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Poly(3,4-ethylenedioxythiophene):poly(4-styrenesulfonate) ratio: Structural, physical and hole injection properties in organic light emitting diodes

Paolo Vacca [a,*], Mario Petrosino [b], Riccardo Miscioscia [a], Giuseppe Nenna [a], Carla Minarini [a], Dario Della Sala [a], Alfredo Rubino [b]

[a] *Enea C.R. Portici, v. Vecchio Macello, 80055 Portici (NA), Italy*
[b] *Dip. Ing. dell'Informazione ed Ing. Elettrica, Università di Salerno, v. Ponte Don Melillo 1, 84084 Fisciano (SA), Italy*

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Abstract

We report on the employ of several kinds of poly(3,4-ethylenedioxythiophene):poly(4-styrenesulfonate) (PEDOT:PSS) dispersions as a hole injection layer to increase the stability and the charge injection in organic light emitting diodes (OLEDs). The PEDOT:PSS dispersions have been characterized in solution and thin film by means of dynamic viscosity, Dynamic Light Scattering, profilometer, contact angle measurement, UV–Vis–NIR transmittance and current–voltage characteristics. Then, the dispersions have been employed to manufacture OLEDs with structure: *indium tin oxide (ITO)–PEDOT:PSS–poly(9,9-dihexyl-9H-fluorene-2,7-diyl–Tris (8-hydroxy)quinoline aluminium–Al*. Device electrical and optical properties have been extensively investigated and discussed in function of PEDOT:PSS ratio. We have found that the hole barrier at the ITO–PEDOT:PSS interface plays a key role in electrical transport and in setting the external quantum efficiency.

Keywords: PEDOT:PSS; Work function; OLEDs; Electrical transport

1. Introduction

Poly(3,4-ethylenedioxythiophene):poly(4-styrenesulfonate) (PEDOT:PSS) is widely used in the fabrication of organic light emitting diodes (OLEDs) [1–12]. The polymer film, which is generally inserted between the anode, usually made of indium tin oxide (ITO), and an organic layer, hole transporter or electron transporter (ETL), has two distinct functions. The first one is to prevent a direct contact between the anode and the upper organic layer. This role is very important when the upper layer is an ETL because it avoids a fast degradation of the devices due to the interactions between the two materials. The second purpose of PEDOT:PSS is to enhance the injection of holes from the anode into the organic layers reducing the barrier height at the ITO–organic interface when it is not low enough. Moreover, the success of the PEDOT:PSS system with high electrical conductivity and low sheet resistance is also demonstrated by commercial use in antistatic coatings, capacitors and Polymer Light Emitting Diodes, and by possible applications in electrochromics [13–15].

PEDOT has a relatively high conductivity in its oxidized form, which can be ascribed to a planar structure allowing effective delocalization of π electrons. It also has good optical transparency in the visible region, but is insoluble. Combination with a poly-electrolyte (PSS) resolved this problem. PSS acts as a charge-compensating counter-ion to stabilize the p-doped conducting polymer, and forms a processable water-borne dispersion of negatively charged swollen colloidal particles consisting of PEDOT and excess PSS [16,17]. PEDOT and PSS chains are linked tightly by ionic interaction and form an ionic polymer complex dispersed in aqueous solution. In the PEDOT–PSS dispersion the polymer chains likely adapt a random coil conformation and can easily be spin-coated resulting in transparent films with grains consisting of doped conjugated polymer coils [18,19] and resulting in low resistivity and high transmittance. Since PSS chains typically consist of a few hundred monomer

* Corresponding author. CR ENEA Portici, Via Vecchio Macello, 80055 Portici (NA), Italy. Tel.: +39 081 7723386; fax: +39 081 7723344.
E-mail address: paolo.vacca@portici.enea.it (P. Vacca).

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units, the polymer grains are probably defined by the PSS random coil with PEDOT ionically attached along them. The area between the grains possibly consists of exceeding PSS. Previous Atomic Force Microscope (AFM) studies have confirmed a grain-like structure of PEDOT–PSS films [18], where a non-homogeneous distribution of the PEDOT and the PSS species within the grains was proposed (PEDOT–PSS core surrounded by a PSS-rich shell). It has been previously estimated that the layer of excess PSS surrounding the PEDOT–PSS grains is on the order of 30 Å thick [20]. Decreasing the thickness of surrounding PSS would enhance the connectivity of the conducting PEDOT–PSS domains in the film and thereby dramatically increase conductivity due to better connecting network through the film. For this reason, varying the PSS content in the PEDOT–PSS layer, it is possible to reduce the area between the grains and to increase the composite conductivity [9].

To understand the influence of PEDOT:PSS ratio on the OLED performances, three dispersions have been chosen in order to obtain hole injection layers different in conductivity, work function and morphology. We have first investigated the physical, morphological and electrical properties of thin films by means of UV–Vis–NIR transmittance, contact angle measurements, surface profilometry and current–voltage (I–V) characteristics. Then, the PEDOT:PSS dispersions have been used to manufacture multilayer ITO–PEDOT:PSS–poly(9,9-dihexyl-9*H*-fluorene-2,7-diyl (PF6)–Tris (8-hydroxy)quinoline aluminium (Alq_3)–Al OLEDs and the device electrical and optical properties have been extensively investigated and discussed in function of PEDOT:PSS ratio.

2. Experimental details

Three commercial dispersions with different PEDOT–PSS molar ratios have been analyzed and employed to manufacture multilayer OLED structures.

The dispersions have been analyzed in dynamic viscosity and particle size dimensions. Dynamic viscosity measurements have been performed by using a Visco Basic Plus with concentric cylinder configuration and a shear rate of 1 rpm/s. Particle size distribution has been analyzed by means of Dynamic Light Scattering (DLS) technique using a Malvern Instrument HPPS ET. In detail, DLS measures Brownian motion and relates this to the size of the particles. It performs that task by illuminating the particles with a laser and analyzing the intensity fluctuations of the scattered light. The film thickness and roughness have been evaluated by a KLA Tencor P-10 Surface Profiler. For UV–Vis–NIR optical transmittance analysis, PEDOT:PSS layers have been deposited on quartz substrates and measurements have been carried out by using Perkin-Elmer lambda 900 spectrophotometer.

Contact angle measurements have been performed with Dataphysics OCA 20 equipment at 21 °C and 50% relative humidity. We have used water (polar) and diiodomethane (non-polar) solvents to evaluate the polar and dispersion components of the surface energy. The standard error of contact angle measurements is ±0.1°.

The resistivity of PEDOT:PSS coating has been measured according to ASTM procedure [21]. In detail, the electrodes have been painted with silver on the PEDOT:PSS layers deposited on glass and arranged as shown in Fig. 1. The electrodes are 1.5 mm wide, 20 mm long, and 20 mm apart.

To manufacture OLED structures, commercial ITO (200 nm) coated glass substrates have been used as transparent conductive anode. In order to create contact areas and to prevent the formation of shorts during the top electrode contact soldering, the ITO layers have been patterned by a photolithography process.

To improve the ITO performance, a double treatment of ITO surface has been developed. First, for a UV ozone treatment, the substrates have been exposed to a 50 W UV light source (wavelength range 250–300 nm) 10 cm away distance under oxygen flow for 30 min. Later a 12% (v/v) HCl water solution has been prepared for acid treatment and the substrates have been dipped in the solution at room temperature for 15 min. Finally the ITO substrates have been rinsed in distilled water and finally dried with nitrogen [22].

To manufacture multilayer structures, ITO–PEDOT–PF6–Alq3–Al OLEDs have been manufactured employing three kinds of PEDOT:PSS commercial dispersion. The three dispersions have been chosen to have different PEDOT–PSS molar ratios, since the amount of PEDOT in a film is expected to strongly influence electrical properties. In detail, to realize a PEDOT:PSS layer in “A device”, a 3.0 wt.% dispersion in water and PEDOT:PSS ratio 1:20 (w/w) was spun on the substrates at 2000 rpm for 30 s and the obtained 70 nm thick film was backed under nitrogen flow at 120 °C for 15 min. To realize a PEDOT:PSS layer in “B device”, a 1.8 wt.% dispersion in water and PEDOT:PSS ratio 1:6 (w/w) was spun on the substrates at 2000 rpm for 30 s and the obtained 70 nm thick film was backed under nitrogen flow at 120 °C for 15 min. To realize a PEDOT/PSS layer in “C device”, a 1.4 wt.% dispersion in water and PEDOT:PSS ratio 1:2.5 (w/w) was spun on the substrates at 3000 rpm for 20 s and the obtained 70 nm thick film was backed under nitrogen flow at 120 °C for 15 min.

After the PEDOT:PSS layer baking, PF6 has been used as a hole transporting material and spun over PEDOT:PSS layer at 1000 rpm for 30 s from a 1.0% (w/w) chlorobenzene solution. After deposition the PF6 film 70 nm thick has been backed in vacuum at 50 °C for 3 h. The spin coating process has been

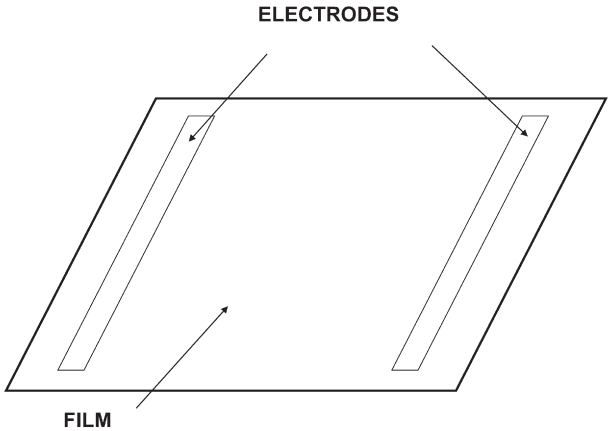

Fig. 1. Electrode arrangement for measuring the resistivity.