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MATERIALS ENGINEERING | RESEARCH ARTICLE

Spray deposition of organic electroluminescent coatings for application in flexible light emitting devices

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Abstract: Organic electroluminescent (EL) films of tris(8-hydroxyquinolinato)aluminum (Alq_3) mixed with polystyrene (PS) binder were produced by spray deposition. The influence of the substrate temperature on the layer's morphology and uniformity was investigated. The deposition conditions were optimized and simple flexible light-emitting devices consisting of indium-tin oxide/Alq3:PS/aluminum were fabricated on polyethylene terephthalate (PET) foil to demonstrate the advantages of the sprayed organic coatings. Same structure was produced by thermal evaporation of Alq3 film as a reference. The influence of the deposition method on the film roughness and contact resistance at the electrode interfaces for both types of structures was estimated. The results were related to the devices' efficiency. It was found that the samples with sprayed films turn on at 4 V, which is 2 V lower in comparison to the device with thermal evaporated Alq3. The current through the sprayed device is six times higher as well (17 mA vs. 2.8 mA at 6.5 V), which can be ascribed to the lower contact resistance at the EL film/electrode interfaces. This is due to the lower surface roughness of the pulverized layers.

Subjects: Material Science; Coating & Thin Films-Materials Science; Materials Processing; Polymers & Plastics

Keywords: spray deposition; organic coatings; flexible displays; electroluminescence; thin films

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PUBLIC INTEREST STATEMENT

Organic electroluminescent structures with potential application as foldable pocket type displays were successfully fabricated on PET foil by applying spray deposition method. Pulverization was adapted for first time for small crystals on flexible substrate as it is typically applied for glass-based polymeric devices. By using spray coating, we achieved high quality uniform films. As a result, better electrical contact between the electroluminescent layers and the power supplying electrodes was obtained and the activation voltage of the light emitting process decreased. The consequence was 33% lower power consumption achieved in comparison to the conventional OLEDs, containing thermally evaporated films.

1. Introduction

Recently, organic optoelectronic devices have been received high popularity, especially organic light emitting displays (OLED) produced on flexible substrates (Wang, 2007). By using flexible foil for substrate, the devices become lighter, thinner, and highly reliable against breakage. The main reason for synthesis of organic materials and development of organic semiconductor coatings is their easy processing by simple and cheap deposition methods, such as spin coating, spray deposition, and ink jet printing. (Abdellah, Fabel, Lugli, & Scarpa, 2010; Lee, Seo, Choi, Kim, & Ha, 2008; Perelaer, & Schubert, 2012). The problem with the short lifetime of organic-based devices has not been solved yet. It is due to degradation of the intra- and intermolecular bonds, which often can be caused by increased temperature. In some cases overheating can occur when high temperature process is applied for the deposition of the organic coating. For example, at vacuum thermal evaporation of low molecular weight compounds for flexible electroluminescent structures, dark spots are consequently formed, because of the partially decomposed chemical bonds (Aleksandrova, 2012). Furthermore, thermal and mechanical stress is revealed in the widely used plastic substrates, such as polyethylene terephthalate (PET), because of their low melting point and high thermal expansion (Lee et al., 2011). Therefore, the high temperature deposition processes have to be replaced by low temperature ones such as, for example, solution-based process or screen printing of inks (Coya, de Andrés, Gómez, Seoane, & Segura, 2008; Lee, Choi, Chae, Chung, & Cho, 2009).

For pulverization aerosol flow generated from airbrush is usually used. It has reservoir containing diluted organic solution. This method allows precise control of the aerosol flow and production of uniform thin films after proper setting of the air pressure, the angle and the distance of spraying. The temperature is one of the most important factors to control layer's roughness and defects density on nanosized level. Different varieties of this technology have been already used for several polymeric-based devices (Hwang, Xin, Cho, Cho, & Chae, 2012; Rietveld, Kobayashi, Yamada, & Matsushige, 2006; Susanna et al., 2011). However, by our knowledge, spray deposition is not applied yet for small molecular electroluminescent materials mixed with polymer and in particular for Alq3 based flexible OLED.

In this paper, flexible OLEDs containing spray deposited electroluminescent (EL) film of tris (8-hydroxyquinolinato)aluminum (Alq3) mixed with polystyrene (PS) were tested. Alternative flexible OLED device was prepared by vacuum deposition of Alq3 as a reference. Interface current injection and device luminance efficiency were found to be strongly affected by the layers morphology.

The novelty in our work consists in study of the electro-optical behavior of OLEDs with sprayed organic coatings and measurement of their contact resistance, current–voltage characteristics and luminous efficiency after optimization of the spray deposition conditions for the organic EL films.

2. Materials and methods

Alq3 (Mw = 459.43 g/mol) and PET flexible foil (230 μm thick) were purchased from Sigma–Aldrich. PET pieces with sizes 3 × 3 cm were cut and cleaned by isopropyl alcohol before transparent electrode deposition. On the PET substrates, indium-tin oxide (ITO) film was deposited by low temperature RF sputtering at oxygen partial pressure 2×10^{-4} Torr and total gas pressure (sputtering argon + reactive) 2.5×10^{-2} Torr. The sputtering power varies between 75 and 105 W with rate 0.5 W/s during deposition of the initial ITO monolayer to avoid overheating and melting of the substrates from the plasma. Sheet resistance was decreased from 45 to 19.2 Ω/sq after exposure of ITO by UV light (UV 365 nm, source power 250 W) for 10 min. The organic dust was dissolved in solvent mixture chloroform:methylethylketon heated to 40°C. Solution was treated for 20 min in ultrasonic bath for stirring and stayed one night until fully dissolving of the particles. PS was added to the solution in weight ratio PS:Alq3 = 1:10 and presents as a binder, increasing the adhesive strength of the organic particles to the ITO electrode. For spraying of this solution, atomizer having nozzle with regulating orifice up to 200 μm was used. The capillary was made of stainless steel with a flat tip at whose end the orifice is. Liquid flow pressure is set by dry pressured air incoming to the airbrush through reducing valve and may has value between 0.5 and 4 bars (4 bars were set for this experiment). Temperature regulator defines the heater temperature, which must be lower than 85–90°C to prevent melting of

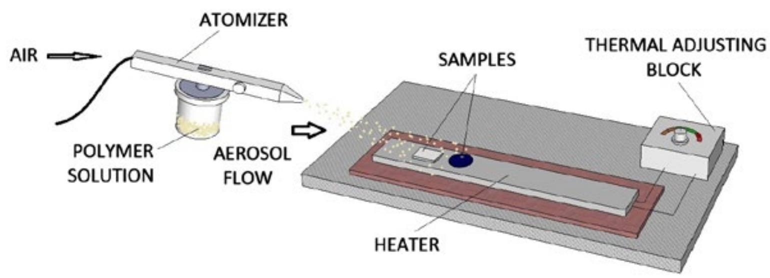


Figure 1. Spray coater for organic solutions pulverization.

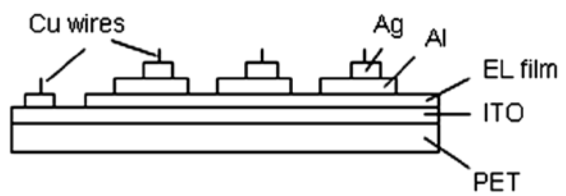


Figure 2. Prepared flexible OLED structure with sprayed organic layer.

the PET substrates. The mixture of organic solvents was selected, according to their evaporation at temperatures lower of the PET's melting point. To ensure full solvent vapor removing after spraying, the experiments were conducted in box with continuously air conditioned ventilation. All samples were sprayed at temperatures in the range 40–80°C with 10°C increasing step. The distance between the nozzle and the heater was set to 12 cm and the air pressuring the aerosol flow was fixed to 4 bars. Solution concentration was 5 ml/mg. The feed rate of the spray was 10 ml/min. It is expected that the droplet size is uniformly distributed in the middle zone versus the nozzle orifice and not so regular in the periphery. However, at experimentally set distance between the nozzle and the substrate (12 cm) and if the substrate size is 3 × 3 cm, it can be seen that the middle zone of the aerosol flow reaches the surface. Therefore, it was assumed that the droplets size distribution is uniform and constant, so it is not variable for the process and doesn't affect the contact condition. The uniformity of the spray was controlled by precise control of the air pressure and using of long nozzle with narrow slit at the end. The spray deposition setup is presented in Figure 1. On the top of the electroluminescent coatings, aluminum electrodes (280 nm) were deposited by vacuum evaporation through a shadow mask. The electrical connection between the formed electroluminescent areas and the measurement equipment was made by cupper wires, connected by silver paste to the aluminum cathodes and ITO anode. The OLED structure is presented schematically in Figure 2.

OLED structure with thermal evaporated Alq3 layer was prepared for comparison of the current–voltage (I–V) and brightness voltage characteristics, as well as for estimation of the luminance efficiency. After preparation, films were imaged by SQF DE Stereo 3D microscope at magnification 500. The thickness of the emissive layer in both types of OLEDs structures was the same—average 500 nm, measured by profiler Tencor Alpha Step 100, together with the surface roughness. The current was measured by a Keithley 6485 ammeter, the brightness was detected by luminance meter with color correction factor Konica Minolta LS-110 and the contact resistance was extracted from the impedance characteristics measured by Instek RLC analyzer in the frequency range 100 KHz–1 MHz at zero bias voltage.

3. Results and discussion

Figure 3(a–c) shows the surface morphology of the sprayed EL coatings at different substrate temperatures. At 40°C, the samples were relatively wet and visibly the layer's morphology is consisted by separated droplets with very different sizes (Figure 3(a)). The results were similar for 50°C, although the spraying cycles are repeated after pause of 5 s for evaporation of the solvent. Data about roughness couldn't be determined. When the temperature is closer to the allowable value for the plastic foil (80°C), the thermal field over the surface causes fully evaporation of the solvent and over drying, which results in formation of dust particles, irregularly distributed on the surface (Figure 3(b)). After decreasing the

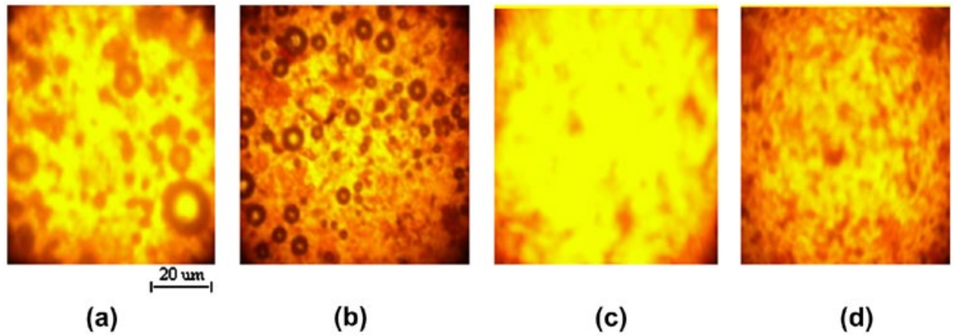


Figure 3. Microscopic images of PET/ITO surface covered with Alq3, spray deposited at different substrate temperatures, and thermal evaporated: (a) sprayed at *T* = 40°C; (b) sprayed at *T* = 80°C; (c) sprayed at *T* = 70°C; and (d) thermal evaporated organic coating.

temperature slightly to 70°C, revealing of strong thermal field was avoided and the solvent was evaporated after the aerosol flow achieves and distributes on the surface as a liquid. This favors the wettability of the substrate and leads to smooth, uniform, and continuous layer formation, consisting of well dissolved organic small molecules, which cannot be distinguished as separated clusters (Figure 3(c)). This is the reason to consider this value as an optimum temperature in the technological mode and to use it further for preparation of the samples for the electro-optical measurements. Microscopic view of thermal evaporated Alq3 is presented in Figure 3(d) for comparison. As was expected the microstructure is fine and the surface distribution of the particles is uniform. It can be seen that the coating produced at optimal spraying temperature on the same substrate and with the same thickness has similar features.

Furthermore, the surface profiles of the organic coatings, deposited by different methods and modes were measured and compared in Figure 4(a–c). Surface roughness is crucial for the contact properties when multilayer structures are fabricated. In the case of optoelectronic devices, it determines the contact resistance at the electrode interface, the charge carrier injection intensity and therefore the EL efficiency.

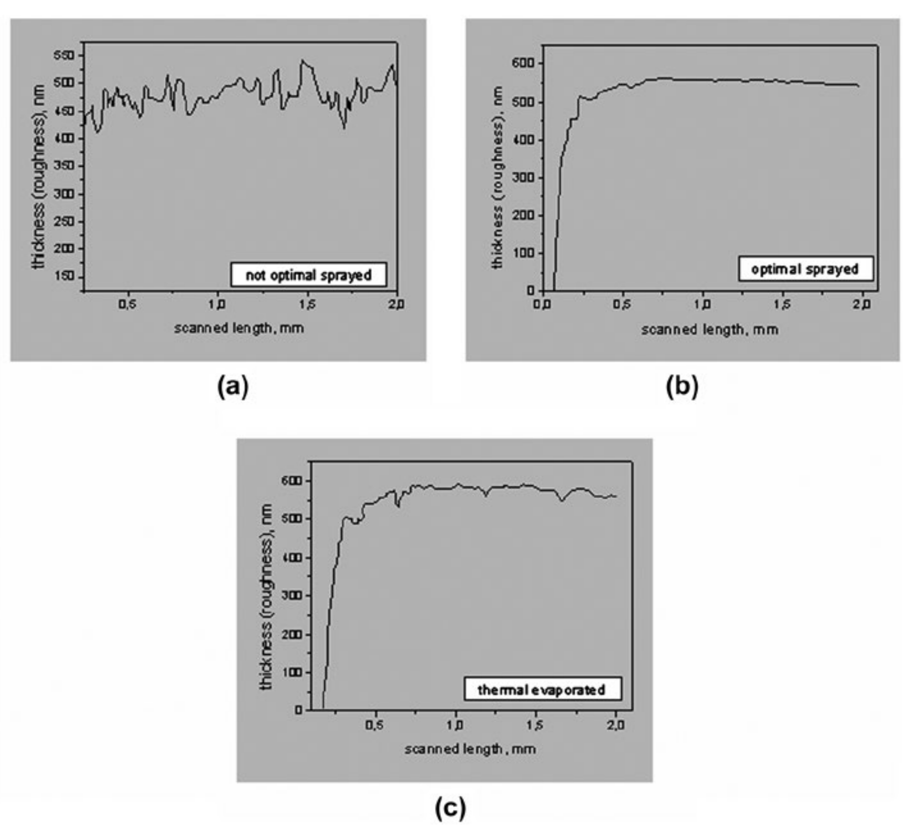
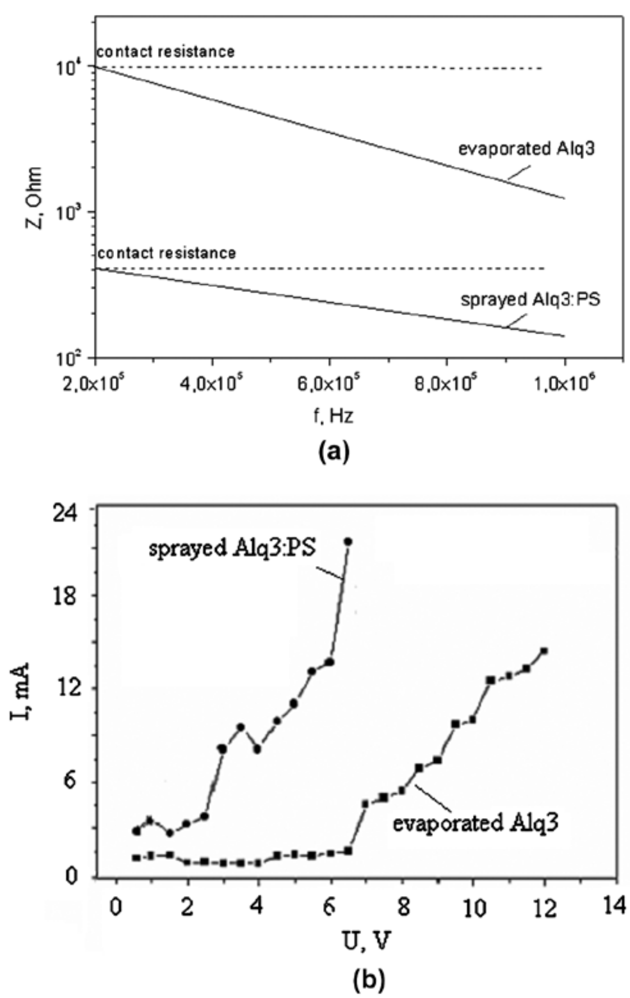


Figure 4. Profiles of PET/ITO surfaces covered with Alq3: (a) spray deposited at substrate temperature of 80°C; (b) at substrate temperature of 70°C; and (c) thermal evaporated.

At substrate temperature of 80°C high roughness value of 29.2 nm was measured due to non-homogeneous distribution solidified particles with large and not regular sizes. The peaks on the profilogram indicate fragmented particles and voids between them in consistent with the microscopic image (Figure 4(a)). Figure 4(b) shows that the average roughness was the lowest (12.6 nm) for the film pulverized at substrate temperature of 70°C. For thermal evaporated Alq3 film, produced here, the roughness was ±19.9 nm (Figure 4(c)). The obtaining of smooth coating at 70°C is ascribed to the droplets ability to form liquid flow, which is related also to the initial solution's viscosity and the resultant vapor pressure of the used solvent mixture. It seems that this temperature is suitable for the quality of the films, as the solvent vaporizing rate rises gradually near the substrate surface. As can be seen from the profiles, coating's average roughness at optimized spray deposition conditions is comparable to the roughness for thermal evaporated Alq3 film. This give us reason to consider spray deposition as a good alternative for replacing of the thermal evaporation for flexible OLED samples.

For further clarification of the OLED behavior impedance measurements were conducted and the contact resistances were extracted from the real part of the structures' impedances $Z(f)$. It was found that the contact resistance at the electrodes interfaces is strongly influenced by the roughness of the electroluminescent layers. To estimate quantitatively how the film's morphology affects to the electrical contact at the interfaces the real part of the impedance was considered for analysis for the optimized sprayed sample and for the reference. Figure 5(a) shows the active resistance of the impedance for both structures. The reactive component (or imaginary part) of the impedance

Figure 5. (a) Real part of the impedance and (b) I–V characteristic of PET/ITO/Alq3/Al device with organic layer deposited by spraying and evaporation.

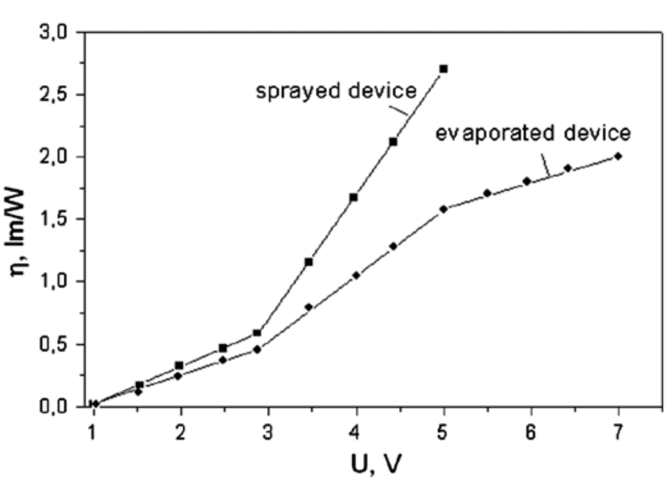


shows the capacitive behavior of the devices. It is related to the junction capacitance, which affects mainly on the delay times at on-off switching conditions and vice versa. However, the process of interfacial capacitance recharging is out of the scope of this work and it is not given.

Relatively low contact resistance (~400 Ω) was achieved between the electrodes and the sprayed at optimum substrate temperature organic film, because of the higher common contact area between the layers mainly due to the low roughness and defect free surface of the spray coated film. It is expected that the thermal evaporated structure will exhibit closer but higher contact resistance, because of the higher measured roughness. However, the contact resistance is almost 10 kΩ. Further investigation of this phenomenon is necessary. It was suggested that additional transporting layer is needed between the ITO anode and the EL film for energy level alignment and suitable dipoles orientation at the interface for compensation of the space charges and contact resistance decreasing (Dinh, Thanh, Long, & Trung, 2004). It seems that the incorporation of PS also influences the interfacial states, although additional analyses should be conducted for support of this hypothesis. The interfacial optimization results in improvement of the electrical conductivity through the structure and lower voltage drop over the contact area as can be seen from the measured current–voltage characteristics. The device with sprayed Alq3 was turned on at 4 V, while the device with the thermal evaporated Alq3 initiated light emission at 6 V. The current density was six times higher at certain voltage compared to the reference device (Figure 5(b)). This confirms for the good quality of the films, and suggests lack of defects and uniform contacts over the entire electrode interfaces areas. Some variations and deviations from the typical diode characteristic (just before device turning on) can be explained with contamination particles fallen into the deposition zone and incorporated in the film due to the lack of clean (vacuum) environment during film growth.

At breakdown voltage of ~6 V the current through the sprayed OLED increased sharply to values higher than 20 mA, which led to device overheating and thermal deformation of the PET foil, due the heat dissipated. This restricted the current–voltage working range of the flexible OLED with small molecule:polymer spray deposited EL films. The current through the sprayed sample is recommended to be limited by outer balance resistance to prevent electrical and thermal breakdown of the inner structure. The power consumption in this region increased to 120 mW, instead of the typically for such devices 50–60 mW that were achievable at our structures at 5 V, where the current flow was 12 mA. For comparison, the working voltage region of the OLED with thermal evaporated Alq3 film was wider and reached up to 12 V. However, the turn on voltage is slightly higher than 6 V. This is the reason for power consumption to reach average value of 80 mW. Although the Alq3 is mixed with PS, the current through the structure with sprayed layer is higher, which suggest suitable ratio between both components.

Figure 6. Quantum efficiency of single layer PET/ITO/Alq3/Al device with organic coating deposited by spraying and evaporation.



The resulting luminance efficiency for both devices is shown in Figure 6. As can be seen for the device with sprayed layer the throughput can be increased average by 30%. This is ascribed to the optimized spray deposition conditions, leading to smooth and uniform EL films and resulting in lower contact resistance, higher conductivity, and smaller voltage drop at the electrode interfaces in comparison to OLED with thermally evaporated EL films.

4. Conclusion

It was proven that it is possible to achieve efficient simple flexible OLED by replacing the thermal evaporation as a deposition technique for small organic crystal electroluminescent compounds by spraying. After proper set of the spray deposition conditions and mostly of the substrate temperature, highly uniform, and smooth thin Alq3 films can be produced. By involving sprayed films in the OLED device, the interface resistance can be greatly reduced, which leads to turn-on voltage decreasing and improves the conductivity of the structures. In this way, the quantum efficiency can be increased by ~30% and reaches values comparable to the bilayer OLEDs, containing thermal evaporated organic films.

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