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Morphological Characterization of Sb-Doped SnO_2 Thin Films Developed by Spray Pyrolysis

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Abstract

In the present work, we have successfully deposited Sb antimony doped tin dioxide (SnO_2) thin films with different concentrations (0 at%, 1 at%, 3 at% and 5 at%) from a stannous (II) chloride dihydrate solution ($SnCl_2.2H_2O$), by the pyrolysis chemical spray deposition technique on ordinary microscope glass substrates preheated to a fixed temperature of 350 °C. After deposition, the films were annealed at temperatures 400 °C for 4h. The aim of this work is on the one hand to study the morphological properties of pure and doped tin dioxide thin films and to determine the different morphological parameters such as: the roughness Ra, Rq and on the other hand to study the effect of Sb doping on the morphological properties of SnO_2 thin films. To achieve this purpose, the thickness of all the films was estimated by profilometer with standard scan type. The morphology of the films was examined by atomic force microscope (AFM) in contact mode at room temperature to visualize the surface of our samples (the structure, size and morphology of crystallites ... etc). The 2D and 3D AFM images confirm the formation of nanostructures on the surface, with shapes and dimensions influenced by the amount of antimony doping. All the samples show a polycrystalline morphology, and the grain size progressively decreases with the increase of the Sb concentration (1% and 3%). On the other hand, for high antimony doping (5% Sb) the grains are larger than those observed at 3% doping. The root mean square (RMS) surface roughness values for samples with Sb concentrations (5%) were found to be 8.334 nm

Keywords: *Thin films, SnO_2 tin dioxide, Spray Pyrolysis, AFM atomic force microscopy, annealing temperature..*

1. Introduction

Transparent conducting oxides (TCO) like In_2O_3, SnO_2, ZnO, In_2O_3: Sn … etc have been the subject of research over a number of years due to their promising properties. Tin oxide SnO_2 is a n-type semiconductor with wide bandgap E_g = 3.6 eV at 300K [1], and electrical resistivity varying from 10 to 10^6 Ωcm, depending on the temperature and the stoichiometry of the oxide [2]. In the thin films form, SnO_2 is a transparent material, characterized by high optical transmission in the visible range ~90%, these properties make it very attractive for several applications, like solar cells, optoelectronics devices, thin film resistors, antireflection coatings, photochemical devices, electrically conductive glass. SnO_2 material is usually used in the field of monitoring air pollution and toxic gas detection [3]. Doped and undoped SnO_2 thin films have been prepared by various techniques such as sol gel [4-6], reactive radio frequency sputtering (RF) [7], direct current (DC) magnetron sputtering [8],

In the present study, SnO_2 thin films are deposited by employing a spray pyrolysis technique. We are principally interested by this chemical technique for their advantages like ease of adding dopant material, reproducibility, high growth rate and mass production capability for uniform large area coatings, which are desirable for industrial, solar cell and gas sensor applications. We have made an attempt to synthesize pure and Sb doped SnO_2 thin films on glass substrates by the chemical spray pyrolysis technique and the influence of antimony dopant concentration on the morphological properties of the prepared films is reported.

2. Experimental methods

Thin films preparation. The substrates of dimensions 7.6 cm × 2.6 cm × 0.1 cm were carefully initially cleaned chemically, by keeping in distilled water, acetone and ethanol individually each for 5 min. These substrates were further treated ultrasonically with pure water for 9 min to remove surface contamination and dried at room temperature. The substrates were preheated to the required temperature, prior to deposition. Undoped and antimony doped tin oxide thin films were deposited on glass substrates by using a spray pyrolysis system HOLMARC Model HO-TH-04. The chemical reagents used were stannous (II) chloride dihydrate ($SnCl_2.2H_2O$, 97%, BIOCHEM Chemopharma, Quebec Canada) and antimony trichloride ($SbCl_3$, 99%, BIOCHEM Chemopharma, France) as host and dopant precursors. Initially, 0.1M of $SnCl_2.2H_2O$ and $SbCl_3$ solutions were made separately by dissolving in appropriate amounts of deionized water and methanol CH_3OH volume proportion: 13 ml: 13 ml with adding a few drops of hydrochloric acid HCl to obtain a standardized and transparent working solution. Then the solution was prepared by mixing the existing solutions in appropriate volume ratios, to obtain the targeted concentrations 0 at.%, 1 at.%, 3 at.% and 5 at.% of Sb doped SnO_2 thin films. The solution was stirred continuously at room temperature for 15 min, until it became transparent and homogeneous. After that, the resulting solution was sprayed on the glass substrate at an optimized substrate temperature of 350 °C with an accuracy of ± 1 °C for 10 min with a compressed air pressure of 2 bars. The normalized distance between the spray nozzle and the substrates, the flow rate and the total quantity of spray solution were 12 cm, 200 µl/min and 30 ml respectively. During the spraying, the nozzle moved with longitudinal and transverse speeds $v_x = 400$mm/s and $v_y = 8$ mm/s respectively. The substrates temperature was maintained using a digital temperature controller. After deposition, the films were annealed in a programmable tubular oven under air and with a heating rate of 10°C/ min at temperatures 400 °C for 4h.

Thin films characterization. A set of complementary investigation methods has been used to characterize the thin films prepared. The thickness of all the films was estimated by BRUKER Dektak XT profilometer with standard scan type. The morphology of the films was examined by atomic force microscope (AFM) Nano surf C3000 in contact mode at room temperature.

3. Results and discussion

The thin films of undoped and Sb doped SnO_2 at 1 at.%, 3 at.% and 5 at.% respectively, annealed at 400 °C for 4h were examined by the AFM device to characterize the surface roughness. The AFM measurements are carried out in air in "contact mode". Fig. 1 displays the 2D and 3D AFM images of Sb-doped SnO_2 thin films annealed at 400 °C with a Sb concentrations of 0 (undoped), 1 at.%, 3 at.% and 5 at.% obtained over an area of 2 × 2 μm^2. The average roughness R_a and the root mean square R_q (RMS) parameters were calculated from AFM data using the following relations:

$$R_a = \frac{1}{l}\int_0^l |Z(x)|dx, \quad (1)$$

$$R_q = \sqrt{\frac{1}{l}\int_0^l Z^2(x)dx}, \quad (2)$$

Where Z(x) is the function, that describes the surface profile, analyzed in terms of height Z and position x of the sample over the evaluation length l. The results are collected in table 1, with thickness values measured by a profilometer as a function of Sb doping. All samples show a polycrystalline morphology, and the grain size gradually decreases with an increase of Sb concentration. The grain size is seen to be larger than the crystallite size estimated from XRD measurements; however, this is also attributable to agglomeration of smaller crystallites. Also, we see from the AFM images, a trend of formation of nanostructures in the form of aggregate with different size in relation with doping concentration.

It have been suggested that there is a homogeneous granulates in all surfaces of the films, these results are in very good agreement with previous works [18]. The root mean square (RMS) surface roughness values for samples with Sb concentrations of 0 (undoped) and 1 at.%, 3 at.% and 5 at.% were found to be 7.707 nm and 13.563 - 5.725 - 8.334 nm, respectively.

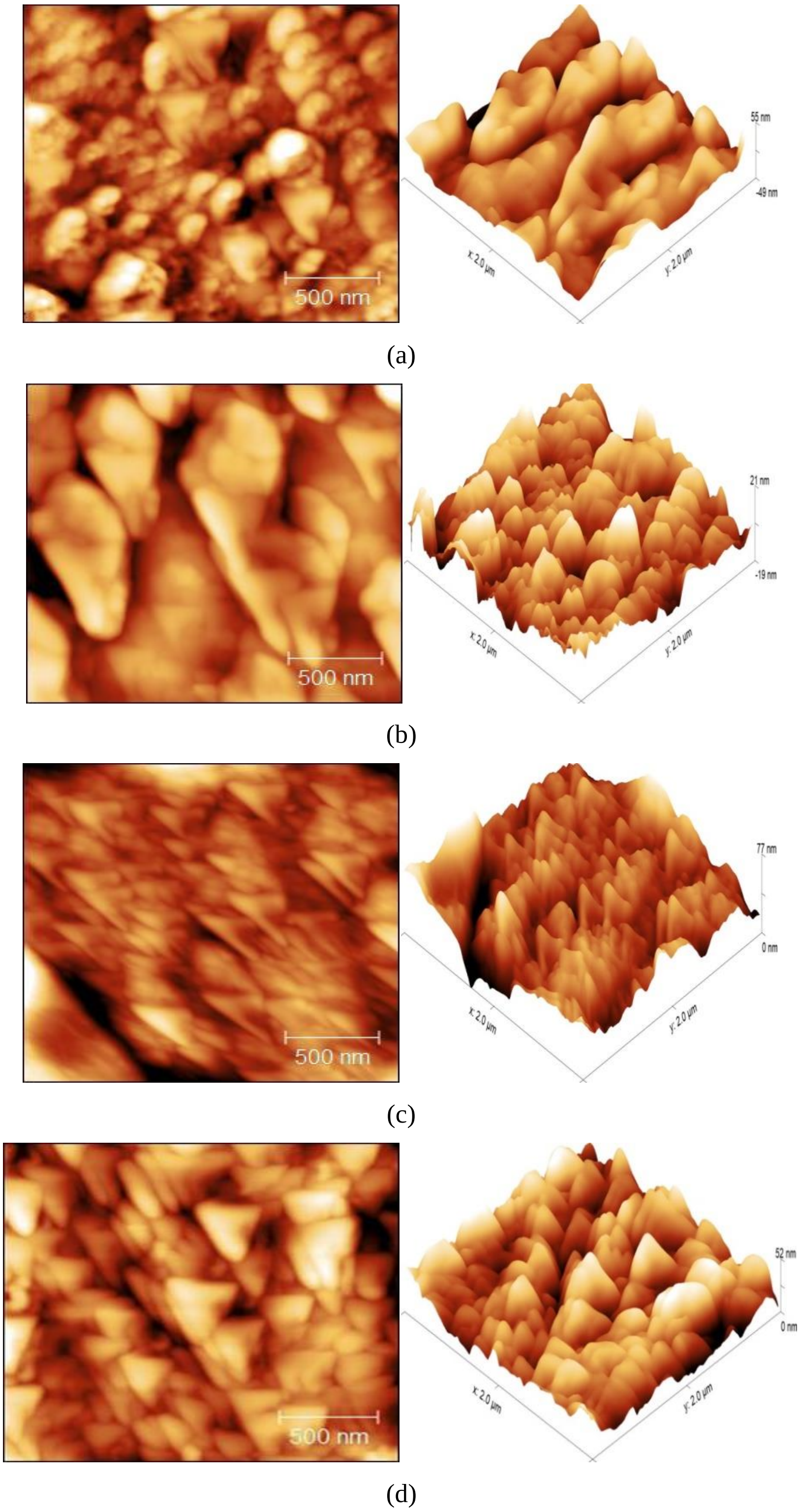

Figure 1: 2D and 3D AFM images of Sb-doped SnO_2 thin films annealed at 400 °C with Sb concentration of 0 (undoped) (a), 1 at.% (b), 3 at.% (c) and 5 at.% (d).

Table 1. Surface roughness parameters and thickness of undoped and Sb doped SnO_2 thin films annealed at 400°C for 4h.

Sb-doping concentration (at. %)	Thickness (nm)	R_a (nm)	R_q (nm)
0	340	5.709	7.704
1	155	10.793	13.563
3	141	4.580	5.725
5	306	6.694	8.334

4. Conclusion

In our study, transparent conducting SnO_2 thin films with different concentrations of Sb have been successfully fabricated on glass substrate by using the chemical spray pyrolysis technique. AFM measurements confirmed a polycrystalline rutile structure for all samples improved with XRD analysis and showed that the maximum roughness was noted for SnO_2: 1 at. % Sb thin films.

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