Sensors & Transducers Journal, Vol. 101, Issue 2, February 2009, pp. 22-30

www.sensorsportal.com

Sensors & Transducers

ISSN 1726-5479

http://www.sensorsportal.com

Aquaregia and Oxygen Plasma Treatments on Fluorinated Tin Oxide for Assembly of PLEDs Devices Using OC_1C_{10}-PPV as Emissive Polymer

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Received: 25 January 2008 /Accepted: 20 February 2009 /Published: 28 February 2009

Abstract: In this work were carried out treatments with oxygen plasma and aquaregia on fluorinated tin oxide (FTO) films varying the treatment times. After treatments, the samples were analyzed by techniques measurements: sheet resistance, thickness, Hall effect, transmittance and superficial roughness. Devices using FTO/PEDOT:PSS/OC_1C_{10}-PPV/Al were assembled. In this experiment some variations were observed by sheet resistance and thickness and Hall effect measurements indicated most elevated carriers concentration and resistivity for aquaregia than that oxygen plasma. The roughness was elevated for the first minutes with treatment by aquaregia too. In the I-V curves the aquaregia devices presented the lowest threshold voltage for 30 minutes and devices treated by oxygen plasma presented a behavior most resistivity different of typical curves for PLEDs devices.

Keywords: FTO, Aquaregia, Oxygen plasma, OC_1C_{10}-PPV

1. Introduction

FTO (fluorinated tin oxide) has similar characteristics as ITO (indium tin oxide) films that are very used for polymeric or organic electroluminescent devices. Favorable characteristics of the films that

contribute in the performance these devices are: transparency, easy etchability, low resistivity, good chemical stability and adherence on substrates.

Some superficial treatments that change electrical and morphological properties of ITO films have been researched. These techniques used are known in the literature as: oxygen plasma [1], aquaregia [2] and ultraviolet-ozone [3]. They contribute in the performance of electroluminescent polymeric devices decreasing of threshold voltage operation and improving the lifetime [4] eliminating contaminants on the surface of TCOs as carbon or hydrocarbon [5]. For example, on the ITO films the treatments decrease the oxygen vacancies reducing these contaminants and consequently occur increase of the work function [6] improving carrier injection holes inside of adjacent polymeric layer.

The objective of this work is study comparing aquaregia and oxygen plasma treatments on the FTO instead of ITO film used in construction of PLEDs devices, varying the treatment time parameter of techniques.

2. Experimental

2.1. Treatment Techniques

The FTO films on glass were patterned in substrates of 10 x 10 mm^2 (for optical and electrical analysis) and 25 x 25 mm^2 (for construction of devices). On each sample four devices were mounted. Before of treatments the samples were cleaned using solutions: trichloroethylene, acetone, isopropyl alcohol and finally dried with nitrogen flow.

- Oxygen plasma treatment was used a RIE (reactive ion etch) reactor and processes parameters as: oxygen flow rate of 50 sccm, pressure of 100 mtorr, source power supply of 100 W and temperature inside the chamber at 293 K (~ 20 ºC).
- Aquaregia treatment was carried out at room temperature and samples were immersed with the film facing up into solution: $1HNO_3$ + 3 HCl + 20 H_2O (distilled) [7]. After treatment the FTO films were rinsed with deionised water and consequently dried by nitrogen flow.

For both techniques were used treatment times from 10 to 60 minutes. An untreated sample was used as reference.

2.2. Measurement Techniques

After treatments the samples were submitted to characterization measurement at room temperature: sheet resistance with four point probe Veeco Instruments model FPP-100; thickness by profilometer Alfa Step 500 Surface and Hall Effect with power source model MPS-50 and Van der Pauw controller model H-50 of Advanced Energy. In this last technique four circular silver paint pads (with ~ 2 mm diameter) were made with a symmetric arrangement at the corner of the samples. The measurement was used with a standard Van der Pauw configuration with AC current and magnetic field with intensity B = 0.35 Tesla and current of 1 mA. The optical measurement was performed using transmittance by UV-VIS Spectroscopy technique Shimadzu model UV-1650 PC. In this technique the FTO film was completely etched using HCl solution and zinc powder and glass substrate was used as reference sample. Atomic force microscopy (AFM) Nanoscope III-A of Digital Instruments was used for measurements of superficial roughness. The images were obtained through of SPM (Scanning Probe Microscopy) by contact mode using Scanner E and the image size in 15 x 15 μm^2. The analysis by roughness was calculated by root-mean-square using specific software. The I x V curves of devices were obtained using parameter analyzer Hewlett Packard model 8453.

2.3. Assembly of Devices

Spin-coating [8] technique was used for deposition of polymeric layers and untreated sample was used as reference. For treated FTOs (including an untreated sample) devices were mounted using: a HTL (hole transport layer) of PEDOT:PSS (poly (3,4 ethylenedioxy-thiophene) (manufactured by Baytron) with ~ 80 nm thick (1,500 RPM by 30 seconds) and annealing by 60 minutes at 373 K (100 ºC). Then an emissive layer of OC_1C_{10}-PPV (poly (2-methoxy-5-(3-,7-dimethyl-octyloxy)–1,4–phenylene vinylene) (manufactured by Covion) was deposited with ~ 190 nm thick (3,000 RPM by 60 seconds) and annealing by 120 minutes at 323 K (50 ºC). Finally on the emissive polymer was deposited an aluminium layer as cathode electrode by thermal evaporation of ~ 50 nm thick. All devices were encapsulated under argon ambient into a glove box system decreasing the oxygen and moisture concentrations causing much less degradation of emissive polymer [9] and using glass and epoxy for encapsulation of devices.

3. Results and Discussion

Comparing all results of sheet resistance was verified a dispersion before of treatments. After treatments by oxygen plasma and aquaregia this dispersion was kept but a little variation for each sample revealed the effect caused by treatments. In the oxygen plasma this variation can be attributed due to the formation of a thin oxygen simulator layer with few angstroms during the treatments. This characteristic was reported by B. Low et al. [10] that used ITO films treated by oxygen plasma. In the aquaregia treatment this variation may has been caused by aggressive attack of the acid elements directly on surface of film, because this solution dissolves also gold or platinum [11,12] without dilution. In the literature is also mentioned that the excess of F atoms not occupied into the crystal lattice contributes with free carrier concentration, but if the oxygen concentration increases into of the crystal lattice there is decrease of free carrier number increasing the sheet resistance and electrical resistivity [13]. For sheet resistance was used one sample for each treatment time with thirty four measurements. The Fig. 1(a) and (b) shows the sheet resistance results.

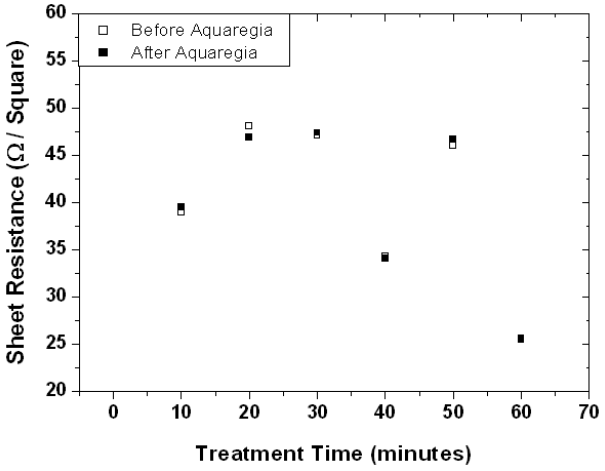

Fig. 1(a). Samples before and after of aquaregia treatment for sheet resistance vs. treatment time.

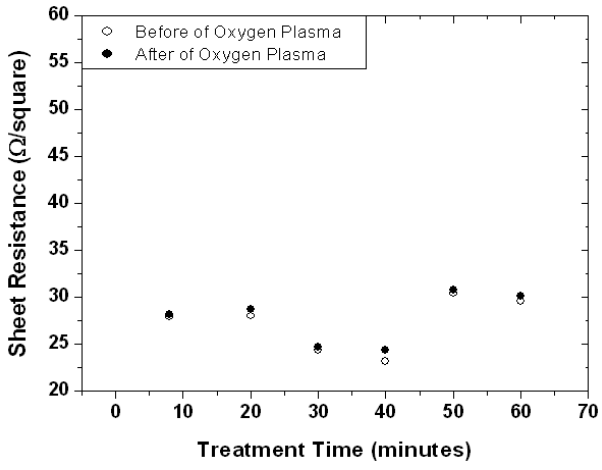

Fig. 1(b). Samples before and after of oxygen plasma treatment for sheet resistance vs. treatment time.

In the thickness compared before and after treatments using both techniques was observed also a little variation of the thickness. When the ITO films are treated by oxygen plasma occurs an ion oxygen bombardment on surface causing damage.

This fact may has occurred also for FTOs films, because the thickness is dependent of sheet resistance and electrical resistivity as shown in the relation presented by Kulkarni et al. [14]. In the experiment the chemical attack caused by aquaregia was most pronounced than that oxygen plasma causing a reduction of the thickness. Before of treatments the samples presented color variability with different tonalities already revealing a dispersion of sample-by-sample. For thickness was used one sample for each treatment time with three measurements. The Fig. 2(a) and (b) shows the thickness results.

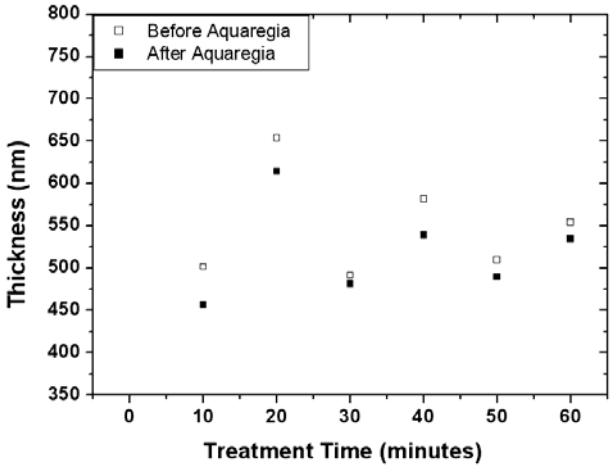

Fig. 2(a). Samples before and after of aquaregia treatment for thickness vs. treatment time.

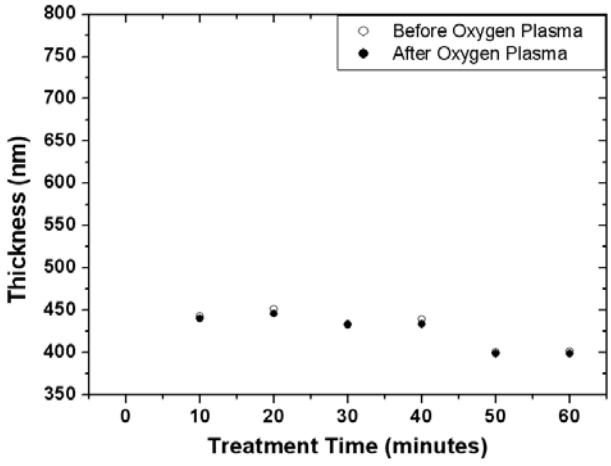

Fig. 2(b). Samples before and after of oxygen plasma treatment for thickness vs. treatment time.

J. S. Kim et al. [15] related although of Hall effect measurements that the high carrier concentration is preferred than that large mobility, in order to achieve the same ITO resistivity. This characteristic can be a suggestion in results of FTO films too. The increase of carriers concentration for FTO film is a good indicative that occurred increases of work function and this characteristic is much more evident for aquaregia than that oxygen plasma treatment.

Table 1. Hall effect measurement for samples treated by aquaregia and oxygen plasma.

Treatment Techniques	**Treatment Time (minutes)**	**Hall Mobility (cm^2 / V / s)**	**Carriers Concentration ($10^{20}.cm^{-3}$)**	**Electrical Resistivity 10^{-4} (Ω .cm)**
Aquaregia	10	7 ± 1	5 ± 0	2 ± 0
	20	5 ± 1	5 ± 1	3 ± 1
	30	6 ± 1	5 ± 0	2 ± 1
	40	7 ± 1	6 ± 0	2 ± 0
	50	6 ± 2	6 ± 1	2 ± 1
	60	11 ± 2	5 ± 1	1 ± 0
Oxygen Plasma	10	20 ± 7	3 ± 1	1 ± 0
	20	26 ± 7	2 ± 1	1 ± 0
	30	26 ± 8	3 ± 1	1 ± 0
	40	25 ± 14	4 ± 1	1 ± 0
	50	22 ± 7	3 ± 1	1 ± 0
	60	14 ± 4	4 ± 1	1 ± 0
	An Untreated	19 ± 4	3 ± 1	1 ± 0

A. S. Gilmore et al. [16] and Jianping Xi [17] made FTO films by APCVD (Atmospheric Pressure Chemical Vapor Deposition) technique and also found carriers concentration values in the same order of magnitude with a variation in the mobility Hall results. They verified that the thickness of samples can be varied independent of carrier concentration or Hall mobility.

The amount of fluoride mixed with tin oxide changes the electrical parameters of the films investigated by of Hall effect, observed by E. Elangovan et al. [**Error! Bookmark not defined.**] and also on the transmittances of FTOs.

Results of transmittances revealed that the oxygen plasma presents highest and lowest values of 88 to 73 % respectively, related by highest emission peak of emissive polymer (OC_1C_{10}-PPV) and aquaregia of 87 (highest) to 60% (lowest). This variation is due to the doping with fluorine on the tin oxide, but these values are very similar as found by A. Romeo, et al. [18] which produced FTO films for solar cells and also found by E. Elangovan et al [**Error! Bookmark not defined.**]. The Fig. 3(a) and (b) shows the transmittance results.

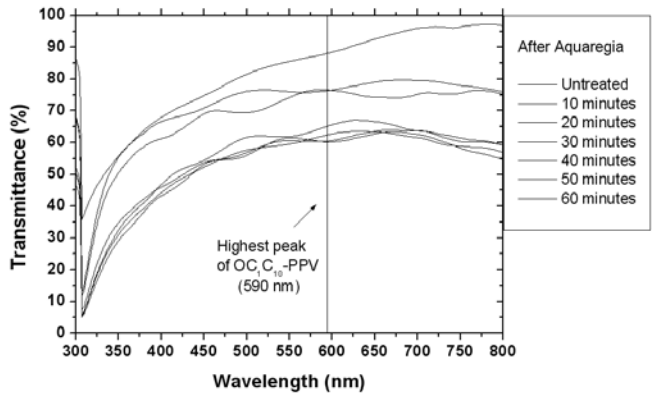

Fig. 3(a). Samples treated by aquaregia for wavelength vs. transmittance.

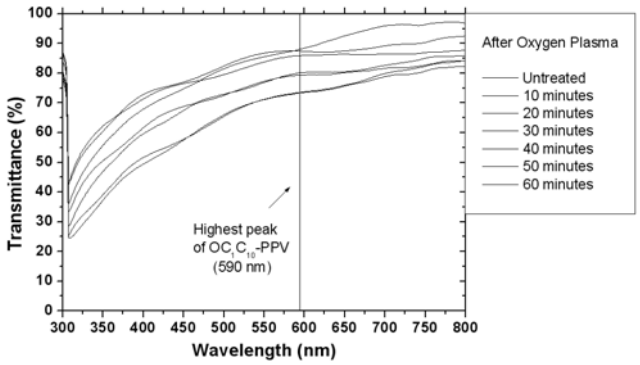

Fig. 3(b). Samples treated by oxygen plasma for wavelength vs. transmittance.

The AFM images revealed changes on superficial roughness of samples by oxygen plasma and aquaregia treatments compared with an untreated sample:

Untreated: 42 nm
Oxygen Plasma: 10 minutes – 27 nm / 60 minutes – 32 nm
Aquaregia: 10 minutes – 37nm / 60 minutes – 19 nm

The Fig. 4(a) to (e), shows the roughness results.

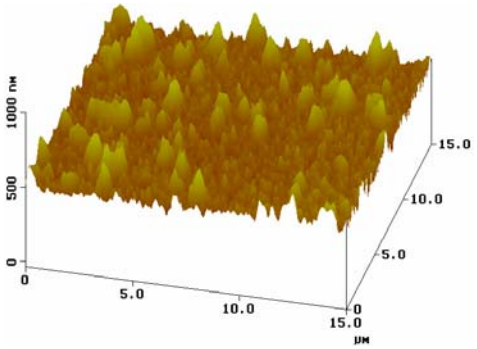

Fig. 4(a). Roughness of untreated sample.

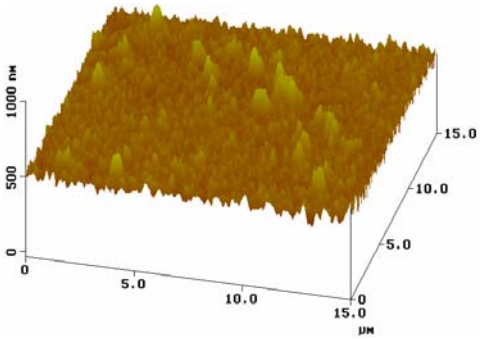

Fig. 4(b). Roughness of treated sample with oxygen plasma by 10 minutes.

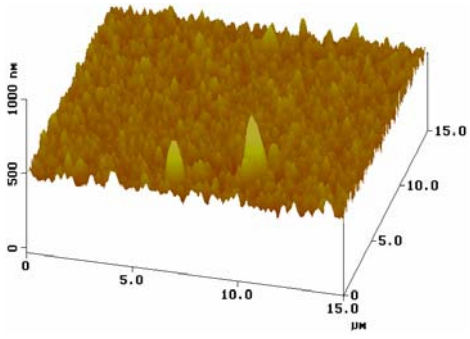

Fig. 4(c). Roughness of treated sample with oxygen plasma by 60 minutes.

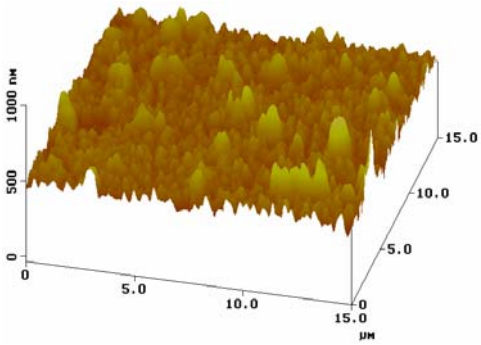

Fig. 4(d). Roughness of treated sample with aquaregia by 10 minutes.

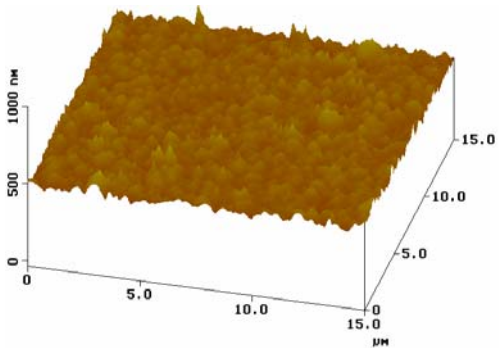

Fig. 4(e). Roughness of treated sample with aquaregia by 60 minutes.

For aquaregia treatment was found to decreasing of roughness increasing the treatment time that can be explained due to the solution in the first minutes has its corrosive properties much more intense [19] attacking quickly the FTO films, but it is known that its corrosive properties decrease by increase of treatment time and consequently the attack is less aggressive. The FTOs treated by oxygen plasma, it is known that the collision caused by oxygen ion bombardment on the surface increase the roughness [20] increasing the treatment time and consequently, there is an increase of superficial area. The fact of an untreated sample presents roughness much more elevated can be due to that it was chosen at randomly between very samples with different values of roughness. Figs. 5 and 6 shows most significant results of I vs. V curves for devices using architecture: FTO/PEDOT:PSS/OC_1C_{10}-PPV/Al treated by oxygen plasma and aquaregia treatments respectively.

For devices with FTO treated by 20 minutes of oxygen plasma presented the lowest threshold voltage than that 10 minutes and also untreated sample. It was verified that these devices presented a resistivity behavior due to the range of large curves.

In devices with aquaregia was observed that 30 minutes presented the lowest threshold voltage than that 40 minutes and also an untreated sample. These devices presented no resistivity behavior with similar aspect of I vs. V curves of PLEDs devices.

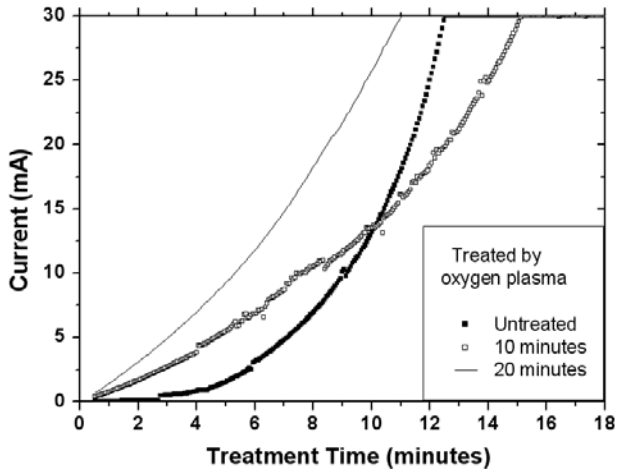

Fig. 5. I vs. V curves for PLEDs devices using FTO treated by oxygen plasma.

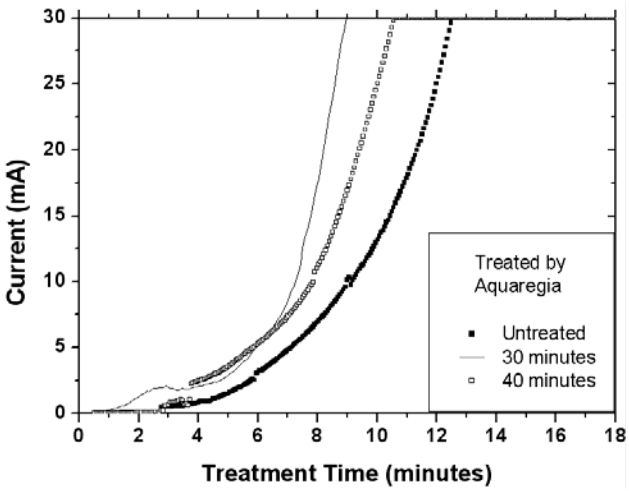

Fig. 6. I vs. V curves for PLEDs devices using FTO treated by aquaregia.

4. Conclusion

Samples presented random sheet resistance values before of treatments. After treatments for each sample was verified though of thickness measurement a decrease much more pronounced for aquaregia than that oxygen plasma. In Hall effect measurements with carriers concentration and electrical resistivity was observed a significant increase compared with oxygen plasma and an untreated sample. Transmittance results of samples showed also influences caused by both techniques, but it did not revealed damage on the transparency. Roughness images by AFM revealed that the aquaregia attacked much more the FTO films during the first 10 minutes, but the elevation of treatment time to 60 minutes decreased its corrosive properties attacking less the surface.

For I vs. V curves of oxygen plasma devices was verified that the PLEDs presented a resistivity behavior (format curves) and aquaregia revealed similar curves of PLEDs devices presenting lowest threshold voltage for sample treated by 30 and consequently 40 minutes compared with an untreated sample.

Acknowledgements

Thank to Ministério da Ciência e Tecnologia, CNPq, Instituto Multidisciplinar de Materiais Poliméricos, Fapesp by financial support, MBE (Molecular Beam Epitaxy Laboratory) by Hall effect measurements, LSI (Laboratório de Sistemas Integráveis) by AFM images, Departamento de Engenharia de Materiais and Laboratório de Microeletrônica of Universidade de São Paulo by sheet resistance, transmittance and thickness measurements and installations.

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- Sensor instrumentation;
- Virtual instruments;
- Sensors interfaces, buses and networks;
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