

Dip coated ITO thin-films through sol–gel process using metal salts

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Abstract

Indium tin oxide (ITO) thin-films were deposited on soda-lime-silicate glass using sols prepared from alcoholic solutions of indium chloride and stannic chloride with different In:Sn atomic ratios, namely 95/5, 90/10, 85/15 and 80/20. The electrical properties, structure and morphology of the thin-films were investigated. All the films studied, with a thickness range of 10–490 nm were polycrystalline with grain sizes in the range of 25–60 nm. Uniform and dense microstructure apparently devoid of cracks and voids were observed. Only cubic In_2O_3 phase was observed in the X-ray diffraction (XRD) and transmission electron microscopy (TEM). SnO and SnO_2 phases were not detected. The sheet resistance values decreased with increase in coating thickness. A significant decrease in the resistance values was also noted after annealing in $\text{N}_2 \setminus \text{H}_2$ (96–4%) atmosphere. The minimum sheet resistance values were noted for Sn concentration of 10 at.%. The lowest value, 11 ohms per square, was obtained after annealing for a 490-nm film. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Indium tin oxide; Coating; Electrical properties and measurements; Scanning electron microscopy

1. Introduction

Transparent conducting oxide films with controlled electrical and optical properties have been extensively used in a variety of electronics and optoelectronics applications including window heaters, solar cells, liquid crystal devices etc. [1–3]. Most of the effort has focussed on the oxides of indium, tin and zinc with small amount of other elements as dopants, e.g. $\text{In}_2\text{O}_3/\text{Sn}$, SnO_2/F and ZnO/Al . Of all the above options thin-films of indium tin oxide (ITO) has been most extensively studied [1–4]. The basic physics of all these systems is similar where the desirable property results from all the oxides being n-type semiconductors with a band-gap between 3 and 4 eV, doped to give electron gas in the conduction band [4]. Electronic

conduction in undoped indium oxide is due to the presence of oxygen vacancies, as each of these vacancies contribute two electrons for conduction. In tin doped indium oxide, tin substitutes for indium as Sn^{4+} , giving rise to an additional electron for conduction [5]. Mössbauer analysis [6] have indicated that tin is tetravalent in all high quality ITO films. The presence of divalent tin state is known to increase the resistivity of the films [7].

Various methods [8–12] like r.f. magnetron sputtering, reactive d.c. sputtering, electron beam evaporation, spray pyrolysis etc. have been used for obtaining high quality films. The relatively inexpensive sol–gel method has also been used [13–18] but apparently the full potential of this method using inorganic sol precursors has not yet been utilized. The present work examines the possibilities of obtaining ITO films on soda-lime-silicate glass: (i) using a sol–gel dip coating technique with sols (non-alkoxide) starting from inorganic salts; and (ii) examining the electrical and optical properties,

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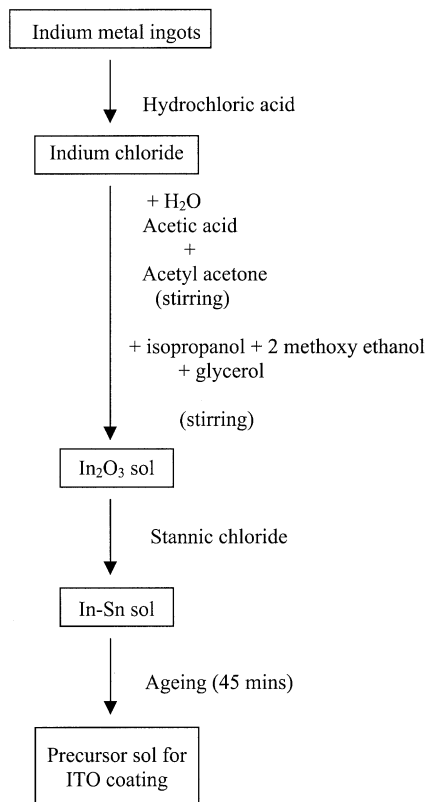


Fig. 1. Schematic representation of precursor sol preparation for ITO coatings.

structure and morphology of the films. The aim of the work was to develop low resistance coatings by dipping method from inexpensive inorganic sol precursors.

2. Experimental

Indium metal ingots (Fluka, Switzerland) and stannic chloride ($\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$, Poole, England) were used as starting materials. The indium metal ingots were dissolved in concentrated hydrochloric acid (12 N) (Merck, Darmstadt, Germany) to obtain indium chloride crystals. A measured amount of distilled water was then added to prepare the indium chloride stock solution. Sols corresponding to 6.0 wt.% In_2O_3 were prepared. A schematic representation of the processing steps is shown in Fig. 1. The desired amount of InCl_3 solution was weighed out and acetic acid (In component in solution/acetic acid = 1:0.5) and acetylacetone (In component in solution/acetylacetone = 1:0.5) were added as complexing agent. After 0.5 h stirring, desired volume of isopropanol, 2-methoxyethanol and glycerol was added to prepare 6.0 wt.% In_2O_3 sol. The required amount of $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ was then added to maintain the In/Sn atomic ratios as 95:5, 90:10, 85:15 and 80:20. The final solution was stirred for another 0.5 h to achieve the dipping sol.

ITO films were prepared on soda-lime silicate mi-

croscopic glass slides by multiple coating. Dip coating was performed at room temperature with substrate withdrawal speed of 7.0 cm/min. After each deposition the films were heat-treated in air at 500°C for 1 h. After 1–20 layers had been deposited, the films were annealed in N_2/H_2 atmosphere (96 N_2 –4% H_2) at 550°C with a soaking of 0.5 h followed by cooling to ambient atmosphere.

The viscosity of the coating sol was measured using Haake VT 550 viscometer. Physical thickness of the films was measured by the stylus method using Surf-corder SE-40G stylus profilometer. The visible transmission was recorded on a Hitachi U-2000 spectrophotometer. The crystalline phases were detected with a Philips PW 1820 X-ray powder diffractometer with CuK_α radiation. The mean crystallite size of the films was evaluated from line broadening of (222) X-ray diffraction (XRD) peak of ITO using Scherrer's equation:

$$T = 0.9\lambda / (B_M^2 - B_S^2)^{1/2} \cos\theta,$$

where λ is the X-ray (CuK_α) wavelength, θ the diffraction angle, B_M (in radian) the half width measured for the (222) peak and B_S (in radian) the half width of the standard (Si single crystal). The error of the estimated value is within 5%. The microstructure was studied under scanning electron microscope Cambridge S200. The transmission electron micrograph was obtained on a JEOL JEM 200CX transmission electron microscope. The sample was prepared by etching out a single layer film from the glass substrate and mounting it on copper grid for examination. The sheet resistance values of the samples were measured using a four-point probe method and the carrier concentration was measured using Vander Pauw method.

3. Results and discussion

The viscosity of the coating sol was 8cP. The sols had a shelf life of more than 2 months. However, all the coatings were prepared within a week of the sol preparation.

The prepared coatings appeared to be homogeneous and transparent under visual inspection. The thickness of the coatings increased with multiple dipping although the relationship between the value of thickness and the number of layers was not linear (Fig. 2). The measurements were carried out 5 times each for different points on the coating surface. The mean values are plotted in Fig. 2. The error was $\pm 5\%$. The transmission (% T) decreased with increase in the coating thickness. Fig. 3 shows the changes in the visible transmission behavior for the coatings having thickness of 113 and 490 nm. The $T\%$ values include the contribu-

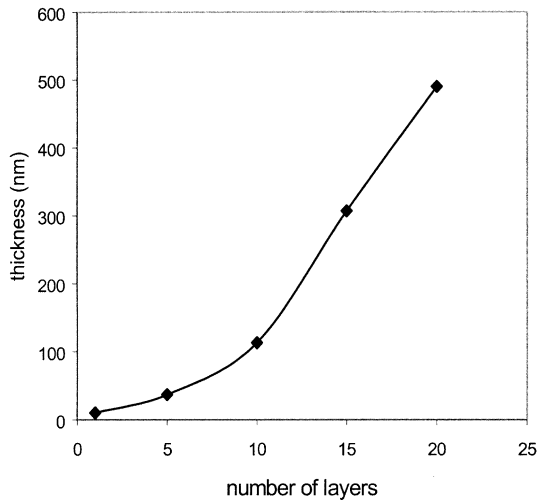


Fig. 2. Variation of film thickness with an increase in number of layers.

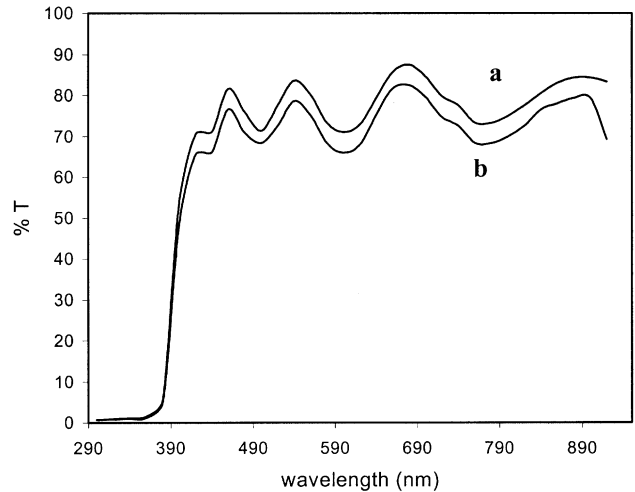


Fig. 3. Visible transmission spectra of ITO films corresponding to In/Sn = 90:10, (a) 113 nm and (b) 490 nm.

tion from the base glass and were carried out on samples that were coated on both sides. Variation of %T from 75 to 90%, in the visible region, has been reported for ITO films of varying thicknesses, by various researchers [16–20].

The XRD pattern of all the samples irrespective of the tin concentration matched with those for cubic

In_2O_3 (ASTM card 6-0416). The crystal orientation did not show any preference for any preferred direction. No phases corresponding to oxides of tin were detected. Fig. 4 shows the XRD pattern of the film (490 nm) corresponding to In/Sn atomic ratio 90:10, which is characteristic of all the other films. The pattern

Table 1
Changes in the crystallite size of the ITO films, for different Sn at.%, air baked and annealed in $\text{N}_2 \setminus \text{H}_2$ atmosphere

Thickness (nm)	Mean crystallite size in (nm) for In:Sn =							
	80:20		85:15		90:10		95:5	
	Heat-treated in							
	Air	$\text{N}_2 \setminus \text{H}_2$	Air	$\text{N}_2 \setminus \text{H}_2$	Air	$\text{N}_2 \setminus \text{H}_2$	Air	$\text{N}_2 \setminus \text{H}_2$
113	21	22	23	23	29	30	24	24
307	25	26	26	27	34	34	28	30
490	29	28	31	32	38	39	32	32

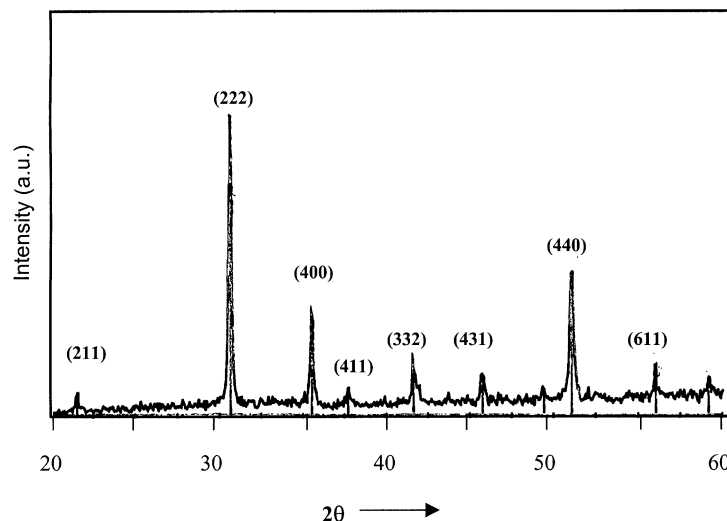


Fig. 4. XRD pattern of the film (490 nm) with In/Sn = 90:10 annealed in $\text{N}_2 \setminus \text{H}_2$ atmosphere.

remained unchanged even after annealing in N_2/H_2 (96–4%) atmosphere. It is known [21,22] that in high quality ITO material, tin is tetravalent, each Sn^{4+} replacing an In^{3+} substitutionally, thereby, donating a free electron for the conductivity in the process. At normal pressure In_2O_3 crystallizes in a cubic structure of the bixbyite of Mn_2O_3 type. ITO materials are known to retain the cubic In_2O_3 structure up to the solid solubility limit of SnO_2 in In_2O_3 [23–26] which is at (6 ± 2) at.% of Sn for powder mixture. In case of thin-films, however, no detectable phase of SnO_2 has been observed up to doping concentrations of 60 at.% Sn [23–25], which was associated with the SnO_2 remaining in finely dispersed form [25]. Different researchers [24,26] have noted preferred orientation of In_2O_3 crystals towards the {111} or {100} plane although it did not have any direct effect on the reduction of the resistivity of the films. The mean crystallite size increased with decrease in resistance as observed earlier by Takahashi et al. [14]. However, there were no significant changes in the crystallite sizes after annealing. Table 1 shows the values for the crystallite sizes for coatings of different thickness before and after annealing.

Scanning electron microscopy (SEM) studies showed that the morphology of the ITO films did not vary significantly for the different In:Sn ratios. Fig. 5a shows the SEM micrograph corresponding to the sample with In/Sn atomic ratio 90:10, after annealing. Surface view of the film (Fig. 5a) shows presence of uniform and dense microstructure apparently devoid of any cracks and voids although it is possible that some microscale porosity is present in the films. The cross-sectional view of the fractured sample in Fig. 5b showed the presence of columnar grains. The transmission electron micrograph (Fig. 5c) shows an apparently hexagonal and elongated spherical morphology of the microcrystallites with grain size between 25 and 60 nm. This is probably because the transmission electron microscopy (TEM) study was done for single layer films. The multilayer films (Fig. 5b) had well-developed columnar structures [14]. The electron diffraction (not shown here) of the films also showed the presence of rings attributed to In_2O_3 only. No diffraction rings for any phase of Sn oxides were noted.

For the sheet resistance measurements five readings were taken for each thickness and the mean values are plotted. The error was between $\pm 2\%$. The sheet resistance values decreased with increase in the coating thickness. This was associated with an increase in the carrier concentration and an accelerated growth of ITO crystals, which increased the conductivity of the formed films [14,27]. The resistance values also decreased significantly after annealing in $N_2 \setminus H_2$ atmosphere. As there were no changes in the crystalline orientations after annealing the air baked films the

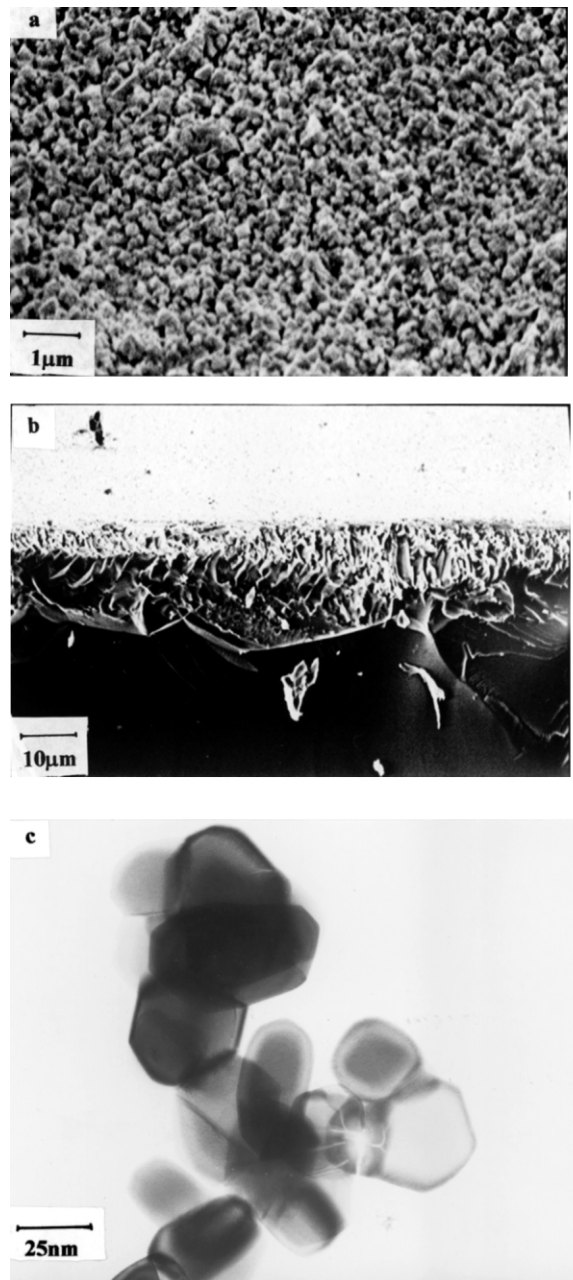


Fig. 5. Micrographs of films corresponding to In/Sn = 90:10 annealed in $N_2 \setminus H_2$ atmosphere, (a) surface microstructure, (b) cross-sectional view of the ITO film and (c) TEM picture of ITO microcrystallites.

significant decrease in the sheet resistance values after annealing could be attributed to the increase in oxygen vacancies resulting in the increase in the carrier concentration and lowering of the overall resistivity. The carrier concentration of the 490-nm film corresponding to In:Sn = 90/10 was 2.3 and $6.1 \times 10^{20}/cm^3$ for the air-baked and annealed films, respectively. The changes in sheet resistance values with changes in coating thickness, for coatings prepared with different In:Sn ratios, before and after annealing are shown in Fig. 6a–d. The

Table 2
Changes in the sheet resistance values for different Sn at% for films air baked and annealed in $N_2 \setminus H_2$ atmosphere

Thickness (nm)	Mean crystallite size in (nm) for In:Sn =							
	80:20		85:15		90:10		95:5	
Heat-treated in								
	Air	$N_2 \setminus H_2$	Air	$N_2 \setminus H_2$	Air	$N_2 \setminus H_2$	Air	$N_2 \setminus H_2$
10	1811	620	1347	481	943	471	994	497
37	665	190	506	101	353	79	384	86
113	438	88	329	74	234	52	276	62
307	436	85	291	65	175	40	250	56
490	400	80	260	58	95	11	210	47

details are provided in Table 2. The mean values of the sheet resistance are provided. Studies of ITO films with various In:Sn ratios (from 100/0 to 0/100) have been reported [14,17,18,24,25,27,28]. Different researchers have made different conclusions regarding the opti-

imum concentration of Sn to obtain best electrical resistivity [14,24,25,27,28]. In the present study, the sheet resistance (and resistivity) values decreased with increase in Sn at.% from 5 to 10, but increased upon further increase in Sn at.% to 15 and 20. The lowest

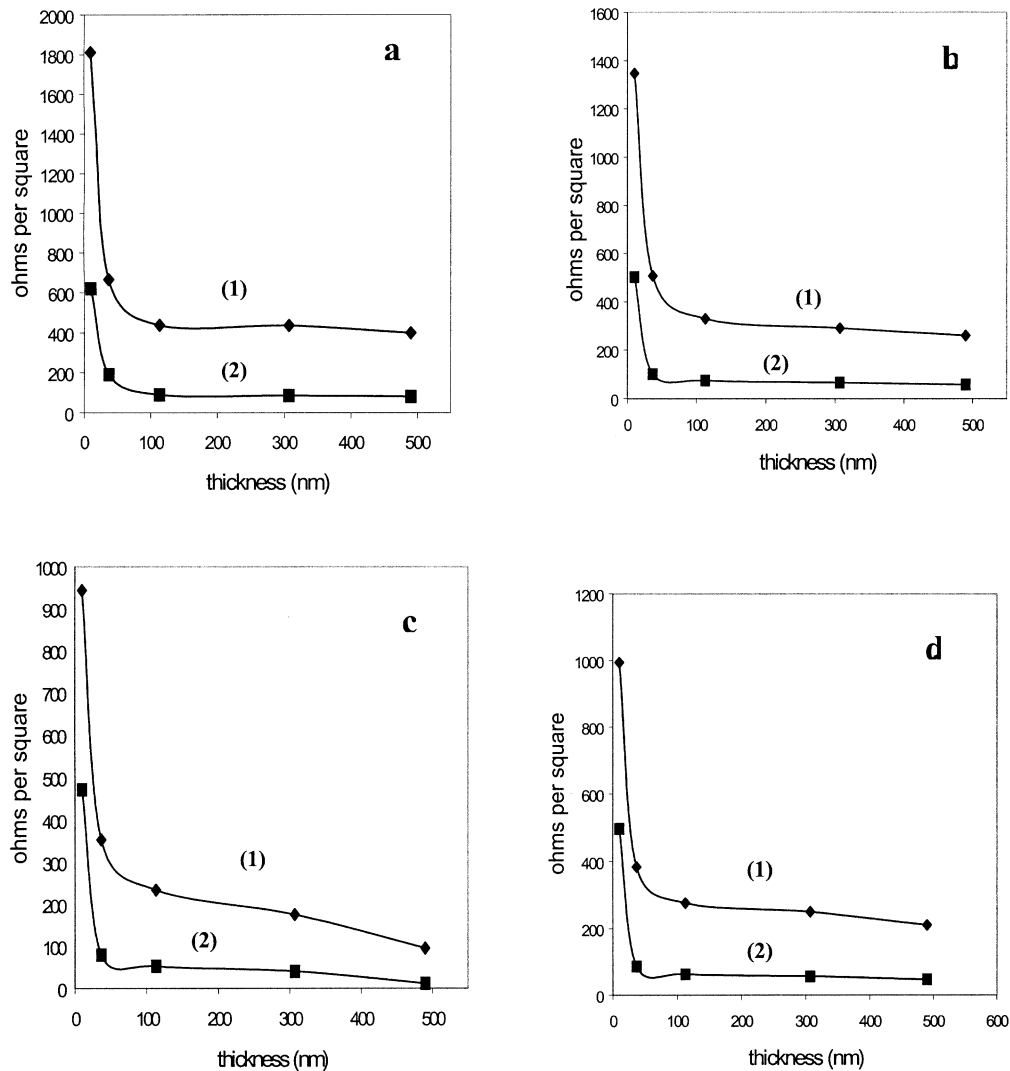


Fig. 6. Variation in the sheet resistance values as a function of film thickness, (i) air baked (ii) annealed in $N_2 \setminus H_2$. (a) In/Sn = 80:20, (b) In/Sn = 85:15, (c) In/Sn = 90:10 and (d) In/Sn = 95:5.

values were recorded for 10 at.% Sn (Table 2). The minimum value of 11 ohms per square (resistivity $5.4 \times 10^{-4} \Omega \text{ cm}$) was observed for the 490-nm thick film. ITO films with resistivities in the range of 10^{-3} – $10^{-4} \Omega \text{ cm}$ has been reported by various authors [2–9,17,19,20] for different preparative techniques. Sheet resistance values of 25–400 ohms per square have been noted for sol–gel derived ITO films [13,16–18,20]. The comparatively low values of sheet resistance recorded for the present coatings may also be associated with the presence of columnar grains which enhances the conductivity of the coatings because of easier movement of carriers due to lesser grain boundaries. The increase in the resistivity of the films with increase in dopant concentration beyond a certain value (10 at.% in the present case) has been associated with segregation of the dopant ion components at the grain boundaries [29,30]. Some researchers have reported that [13,20] a barrier layer of SiO_2 to prevent alkali diffusion is necessary prior to deposition of ITO films in order to increase the conductivity of the films. In the present case, ITO films were also deposited on glass slides pre-coated with a silica layer, for comparison. However, the presence of the silica layer did not produce any significant changes in the final sheet resistance values. This may probably be due to the reason that the final thickness of 490 nm was high enough to prevent alkali diffusion to affect the surface resistance. The resistivities of dip coated ITO films have been reported [14] to increase with storage time. For the present study, the sheet resistance was measured within a day of deposition. However, it was observed that after 6 months the sheet resistance values increased between 2 and 5% of the values recorded after 1 day of storage.

4. Conclusions

Transparent conductive ITO films were deposited on soda-lime silica glass slides from sols prepared using chlorides of In and Sn with different In:Sn atomic ratios. Only crystalline phases corresponding to In_2O_3 were observed. The lowest sheet resistance values were recorded for films with 10 at.% Sn. The minimum sheet resistance value obtained was 11 ohms per square for a 490-nm thick film prepared from sol corresponding to In:Sn atomic ratio 90/10. The SEM pictures showed presence of uniform and dense microstructure apparently devoid of any voids and cracks. The TEM picture showed microcrystallites with hexagonal and elongated spherical morphology with grain size between 25 and 60 nm. The present work shows that ITO films of significantly low sheet resistance values could be prepared starting from the relatively inexpensive metal salts rather than the highly expensive alkoxides.

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