Influence of the Transparent Conductive Oxides on the P-OLEDs Behavior

E. R. Santos[a], F. C. Correia[a], E. C. B. Junior[b], R. K. Onmori[c], S. H. Wang[a]

[a] Escola Politécnica da Universidade de São Paulo, Departamento de Engenharia Metalúrgica e de Materiais, São Paulo, SP, 05508-970, Brazil
[b] Instituto de Eletrotécnica e Energia da Universidade de São Paulo, São Paulo, SP, 05508-010, Brazil
[c] Escola Politécnica da Universidade de São Paulo, Departamento de Sistemas Eletrônicos, 05508-900, Brazil

Multilayer polymer light emitting devices (P-OLEDs) were assembled having different transparent conductive oxide (TCO) and aluminum as the anode and cathode, respectively. Two types of TCOs, ITO (indium tin oxide) or FTO (fluorine tin oxide), with different sheet resistances, from 10 to 61 Ω/□, were used. A blend of poly[(1,4-phenylene)-alt-2,7(9,9-dioctylfluorene)] and an europium complex (20 %) was used as the polymeric photoactive layer of the devices. The performance of P-OLEDs devices showed that the FTO films with the lowest sheet resistance presented the lowest threshold voltage, while the ITO with the lowest sheet resistance presented the highest luminance among all the devices prepared.

Introduction

The P-OLEDs (polymeric-organic light emitting diodes) are devices comprised by different materials usually mounted layer-by-layer on a rigid (as glass) or flexible (as plastic) transparent substrate. On these substrates, a thin transparent conductive oxide (TCO) film is deposited, which functions as anode during the polarization of the device. Indium tin oxide (ITO) and fluorine tin oxide (FTO) are the most common TCOs in displays.

The initial pre-cleaning process of the TCO surface for the removal of powder and micro particles is followed by an oxidative treatment using UV-Ozone, for the elimination of hydrocarbon compounds on the surfaces, The TCO cleaning procedure has been shown to decrease the threshold voltage and increases the luminance of P-OLEDs (1).

The main goal of this work is to investigate the influence of different TCOs on the performance of a P-OLED. In the photoactive layer of the devices, a blend of polyfluorene and an europium complex (2,3) was used (4,5), which is known to present high electroluminescence. (6,7).

Experimental

Synthesis of poly[(1,4-phenylene)-alt-2,7(9,9-dioctylfluorene)]

The copolymer was prepared following the procedures described in the literature (8). In a three-necked flask, a mixture of 9,9-dioctyl-2,7-dibromofluorene

(0.548 g, 1 mmol), 1,4-phenylenebisboronic acid (0.165 g, 1 mmol)) and $Pd(PPh_3)_4$ (0.0116 g, 0.5–1.5 mol %) were added to a degassed mixture of toluene (9 mL), benzalkonium chloride (0.143 g) and 6 mL of K_2CO_3 2M (1.65 g) (9). The mixture was vigorously stirred at 85 - 90 °C for 48 h under a nitrogen atmosphere. Then, phenylboronic acid (0.025 g, 0.2 mmol) was added as an end capping agent and the mixture was heated for an additional 24 h. After cooling to room temperature, the copolymer was dissolved in chloroform and precipitated in methanol. After purification 0.107 g (yield = 21.5 %) of copolymer was obtained. M_n: 1,413x10^3 g/mol and M_w: 2,313x10^3 g/mol.

Chemical pre-cleaning method of TCOs

Commercial ITO and FTO films deposited on glass substrates having different sheet resistances were used. The ITO films presented sheet resistance of 15 and 30 Ω/□ and FTO films, 10 and 61 Ω/□. The substrates were previously cut to 1 x 1 inch, then submitted to a chemical pre-cleaning procedure using detergent and then ultrasonic bath for 20 minutes in isopropyl alcohol and acetone, sequentially. .

Assemblage of P-OLEDs

After the pre-cleaning process, the TCOs were exposed to UV-Ozone during 5 minutes. The UV-ozone treatment was performed with the aid of a homemade UV-ozone generator (10).Soon after the UV-Ozone treatment, the PEDOT:PSS films were deposited by spin-coating, which was thermal annealed at 373 K for 10 min. Also the emissive polymer layer (EL), blend of poly[(1,4-fenylene)-alt-2,7(9,9-dioctylfluorene)] and an europium complex, was deposited, thereafter, and annealed at 328 K. Finally, butyl-2-(4-biphenylyl)-5-(4-tert-butylphenyl)-1,3,4-oxadiazole (butyl-PBD) (electron transport layer – ETL) and aluminum film were sequentially deposited by thermal evaporation under reduced pressure.

P-OLED's design

Four P-OLEDs devices were mounted at the same time on each 1" x 1" slide, according to Fig. 1. The size of the active area is 0.12" x 0.12". In this layout, each P-OLED had its respective electrodes (anode and cathode) completely independent.

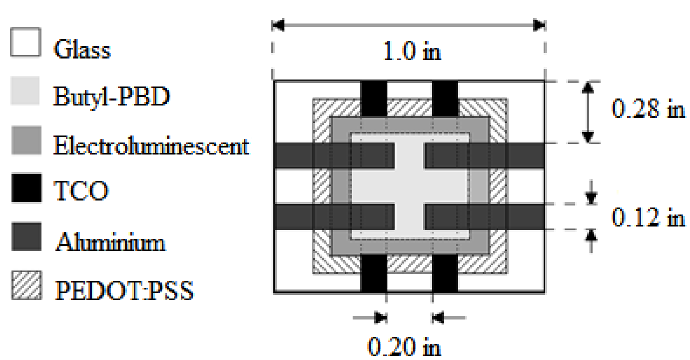


Figure 1. Architecture of the P-OLEDs devices mounted.

Optical characterization of TCOs

Contact angle of TCOs' surfaces, previously submitted to UV-ozone treatment, were determined by using a webcam Philips model SPC530NC with 1.3 mega pixels resolution. A droplet of PEDOT:PSS was deposited by a micro syringe and its image was captured for the contact angle measurement.

Transmittance of TCOs films were carried out using an UV-Vis spectrophotometer (Shimadzu model UV 1650). The surface was also observed by FEG-SEM (FEI Co. model Nova 400) with magnification up to 50,000 x.

Electrical characterization of P-OLEDs

Polarization of P-OLEDs and the correspondent current-voltage curves were obtained by using a source meter manufactured by Keithley, model Series 2420. The voltage range was set from 0 to 20 V at 0.5 V steps. A chroma meter manufactured by Minolta, model CS100 A was connected simultaneously to the source meter and a correspondent luminance value was obtained for each voltage-current result. The electroluminescence spectra of the devices were measured by a spectrophotometer manufactured by Ocean Optics, model HR 2000+, with the aid of an optical fiber positioned on the active region of the P-OLED polarized at 10 V.

Results

The transmittance spectra of the slides having different TCOs are shown in Fig. 2. The ITO 30 Ω/□ slide presented the highest transmittance in the whole visible light range. A reference line at 520 nm correspondent to the polyfluorene emission is included.

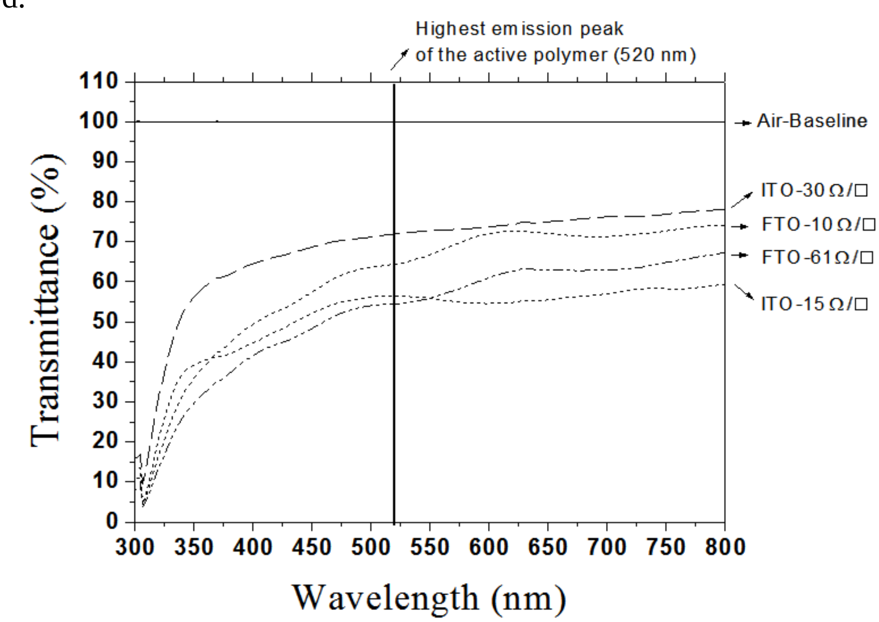


Figure 2. Transmittance vs. wavelength for different TCOs.

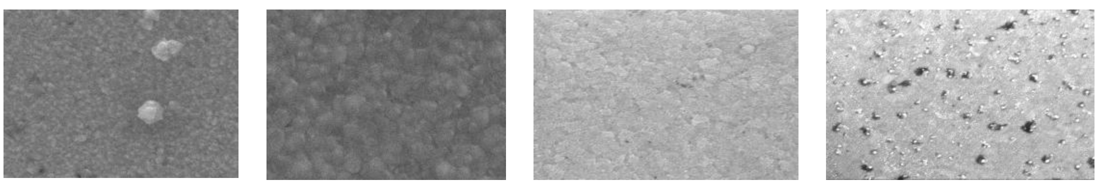
Usually, for the same chemical composition lower sheet resistances are observed for thicker film. However, the transmittance results suggest that the FTO 10 Ω/□ slide might present a thinner film compared to that of FTO 61 Ω/□.

A 20 % difference in transmittance is observed between the most translucent (ITO 30 Ω/□) and less (FTO 61 Ω/□) transmittance at 520 nm.

Table I shows the observed contact angles and Figure 3, the images of the surface observed by FEG-SEM. Both techniques are complementary; in general, they are able to measure the surface roughness. In this case, only the FTO samples presented conclusive results, as the observed standard deviations are acceptable. For these samples, a correlation between the surface smoothness and the contact angle is obtained.

TABLE I. TCO types and contact angle (with standard deviation).

TCO Type	Contact Angle (±Standard Deviation)
ITO 15 Ω/□	45 ± 7
ITO 30 Ω/□	38 ± 5
FTO 10 Ω/□	38 ± 3
FTO 61 Ω/□	29 ± 3



(a) (b) (c) (d)

Figure 3. FEG-SEM images of TCOs films surfaces: (a) FTO 61 Ω/□, (b) FTO 10 Ω/□, ITO 15 Ω/□ and ITO 30 Ω/□.

Two devices from each slide were tested and the correspondent current-voltage curves are shown to be similar (Fig. 4). The P-OLEDs are distinguished by the TCO. The P-OLED with FTO 10 Ω/□ presented the lowest threshold voltage (≈ 3.5 V), followed by that with ITO 15 Ω/□, ≈ 5 V. Those P-OLEDs with ITO 30 Ω/□ and FTO 61 Ω/□, presented similar behavior, characterized by comparable threshold voltage and low electrical current density, even after increasing the voltage. Nonetheless, the overall results indicate a clear dependence of the current density response on the TCO sheet resistance.

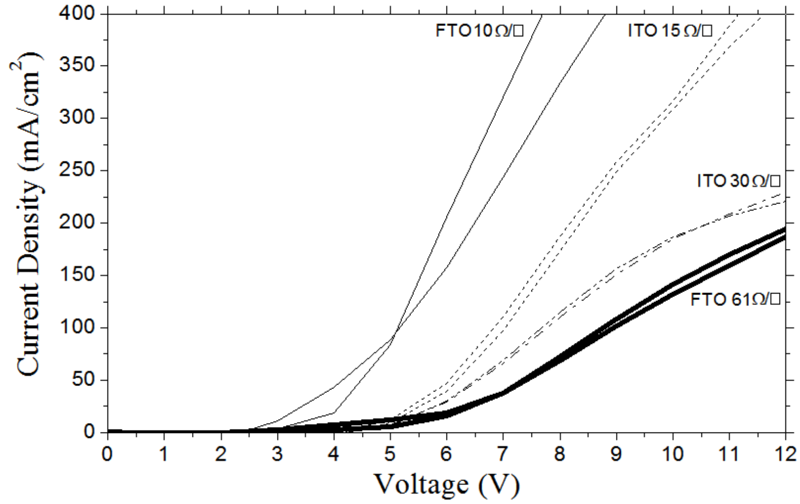


Figure 4. Current density vs. voltage curves for P-OLEDs devices with different TCOs.

The electroluminescence behavior of the devices is shown in Fig 5. Although FTO 10 Ω/☐ device presented the highest current density among the four types of P-OLEDs, its electroluminescence response is much worse than that of ITO 15 Ω/☐ and besides its lower threshold voltage, its behavior is close to those observed for the devices prepared from ITO 30 Ω/☐ and FTO 61 Ω/☐. Compared to the others, the ITO 15 Ω/☐ device presented a three times higher electroluminescence.

This behavior indicates that the ITO 15 Ω/☐ improves the balance of the injected charge carriers contributing to the increase of the recombination of electrons-holes inside the active layer of the device, while the presence of FTO 10 Ω/☐ in the devices, allowed an increased hole injection, observed as a lower threshold voltage, although no contribution to the number of hole-electron recombination has resulted.

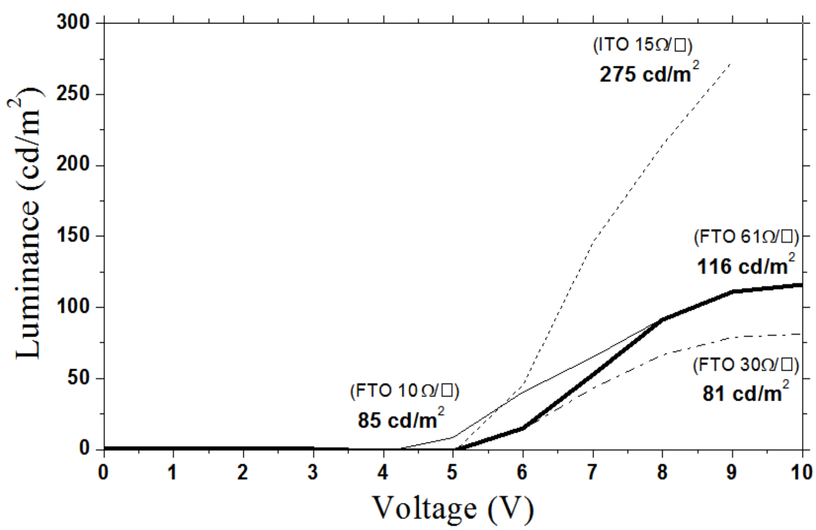


Figure 5. Luminance vs. voltage curves for P-OLEDs devices with different TCOs.

The Figure 6 shows the electroluminescence spectra for two P-OLEDs polarized at 10 V and 50 mA. All P-OLEDs presented the same electroluminescence spectrum with maximum emission at 520 nm, however that from ITO 15 Ω/☐ presented the highest intensity, as expected. It is important to note that at 520 nm, the ITO 15 Ω/☐ and FTO 61 Ω/☐ present a transmittance that is 20 % lower than that observed for ITO 30 Ω/☐ (Fig. 2).

The electroluminescence spectra revealed also that the emission peak is characteristic of polyfluorene and no emission due to the europium complex was observed, which characteristic emission peak appears at 615 nm.

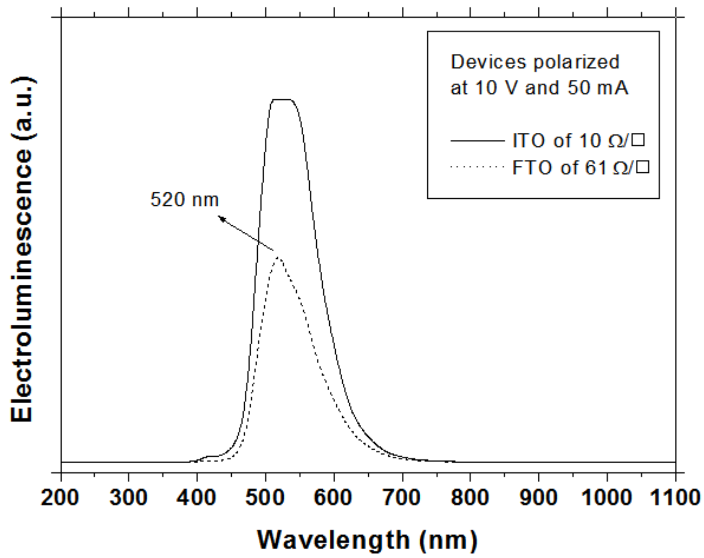


Figure 6. Comparison of electroluminescence vs. wavelength for two P-OLEDs polarized at 10V and 50 mA with ITO of 15 Ω/□ and FTO of 61 Ω/□.

Conclusion

The poly[(1,4-phenylene)-alt-2,7(9,9-dioctylfluorene)]/europium complex (20%) blend presented an electroluminescence spectrum in the visible wavelength range with a peak maximum at 520 nm.. Although the FTO 10 Ω/□ device presented the lowest threshold voltage, the devices with ITO 15 Ω/□ presented the highest electroluminescence, about three times more intense. The observed results are attributed to the FTO better hole injection ability, due to a lower potential barrier between the materials, resulting in a decreased threshold voltage. On the other hand, the ITO film promotes an increased number of recombination of electrons and holes improving the emission of P-OLEDs devices. The transmittance results indicated significant differences among the TCOs, but it is not directly responsible for the emission intensity observed for the P-OLEDs.

References

1. E. R. Santos, F. C. Correia, S. H. Wang, P. Hidalgo, F. J. Fonseca, E. C. Burini, A. M. Andrade, *Quim. Nova*, **33**, 1779 (2010).

2. N. Miyaura and A. Suzuki, *Chem. Rev.*, **95**, 2457 (1995).
3. A. Suzuki *J. of Organom. Chem.*, **576**, 147 (1999).
4. U. Scherf and E.J.W. List, *Adv. Mater.*, **14**, 477 (2002).
5. J. Kang, J. Jo, Y. Jo, S.–Y. Lee, P. E. Keivanidis, G. Wegner, D. Y. Yoon, *Pol.*, **49**, 5700 **(**2008).
6. G. Santos , F. J. Fonseca , A. M. Andrade, V. Deichmann, L. Akcelrud, S. S. Braga, A. C. Coelho, I. S. Gonçalves, M. Peres, W. Simões, T. Monteiro, L. Pereira, J. of Non-Cryst. Sol. 2008, 354, 2897.
7. K. Yoshino, Y. Manda, K. Sawada, S. Morita, H. Takahashi, R. Sugimoto, M. Onoda, *Phys. J. Phys. Soc. Jpn.*, **58**, 1320 (1989).
8. W. S. Hui, F. C. Correia, Patent: P.I. 1.002.492-1, - RPI 2011, 2098, 150 (2010).
9. Y. Li, J. Ding; M. Day, Y. Tao, J. Lu, M. D'iorio, *Chem. Mater.*, **16**, 2165, (2004).
10. E. R. Santos, E. C. Burini, S. H. Wang, Ozone: Sci. & Eng., **34**, 129 (2012).