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FLUORINE-DOPED SnO_2 THIN FILMS IN SOLAR CELL APPLICATIONS. MORPHOLOGICAL, OPTICAL AND ELECTRICAL PROPERTIES

This study examines the optimal parameters for obtaining fluorine-doped SnO_2 (FTO) films with promising potential for photovoltaic applications. Due to its properties, tin oxide is used in a wide range of technologies, among which the manufacture of solar cells is one of the most important. Being doped with fluorine, tin dioxide becomes a good transparent and conductive electrode, suitable for solar cell applications. The chemical stability and low cost of the doped SnO_2 makes it an advantageous alternative to tin-doped indium oxide (ITO). Among the most important characteristics of FTO thin films are high photoconductivity under sunlight irradiation and strong UV absorption. The SnO_2 compound, doped with fluorine, exhibits a considerable chemical and physical stability, good electrical conductivity and high transmission (over 85%) in the visible range. The spray pyrolysis technique is the most preferable and efficient deposition method of fluorine-doped SnO_2 thin films. This work aims to identify the optimal parameters for the spray pyrolysis of SnO_2:F films and to analyze the morphology, transparency and strength of as obtained films in relation to the doping amount in the precursor solution, spraying distance and film thickness.

Keywords: fluorine tin oxide (FTO); thin films; spray pyrolysis; solar cells

1. Introduction

The aim of this study is to improve the properties of FTO thin films and to identify the optimal parameters for their deposition through spray pyrolysis method. The Sn-doped indium oxide (In_2O_3:Sn) (ITO) and fluorine-doped tin oxide SnO_2:F (FTO) are among the best known and most commonly utilized transparent and conductive oxide (TCO) materials, being used in various applications including solar cells, liquid crystal displays, organic diodes, and thermal mirrors [1,2]. Nevertheless, ITO is thermally and electrically unstable and involves high costs. In photovoltaic applications, the alternative to TCO is fluorine-doped tin oxide (FTO), which can be used as a transparent electrode. This material is thermally stabile, resistant to abrasion, adheres well to glass, exhibits chemical stability, optical transparency and high electrical conductivity [1-5].

2. Experimental details

The spray pyrolysis method involves, in the present case, the formation of a thin film by spraying an aqueous solution of tin chloride ($SnCl_4 \cdot 5H_2O$) on a heated surface. In order to perform fluoride doping, ammonium fluoride (NH_4F) was added to the precursor solution,consisting of 0.2 M $SnCl_4 \cdot 5H_2O$, 0.14 M NH_4F and CH_3CH_2OH (98%) [1,6]; it was sprayed at a constant flow on glass substrates/slides with an area of 1.25×1.25 cm^2 and a thickness of 2 mm. The glass substrates were preheated and kept at a temperature of 460°C during the deposition. Compressed air was used as the carrier gas. The nozzle-to-substrate distance (d) varied between 10 and 50 cm, and the carrier gas pressure was kept constant for all samples. The deposition time (t) varied between 6 and 45 minutes. The substrate temperature was measured and controlled electronically (Enda 4420 controller) with a K-type thermocouple.

Using the spray pyrolysis technique, three series of films of 5 samples each were deposited. The variable parameters were doping concentration and the nozzle-to-substrate distance

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TABLE 1

Experimental conditions of spray pyrolysis technique

ID		T (°C)	C ($SnCl_4$, mol×l^{-1})	Solution flow (ml×min^{-1})	D (cm)	Time (min)	C (F, %)
Series 1	P_1	460	0.2	2	30	6	0.81
	P_2						1.04
	P_3						1.26
	P_4						1.49
	P_5						1.71
Series 2	C_1	460	0.2	4	30	15	0.55
	C_2						0.61
	C_3						0.67
	C_4						0.73
	C_5						0.85
Series 3	D_1	460	0.2	4	10	45	0.67
	D_2				20		
	D_3				30		
	D_4				40		
	D_5				50		

(TABLE 1). All samples were sprayed continuously throughout the deposition process.

The SnO_2:F thin films were morphologically, structurally, optically and electrically analyzed, all the measurements being conducted at room temperature. The thickness of the films was determined with a Veeco Dektak 6M Stylus Profilometer. The transmission spectra were recorded with a Lambda 19 UV/Vis spectrophotometer in the range of 280-1100 nm, using unpolarized light. The crystal structure of FTO films was determined by X-ray diffractometry (XRD) (D/MAX-rB apparatus, operated at 40 kV and 200 mA) with CuKα radiation (λ = 0.15406 nm), in Bragg-Brentano configuration ($\theta/2\theta$ mode). The electronic structure of as obtained films was studied by means of X-ray photoelectron spectroscopy (XPS). Measurements of the electrical resistivity of thin-filmsamples were also performed.

3. Results and discussions

3.1. Profilometry

As revealed by profilometry study of FTO films deposited under the abovementioned experimental conditions on glass substrates, the decrease in the nozzle-to-substrate distance results in the growth of the thickness of deposited layers (Fig. 1), that become more porous and opaque, which affects the optical characteristics of the films.

According to [6-13] and as the results of the actual research show, the optimal spraying distance of the precursor solution is between 30 cm and 40 cm. The spraying distance for the samples from 1st and 2nd series was of 30 cm. Additionally, the experimental data reveals the tendency to saturation of the precursor solution. For the 1st and 2nd series the optimal concentration of dopant in the solution is between 1.4% and 1.8%, while for the 3rd series it is between 0.67% and 0.73%.

3.2. Spectrophotometry

The obtained transmission spectrum confirms that FTO thin films are transparent. A transmittance of over 80% in the visible range (from 350 nm) is registered (Fig. 2).

In the 1st and 2nd series of samples, the values of transmittance grew with the increasing fluoride doping concentration, while in the third series the increase of the nozzle-to-substrate distance leads to the improvement of the optical transmittance

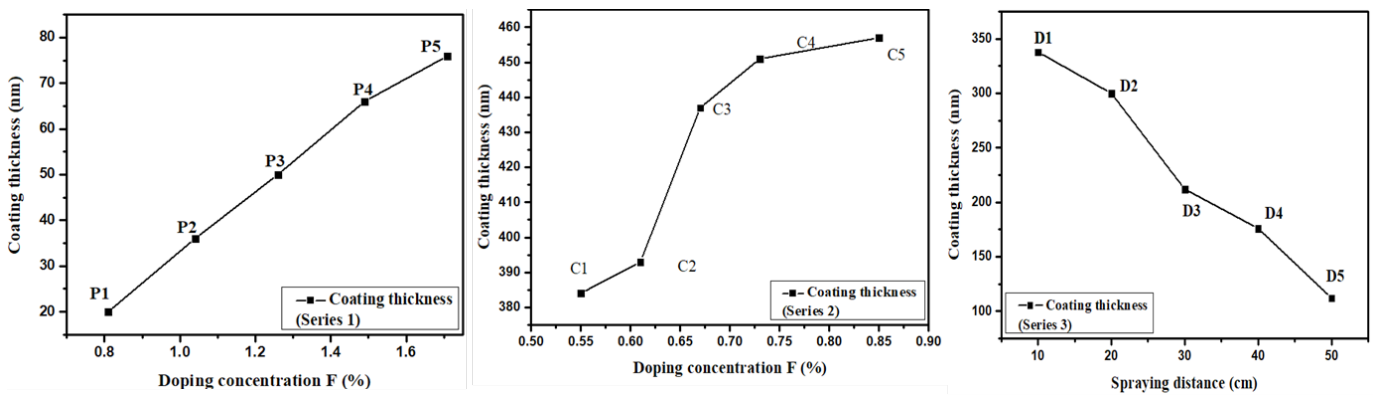

Fig. 1. Influence of different deposition parameters for a) 1st; b) 2nd; c) 3rd series

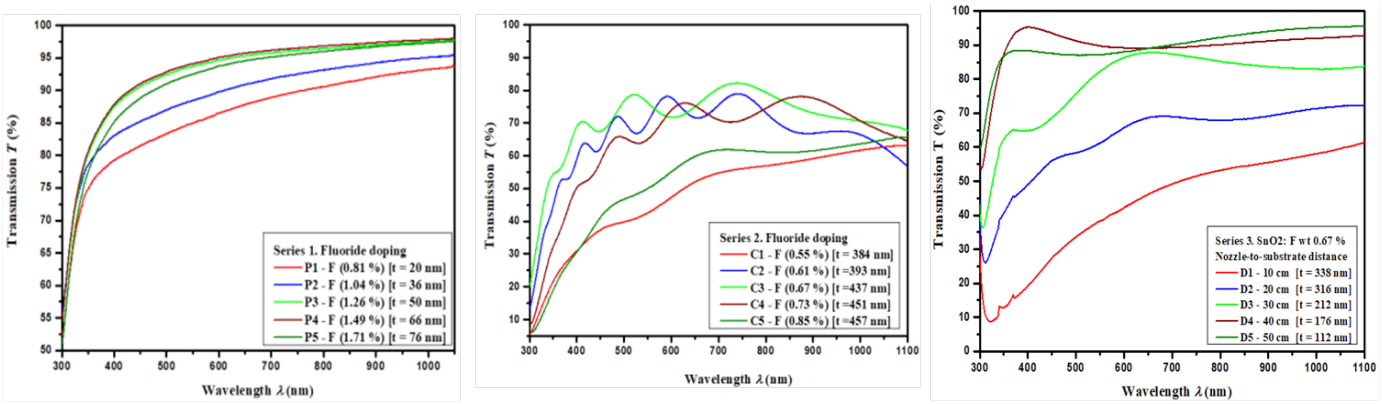

Fig. 2. Transmission spectrum of F-doped SnO_2 thin films: a) 1st; b) 2nd; c) 3rd series

of the films. The optical properties of thin films strongly depend on the film thickness, which is determined by the fluoride concentration and by the nozzle-to-substrate distance [10-17]. The transmittance spectra exhibit a marked absorption, with different values depending on depositions conditions. The best transmittance values, between 60 and 80%, were registered in the region of 400-800 nm, which reveals that the FTO films can meet the requirement of high transparency in the visible range for solar cells applications.

The values of the energy band gap were determined by using the optical absorption spectra of films (Fig. 3). The linear portion of the dependences was extrapolated to zero absorption, according to Tauc method. Its intersections with the abscissa axis (photon energy) correspond to the E_g values. Thus, values between 3.54 and 3.95 eV were obtained (TABLE 2) [7,17-21].

The decrease in the optical band gap values can be explained by the presence of some structural defects in material, which could increase the density of electron states located in the semiconductor band gap.

3.3. X-ray diffraction

The observed diffraction patterns (Fig. 4) for all three series of samples were indexed using the ICDD/JCPDS database (PDF41-1445 card) for SnO_2. The obtained XRD patterns reveal that the FTO films have a polycrystalline nature, with a tetragonal structure. Reflections on (110), (101), (200), (211), (310) and (301) lattice planes have been reported in literature [14,26-28], among which the (200) diffraction line corresponds to a preferential orientation in FTO thin-film samples. Also, there were not detected other phases related to fluorine, which indicates that oxygen (O^{2-}) ions have been successfully replaced by fluorine ions (F^{1-}) [18,21].

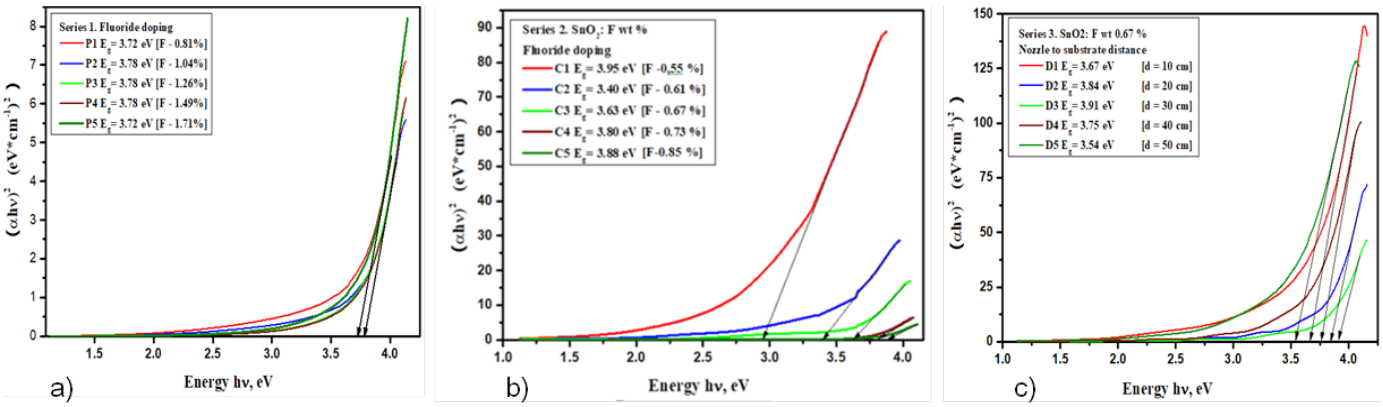

Fig. 3. Band gap energy of FTO films according to the Tauc method: a) 1st; b) 2nd; c) 3rd series

TABLE 2

Experimental values for the optical band gap, E_g, and thickness, t, of FTO samples

ID		t (nm)	E_g (eV)	ID		t (nm)	E_g (eV)	ID		T (nm)	E_g (eV)
Series 1	P1	20	3.72	Series 2	C1	384	3.59	Series 3	D1	338	3.67
	P2	36	3.78		C2	393	3.40		D2	316	3.84
	P3	50	3.78		C3	437	3.63		D3	212	3.91
	P4	66	3.78		C4	451	3.80		D4	176	3.75
	P5	76	3.72		C5	457	3.88		D5	112	3.54

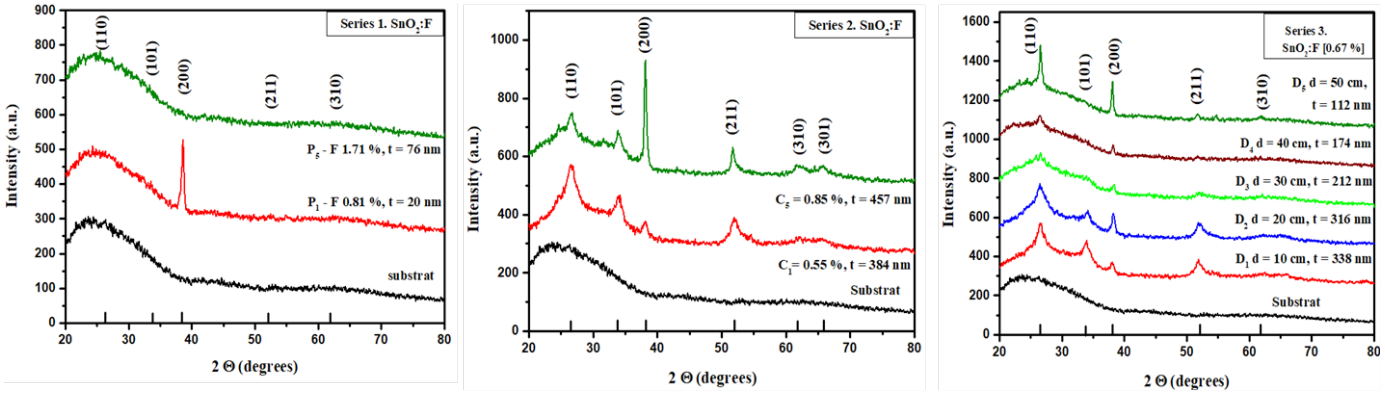

Fig. 4. XRD patterns of spray pyrolysed FTO thin films

The differences between the Bragg positions of the diffraction peaks in Figure 4 reflect the doping effect of the solution. Thickness is one of the most important parameters that can substantially change the physical properties of thin films. A comparison of the data from recorded diffractograms (Fig. 4) shows that as the films become thicker the crystallinity improves.

Based on the 1st and 2nd series it can be observed that the peak intensity of the reflections increased as a result of the increasing doping level in the solution.

3.3. X-ray photoelectron spectroscopy

The chemical composition and the characteristics of the chemical bonds for the FTO thin films were identified by using the XPS spectroscopy. The inspection was performed on two typical samples from each series. The main detected elements were O, Sn, F and C. The presence of carbon in the composition of the thin-film surface was caused by contamination.

The Figs 5-7 below show the XPS spectra of the baseline levels (Sn3d, O1s, F1s and C1s) for the investigated series of samples.

The presence of Sn MNN and O KLL emission lines indicates an Auger electron emission caused by the relaxation of excited ions. The XPS spectrum contains multiple emission lines explainable through multiple interactions occurring during the photoemission process [22].

The Sn3d orbital is related to one of the most important spin-orbit coupling interactions, which is registered when an electron is emitted from Sn3d and an unassociated electron is left behind with spin $m_s = \pm 1/2$. The spin of the unpaired electron can be parallel or antiparallel to angular momentum l, and it results in an angular momentum of either j ($j = l + m_s$) of 5/2 or $j = 3/2$. The intensity ratio of the two emission lines in the spectrum is

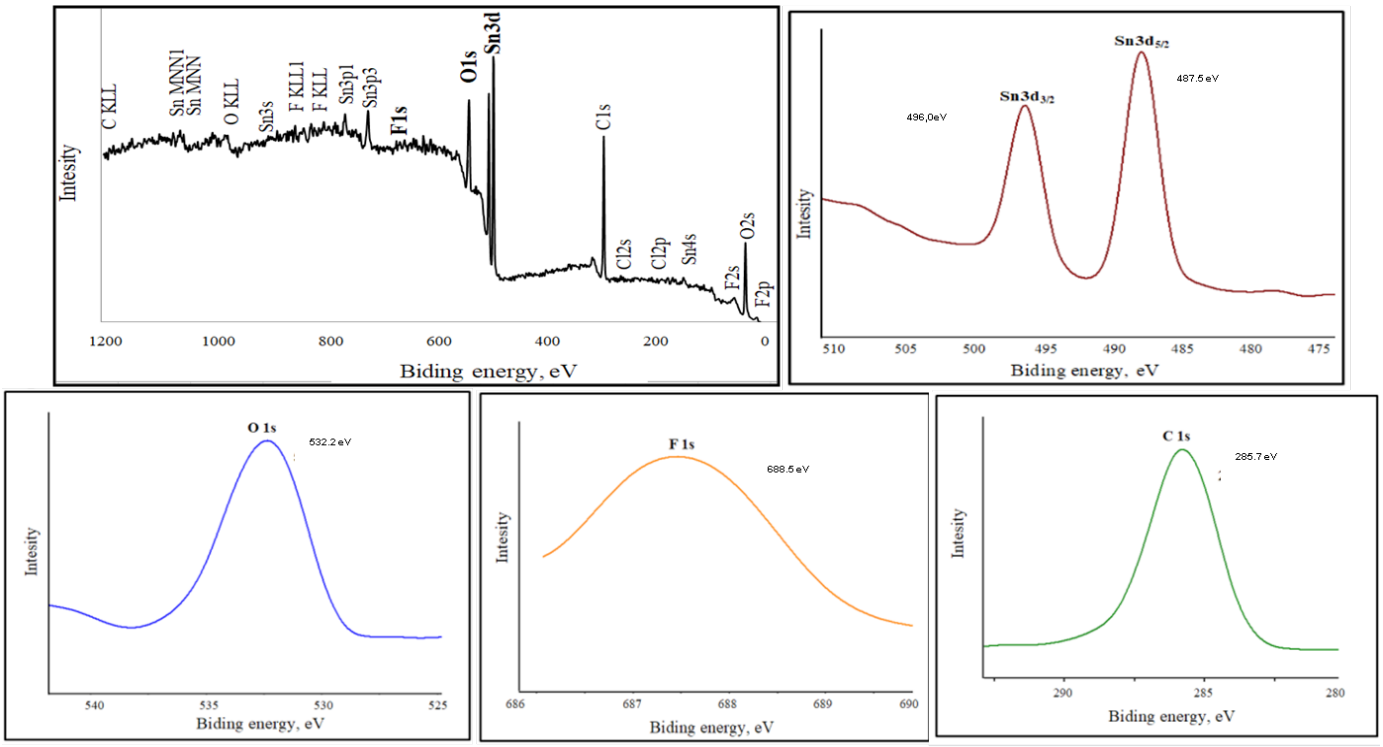

Fig. 5. Base level spectrum (Sn3d, O1s, F1s and Cs1) for series 1, P1 (F 0.81%)

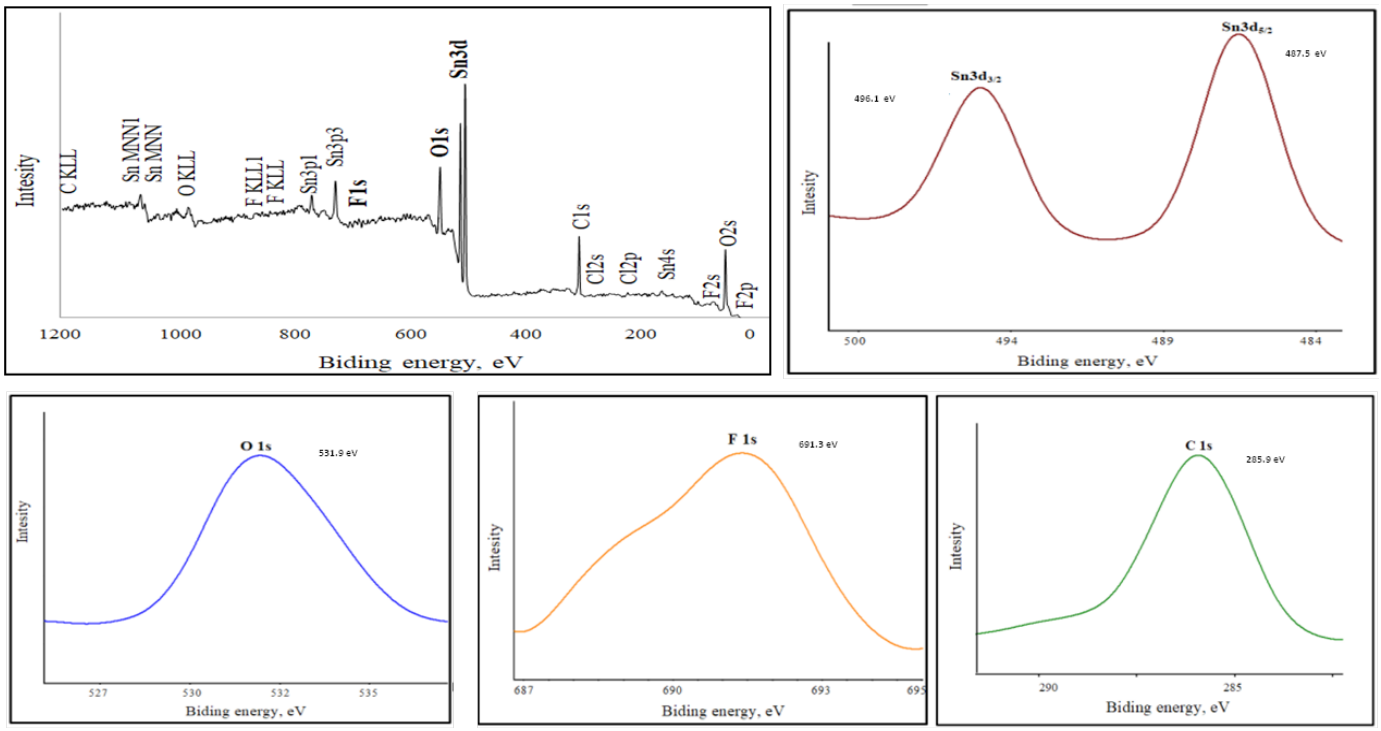

Fig. 6. Base level spectrum (Sn3d, O1s, F1s and Cs1) for series 2, C1 (F 0.54%)

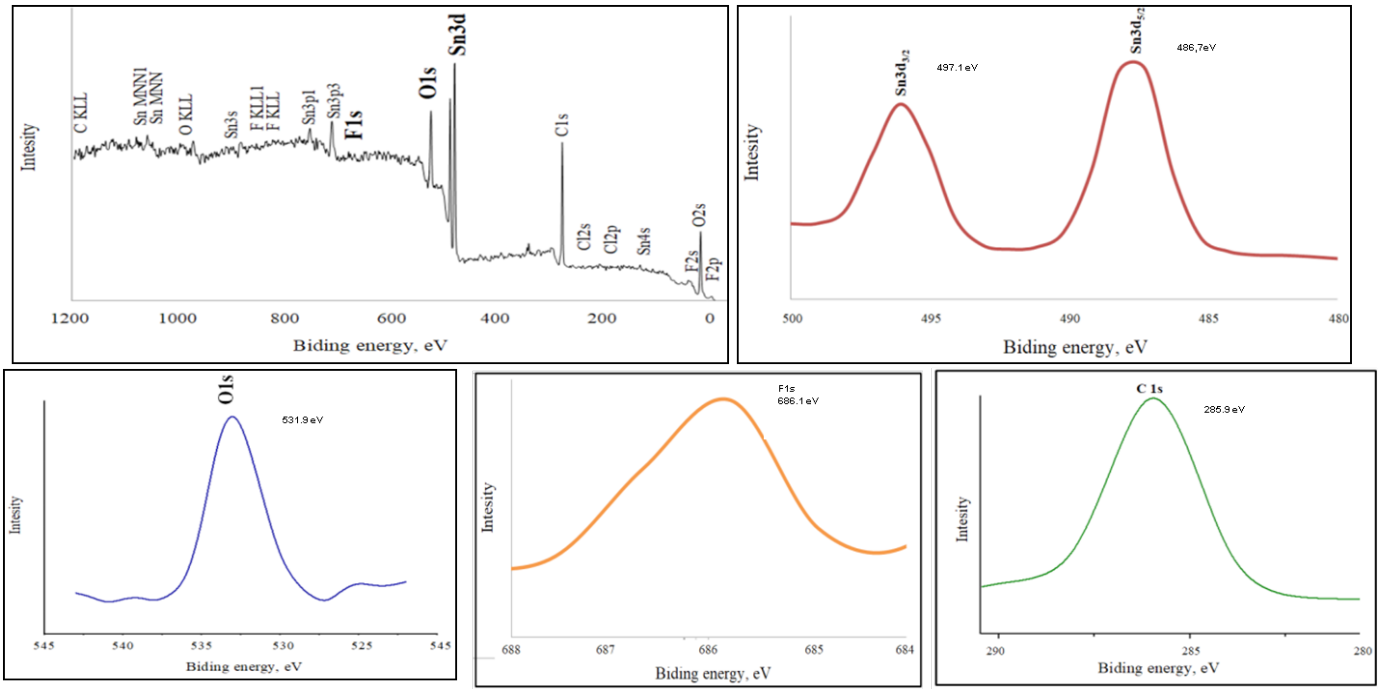

Fig. 7. Base level spectrum (Sn3d, O1s, F1s and Cs1) for series 3, D1 (d = 10 cm)

determined by the degeneration $(2j + 1)$ of the final state and thus is equal to 6:4 for $Sn3d_{3/2}$ and $3d_{5/2}$ [22-25].

The $Sn3d_{3/2}$ photoelectron registered energies in the XPS spectrum were: P1 – 496.0 eV; C1 – 496.1 eV; D1 – 497.1 eV. For the $3d_{5/2}$ photoelectron the values were: P1 – 487.2 eV, C1 – 487.5 eV, D1 – 486.7 eV. The available data suggest that the Sn element in the compound SnO_2 is an ionic species similar to Sn^{4+}. The binding energy of the $Sn3d_{5/2}$ peak at 487.5 eV indicates the presence of SnO or SnO_2, which have similar binding energy. The O1s spectrum registers the main peaks at 532.2 and 531.9 eV. The degree of oxidation of Sn in the oxide film depends on the energy difference between Sn levels ($3d_{5/2}$) and the X (O) peaks that can be used as oxidation degree for Sn. The binding energy of $3d_{5/2}$ was similar to that of Sn^{4+} in SnO_2 (486.6 eV) and higher than that of Sn^{2+} in SnO (485.9 eV). This finding confirms that Sn^{4+} is the dominant ionic species in the SnO_2 compound.

TABLE 3

Peak parameters for FTO samples

XPS $Sn3d_{5/2}$ peak parameter	ID	Components	
		Sn^{2+}	Sn^{4+}
Binding energy (eV)	P1	485.9	487.5
	C1	485.9	487.5
	D1	485.9	486.7
XPS O1s peak parameter		**O-Sn^{2+}**	**O-Sn^{4+}**
Binding energy (eV)	P1	529.8	532.2
	C1	529.8	531.9
	D1	529.8	531.9
XPS F1s peak parameter		**Sn-F**	
Binding energy (eV)	P1	688.5	
	C1	691.3	
	D1	686.1	

In the case of $Sn3d_{5/2}$, the XPS spectrum was composed of two lines corresponding to the Sn-O and Sn-F bonding states. For baseline O1s, the measured values were 531.9 and 532.2 eV for SnO_2. The binding energy of O1s was similar to that of SnO_2 (530.5 eV) and different from the energy in SnO (529.8 eV), which suggests that the O ions formed bonds with the Sn^{4+} ions and direct bonds with positively charged tin ions. The results of the XPS analysis confirm that the films deposited by spray pyrolysistechnique are composed of F-doped SnO_2 [7,18,25-33].

3.4. Electrical properties

Fig. 8 shows that the lowest value of electrical resistance was obtained in thin films with fluoride dopant concentrations of 0.61% and 0.67%, with values of 0.50×10^{-3} Ω×cm and

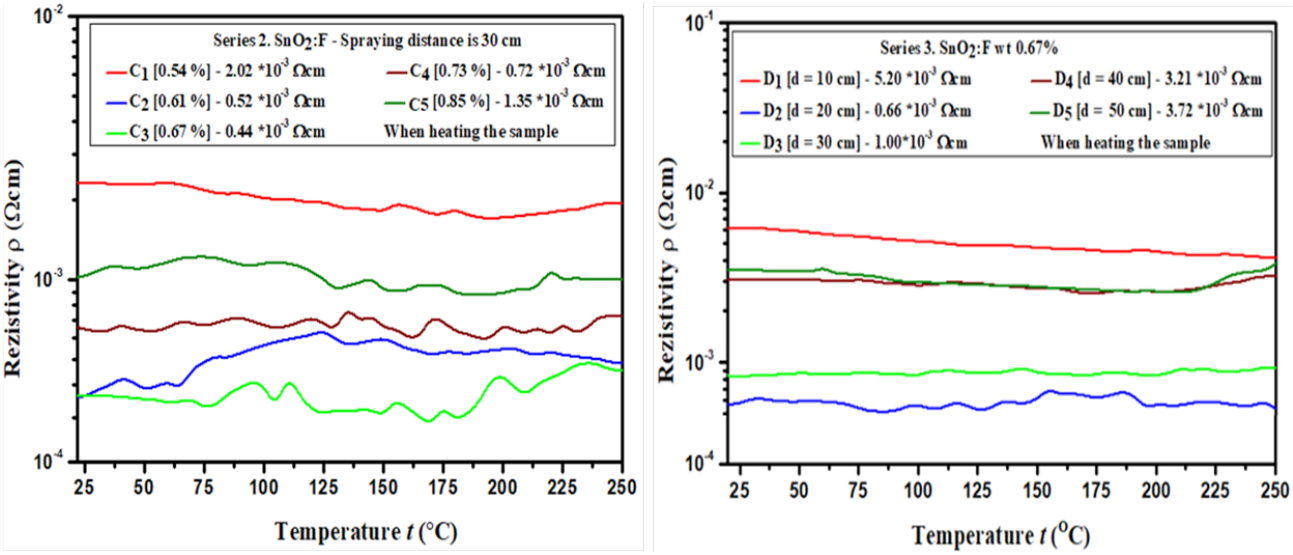

Fig. 8. Temperature dependence of electrical resistivity of FTO samples as a function of temperature during samples heating between 25 and 250°C

TABLE 4

Correlation of deposition parameters and experimental results obtained

ID		*C* ($SnCl_4$, mol×l^{-1})	*C* (F,%)	Nozzle-to-substrate distance (cm)	*T* (°C)	*D* (nm)	*r* (10^{-3} Ω×cm)	E_g (eV)
Series 1	**P1**	0.2	0.81	30	450	20	30.21	3.72
	P2		1.04			36	27.32	3.78
	P3		1.26			50	23.10	3.78
	P4		1.49			66	24.30	3.78
	P5		1.71			76	23.11	3.72
Series 2	**C1**	0.2	0.55	30	460	384	2.02	3.59
	C2		0.61			393	0.52	3.40
	C3		0.67			437	0.44	3.63
	C4		0.73			451	0.72	3.80
	C5		0.79			457	1.35	3.88
Series 3	**D1**	0.2	0.67	10	460	338	5.20	3.67
	D2			20		316	0.66	3.84
	D3			30		212	1.00	3.91
	D4			40		176	3.21	3.75
	D5			50		112	3.72	3.54

0.37×10^{-3} Ω×cm, respectively. The samples with fluoride concentrations of 0.61% and 0.67% had the highest transmittance compared to the other samples, equal to 70-80%. While the highest value of electrical resistance was obtained at a dopant concentration of 0.54%, but corresponded to the lowest value of transmittance, of 55-60%.

The data presented in Fig. 2 indicate that the transmittance increases as the distance between the sprayer and the sample grows. This correlation is caused by the fact that the increase in film thickness leads to a higher dopant concentration in the conductive layer. The decrease in the resistance is explainable by the increase of the fluorine concentration, resulting in an increased number of O^{2-} anions substituted with F^{1-} anions, which creates more free electrons.

4. Conclusions

In the present work the tin oxide thin films with different concentrations of fluorine dopant were deposited on glass substrates at a temperature of 460°C, using the spray pyrolysis technique. The FTO films with fluoride concentrations of 1.26% and 0.67% [from series 1 (P3), 2 (C3) and 3 (D2)] that was sprayed from a distance of 30 cm and 20 cm, exhibit the best crystal structure and optical transparency (~90, 70 and 60%, respectively). The obtained experimental results suggest that the structure, morphology, transparency and strength of the FTO films depend on the doping amount in the precursor solution, spraying distance and film thickness. All the deposited films are very smooth, exhibit a polycrystalline nature and a tetragonal structure with preferential orientation (200). The XPS analysis shows that the actual spray pyrolysed films are composed of SnO_2 doped with fluoride. The lowest values of resistance were found for 2nd and 3rd series, equal to 0.44×10^{-3} Ω×cm and 0.66×10^{-3} Ω×cm, respectively. These films, with the thickness of 437 nm and 316 nm, respectively, were deposited at spraying distances of 30 cm and 20 cm, respectively. The values of transmittance in the visible range were of 80.23% and 75.11%, respectively. The average visible transmittance (400-700 nm range) of the actual films is ranging between 50.4% and 94.3%. The revealed properties of the as-deposited FTO films prove the convenience, in terms of both price and ecological cleanliness, of the use of these films as transparent electrodes in solar cell applications.

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Author's contributions

Petru Lisnic, Laura Hrostea, Liviu Leontie, Mihaela Girtan contributed to the design and implementation of the research, to the analysis of the results and to the writing of the manuscript.

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