EFFECTS OF NANOPARTICLES IN THIN FILMS OF ORGANIC SEMICONDUCTOR MATERIALS

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ABSTRACT

The electronics industry is developing flexible organic devices using flexible organic material such as substrate for the deposition of organic semiconductor materials (OSM). Flexible organic material based in Polypropylene and Polyvinylidene Fluoride were used as substrates for deposition of the OSM based in Polyaniline and Polypyrrole. The ITO layer was deposited between the flexible substrate and OSM for electrical contact in device. The OSM and the flexible substrates were characterized by Spectroscopy UV-Visible (UV-Vis), electrical measurements (EM) and Scanning Electron Microscopy (SEM). The films of polyaniline and polypyrrole prepared with organic solvents were identified after electrodeposited by PANI-X1 and PPY-X1. The results obtained by UV-Vis shows that the PANI-X1 and PPY-X1 does not have displacement of optical absorption for wavelengths greaters after electrodeposition. After 500 hours of electrical testing of devices with only PANI-X1, there was visible growth of nanoparticles in the SEM images due to migration of OSM.

1. INTRODUCTION

The synthesis and application of new organic semiconductor materials for technology development in organic devices have attracted great interest in the scientific community. Currently, the electro-electronic market has the first products using polymer electronics manufactured using organic semiconductors materials, for example, there is the electrochromic devices, organic solar cells, organic batteries, organic transistors, organic light emitting diodes (OLEDs) and Organic Displays [1][2]. The research studies to synthesize and characterize components of this new class of materials are currently in a continuous process of technological advance in the search for new conductive polymers. Thin films made of organic semiconductor materials have attracted the interest of research groups, owing to its enormous potential for application in various industries and the impact that their results can give to technological development. The characterization and application of new techniques for deposition of organic semiconductor materials are the focus of a large number of studies and essentials to reduce production costs this devices [3]. The

developing flexible organic devices using organic materials flexible such as substrate for the deposition of organic semiconductor materials (OSM), is being widely used by the electronics industry in the manufacture of new technological products [4]. The objective of this work is the development of flexibles organic electrodes for the OSM electrodeposition and characterization layer deposited by UV-Vis, MS and SEM.

2. FLEXIBLE ORGANIC ELECTRODES

The Flexible Organic Electrode developed in this work were constructed using as substrate flexible organic material covered on the surface with Indium Tin Oxide (ITO) deposited by sputtering. The ITO has a high conductivity and high transmittance in the visible region of the electromagnetic spectrum which enables to their use, for example as, organic solar cells, gas sensors, anti-glare coatings and electrochromic devices [5]. The flexible substrate, based in Polypropylene (PP) and Polyvinylidene Fluoride (PVDF), used for the electrodeposition of Polyaniline (PANI) and Polypyrrole (PPY) is covered by a layer of ITO with a thickness of 400 nm. The active layer of flexible organic electrode was prepared using PANI and perchloric acid ($HClO_4$) or PPY and perchloric acid ($HClO_4$). This active layer is the Organic Semiconductor Material of the flexible organic electrode developed. The process of electrodeposition of active layer is based on the application of voltage versus time, for obtain a homogeneous layer of thin film. Figure 1 is represented schematically the voltage source, square wave generator and electrodeposition system used.
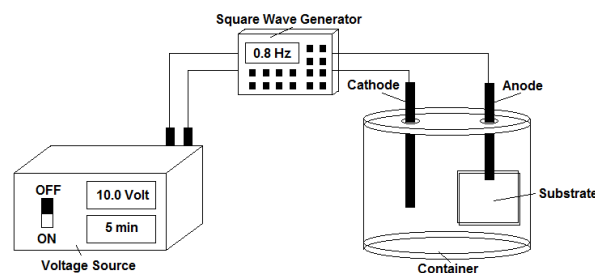

Figure 1. Voltage source, square wave generator and electrodeposition system.

The electrochemical growth of films was used by potential pulse modulated for the square wave, from a value where there was no anodic oxidation of organic material (1.0Volt) and frequency modulation of the potential of 0.8 Hertz. The electrodeposition of PANI solution prepared with perchloric acid (HClO₄), with applying voltage of 10.0 Volts for 5 minutes, resulted in an active layer of PANI-X1 with thickness between 180 nm and 220 nm. The electrodeposition of PPY solution prepared with perchloric acid (HClO₄), with applying voltage of 10.0 Volts for 5 minutes, resulted in an active layer of PPY-X1 with thickness between 150 nm and 200 nm. The electrodeposition of PANI and PPY in acid solvent on the ITO layer originated the active layer of PANI-X1 and PPY-X1. Figure 2 shows the multilayer structure developed for the ODOT. Figure 2 shows the multilayer structure developed for the Flexible Organic Electrode.

The ODOT with active layer of the PANI-X1 were characterized by Ultraviolet-Visible Spectroscopy (UV-Vis), Electrical Measurements and Scanning Electron Microscopy (SEM). Figure 2 shows the multilayer structure developed for the Flexible Organic Electrode, with (a) PANI-X1 and with (b) PPY-X1.
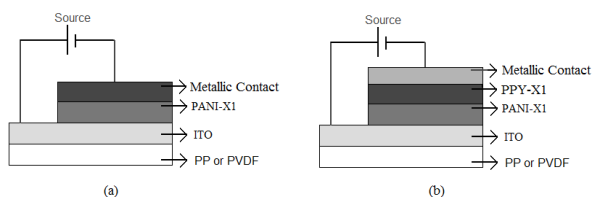

Figure 2. Multilayer structure developed for the flexible organic electrode. (a) PANI-X1 and (b) PPY-X1.

3. RESULTS AND DISCUSSION

The analysis of a sample by ultraviolet-visible spectroscopy is the result in a spectrum of light, obtained by a graph of wavelength or frequency versus the intensity of absorption (absorbance or transmittance) [6]. The absorption spectrum in the spectral region of 200-1100 nm of the electrode flexible organic with PP, ITO and PANI-X1, are shown in Figure 3 (a) and of the electrode flexible organic with PVDF, ITO and PANI-X1, are shown in Figure 3 (b). This result indicates no significant change in the optical absorption spectrum for flexible substrates of PVDF. The absorption spectrum in the spectral region of 200-1100 nm of the electrode flexible organic with PP, ITO, PANI-X1 and PPY-X1, are shown in Figure 4 (a) and of the electrode flexible organic with PVDF, ITO, PANI-X1 and PPY-X1, are shown in Figure 4 (b). This result indicates an increase in optical absorption for flexible substrates of PP or PVDF, due to the presence of the layer of PPY-X1. The deposition of a layer of PPY-X1 on the substrate PP/ITO/PANI-X1 or PVDF/ITO/PANI-X1 resulted in displacement of the optical absorption for wavelengths greaters, as shown in Figure 4 (a) and Figure 4 (b). This

result qualifies the electrode flexible organic of the PP/ITO/PANI-X1/PPY-X1 or PVDF/ITO/PANI-X1/PPY-X1 to be used in organic devices operating in the spectral region of 400-1100 nm.
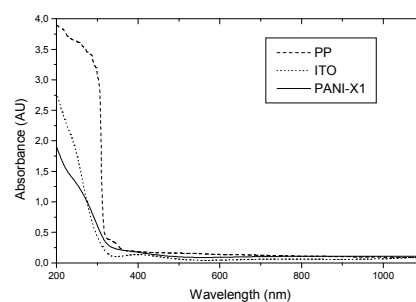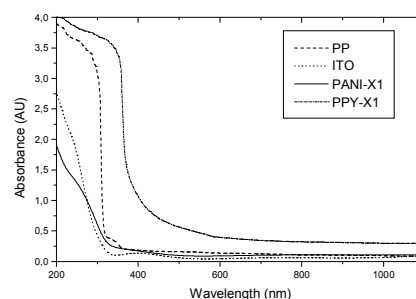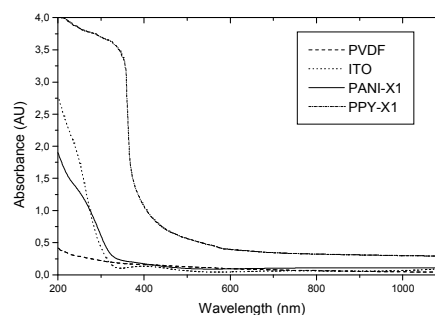

(a)
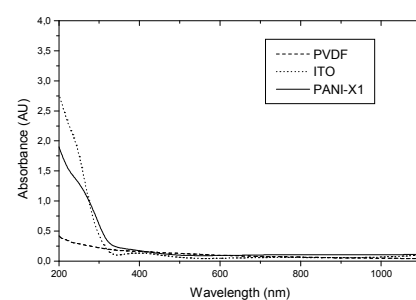
(b)

Figure 3. UV-Vis spectroscopy of (a) PP/ITO/PANI-X1 and (b) PVDF/ITO/PANI-X1.

(a)

(b)

Figure 4. UV-Vis spectroscopy of (a) PP/ITO/PANI-X1/PPY-X1 and (b) PVDF/ITO/ PANI-X1/PPY-X1.

The electrical measurements of organic flexible electrodes indicated that the electrical resistivity of the organic semiconductor material, with deposition of PANI-X1, is the order of 10^{-1} Ω.cm. Already the electrical resistivity of the organic semiconductor material, with deposition of PANI-X1 and PPY-X1, is the order of 10^{-3} Ω.cm. The deposition of PANI-X1 and older layers of PPY-X1, did not significantly alter the electrical resistivity of PP/ITO and PVDF/ITO, keeping the same order of magnitude these flexible electrodes. However, the flexible electrode of PVDF was the only one that presented the lowest optical absorption. This result selects the flexible electrodes with substrate of PVDF to characterization for by EM and SEM.

The microscopic analysis performed in these flexible electrodes, for Scanning Electron Microscopy, allows us to observe the changes induced on the surface of the samples before and after application of voltage. The Figure 5 shows the micrograph of these flexible electrodes, without applying voltage, for the (a) PVDF/ITO/PANI-X1 and (b) PVDF/ITO/PANI-X1/PPY-X1. It is observed that the surface of the flexible electrodes has a homogeneous aspect, plan and without changes.
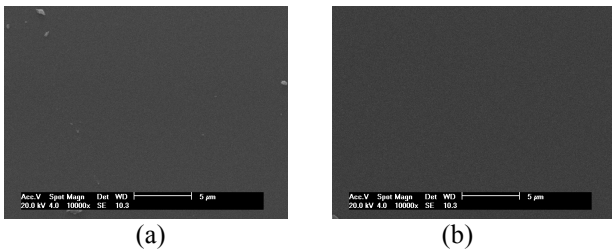

(a)   (b)

Figure 5.   SEM of (a) PVDF/ITO/PANI-X1 and (b) PVDF/ITO/PANI-X1/PPY-X1 without applying voltage.

The Figure 6 (a) PVDF/ITO/PANI-X1 and (b) PVDF/ITO/PANI-X1/PPY-X1, shows the micrograph of these flexible electrodes after application of voltage between 0.0 volts and 5.0 volts, during 500 hours. Can observe in this micrograph the surface of these flexible electrodes the aspect irregular, with holes and cracks. Can observe the formation of nanoparticles only in the flexible electrodes with one layer the PANI-X1, due to the migration of organic semiconductor material. Also can observe with increase of the time of use of device and with increasing application of the voltage, that there is an increase in the formation of nanoparticles, only in the PVDF/ITO/PANI-X1 electrode. These nanoparticles can contribute to reducing the lifetime of these flexible electrodes, since the accumulation of OSM may cause short circuit in the device. However, the flexible electrode layer of PANI-X1 and PPY-X1 did not show the formation of nanoparticles. This new multilayer structure reduces the formation of nanoparticles and increases the lifetime of the device. This new multilayer structure reduces the formation of nanoparticles and increases the lifetime of the device, because it lessens the possibility of short circuit between the OSM and the metallic contact

layer. The proposal this active layer for the flexible electrode with PANI-X1 and PPY-X1, can be applied to organic devices that work in mode reflection and transmission.
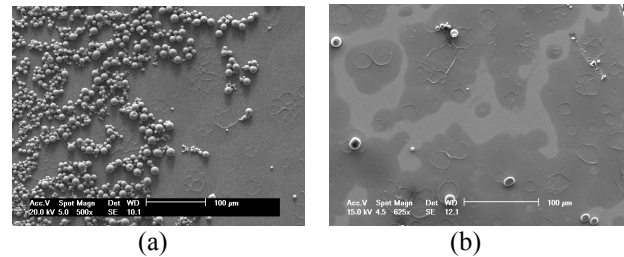

(a)   (b)

Figure 6.   SEM of (a) PVDF/ITO/PANI-X1 and (b) PVDF/ITO/PANI-X1/PPY-X1 with applying voltage.

4. CONCLUSION

Metallic contacts of microelectronic devices when subjected to high densities of electric current, undergo changes in the microstructure that favor the manifestation of the phenomenon of electromigration. This phenomenon causes the growth of vacancies (hillocks), forming cavities (voids) which can grow and eventually lead to the rupture of metallic contacts [7] [8]. The new phenomenon of migration observed in flexible electrodes showed similarities with that observed in microelectronic devices. In organic devices this new migration mechanism that arises with the passage of electric current can influence the reduction in the lifetime of the devices. However, the additional layers of PPY-X1 in the structure of the flexible electrode minimized the effects of migration observed in conventional organic devices.

5. REFERENCES

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