

Nanostructured Zn-Sn-O films obtained by dip coating technique

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Abstract

Oxide compounds belonging to Zn-Sn-O (ZTO) system with the rutile (SnO_2), wurtzite (Zn), perovskite (ZnSnO_3) and inverse spinel (Zn_2SnO_4) type structure with outstanding electrical and optical properties have become recently extremely attractive, to obtain transparent conducting oxide (TCO) films. It is well known that TCO films are playing an increasingly main role in many applications as transparent electrode of solar cell, the flat panel devices, infrared (IR) reflectors, organic light emitting diode (OLED) and thin film transistor-liquid crystal display (TFT-LCD).

The aim of this work is to obtain Zn-Sn-O films by sol-gel dip coating method.

Stable sols with concentrations ratio of $[\text{Sn}] / [\text{Sn}] + [\text{Zn}] = 1;0.5;0.33$ and 0 were obtained starting from Sn(II) 2- ethylhexanoate and zinc acetate dehydrate in ethylic absolute alcohol (as solvent) and triethanolamine (as chelating agent).

Mono- and multi- layer films were deposited on glass and silicon substrates.

The structural and morphological characteristics of the as- prepared and consolidated films, were determined by IR-Spectroscopy, X-Ray Diffraction and Scanning Electron Microscopy. The surface topography and roughness were estimated by Atomic Force Microscopy. The optical properties were determined by Spectroellipsometry measurements and Fluorescence Spectroscopy. The structure, morphology and optical properties of the obtained films depend on the composition, number of deposition and the thermal treatment temperature.

Introduction

Transparent conductive films (TCO) play a main role in many optoelectronic devices. Although for these applications the TCO films of $\text{In}_2\text{O}_3:\text{Sn}$ (BTI), $\text{SnO}_2:\text{F}$ or $\text{SnO}_2:\text{Sb}$ (FTO or ATO) and $\text{ZnO}:\text{Al}$ (AZO) are already established and are obtained at industrial scale, it remains important to find new approaches for existing ones or even for new TCO materials to improve function, mobility and electronic transparency.

The ternary oxide compounds like Cd_2SnO_4 , ZnSnO_3 , Zn_2SnO_4 , ZnGa_2O_4 and GaInO_3 were mentioned in the literature data for TCO coatings obtained by different methods [1-3]. In the literature data are few references about sol-gel deposition of the thin films such as Cd_2SnO_4

[4,5], $ZnGa_2O_4$ [6], In_6WO_{12} [7] and Zn_2SnO_4 [8]. Thick-film sensors, around 500nm, were obtained using Zn_2SnO_4 particles prepared by the sol-gel method [9]. Transparent conductive films of $ZnSnO_3$ and Zn_2SnO_4 obtained by sol gel method were studied by Kurz and Aegerter [10].

This work aims to obtain mono component powders and films in the $ZnO-SnO_2$ system by sol gel method. This paper presents the results obtained in the $Zn-Sn-O$ system for $[Sn]/([Sn]+[Zn])$ concentration ration of 1; 0,5 ; 0,33; 0.

Experimental

The starting materials for obtaining precursor solutions are following SnO_2-ZnO materials: Sn (II) 2- ethylhexanoate (SIGMA) $-Sn(C_7H_{15}COO)_2$, zinc acetate dehydrate (p.a reagent grade) $-Zn(CH_3COO)_2 \cdot 2H_2O$. The solutions were obtained in absolute ethanol (Merck) - CH_3CH_2OH using as chelating agent triethanolamine (BAKER ANALYZED) - $(CH_3CH_2OH)_3N$. Table 1 presents the preparation conditions of the tin and zinc sols are presented.

Table 1 The preparation conditions of the studied sols

Solution	Concentration		Molar ratio precursor/TEA	T [°C]	Reaction time [min]
	$Sn(C_7H_{15}COO)_2$	$Zn(CH_3COO)_2 \cdot 2H_2O$			
T	0.1 M	-	5	40	120
TZ	0.05 M	0.05 M	5	50	120
TZ2	0.033 M	0.067 M	5	50	120
Z	-	0.1 M	5	50	120

The prepared sols were identified by abbreviation: T-S; TZ-S; TZ_2-S and Z-S depending on the starting solution. The abbreviations for the powders obtained from dried gels were: T-P; TZ-P; Z_2-P and Z-P depending on the starting solution.

The as obtained sols were deposited by dip-coating technique on glass and silicon supports.

Powders were obtained after thermal treatment of the gels formed by gelation of the solution in air, at room temperature.

In Table 2 the deposition conditions by dip coating of the sols are presented.

Table 2 Deposition and densification conditions of the films

Deposition and densification of the films	
Withdrawal speed (cm/min)/withdrawal temperature (°C)	5/20
Storage time of the sols before first deposition (hours)	24
Number of depositions	1-4
Thermal treatment of the films (°C)/time (h)	500/1

The films were labeled such as: SnO₂ films as T-F; ZnO films as Z-F; Zn-Sn-O films with [Sn]/([Sn]+[Zn]) concentration ratio =0,5 as TZ -F; Zn-Sn-O films with [Sn]/([Sn]+[Zn]) concentration ratio =0,3 as TZ₂-F and T-Fn, Z-Fn, TZ-Fn and TZ₂-Fn consolidated films where n=1, 2, 3, 4 is the number of depositions.

The sols evolutions were observed by Fluorescence Spectroscopy with Perkin Elmer 204 spectrofluorimeter (having a Xe lamp of 150 W), interfaced to a computer, permitting a prestabilized reading time of the data. Usually the time range between two measurements is 550 ms. The spectral measurements (emission fluorescence spectra) were performed at room temperature.

The obtained gels were investigated by DTA and TG/DTA with a Mettler Derivatograph in the 20-1000 °C temperature range with a heating rate of 5°C/min and by FT-IR Spectroscopy with a Nicolet 6700 apparatus in 400-4000 cm⁻¹ domain.

The unconsolidated and consolidated films were characterized by Fluorescence Spectroscopy and Atomic Force Microscopy (AFM). The AFM experiments were carried out based on the Dynamic Force Module / Intermittent contact mode, using an EasyScan 2 model from Nanosurf® AG Switzerland. The phase contrast working mode was used for the samples imaging by means of a 10 µm x 10 µm high resolution scanner with vertical range of 2 µm, z-axis resolution 0.027 nm and a X-Y linearity mean error of less than 0.6%. The scan rate was around 1 Hz. The cantilever (NCLR type from Nanosensors™) was with spring constants of around 32 N/m and vibrating frequency of 166 kHz.

Results and discussions

Transparent sols of T-S, Z-S, TZ-S and TZ₂-S were obtained in the conditions presented in Table 1. The sols are transparent over 90 days at room temperature.

The evolution of the sols during the storage was observed by Fluorescence Spectroscopy. Figure 1 presents the fluorescence emission spectra of the sol from zinc acetate dehydrated. As can be seen, with a light of 270 nm as excited light, the emission spectra have one structured emission band at about 308 nm.

The zinc sol (Z-S) initially presents a weak fluorescent signal, which increases by storage of the solution at room temperature. No change in the maximum emission wavelength is observed. The fluorescence intensity increases through three days storage at room temperature probably due to the formation of hydrogen bonds in the presence of triethanolamine. The fluorescence emission is quenched after four days of Z-S stored at room temperature. It was found that the fluorescence intensity value of Z-S stored four days at room temperature is almost nine times lower than the value of Z-S (initially). Moreover, the fluorescence emission wavelength is 3 nm red-shifted, fact that could be attributed to the coordination of zinc ions with triethanolamine.

Table 3 shows the fluorescence parameters of the TZ-S and TZ₂-S sols with molar ratio Sn/Zn=1 and 1/2 respectively. Unlike Z-S sol, for TZ-S and TZ₂-S sols a continuous increase of the relative fluorescence intensity even in the fourth day was observed.

Also, it could be noticed a slightly red-shift of the fluorescence emission maximum. This could be attributed to the formation of preferential links between zinc ions and triethanolamine.

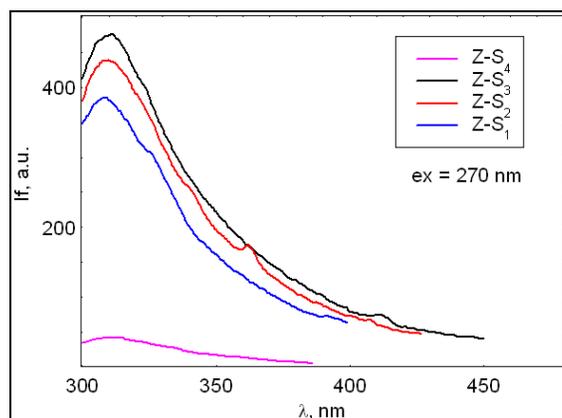


Fig.1. The evolution of the fluorescence emission spectra of the Zinc sols (Z-S) stored at room temperature for four days (S1 – S4)

Table 3 The fluorescence parameters (emission maximum, λ_{em} , and the relative fluorescence intensities, If) of the TZ-S and TZ₂-S samples stored at room temperature 1-4 days; λ_{ex} = 350nm

Sample	Stored period	Emission maximum, λ_{em}, nm	Relative intensities If, a.u.
TZ-S	1 day	405,99	35,64
TZ2-S		412,50	49,00
TZ-S	2 days	410,80	59,90
TZ2-S		415,52	76,73
TZ-S	3 days	411,84	74,13
TZ2-S		416,08	96,95
TZ-S	4 days	412,17	126,73
TZ2-S		413,80	167,32

The gels obtaining after removal of the solvent at room temperature, from T-S sol was analysed by thermal analysis DTA / TG in the range temperature 20-1000 °C.

The curves are shown in Fig. 2. It can be seen the decomposition steps of the gels. The first two endothermic effects at 76 and 133 °C respectively are due to desorption of ethanol and water.

The decomposition of the acetate reformed in the Z-P gel after gradual removal of solvent takes place around 300 °C with a weight loss of 47.7%. In the temperature range 320-480 °C occurred removing organic component from the studied gel.

After 500 °C TG curve remains constant suggesting, that a thermal treatment at this temperature is enough to obtain ZnO.

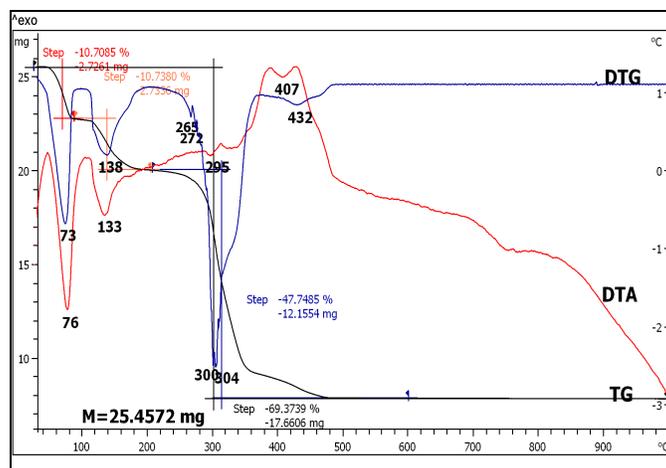


Fig.2. DTA/ TG analysis of the Zn-P gel (obtained at room temperature after evaporation of the solvent)

Reforming of zinc acetate after removal by evaporation of the ethylic alcohol in the Z-P gel is outlined in the FT-IR spectrum shown in Fig. 3.

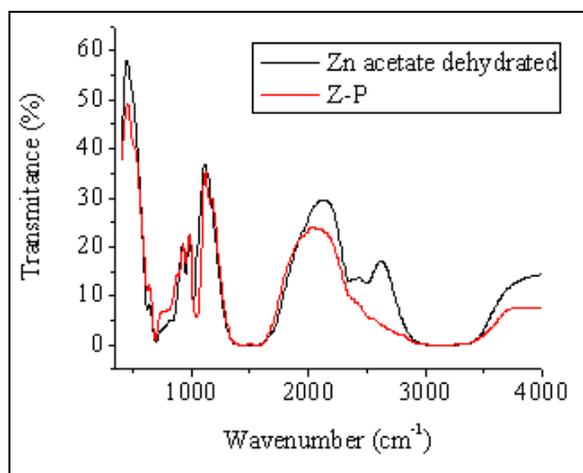
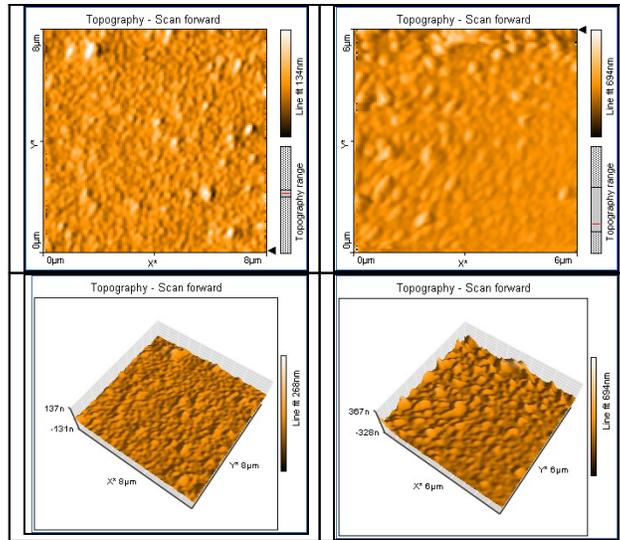


Fig. 3 FT-IR spectra of Z-P powder and zinc acetate used as precursor

It is established an overlapping of transmission bands for both samples studied in 400-2200 cm⁻¹ domain.

In the Figs. 4 and 5 (a,b) are presented AFM images in the 2D (Image plane) and 3D (three-dimensional picture) representation of the films deposited on the silica support.



a.) b.)
 Fig.4. AFM 2D and 3D images of the Z-F₄ (a) and T-F₄ (b) films;
 upper part 2D images; lower part 3D images.

*Z-F₄ is ZnO films obtained after four layers deposition from the Z-S sol consolidated at 500 °C, 1h;
 T-F₄ is SnO₂ films obtained after four layers deposition of T-S sol and consolidated at 500 °C, 1h*

As can be seen in the Fig. 4 (a and b), the ZnO and SnO₂ films obtained in the conditions previous presented are adhesive, continuous and homogenous.

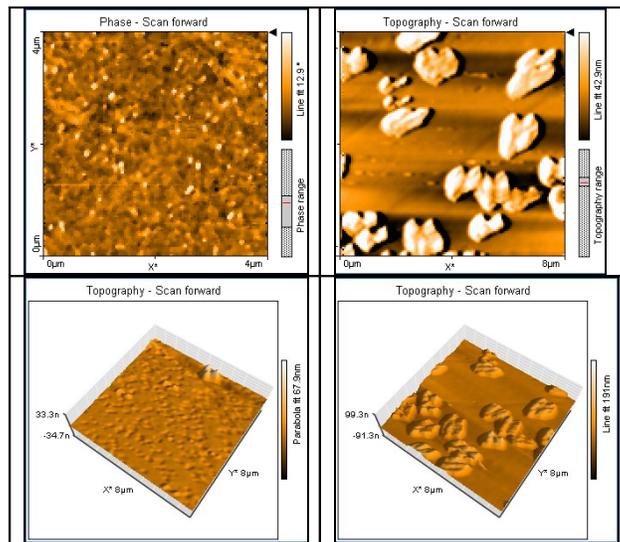


Fig.5. AFM 2D and 3D images of the TZ-F₄ (a) and TZ₂-F₄ (b) films;
 upper part 2D images; lower part 3D images.

*TZ-F₄ is Zn-Sn-O films obtained after four layers deposition from fTZ-S sol consolidated at 500 °C, 1h;
 TZ₂-F₄ is Zn-Sn-O films obtained after four layers deposition of TZ₂-S sol and consolidated at 500 °C, 1h*

From AFM images presented in Fig. 5 it is observed a distinctive morphology for the TZ-F4 and TZ₂-F4 films which suggests the formation of ZnSnO₃ and Zn₂SnO₄ compounds respectively.

Moreover Kurz and co. [10] has been emphasized by X-rays diffraction the formation of two compounds starting from sols with similar atomic ratio Sn /Zn. At 450 °C ZnSnO₃ is amorphous while Zn₂SnO₄ compound presents bands characteristic of inverse spinel structure.

All films exhibit emission fluorescence excepting with SnO₂ (T-F_{1.4}) films. The emission fluorescence spectra of the films after four depositions, thermally consolidated at 500 °C, for 1 hour, compared with similar ones obtained after one deposition and without consolidation are presented in Fig.6.

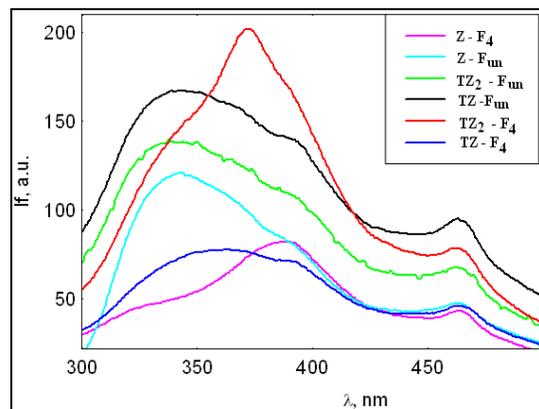


Fig.6 . Fluorescence emission spectra of the films deposited on glass support

The as prepared films, abbreviated Z-F_{un}, TZ -F_{un} and TZ₂-F_{un}, present fluorescence emission bands in the broad field of 300-400nm.

The thermally treated consolidated films exhibit distinctive bands according to the initial composition of the sol. Z-F₄ film presents an emission band in the 350-420nm domain, assigned to zinc oxide format. The large band of low-intensity of the fluorescence spectrums for TZ-F₄ film could be assigned of the formation of ZnSnO₃. TZ₂-F₄ film presents a fluorescence emission band well definite intense in the 350-420nm domain.

Florescence spectrum of Zn₂SnO₄ obtained by solid phase reaction from ZnO and SnO₂ at 1000 °C, for 10 hours is similar to that obtained for TZ₂-F₄ film and could constitute an argument for the assertion made earlier that the Zn₂SnO₄ compound is viewed in AFM images of Fig. 5 (b).

Conclusions

Stable transparent sols were obtained under soft conditions starting from organic tin and zinc salts in absolute ethylic alcohol, using triethanolamine as chelating agent.

Adherent, continuous and homogenous films deposited on the glass and silicon supports were obtained by dip coating method.

The microstructure and optical characteristics of the obtained materials are strongly influenced by the Sn/Zn atomic ratios.

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