M. A. Hempenius, G. Julius Vancso, Adv. Mater., **17**(2), 31 (2005).
[9] K. Tada, M. Onoda, Current Applied Physics, **5**, 5–8 (2005).
[10] K. Tada, M. Onoda, Thin Solid Films, **499**, 19 (2006).
[11] S. Maenosono, T. Okubo, Y. Yamaguchi, J. Nano Res., **5**, 5 (2003).
[12] K. Tada, M. Onoda, Adv. Func. Mater., **14**(2), 139 (2004).
[13] S. Ouro Djobo, J. Bernede, K. Napo, Y. Guellil, Materials Chemistry and Physics, **77**, 476 (2002).

---

[*] Corresponding author: izhiv@clf.bas.bg