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CHARACTERIZATION OF ITO NANOSCALED LAYERS APPLIED TO THE ENVIRONMENT PROTECTION

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ABSTRACT. The ITO (indium doped SnO_2) is an n-type semiconductor material, which belongs to the transparent conductive oxides category (TCO). ITO presents also excellent features, such as good electrical conductivity, high mechanical resistance, antistatic effect, outstanding chemical resistance, optical transparency in the range of visible, protective properties against electromagnetic waves and the capability of reflecting the IR-rays and absorbing solar energy. Another advantage comes from its possibility of covering different materials such as glass, metal or flexible plastics at low temperatures. This paper reports a study regarding the ITO structure and several ITO film properties (electrical conductance, VIS transmittance and anticorrosive stability) when deposited on glass substrates by pyrosol method, next to its application in environmental protection after used as a long life resistant anode for destroying different organic pollutants by electrochemical oxidation.

Keywords: *ITO films, characteristics, environmental protection applications.*

INTRODUCTION

The ITO (indium doped SnO_2) is an n-type semiconductor material, which belongs to the category of transparent conductive oxides (TCO). ITO shows excellent properties such as good electrical conductivity [1], outstanding mechanical and chemical resistance, optical transparency in the range of visible [2], protective properties against electromagnetic waves [3], antistatic effect and also the capability of reflecting IR-rays and absorbing solar energy [4]. More benefits comes from the possibility of covering different surfaces (glass, metal or flexible plastics) with ITO films at low-temperatures [5, 6]. For this reason ITO coatings are widely used in a large number of technical applications, e.g. for constructing window electrodes in solar cells [7, 8], transparent electrodes

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in display devices (liquid crystal display [9], electro-luminescent display, and electro-chromic and LED displays [10]), conductive windscreens for aircraft, or EMI shielding [3, 11], also in architectural applications (e.g. IR reflective coatings and heat mirrors) and recently employed in environmental protection as a sensor for detecting the hydrogen gas above 50^{o} C [12], or as biosensor substrate for detection of the virus bovine diarrhea [13]).

This paper reports a study upon the structure and several ITO film properties (electrical conductance, VIS transmittance and anticorrosive stability) when deposited on glass substrate by using the pyrosol method, along with its application in environmental protection as a long life resistant anode used for destroying organic pollutants by electrochemical oxidation.

RESULTS AND DISSCUSIONS

Table 1 presents the characteristics of the ITO film depending on the doping level with indium.

Table 1. Characteristics of the ITO film depending of the doping level.

In^{3+} mol %	CHARACTERISTICS			
	Grain size (nm)	Resistivity (Ω*cm)	Charge carrier number/cm^3	VIS transmittance (%)
3,5	120	45	$4,0x10^{20}$	76
4,5	80	35	$4,8x10^{20}$	82
6,5	174	52	$3,2x10^{20}$	70

This values show that the best transmittance and the best electrical conductance are obtained for a doping level of 4,5 mol % In^{3+}.

Figure.1 shows the presence of a uniform deposited nanoscaled film, with a globular shape of the grain particles.

The corrosion resistance of ITO films is very important for numerous applications in environmental protection. For that reason in figure 2 are presented the results of best ITO film stability in three different chemical media: H_2SO_4 (1M), NaOH (1M) and HOCl (1M).

The graphics illustrated in figure 2 confirms a good stability after 30 days in all three media. In H_2SO_4 media the variation of both resistance (R) and corrosion potential (E) were smaller comparing to NaOH. After 60 days the largest variation of studied properties for the exposed films was detected in HOCl media. On the other hand, these films have shown a very good stability in H_2SO_4, thus demonstrating an excellent long life of over two months.

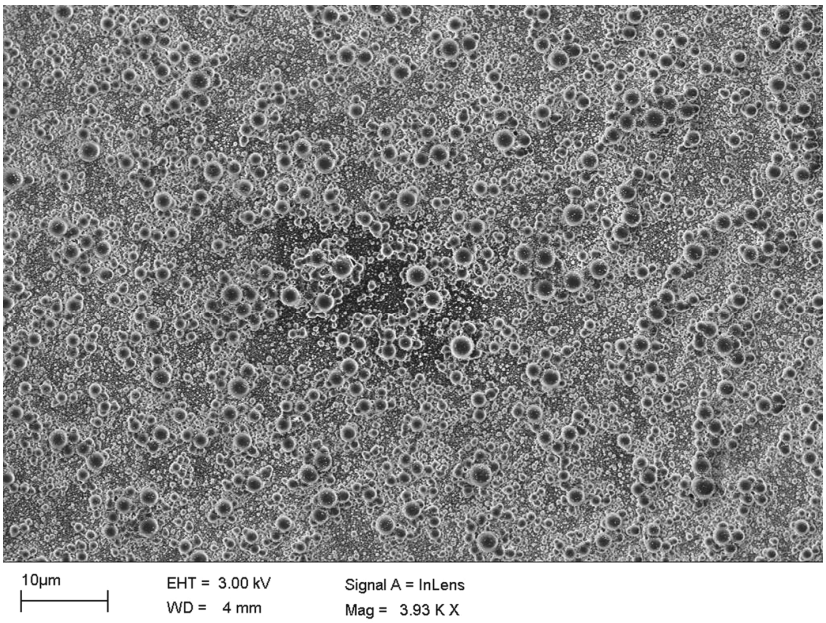
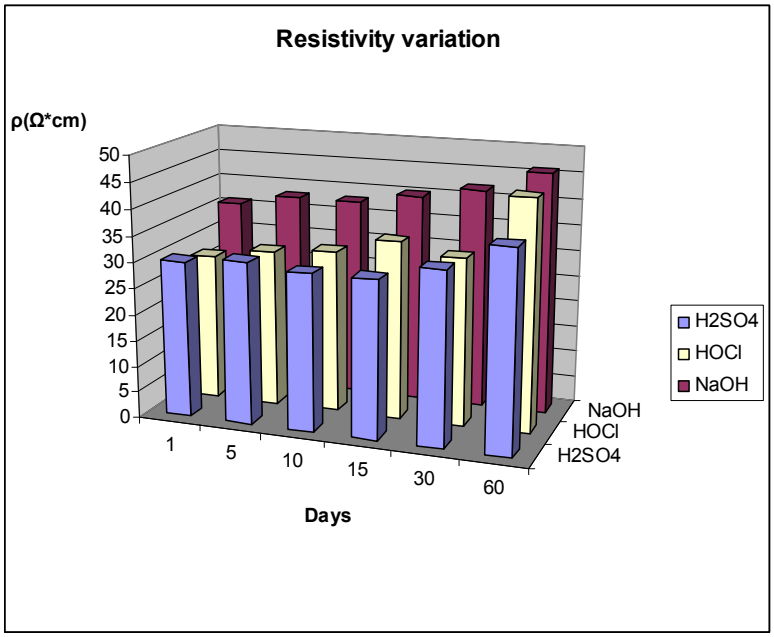


Figure 1. SEM images of ITO films structure.



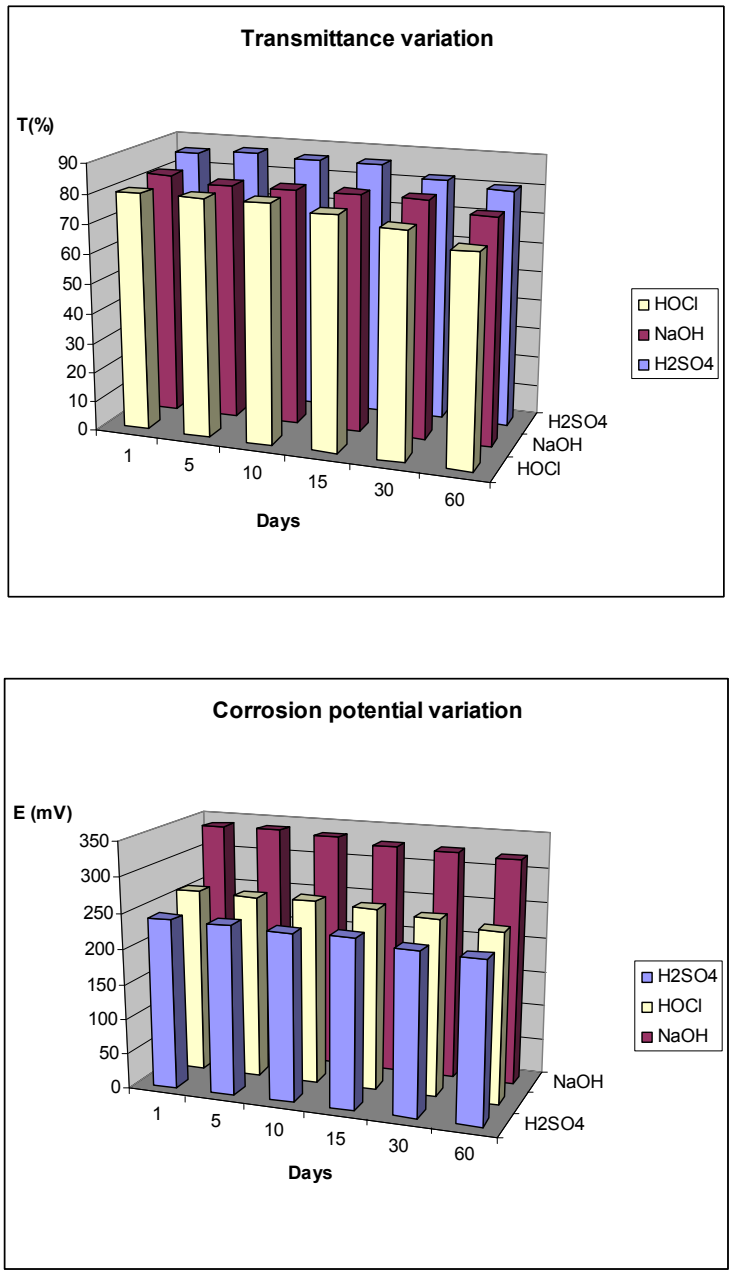


Figure 2. ITO corrosion.

Another TCO films we previously prepared and analyzed [14] was an ATO type (antimony doped tin dioxide) film. The data presented in table 2 compares the characteristics of the ATO and ITO films which we prepared.

Table 2. Comparison of the ITO and ATO films characteristics, with best doping level.

Characteristics	**ITO 4,5%**	**ATO 2%**
Grain size (nm)	80	85
Resistivity (Ω*cm)	35	42
Charge carrier numbers/cm^3	4,8x10^{20}	4,0x10^{20}
VIS transmittance (%)	82	76
Stability (days)	60	54
Preparation temperature (^{o}C)	200	425
Preservation temperature (^{o}C)	25	25
Electrocatalytical activity (%)	30	65

The experimental data presented in table 2 confirms that both TCO films show excellent properties. The ITO film demonstrates a better transmittance and high electric conductivity, while for the chemical stability a small difference can be noticed. Another advantage of the ITO film it is given by the possibility of depositing the film at low temperature (200^{o}C) comparing to ATO film (425^{o}C) [10]. For the ATO film, a more electro oxidation activity has been noticed.

The ITO film we obtain presents a good anticorrosive stability and it was further used for constructing a dimensionally stable anode (DSA) [15] with good electro catalytically properties and then applied in the process of degradation of organic pollutants from waste waters. The general scheme of the DSA it is presented in figure 3.

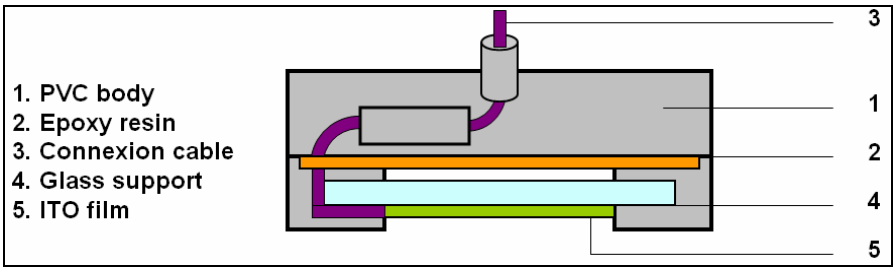


Figure 3. Schematic representation of the DSA anode.

Since formaldehyde is a hazardous waste in the textile industry, it must be eliminated especially for environmental protection. DSA-ITO anode was tested in the electrochemical oxidation of formaldehyde and the cyclic voltammetry results can be seen in figure 4.

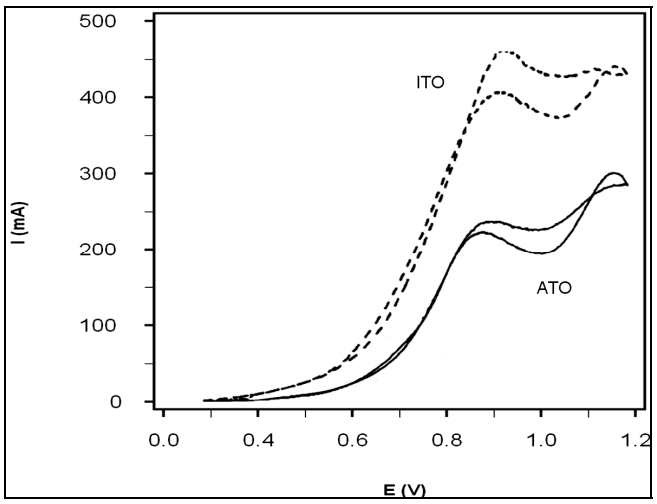


Figure 4. Cyclic voltammetry of formaldehyde oxidation.

The oxidation currents are higher for the ITO electrode versus ATO electrode, which demonstrates that ATO is more electrocatalitycaly active.

CONCLUSIONS

The properties of the TCO films received in the last decade much attention due to their large number of important applications. The nano-crystal films, ITO and ATO deposited on glass substrate give approximately identical stability results. However the ITO film has a low depositing temperature and also the best transmittance in VIS, at the same time as the ATO film demonstrate better electro catalytically properties. Both TCO were employed for constructing the DSA, which further was used to degrade the organic pollutants from waste waters

EXPERIMENTAL SECTION

The preparation of ITO is possible by using the following chemical reactions:

$$SnCl_4 + 4\ ROH \longrightarrow Sn(OR)_4 + 4\ HCl$$

$$Sn(OR)_4 + H_2O \longrightarrow Sn(OR)_3OH + ROH$$

$$Sn(OR)_3OH + Sn(OR)_4 \longrightarrow (RO)_3\,Sn\text{-}O\text{-}Sn\,(RO)_3 + ROH$$

The sol-gel preparation method of ITO by pyrosol technique [16, 17] uses as precursors the following solutions: $SnCl_4$ x $4H_2O$ and $InCl_3$ dissolved in isopropanol. The optimum doping level with $InCl_3$ was obtained by using three indium chloride concentration levels: 3 mol%; 4,5 mol% and 6,5 mol %. The preparation process has followed several steps, which are next presented. The glass substrate (soda lime silica glass plate 5x10 mm) is first pretreated with sulfuric acid for 15 minutes, then with acetone for another 15 minutes and next dried in air, also for 15 minutes. Then, the substrate is calcined for 15 minutes at 200^{o}C. The precursor solution was prepared from 100ml $SnCl_4$, 0.2M dissolved in isopropanol and 15ml $InCl_3$, 0.5M dissolved as well in isopropanol. Both solutions were mixed under constant stirring for 2 hours. The chemical composition has been checked by AAS (atomic spectra absorption). The mixture is further agitated for 1,5 hours with gradual addition of 200 ml of boric acid, 0.2M and then by ultrasonic for 2 hours to get the soil, which is further sprayed with compressed air over the glass substrate for 3 minutes. The spraying process was repeated five times. The coated glass with ITO film is finally heated at 200°C for 30 minutes.

The methods used for characterize of ITO nanofilms were: XRD (X-ray diffraction, Philips PW 3710, Cu Kα radiation) for measuring the grain size n (nm); SEM (scanning electron microscope, Hitachi 20kV accelerate voltage, 1000-10000 magnification) for verifying the film structure; UV-VIS spectroscopy (Pye-Unicam UV-VIS spectrophotometer 200-900 nm spectra transmittance) for confirming the transmittance T (%). and EIS (electrochemical impedance spectroscopy, Solartron 1286) for determining the number of charge carriers (N/cm^3). The carrier charge numbers were determined by the Mott-Schottky equation, measuring impedance at 1000 Hz. For estimation of corrosion potential E (mV) electrochemical potential measurements were made in three-electrode cells equipped with Ag/AgCl, (Radiometer) as reference electrode and platinum sheet as counter electrode (Potentiostat model PG STAT 10 - Autolab). The working electrode was glass covered by ATO films. Cyclic voltammetry was used for determining the electro catalytic activity (CV:BAS 100B, Autolab type) and Van der Pauw method for validating the electrical resistivity: [$\rho = R / A * d$], where R is resistance, A surface area and d the film thickness (ohm*cm). The sheet resistance of the films (ohm/□) was measured by four point method (by using a self made device).

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