

Low cost UV-Ozone reactor mounted for treatment of electrode anodes used in P-OLEDs devices

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Abstract

Low cost UV-Ozone reactor using a high pressure mercury vapor lamp of 80 watts without outer bulb showed good results for treatment of ITO films used as anode electrode in the assembly of P-OLED (polymer-organic light emitting diode) devices. This study revealed 20 minutes as effective treatment time and it was verified also that the effect of UV-Ozone treatment loses its efficiency as the elapsed time increases. It was analyzed with measurements of contact angle using a droplet of PEDOT:PSS polymer. P-OLEDs devices were mounted with architecture: ITO/PEDOT:PSS/PVK/Alq₃/Al. The PVK polymer was diluted in organic solvent of 1,2,4-trichlorobenzene with concentrations of: 5, 10, 20 and 30 mg/mL. Results revealed better performance of P-OLED devices for concentration of 5 mg/mL resulting in lower threshold voltage, elevation of electrical current and similar diode curve.

Keywords: ITO film, PVK, P-OLED, HPMVL, UV-Ozone.

1. Introduction

Layer-by-layer assembly of monochromatic P-OLED (polymer-organic light emitting diode) devices starts with a TCO (transparent conductive oxide) films chemical pre-cleaned, they are used as electrode anodes deposited on transparent substrates. This step is complemented by oxidative treatment using UV-Ozone technique^[1,2]. This treatment on the surfaces of the TCO films changes their chemical structures removing carbon and hydrocarbon groups contributing to improve the performance of devices^[3]. The energy surface is modified by removal of these contaminants increasing the physical contact in the interface between the surface of TCO film and polymeric layer (deposited in posterior step)^[4]. The treatments provide also the increase of the TCO workfunction decreasing the interface barrier to injection of holes between the TCO film and adjacent polymer layer promoting better charge carriers then there is a decrease of the threshold voltage of devices^[5,6].

After UV-Ozone treatment a polymer known as HTL (hole transport layer) is deposited on TCO^[7]. It will inject holes inside the subsequent deposited layer, an emissive polymeric material diluted in any organic solvent^[8].

On the emissive material is deposited the ETL (electron transport layer) formed by organic material that will inject electrons coming from electrode cathode film formed by metal deposited on top^[9]. The last step is the encapsulation to avoid chemical attack by oxygen and moisture^[10].

In this work, studies of two processes required in the P-OLED assembly to improve the performance of devices, good stability of material and low voltage operation are reported^[11]. First, a low cost UV-Ozone reactor assembly due to the lack of manufacturers in Brazil, and second, the use of an organic solvent in different concentrations for the polymer dilution^[12].

2. Materials and Methods

2.1 Assembly and analyses of UV-Ozone reactor

A UV-Ozone reactor was built with high pressure mercury vapor lamp of 80 watts and ballast supplied by Osram Company. The outer bulb was removed to obtain the discharge tube that generates the ultraviolet rays for the production of ozone from oxygen in air^[13]. A metallic box with dimensions: 18.5 × 20.0 × 20.0 cm and two fans held at the lid were used. These fans contribute in the ozone homogenization and help cool the lamp temperature avoiding a possible change of the ozone concentration produced. The Figure 1a shows the image of reactor and Figure 1b shows the scheme of the complete UV-Ozone apparatus.

A monitor manufactured by IndevR 2B Technologies, 205 model was used for the analyses of ozone produced from 0 to 30 minutes^[14]. This procedure was repeated for five times and for each analysis the lamp was cooled to room temperature. A plastic tube with length of ≈1.5 m

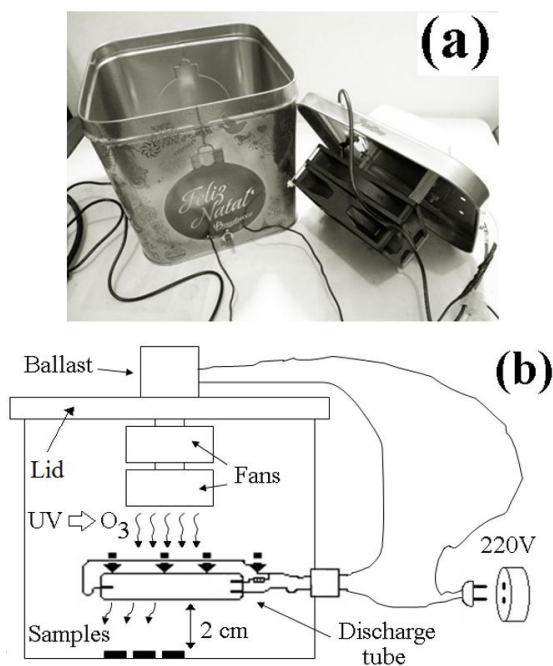


Figure 1. (a) UV-Ozone reactor; and (b) all components used in the UV-Ozone reactor apparatus.

and diameter of ≈ 7 mm was connected at the back of the monitor and the tube tip (inserted underneath the box) was placed ≈ 2 cm from the lamp to collect the ozone produced.

A spectroradiometer manufactured by LuzChem, SPR-03 model connected by optical fiber to the computer, was used to collect the wavelengths produced by the lamp^[15].

2.2 Analyses of TCOs

TCO thin films (ITO - indium tin oxide of $15 \Omega/\square$ deposited on glass) were irradiated at different times in the UV-Ozone reactor and eight droplets of HTL (PEDOT:PSS polymer) were placed on the surface with a micro syringe and contact angle analyses were conducted^[16]. The literature reports that a hydrophilic characteristic of ITO films decreases the droplet spreading without treatment^[17]. After the UV-Ozone treatment, TCO films surface starts adsorbing chemical elements from atmosphere as carbon and/or hydrocarbons decreasing P-OLEDs performance^[18]. UV-Ozone irradiation helps oxygen atoms complete the chemical bonds removed by contaminants from surface resulting in better adherence of the polymer^[19].

A webcam manufactured by Philips Company, SPC 530NC model coupled to lens with 30x magnification was used for contact angle measurement and the images, without distortion, produced by software were printed on paper^[12]. Contact angles were obtained from left and right side measurements of PEDOT:PSS droplet semi-circles using ruler and protractor to obtain tangent lines. The Figure 2a shows the contact angle apparatus and 2(b) the methodology used.

Before contact angles measurement, the surfaces were exposed to UV-Ozone for: 5, 10 and 20 minutes including an untreated sample used as reference. The angle of PEDOT:PSS

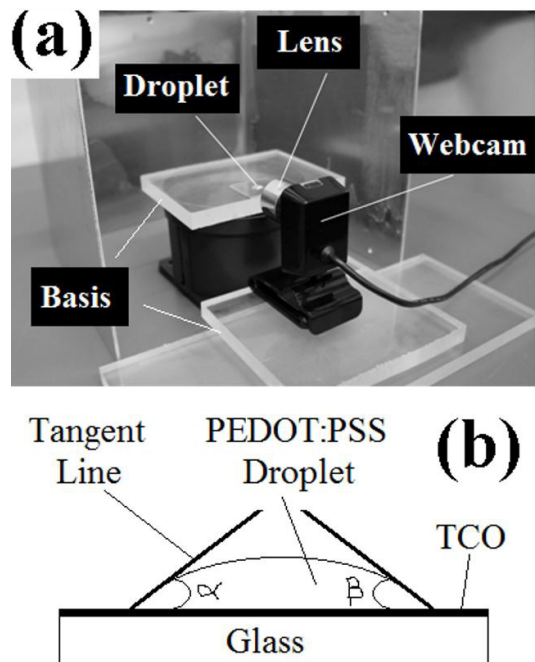


Figure 2. (a) Contact angle apparatus; (b) method used to obtain the contact angle.

droplets on the film were immediately measured. Another study was carried out to obtain the “durability” of cleaning (or treatment time), where the TCOs were treated for a specific time and left in the Petri dishes without lid at room temperature.

The contact angles of the samples were measured immediately after exposition to 10 minutes elapsed time. The irregularities of the analyses were calculated using the equation:

$$Irr = (3 \times sd \times 100\%) \div artm \quad (1)$$

where: Irr is the irregularity, sd is the standard deviation and artm is the arithmetic mean.

2.3 Assembly and analyses of P-OLEDs devices

P-OLED architecture was mounted using: (a) ITO films cleaned with water and common detergent, then the samples were immersed in isopropyl alcohol and acetone by 30 minutes each using ultrasonic bath; (b) UV-Ozone treatment for a specific time; (c) spin-coating deposition of PEDOT:PSS (HTL supplied by Sigma-Aldrich) at 1,700 rpm and dried at 80 °C for 20 minutes; (d) spin-coating deposition of PVK polymer (supplied by Sigma-Aldrich) diluted in 1,2,4-trichlorobenzene (supplied by Tedia) at 1,700 rpm with: 5, 10, 20 and 30 mg/mL concentration and dried at 50 °C for 60 minutes; (e) evaporation of Alq₃ (ETL) synthesized at laboratory; (f) evaporation of electrode cathode formed with aluminum (supplied by Balzers) and (g) encapsulation inside the glove box system at room temperature and humidity below 20% in nitrogen atmosphere. Devices were sealed using glass blades (dimension of 1.7×1.7 cm) with calcium oxide (CaO) layer and double-sided rubber

tape, VHB model (supplied by 3M Company) placed at the edge of the samples^[20-22]. Four devices of each sample were built at the same time. Each device presented active area of 3.0×3.0 mm. A power source was adjusted for the polarization of the P-OLEDs from 0 to 20 V and the respective electrical current was obtained^[23]. The Figure 3a shows the complete architecture of P-OLED device mounted and the Figure 3b shows the sample with four devices.

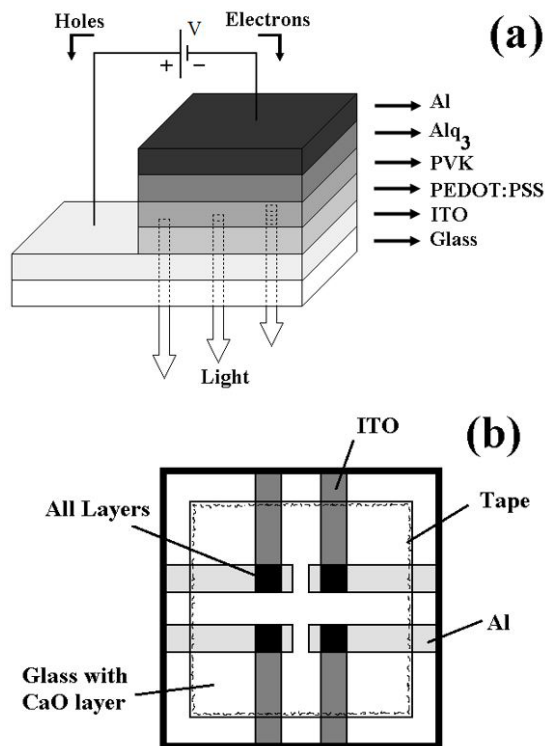


Figure 3. (a) Complete architecture of P-OLED; and (b) sample mounted with four devices.

3. Results and Discussions

Results in the Figure 4a revealed a fast increase of ozone concentration in the first minutes, during this period the lamp is still heating and after ≈ 12 minutes the ozone concentration is more stable ≈ 1.3 ppm (the literature does not report the minimum ozone concentration requirement for the best condition of UV-Ozone used in TCO treatments). The reactor geometry and the lamp operation temperature are very important factors for the ozone production, because these parameters contribute to find the specific time of stabilization transforming the oxygen confined in ozone^[21]. The reactor revealed efficient gas confinement without escaping to ambient during leakage tests. Ozone concentration near the reactor was monitored and it showed similar results to those found in the laboratory ambient with 0.006 ± 0.002 ppm. For example, the literature reports that for papers storage environment the maximum limit of ozone concentration (defined ozone as pollutant gas) is up to 0.010 ppm and the World Health Organization (WHO) indicates that the ozone concentration above of 0.035 ppm causes health problems in human^[17,24].

The literature relates also that the radiation below of 243 nm forms ozone (O_3) and radiation between 240 and 320 nm breaks the ozone molecule and in this case, the lamp spectrum in the Figure 4b revealed ultraviolet emission (UV-A from 315 to 400 nm, UV-B from 280 to 315 nm and UV-C from 100 to 280 nm)^[25,26].

For the untreated sample, the surface of TCO film presented a hydrophobic characteristic (as expected), for samples treated mainly for 20 minutes, a better droplet spreading on the TCO film was observed with relative contact angle decrease and increase of the contact area between the polymeric layer and the TCO surface improving the charge carriers transport promoted by improved chemical bonds. Figure 5 shows the images of PEDOT:PSS droplets on the untreated ITO film and ITO treated for: 5, 10 and 20 minutes. Arithmetic mean, standard deviation and irregularity are reported in Table 1.

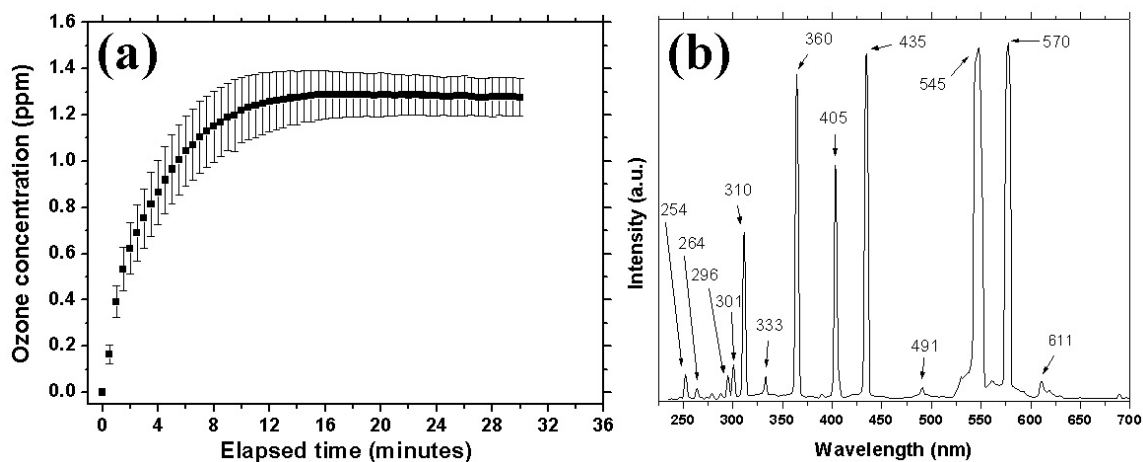


Figure 4. (a) Ozone concentration vs. elapsed time for reactor apparatus; and (b) spectrum of the high pressure mercury vapor lamp of 80 W without outer bulb.

The study carried out by Satoru Yoshida found up to 35 degrees difference between the untreated and treated ITO films deposited on PET (polyethylene terephthalate) using the same measurement method^[27].

To analyze the “durability” of the UV-Ozone treatment, samples were irradiated by 20 minutes and placed in Petri dishes then the contact angles measured from immediately after exposition to 10 minutes elapsed time. The results revealed a significant influence of possible atmospheric elements on the TCO immediately after treatment. Figure 6 shows the contact angles of PEDOT:PSS droplets on the ITO films

Table 1. Results of contact angle measurements for untreated and treated for: 5, 10 and 20 minutes with arithmetic mean, standard deviation and irregularity.

	untreated	5 minutes	10 minutes	20 minutes
Arithmetic Mean ± Standard Deviation (degree)	55 ± 3	54 ± 3	38 ± 3	37 ± 2
Irregularity (%)	15	19	23	13

treated for 20 minutes and analyzed from immediately after exposition to 10 minutes, including the untreated sample.

The Figures 7a to 7d show the I-V (current-voltage) curves of P-OLEDs with PVK diluted in 1,2,4-trichlorobenzene at concentrations of: 5, 10, 20 and 30 mg/mL, respectively.

The I-V curves of P-OLEDs in the Figure 7a mounted with 5 mg/mL concentration solution presented threshold voltages between 10 and 11 V (obtained by curve imaginary tangent line) and electrical current up to 100 mA (the elevation of electrical current is necessary to the light emission increase). A hypothesis for the poor performance in devices mounted with: 10, 20 and 30 mg/mL solution in the Figure 7b to 7d respectively, showed irregularities in curves of diode or increase of voltages with an electrical current up to 50 mA. This aspect can be explained by discontinuity, where incomplete chemical bonds in the polymer causes difficulty in the charge carriers transport increasing the PVK electrical resistance and causing, consequently, increases of the threshold voltage. Another hypothesis is that the all devices emitted light green color and this behavior can be attributed to Alq₃ emission instead of PVK, as this polymer is considered a conductor in the

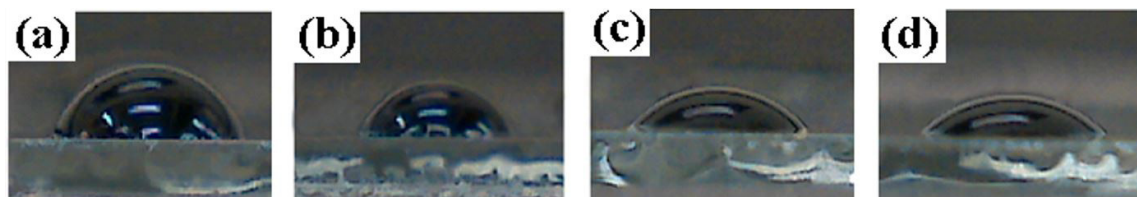


Figure 5. Images of PEDOT:PSS polymer droplets on ITO films: (a) untreated and treated by: (b) 5; (c) 10; and (d) 20 minutes.

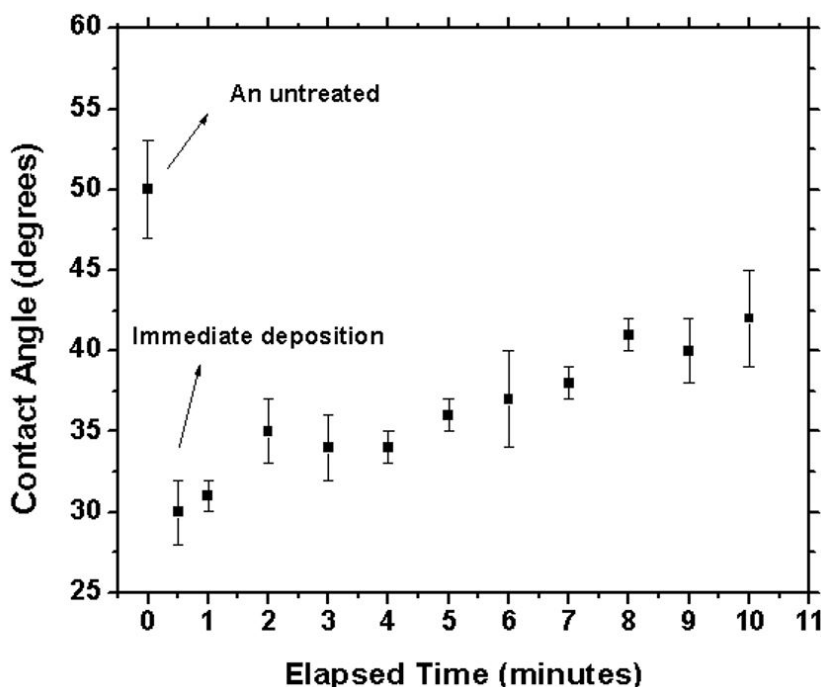


Figure 6. Contact angles of PEDOT:PSS droplets on TCO films treated for 20 minutes and analyzed from immediately after the exposition to 10 minutes, including the untreated sample.

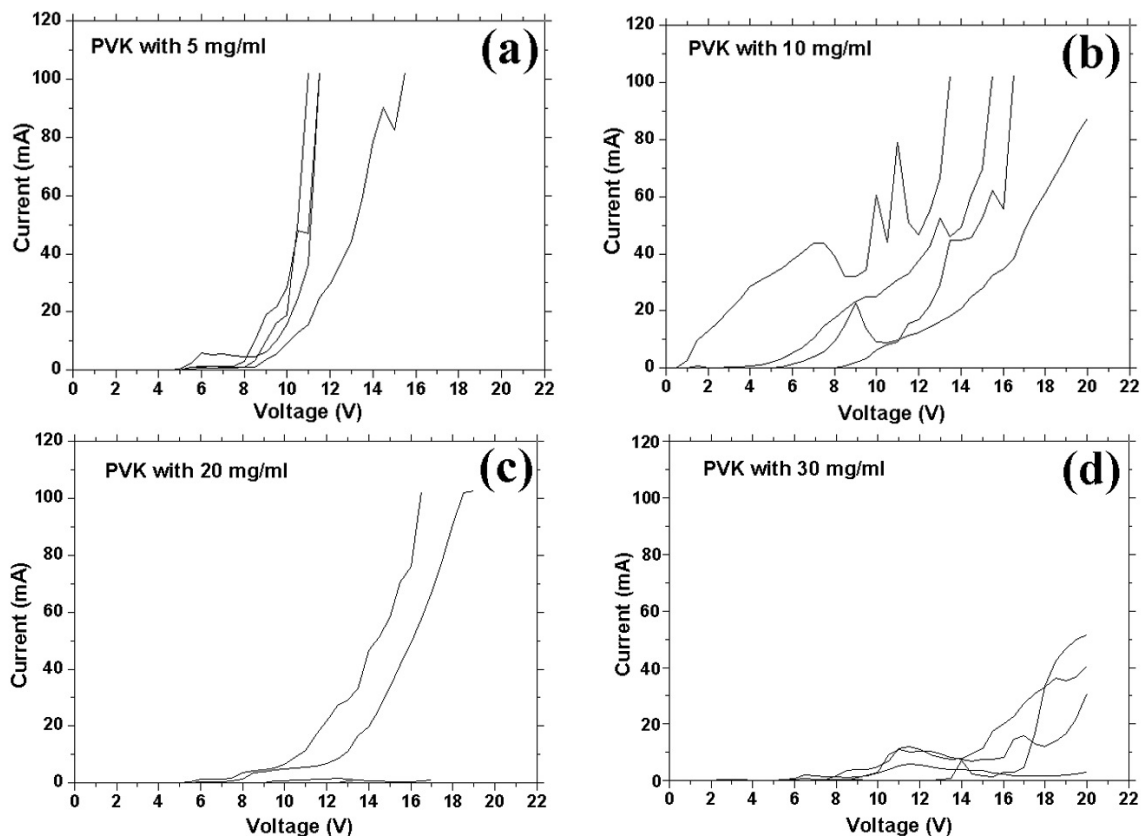


Figure 7. I-V curves of P-OLED devices with PVK diluted in 1,2,4-trichlorobenzene at concentrations of (a) 5; (b) 10; (c) 20; and (d) 30 mg/mL.

literature^[28]. The study carried out by Erick Vendruscolo Guerra using this same architecture, but without Alq₃ layer revealed no luminance in devices. In other devices he used also a different material called Butyl-PBD as ETL and light blue emission was observed^[29,30].

4. Conclusions

The UV-Ozone reactor mounted with modified high pressure mercury vapor lamp of 80 W produced stable ozone by elapsed time from ≈ 12 minutes. In this case, the confined oxygen of the air into reactor (without escape to ambient) and some peak of wavelengths in the range of UV produced by lamp contribute to ozone formation has been mentioned by literature. The analyses of contact angle revealed that the ITO films presented better results for treatment time of 20 minutes improving the spreading of the PEDOT:PSS droplets on the TCO surfaces compared with untreated sample. The analyses showed also that the treatment efficiency decreases after elapsed time of 1 minute. P-OLEDs devices were mounted using ITO films treated with UV-Ozone by 20 minutes and architecture: glass/ITO/PEDOT:PSS/PVK/Alq₃/Al. The devices showed better performance of PVK polymer diluted in organic solvent of 1,2,4-trichlorobenzene using 5 mg/mL compared with other concentrations analyzed. These devices presented

lower threshold voltage, considerable increase of electrical current and similar curve of diode.

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