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Effect of the cathodic polarization on structural and morphological proprieties of FTO and ITO thin films

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ABSTRACT

This paper deals on the influence of the potentiodynamic stress on structural and morphological proprieties of fluorine-doped tin oxide (FTO, SnO_2:F) and indium tin oxide (ITO, In_2O_3:Sn) commercial substrates. The potential range is between 0.0 and −2.0 (V/SCE) using an electrolyte with neutral pH. The electrochemical behavior was investigated from cyclic voltammetry technique and chronopotentiometric curves. These electrochemical results were associated to the X-ray diffraction (XRD) spectra and morphology images acquired by scanning electron microscopy (SEM). The main results show that structural and morphological properties of FTO substrates after cathodic polarization remain near constant when compared with ITO films. The ITO substrates show morphological changes after treatment and the XRD patterns indicate the formation of a crystalline structure with In metallic characteristic, at neutral pH.

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1. Introduction

Transparent conducting oxide films are frequently used with substrates in development of electronics and optoelectronic devices, due to its conductive and optical properties [1–4]. Among these substrates, the fluorine-doped tin oxide and indium tin oxide deposited as thin films on glass stand out in the development of solar cells by its high electrical conductivity, optical transparency to visible radiation and low cost [3–7]. Actually, it is possible to find studies focused in development of solar cells using in its architecture semiconducting metal oxides films deposited on FTO or ITO substrates, such as ZnO and TiO_2 [8,9]. There are several methods for deposition of metal oxides films, among them, the electrodeposition technique [9–12]. In this case, the FTO or ITO electrode is immerse in an aqueous medium and it is submitted to potentiodynamic stress. Some authors show that the surface of the ITO film undergoes chemical and morphological changes during electrochemical treatment, affecting the electric and optic properties of the original substrate [13–15]. Moreover, possible mechanisms associated to these changes for anodic and cathodic potentials in acid conditions, are suggested. On the other hand, there are no previous works to compare the structural and morphological characteristics before and after the electrochemical treatment in FTO films, as well as comparisons between electrochemical stability of the two substrates, considering the same treatment conditions, are not found.

In this communication, we examine the electrochemical stability of FTO and ITO films during application of cathodic potential. The electrolyte used was an aqueous solution of 0.3 M Na_2SO_4 at inedited conditions of neutral pH. The surface condition of the films has assessed by examining the voltammograms and chronopotentiometric curves obtained for potential values between 0.0 and −2.0 (V/SCE). The crystalline structure and morphology of the films before and after treatment were controlled by X-ray diffraction and scanning electron microscopy techniques, respectively. Thus, it was possible to assess the degree of change undergone by films after treatment.

2. Experimental procedure

The FTO substrates were purchased from FlexiTec, with average sheet resistance ≤5 Ω/sq, and the ITO substrates were also commercial products from Delta Technologies Ltd., with sheet resistance varying from 4 to 8 Ω/sq. The thicknesses of the active layers were obtained using a Dektak 150 profilometry: 190 nm and 1000 nm for the ITO and FTO substrate, respectively.

Experiments were carried out in cathodic potentials, using electrolyte in aqueous solution of 0.3 M Na_2SO_4, with natural pH. The cyclic voltammograms and chronopotentiometric curves were carried out in a conventional three-electrode cell using a Autolab PGSTAT302N Potentiostat. The reference electrode used in the

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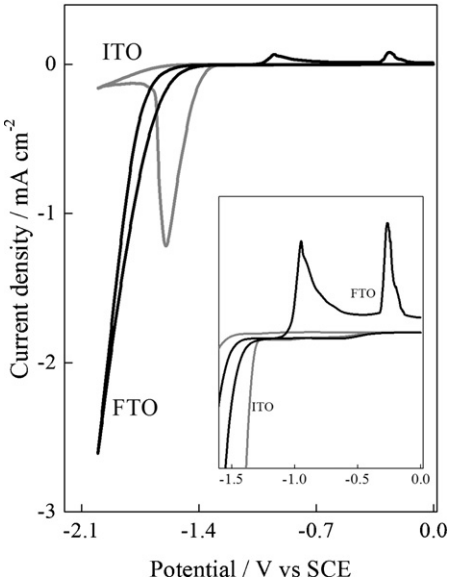

Fig. 1. (a) Cyclic voltammetry obtained for FTO (black line) and ITO (gray line) substrates in 0.3 M of Na_2SO_4, between −2.0 and 0.0 (V/SCE) at a scan rate of 10 mV s^{-1}.

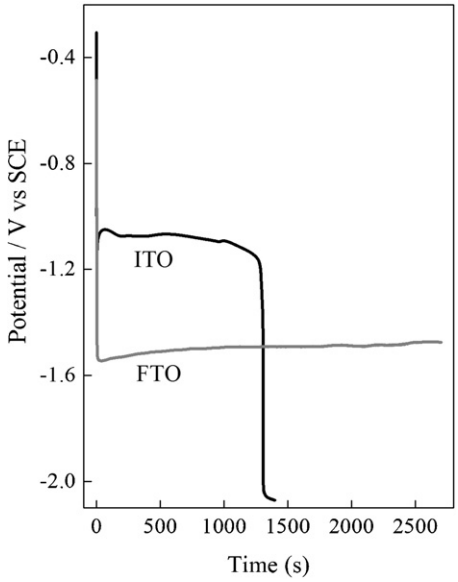

Fig. 2. The chronopotentiometric curves for FTO (gray line) and ITO (black line) substrates using a electrolyte 0.3 M Na_2SO_4 with pH 7.0 and constant current of 130 μA.

procedure was a saturated calomel electrode (SCE) and a large area Pt was used as counter electrode. The samples have an area of 1.0 cm^2, with a region exposed to the cathodic treatment limited at 0.5 cm^2. The crystalline structure of the substrates before and after cathodic treatment were examined by XRD patterns at room temperature using a Panalytical X'Pert Pro MPD model equipment, with a combination of a X-ray mirror and a two-crystal Ge (220) two-bounce monochromator, that provides monochromatic Cu $K\alpha_1$ radiation ($\lambda = 1.540562$ Å). Measurements were taken in a θ–2θ configuration, from 20° to 90°, with a step size of 0.008° and a scan step time of 13 s. In order to increase the signal to noise ratio, each measurement consisted of a sum of 5 scan. Surface morphology of the substrates were controlled on a Phillips XL30 scanning electron microscope and obtained at acquisition modes of secondary (SE) and backscattered electrons (BSE).

3. Results and discussion

3.1. Electrochemical characterization

The electrochemical stability of FTO and ITO films was studied using the cyclic voltammetry technique and the results are presented in Fig. 1. In the voltammogram obtained for FTO was not observed current peak, but a monotone increase in the potential characteristic of the evolution of hydrogen. In the region of the curve associated with negative scanning, it is possible to observe the presence of two current peaks at −0.94 and −0.28 V/SCE (insert in Fig. 1), which may be associated with the formation of hydrous tin oxide/hydroxide in the film [16]. Furthermore, we verified the existence of an anodic no null current, characteristic of valve metals [17] and indicating the formation of a layer of tin oxide. This is only possible if we assume that the FTO film suffered some degree of reduction during negative scan, suggesting a reversible process. For ITO film, the voltammogram to the more negative potential shows a current peak at −1.6 (V/SCE), characteristic of reduction reactions [14]. In the positive scanning is not observed anodic current indicating that oxidation processes are not present. The lack of reversibility observed in the ITO voltammogram, due to absence of oxidation peaks, suggests a possible chemical change in the substrate that occurs during the time range related to the current peak.

Fig. 2 presents the chronopotentiometric curves obtained for the two substrates. The current applied during the study was constant at 130 μA. The curve obtained for ITO film presents a region of constant potential around −1.0 V/SCE. A strong increase in the potential is observed after 1050 s of treatment. From this instant, the tendency of the curve suggests that the potential assumes a value around −2.05 V/SCE. This behavior indicates a total reduction of ITO film, since the system is forced to increase the potential to maintain constant the current. The curve associated to FTO film (Fig. 2) was obtained for a treatment time of 2750 s, since its active layer has a thickness five times greater than the layer of ITO. During the treatment of the FTO substrate the potential remained around −1.5 V/SCE. In other words, the absence of reduction processes suggests that the treatment time was not enough for the total active layer to suffer potentiodynamic stress. In addition, if the FTO layer is also chemically unstable from the initial instant of treatment, from XRD and SEM results it should be possible to observe the product formed and changes in the morphology of the substrate.

3.2. Structural properties

A set of XRD patterns was acquired for both substrates, before and after cathodic polarization. These results are showed in Fig. 3. The pattern obtained for original FTO substrate it is characterized by ten lines associated to the following diffraction peaks: (1 1 0), (1 0 1), (2 0 0), (2 1 1), (2 2 0), (3 1 0), (3 0 1), (3 2 1), (4 0 0) and (4 2 0). After the cathodic treatment, the same set of peaks initially identified was observed, and the relation between the intensities of the peaks also remained constant. In this way, it is possible to conclude that the crystalline structure of FTO film remains stable after the cathodic treatment. However, the XRD patterns for the ITO film present significant differences (Fig. 3b). The pattern obtained for the original substrate has the following diffraction peaks set: (2 1 1), (2 2 2), (4 0 0), (4 1 1), (4 3 1), (5 2 1), (4 4 0), (4 3 3), (6 1 1), (6 2 0), (6 1 1), (6 2 2) and (6 3 1). After cathodic polarization, the set of XRD peaks indicates to a new crystalline structure, corresponding to metallic In: (1 0 1), (0 0 2), (1 1 0), (1 1 2), (1 0 3), (2 1 1) and (2 0 2). In this pattern, it is possible to verify the presence of the same XRD peaks (less intense) that identify the structure of original sample: (2 2 2), (4 0 0), (4 4 0) and (6 2 2). This result is awaited because the sample exposed to the X-ray beam is composed by a treated region and a little area of no treated substrate.

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