Synthesis and Characterization of Highly Transparent and Conductive SnO_2:F and In_2O_3:Sn thin Films Deposited by Spray Pyrolysis

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Highly transparent and conductive thin films of SnO_2:F and In_2O_3:Sn (ITO) have been prepared on glass substrates using the simple pyrolitic (spray) method. Through an exhaustive parameter study and using as diagnostic method for the film quality a figure of merit defined as a function of both, the transmittance and the electric resistivity, the conditions to prepare the SnO2:F and ITO films, with adequate properties to be used as transparent front contact for solar cells, were achieved. A relevant contribution of this work is related with the deposition of SnO_2:F and ITO films with the mentioned characteristics, using a solution synthesized in our laboratory by dissolving the precursor metals in HCl. Transparent conducting oxide (TCO) thin films were obtained, with transmittances greater than 80% and resistivities smaller than $7x10^{-4}\Omega$·cm, results which are comparable with those obtained using commercial reactants. Results concerning the influence of the synthesis parameters on the optical, electrical and structural properties of the TCO films are reported.

Keywords: Thin films; Spray pyrolysis

I. INTRODUCTION

TCO semiconductors exhibit in general high transmission in the visible region, high reflectance in the infrared region and high electrical conductivity. Due to these properties, the TCO materials have been used in a wide range of applications in science and technology, including solar cells [1], heat reflecting mirrors [2], antireflection coatings [3] and a variety of electro-optical devices such as flat panel display devices [4,5]. In the literature, TCO thin films have been deposited by a variety of techniques such as, magnetron sputtering [6], chemical vapour deposition CVD [7], reactive evaporation [8] and spray Pyrolysis [9]. Particularly attractive among these techniques is the spray deposition technique successfully used for TCO thin films; this technique is simple, cheap, and easily adaptable for large area deposition. Among the available TCOs, highly transparent and conducting, SnO2:F and ITO films are promising candidates for photovoltaic and solar thermal energy conversion. In this context, the present study is aimed at preparing SnO_2:F and ITO thin films using the inexpensive spray pyrolysis technique and a procedure which is very cost-effective when compared to others reported for spray pyrolysis of these films. It includes the preparation of the spraying solution in our laboratory by dissolving the precursor metals in HCl, instead of using commercial reactants.

II. EXPERIMENTAL DETAILS

The TCOs films were prepared on soda-lime glass substrates using a conventional spray pyrolysis reactor, with electronic control of the substrate temperature, carrier gas flow rate and motion of the spraying nozzle. The solution flow rate was controlled with a peristaltic pump and the nozzle was made in Teflon with a special design to get an adequate size and droplet distribution.

The ITO thin films were prepared using an alcoholic solution containing indium chloride ($InCl_3$) and tin chloride ($SnCl_2$) as dopant. The SnO_2:F films were deposited by spraying an alcoholic solution containing tin chloride ($SnCl_2$) as precursor and HF as dopant.

The indium chloride and tin chloride solutions (called from now on solution type 1) were prepared using the following procedure:

a) *Indium chloride ($InCl_3$)*: 67 mL of concentrated HCl and 5 droplets of concentrated HNO_3 were added to 22.96 gr (0.2 mols) of metallic In (99.9%). Subsequently, this solution was heated until the In was totally dissolved and the excess of HCl evaporated. The resulting solution was transferred to a volumetric flask of 100 mL and then diluted to volume with ethanol, until reaching the desired concentration of In^{3+}.

b) *Tin chloride ($SnCl_2$)*. 9 mL of concentrated HCl and 5 droplets of concentrated HNO_3 were added to 2.97 gr (25 mmols) of metallic Sn (99.5%) This solution was subsequently heated until the Sn is totally dissolved and the excess of HCl evaporated. The resulting solution was transferred to a volumetric flask of 100 mL and then diluted to volume with ethanol, until reaching the desired concentration of Sn^{2+}. A similar procedure was used to prepare the solutions of $SnCl_2$ from commercial reactants.

In order to find the best deposition conditions, the ITO and SnO_2:F films were prepared varying the synthesis parameters in a wide range, as indicated in table 1.

ITO and SnO_2:F films were also deposited using solutions prepared from commercial $InCl_3$ and $SnCl_2$:$_2H_2O$ (Merk reagent grade), to use them as reference for the samples prepared dissolving of the precursors metals in HCl. This solution will be referred to from now on, as solution type 2.

The transmittance measurements were made using a UV-VIS Perking –Elmer Lambda 2S spectrophotometer. The structural characterization was made using an X-ray diffractometer Shimadzu 6000. The film thickness was determined from the interference fringes of the transmission spectrum, using relation [10]:

TABLE I: Variation range of the synthesis parameters of the ITO and SnO_2:F thin films

Synthesis parameters	Variation range	
	ITO films	SnO_2:F films
In^{3+}-concentration (M)	0.05 – 1.00	
Sn^{2+}- concentration (M)	0.005 - 0.05	0.1 -1.0
HF-concentration (M)		0 – 0.4
Substrate temperature (^{o} C)	300 – 500	250 - 500
Gas (air) flow rate (L min.$^{-1}$)	5	5
Solution flow rate (mL min.$^{-1}$)	4	4

$d = \frac{\lambda_1\lambda_2}{2(n_1\lambda_2 - n_2\lambda_1)}$, where n_1, n_2 are the refractive indexes in two consecutive maxima (or minima) and λ_1, λ_2 the corresponding wave lengths.

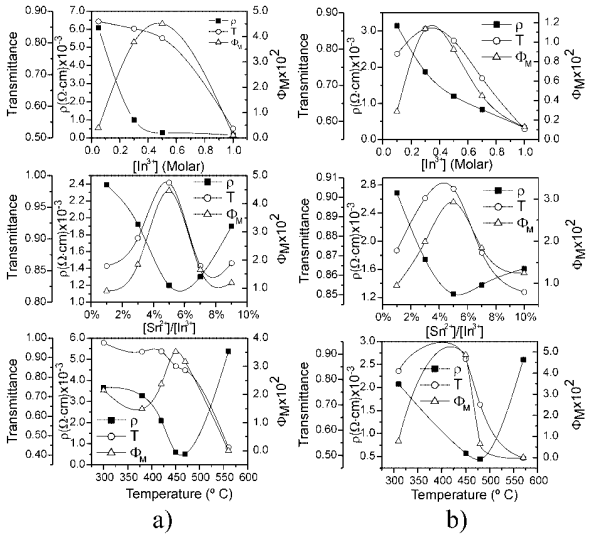

FIG. 1: Influence of the synthesis parameters (Ts, $[In^{3+}]$ and $[Sn^{2+}]/[In^{3+}]$) on the transmittance , resistivity and figure of merit of ITO films synthesised using solutions prepared a) by dissolving the metals in HCl (solution 1) and b) from reagent grade commercial reactants (solution 2).

III. RESULTS AND DISCUSSION

A. *Study of synthesis parameters*

As diagnostic method to determine the best condition to deposit highly transparent and conductive ITO and SnO_2:F thin films, we used a figure of merit Φ_M which includes both, the transmittance T and the resistivity ρ; it is defined as $\Phi_M = T^{10}/\rho$ [11], which gives more weight to the transparency and thus is better adapted to solar cell technology.

The curves depicted in Fig. 1 show the influence of the main synthesis parameters (substrate temperature Ts, molar concentration of the precursor specie, molar concentration of the dopant specie) on the transmittance T (measured at λ=550 nm), resistivity ρ and figure of merit of the ITO thin films, synthesized by spray pyrolysis.

A similar parameter study was made to determine the influence of the synthesis parameters (substrate temperature Ts, molar concentration of the Sn-ions $[Sn^{2+}]$) and concentration of the dopant specie $[F^-]$) on the transmittance, resistivity and figure of merit of SnO_2:F films synthesized using the two types of solutions. In table 2 are listed the best parameter we found for the synthesis of ITO and SnO_2:F thin films grown using both types of solutions. This table also includes results of the best values of T, ρ and Φ_M.

The results indicate that all the studied synthesis parameters, significantly affect the transmittance and the resistivity of the TCO films. However, it was possible to find a parameter set through which is possible to prepare ITO and SnO_2:F thin films with adequate properties for the desired application, using the data of the curves of figure of merit.

In general, the ITO and SnO_2:F films prepared using solution 1 present a better figure of merit than those prepared using solution type 2. However, the results shown in table 2 indicate that both types of solutions give rise to TCO films with adequate values of transmittance and resistivity for using them as transparent front contact of solar cells.

B. *Optical properties*

In Fig. 2 are compared typical transmission spectra of SnO_2:F and ITO thin films prepared using solution type 1 and the parameter values listed in table 2, with those of samples prepared using solution type 2. These results show that independently of the used solution type, the spectral transmittance of both types of TCO films is greater than 80% in the visible and near infrared regions, indicating that from the optical point of view, both the ITO as the SnO_2 films present good properties for using them as optical windows in solar cells. From the *interference fringes observed in the transmission spectra can be deduced that the thickness of the TCO films prepared using solution type 1 is different than that of films deposited with solution 2. This behaviour is due to the fact that the films are deposited using solutions with different molar concentrations and different substrate temperatures (see Table 2). The precursor type used in the spraying solutions does not affect significantly the growth rate of the TCO films.*

The studies carried out in this work indicate that the different procedures used to prepare ITO and SnO2:F thin films give rise to samples with adequate transmittance and electrical conductivity to be used as transparent electrical contact of thin film solar cells. However, from the economic point of view, for the mentioned application, it is recommendable to use SnO_2:F films (prepared using solution type 1) instead of ITO films, because metallic Sn is cheaper than metallic In.

Using the transmission spectra of Fig. 2 and calculations based on a procedure described in detail in reference [12], the optical constants (refractive index n, absorption coefficient α and optical gap Eg) of the ITO and SnO_2 films were deter-

TABLE 2. Values of the parameters leading to the best results for the synthesis of ITO and SnO_2:F thin films using solution type 1 and type 2 respectively.

Material	Solution	Molar Conc. [Ion-Me*]	Molar Conc. [Dopant**]	Sustrate Temp. (° C)	Results		
					T (%)	ρ (Ω·cm)	Φ_M
ITO	$InCl_3$ + $SnCl_2$ (prepared by dissolution of metals in HCl).	0.4 M	0.016 M	440	90	$6.7x10^{-4}$	504
	$InCl_3$ + $SnCl_2$ (from commercial reactants).	0.5 M	0.025 M	450	86	$6.0x10^{-4}$	352
SnO_2:F	$SnCl_2$ (prepared by dissolution of metal in HCl) + HF	0.45 M	0.022 M	360	83	$7.5x10^{-4}$	206
	$SnCl_2$ (prepared using commercial reactant) + HF	0.5 M	0.025 M	350	82	$7.2x10^{-4}$	215

*Ion-Me: In^{3+} and Sn^{2+} for the synthesis of ITO and SnO_2:F filmes respectively.
** Dopant Sn^{2+} and F for the synthesis of ITO and SnO_2:F filmes respectively.

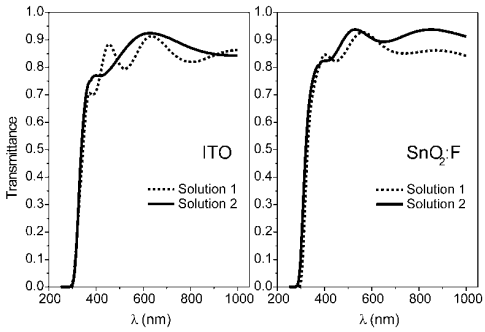

FIG. 2: Comparison of typical transmission spectra of ITO and SnO_2:F thin films prepared using a solution type 1 with those of samples prepared using a solution type 2.

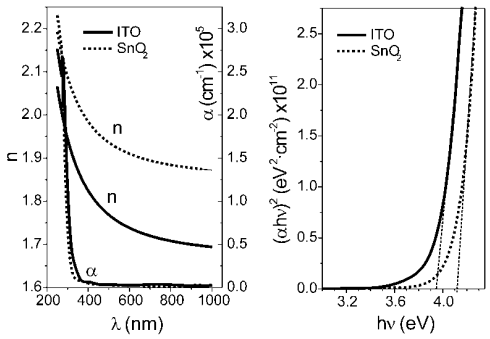

FIG. 3: Curves of n vs λ, α vs λ and $(\alpha h\nu)^2$ vs hν corresponding to highly transparent and conductive SnO2:F and ITO thin films. The curves of $(\alpha h\nu)^2$ vs hν allowed determining the optical gap Eg of both TCO films.

mined. Fig. 3 shows curves of n vs λ and α vs λ, corresponding to highly transparent and conductive ITO and SnO_2:F films deposited by spray pyrolysis. In Fig. 3 are also shown curves of $(\alpha h\nu)^2$ vs hν which were used to determine the optical band gap Eg of the ITO and SnO_2:F films; We have obtained values of Eg = 3.95 eV for ITO and 4.07 eV for SnO_2, which are similar to those reported elsewhere [13]. It is also observed that the refractive index of the SnO_2 films is significantly greater than that the ITO's. A similar behaviour of the n vs λ curves has been reported in the literature for ITO and SnO_2 films deposited by spray pyrolysis [14].

C. *Structural properties*

The structure, phase and lattice parameters of the ITO and SnO_2:F films were determined trough XRD (x-ray diffraction) measurements carried out in the θ - 2θ mode. Typical XRD patterns of highly transparent and conductive ITO and SnO_2:F films are depicted in Fig.4; these results indicate that these films are polycrystalline. The phases exhibited by the TCO films which were synthesized in this work, as well as their respective structures and lattice parameters, were determined with the help of the data reported in the JCPDS data base for these type of compounds.

It was found that highly transparent and conductive TCO films like those prepared using the optimum parameters listed in table 2, present typically, XRD patterns like those depicted in Fig.4. These results indicated that the ITO films grow with cubic structure, whereas the SnO_2:F films grow with tetragonal structure. In some samples, reflections associated to the $Sn_{21}Cl_{16}(OH)_{14}O_6$ (TOCH) phase were identified, which result probably as a consequence of an incomplete chemical reaction. In table 3 are listed data regarding the phase, structure and lattice parameters, of the ITO and SnO2 thin films, whose difractograms are shown in Fig. 4.

IV. CONCLUSIONS

ITO and SnO2:F thin films with adequate properties to be used as electrical contact for solar cells were synthesised by spray pyrolysis, using a cost effective procedure which includes a solution prepared by dissolving the precursor metallic species in HCl. Through an exhaustive parameter study, the conditions to prepare both types of TCO films with the above mentioned properties were found. Spectral transmittances greater than 80% (in the visible and near infrared region) and resistivities lower than 7x10-4 Ω·cm were obtained. Similar results were achieved with ITO and SnO2:F films synthesized using a solution prepared from reagent grade com-

TABLE 3. Phase, structure and lattice constants corresponding to ITO and SnO2 films prepared by spray pyrolysis using the synthesis parameters listed in Table 1.

TCO film	Phases identified	Structure	Lattice constant (Å)	
			a	c
SnO_2:F	TOCH	Hexagonal	10.018	44.030
	SnO_2	Tetragonal	4.735	3.194
ITO	(In_2O_3:Sn)	Cubic	10.117	

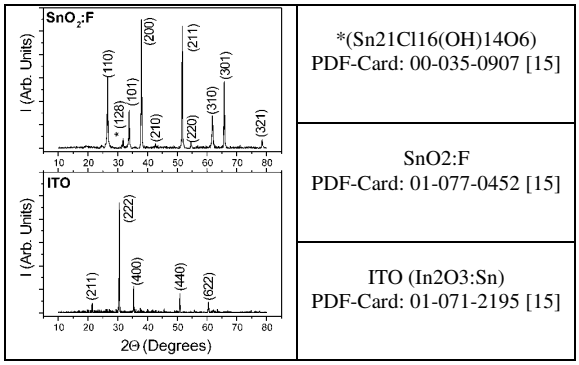

FIG. 4: Typical X-ray diffraction patterns of highly transparent and conductive ITO and SnO2:F films, deposited by spray pyrolysis.

mercial chemicals.

XRD measurements indicated that the ITO films grow with cubic structure, whereas the SnO2:F films grow with tetragonal structure. In some samples, reflections associated to the $Sn_{21}Cl_{16}(OH)_{14}O_6$ secondary phase were identified.

The procedure developed and optimized in this work is of great help to people interested in preparing TCO thin films by spray pyrolysis in countries where commercial reactants are very expensive.

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