Influence of Electrical, Chemical and Morphological Properties of Inorganic/Organic Interface on Light Emitting Devices Performance

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Summary: studies on the influence of chemical and physical treatments on the properties of indium–tin oxide (ITO) thin films are reported. The ITO films are utilized as transparent anodes of organic light-emitting diodes (OLEDs) incorporating poly(9,9-dihexyl-9H-fluorene-2,7-diyl) (PF6) as the hole transporter material and 8-hydroxyquinoline aluminum salt (Alq3) as emitter material. Chemical (HCl, piranha solutions), thermal (vacuum annealing), physical treatments (oxygen plasma, UV ozone) and combined treatments are studied. First, ITO layers with different treatments are characterized by using four point probe method, contact angle measurement, X-Ray diffraction (XRD), surface profilometer, scanning electron microscopy (SEM), UV-Vis-IR transmittance. Later, electrical and optical properties of OLEDs with treated ITO as anode are extensively investigated.

Keywords: contact angle; electrical properties and measurements; electroluminescence; ITO surface treatments; OLED

Introduction

The performance of organic devices has motivated a vast research activity in the field of solid-state physics and in that of the technology of organic molecules. Although a large variety of transparent conducting oxides (TCO) are known, the anode of organic light emitting diodes (OLEDs) is, in the most of the cases, a thin layer of a mixed indium–tin oxide (ITO). ITO is by far the common choice, due to the commercial availability, its good transparency in the visible range and low resistivity. Therefore, the relationship between the properties of ITO modified by various surface treatments and the device performance has been widely studied.[1–6] Indeed, these treatments can increase ITO work function, probably due to surface carbon removal, creation of surface dipoles, changes in ratio of surface constituents. This paper is our contribution for a better understanding of some effects of ITO treatments on OLED performance. Therefore, a series of ITO surface treatments have been performed, i.e.: chemical (HCl, piranha solutions), thermal (vacuum annealing), physical treatments (oxygen plasma, UV ozone) and combined treatments. First, ITO layers with different treatments have been characterized by using four point probe method, contact angle measurement, X-Ray diffraction (XRD), surface profilometer, scanning electron microscopy (SEM) and UV-Vis-IR transmittance. Later, OLED with structure ITO/poly(9,9-dihexyl-9H-fluorene-2,7-diyl) (PF6)/8-hydroxyquinoline aluminum salt (Alq_3)/Al have been fabricated on these ITO and their performance investigated.

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Experimental Part

We have used six different sets of processing techniques for treating the surface of ITO substrates, before spin coating the polymer films i.e.: acid treatment by HCl solution and by piranha solution, thermal treatment by vacuum annealing, physical treatments by oxygen plasma and by UV ozone, and combined cleaning process. Commercial indium tin oxide glass substrate has been purchased by Delta Technologies and cut into 50 × 50 mm samples. HCl solution, 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 times ranging by 5 to 30 min. More, piranha solution, H_2SO_4: H_2O_2 4:1 (v/v) solution has been prepared for acid treatment and the substrates have been dipped in the solution at room temperature for 5 min. For oxygen plasma treatment, pure oxygen has been introduced into a plasma etcher chamber with a 30 sccm flow and at a pressure of 0.200 mbar, at room temperature. The applied forward and reflected powers have been 60W and less than 1W respectively. For UV ozone treatment, the substrates have been exposed to a 50W UV light source (wavelength range 250–300 nm) from 10 cm distance under oxygen flow for times ranging by 5 to 45 min. As combined treatments, we have used UV ozone and HCl solution as these two treatments were reported by many authors as the promoters of highest efficiency and luminance and lowest drive voltage.[7,8] For all the treatments, the ITO substrates have been then rinsed in distilled water and finally dried with nitrogen. For each treatment, we have optimized the treatment time individually. ITO substrate properties without any treatment have been used as a reference. After each treatment, an extensive characterization has been performed for each sample for inspecting its surface properties.

Contact angle measurements have been performed by using a 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 angles measurements is ±2 °. Sheet resistance has been measured with the four-point probe. The crystal structure of some ITO films has been characterized by X-ray diffraction (XRD) measurements carried out in classical θ-2θ configuration with an MPD-XPERT (Philips) diffractometer using a Cu Kα radiation source. The film thickness and roughness have been evaluated by a KLA Tecnor P-10 Surface Profiler. The UV-vis and near-IR optical transmittance has been performed with Perkin-Elmer lambda 900 spectrophotometer.

The ITO substrates treated, as described above, have been used to fabricate double layer devices. For LED fabrication we have carried out the ITO patterning by conventional photolithography to define the OLED geometry. PF6 is a blue emitting polymer and soluble in common organic solvents. It has been used as a hole-transporting material and spun over the substrates at 1000 rpm form a 1.0% (w/w) chlorobenzene solution for 30 s. After deposition the films 700 Å thick have been backed in vacuum at 50 °C for 3h. The spin coating process has been developed using a Brewer Science Model 100 Spin Coater. Tris (8-hydroxy)quinoline aluminum (Alq_3) used as electron-transporting and emitter material, has been deposited by thermal evaporation. The process has been performed in High Vacuum Chamber and the base pressure was 10^{-7} mbar. The layer thickness is 600 Å. Al cathode, 2000 Å thick, has been evaporated as a final layer. The active device area is 12.57 mm^2.

Current-voltage (I–V) characteristics have been measured with a Keithley 4200 Semiconductor Characterization System in constant voltage mode with logarithmic increment steps and a delay time of 200 ms before each measurement point. The spectral radiance has been monitored using a calibrated spectroradiometer by Optronics *OL770* and it has permitted the calculation

Table 1.
Summary of the ITO parameters with different surface treatments.

ITO treatment	Time (min)	*R*s (Ω/□)	RMS roughness (nm)	Spikes (nm)	Surface energy (mJ/m^2)	Polarity X*p*
Untreated	/	10,55	2,4	17,2	32,56	0,49
UV ozone	30	10,00	3,0	24,9	34,40	0,52
HCl (12%)	15	12,31	3,1	14,5	42,36	0,31
UV ozone – HCl (12%)	30 + 15	11,13	2,6	9,4	46,60	0,51
Annealing 200 °C	1440	10,33	2,5	11,9	36,34	0,48
Oxygen plasma	5	10,44	1,8	11,0	38,72	0,65
piranha	15	10,03	4,5	10,7	63,08	0,58

of the chromaticity coordinates (CIE) of the Alq$_3$ emission: $x = 0.3204$, $y = 0.5526$, $z = 0.1236$. All the characterization has been performed in air.

Results and Discussion

We have investigated the effect of different surface treatments on the ITO properties. In Table 1 the results of sheet resistance measurements, surface roughness, ITO spikes, surface energy and its polar component for all the analyzed ITO layers are summarized.

UV ozone (30 min) and *piranha* (15 min) are the only treatments which result in a valuable decreasing of sheet resistance. These results are consistent with a lower near-IR transmittance (Fig. 3) and reveal an increased carrier concentration. All other treatments result in increased sheet resistance.

In according to Kim et al.[2–4] we have obtained that oxygen plasma only result in lowest root-mean-square surface roughness (RMS). Surface roughness of ITO is instead markedly increased by piranha and HCl (6%) treatment. Moreover, we have obtained that ITO spikes dimensions are lowest for oxygen plasma and piranha treatment. Piranha etch is a powerful oxidizer and react violently when placed in contact with organics that are readily oxidized.[9] We suppose that the spikes dimensions could be more important than RMS value for device performances. Indeed, the reduction of spikes dimension is very important to avoid the shorting between the two electrodes, which subsequently result in the dark spots formation. As some authors have pointed out the spikes influence very strongly the device degradation.[10,11]

The wettability analysis of the ITO layers is also very important to understand interface properties. A substrate with a higher surface energy than surface tension of the spin coated solution induces a better wettability and a smaller contact angle. On the other hand, the contact angle should decrease as the quantity of organic residues decreases and the surface energy increases. In detail, the contact angle (θ) between a flat surface and a liquid droplet is given by the Young equation as follows: $\gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cos\theta$, where γ_{SV}, γ_{SL}, and γ_{LV} denote the surface tensions between the various interfaces (S = solid, L = liquid, V = vapour). We have estimated a value of 30 mJ/m^2 in surface tension for the employed PF6 chlorobenzene solution that is lower than the γ_{SV} of employed ITO layers. For the ITO layers, we have observed that all treatments produced an increasing of γ_{SV} and the highest value was obtained for *UV ozone + HCl* treatment. This reveals a rather effective organic residues decreasing. Moreover, we observe a more uniform spreading of thin films of

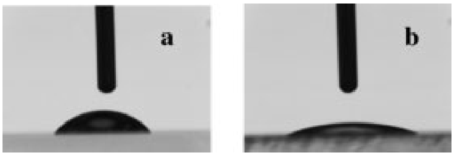

Figure 1.
Contact angle of a chlorobenzene drop on a ITO layer before (a) and after (b) a UV ozono + HCl treatment.

the polymer solutions for the surfaces with the highest polarities (Fig. 1).

We have analyzed the polarity (Xp) as the ratio of the polar component to the total surface energy and we have obtained a decrease of polarity only for HCl treatments.

The XRD patterns of treated ITO layers are shown in Fig. 2. We have analyzed only the samples that could have changed their crystalline structure, i.e.: *annealed* and *UV ozone*. All samples show a cubic structure with diffraction peaks corresponding to (2 1 1), (2 2 2), (4 0 0), (4 1 1) and (6 2 2) in according to other authors.[10] It can be seen that no modification occurs due to the treatments because we have started from a very perfect crystalline structure.

The transmittance spectra in visible and near-IR regions for the ITO layers are shown in Fig. 3. The transmittance in visible light range of ITO layer is closely related with the grain-boundary scattering as discussed by Wu and Chiou.[11] In our study, for wavelength below 1000 nm, the transmittance of the treated samples remains very similar to that of an untreated ITO layer, suggesting that the optical quality of the material in the visible range was not altered by the treating processes. In near-IR region, the carrier absorption becomes important for the transmittance of the ITO layers. We can see that in this range, the transmittance of the ITO layers submitted to *UV ozone* (30 min) treatment is decreased and it can be concluded that this layer have a higher carrier concentration.

All the observed ITO properties are related to the performances of OLEDs with the treated ITO layers as anode. The I–V characteristics for manufactured OLED reveal a clear trend in according with the obtained γ_{SV} values: a higher γ_{SV} induces a better electronic contact and it produces an increased current flow at the same applied voltage. In fact, the combined *UV ozone – HCl* and only *HCl* treatments give the highest operational stability and the lower turn on voltage as we can see in Fig. 4. Further, OLED electroluminescence has been evaluated. Both previous treatments have given highest brightness efficiency

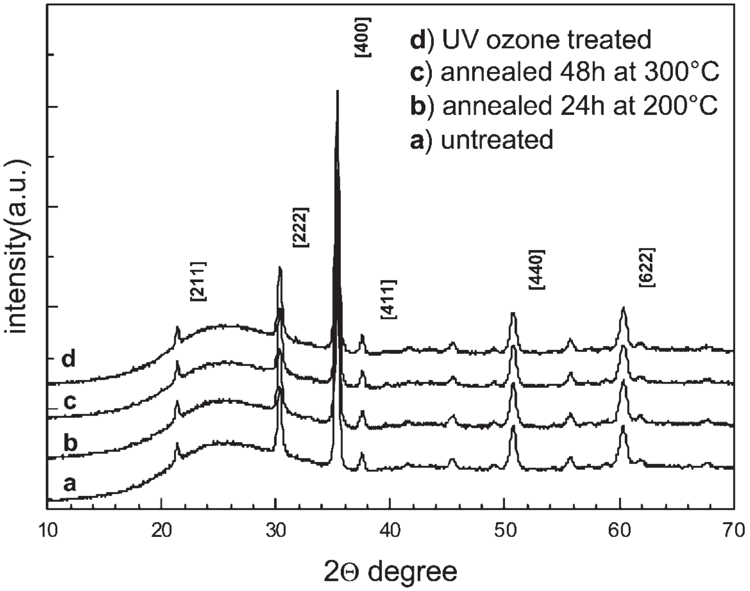

Figure 2.
XRD patterns for different surface treatments of ITO.

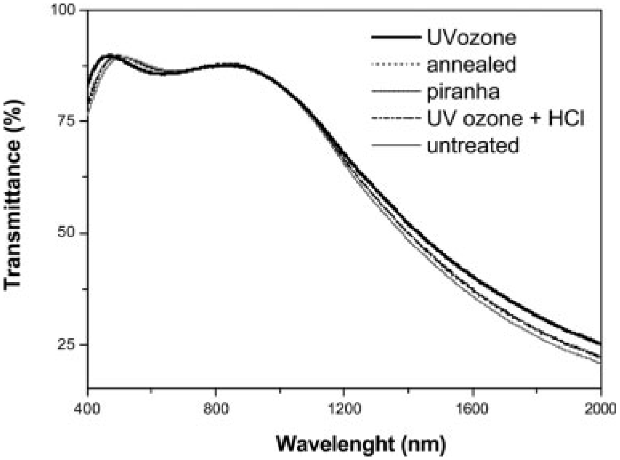

Figure 3.
Transmittance vs. wavelength dependence for different surface treatments of ITO.

(Fig. 5) too. We have also to consider that the only HCl treatment slightly larger surface roughness increased the contact surface between the ITO substrate and the polymer film. The subsequent result is an improved hole injection.

Analyzing the obtained results, we deduce that higher surface energy obtained for these treatments is beneficial for the fabrication of polymer LEDs as it provides a better adhesion of the polymeric hole transporter and reduces the interfacial tension between the hole transporter material and substrate. The result is a better electronic contact between the two materials with a concomitant improvement of charge-carrier injection through the interface, and therefore, of the LED performance. The effect of the increased surface energy is observed for almost all fabricated OLED and the effect is amplified by a high polar component. However, despite the high γ_{SV} of piranha treatment we have observed a decrease of LED performance probably due to a too high value of ITO surface energy compared to the value of the surface tension of the employed chlorobenzene solution.

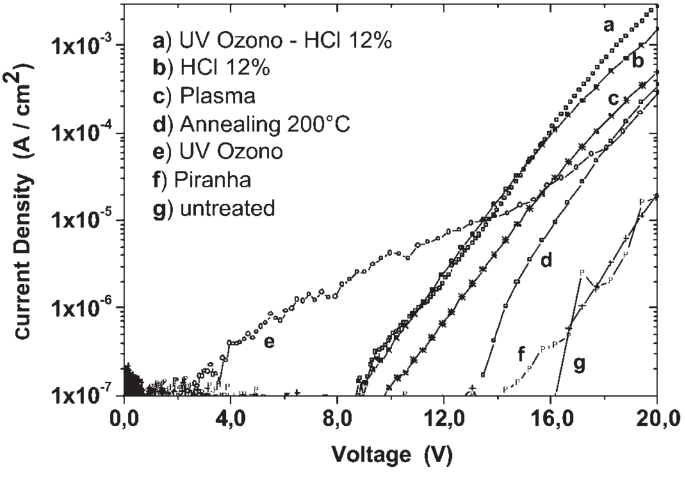

Figure 4.
Current (density) vs drive voltage for ITO/PF6/Alq3/Al OLEDs for different surface treatments of ITO.

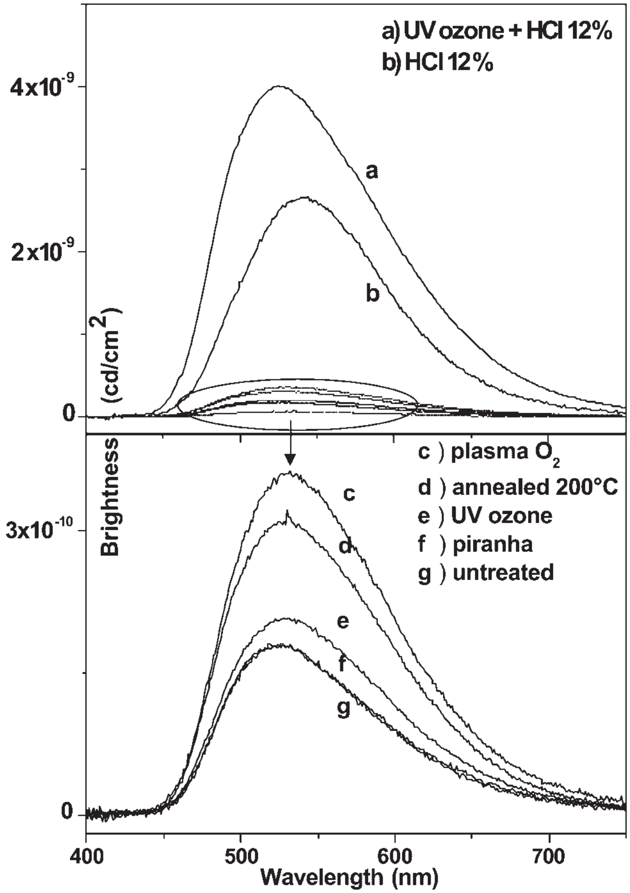

Figure 5.
Brightness vs wavelenght for ITO/PF6/Alq3/Al OLEDs for different surface treatments of ITO.

Our results indicate that the work function and the sheet resistance of ITO are not the only main factors governing the carrier injection and the device performance. We suppose that is also very important to increase the surface energy first and the polarity later of the anode layer to obtain a better electronic contact. The reduction of spikes dimension is also important to assure a homogeneity in current distribution.

Conclusions

In this work we have investigated the effects of acid, thermal and physical treatments by on ITO layers. The most significant changes have been observed for UV ozone + HCl treated samples. The electro-optical characteristics of diodes using PF6 as hole transporter material and Alq3 as an active layer have been significantly improved by this treatment. The obtained improvement could be explained in terms of enhancement of the hole injection from the anode, favoured by a higher surface energy and by a decrement of the potential barrier height. A higher surface energy provides a better adhesion of the polymer and reduce the interfacial tension between the hole transporter material and substrate. A change in morphology with a reduction of spikes dimension has been also obtained for this combined treatment.

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