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Effect of solution concentration on the structural, optical and electrical properties of SnO_2 thin films prepared by spray pyrolysis

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ABSTRACT

The aim of this work is the production of tin oxide thin films with a suitable optoelectronic properties required for application as transparent electrodes. Using a simple and inexpensive homemade spray pyrolysis system of tin chloride ($SnCl_2$) onto glass substrates. The motivation for the use of this technique is its simplicity and effectiveness of preparation. The effect of the molarity (0.05–0.25 mol/l) on structural, optical and electrical film properties was investigated.

The results obtained with several characterization techniques such as DRX, AFM, UV–visible transmission and four probe points measurements are well consistent and suggest that the prepared films were uniform and well adherent to the substrates. All the films are polycrystalline in nature with a tetragonal structure having a preferential orientation along the (1 1 0) plane. The obtained SnO_2 films, not only have an average transmittance greater than 80% in the visible region, but also have an optical band gap between 3.84 and 4.14 eV depending on the spraying solution concentration. Moreover, the measured electrical conductivity at room temperature was found in the order of 10^2 $(\Omega\,cm)^{-1}$.

1. Introduction:

Tin oxide thin films have been used for transparent electrodes in photoelectric conversion devices namely amorphous silicon solar cells, liquid crystal display, gas discharge display, etc. [1,2]. Though tin oxide films may be prepared by various techniques, such as: sputtering [3], electron beam [4], sol–gel [5], chemical vapor deposition [6] and spin coating [7], spray pyrolysis is used to prepare films because of its simplicity and commercial viability [8]. The spraying method involves decomposition of tin chloride solution at high temperatures in the presence of an oxidizing agent. Stannic oxide (SnO_2) condenses in the rutile crystallographic structure. Oxygen deficiency in the crystal lattice of tin oxide can be accounted for by properties revealed in the experimental observation [9].

Doping tin oxide with fluorine, chlorine, antimony etc. [10,11] as donor impurities yields films with low sheet resistance [1]. This paper describes the results of our study in an attempt to correlate the electrical conduction with the grain orientation.

The aim of this research was to establish a relationship between the solution concentration and the film properties. In order to achieve this goal, tin oxide films were prepared by a spraying method at various solution concentrations ranging from 0.05 to 0.25 mol/l. The properties of the films were characterized by X-ray diffraction analysis (XRD), Atomic Force Microscopy, UV–vis spectroscopy and four-point conductivity measurement method.

2. Experimental procedure

The tin oxide films were prepared using a homemade spray pyrolysis system (Fig. 1). In this deposition technique, liquid precursors are sprayed by atomization processes and condensed by thermal decomposition on substrates maintained at elevated temperatures. The sprayed micro-droplets reaching the hot substrate surface undergo pyrolytic decomposition and form a single crystallite or a cluster of crystallites of the sprayed materials Stannous chloride ($SnCl_2{\cdot}2H_2O$) was used as a precursor for tin. This tin precursor dissolved in distilled water with adding few drops of hydrochloric acid (HCl). The precursor concentration was varied from 0.05 to 0.25 mol/l. All spray solutions were magnetically stirred to obtain homogenous solutions. The resultant solutions were sprayed on glass substrates. The normalized distance of 30 cm

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between the spray nozzle and the substrates was maintained. The spray solution quantity of 100 ml was kept fixed during the growth. The filtered compressed air was used as gas carrier. The deposition time was fixed to 3 min for each film. The substrate temperature (working temperature) was maintained at 400 °C and by an electronic temperature controller connected to the heater. After deposition, the coated substrates were allowed to cool down naturally to room temperature.

The formation of SnO_2 films from a $SnCl_2$ solution gives rise to a transitory formation of the compound SnO. The chemical reactions taking place are [12–14]:

$$SnCl_2 + H_2O \rightarrow SnO + 2HCl;$$

$$SnO + 1/2O_2 \rightarrow SnO_2$$

$SnCl_2$ can partly decompose and ionize into Sn^{2+} and Cl^-; it could also form tin based polymer molecules [13]. On the other hand, it is reported that the presence of HCl in $SnCl_2$ solution forms different intermediate molecules in the starting solution. Addition of HCl that results in transparent solution may be due to the breakdown of those tin based polymer molecules. $SnCl_2{\cdot}2H_2O$ is known to react with HCl to give $HSnCl_3$. At the pyrolysis temperature, $HSnCl_3$ is thermally decomposed to form the SnO_2 molecule [12,14].

The structural characterization of the SnO_2 thin films was carried out by X-ray diffraction (XRD) measurements using a BRUKER D8 ADVANCE diffractometer with Cu Kα radiation (λ = 1.541838 Å). The diffractometer reflections were taken at room temperature and the values of 2θ were altered between 20° and 80°. The surface morphology of the films was observed using A100 AFM Atomic Force Microscope A P E Research. The DC electrical resistivity measurement was achieved in dark and at room temperature with four-point probe technique. Film optical transmittance was recorded by using SHIMADZU 1800 UV–visible scanning spectrophotometer in the spectral region between 200 and 800 nm.

3. Results and discussion

Films deposited on glass substrate were physically stable and had a good adherence to the substrates (hardly peeled with scotch tape test).

3.1. Structural properties and morphology

To investigate the crystalline quality of the films with various solution concentration, XRD analysis was made, and the resulted

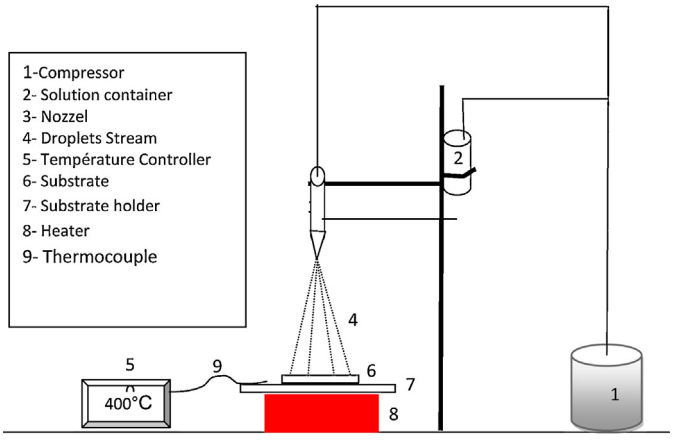

Fig. 1. Experimental set-up schematic of the Homemade Spray Pyrolysis System used to prepare the samples.

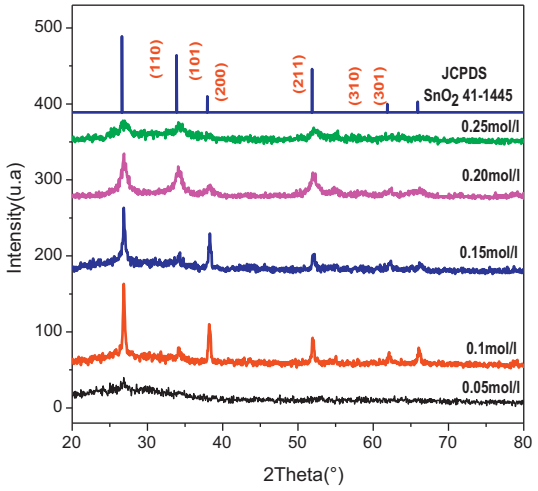

Fig. 2. XRD patterns of solution concentration used to prepare SnO_2 thin films.

Table 1
The textured coefficient (TC) values of SnO_2 thin films.

(*hkl*)	0.1 mol/l	0.15 mol/l	0.2 mol/l	0.25 mol/l
1 1 0	2.290	2.213	1.925	1.466
1 0 1	0.587	0.762	1.379	1.377
2 0 0	1.216	1.377	0.609	0.711
2 1 1	0.851	0.713	1.1229	1.066
3 1 0	0.466	0.491	0.4812	0.755
3 0 1	0.587	0.442	0.4812	0.622

spectrums are shown in Fig. 2. This figure also proves that the film with 0.05 mol/l concentration is not completely crystallized (nearly amorphous). By increasing the molarity, the intensity of peaks is significantly increased due to the improvement of the film crystallinity, and these peaks indicate that the films have a tetragonal rutile phase of tin oxide (JCPDS card No. 041-1445) which belongs to the space group P42/mnm (number 136). It is perceptible from the XRD patterns of Fig. 2. That the matching of the observed and standard '*d*' values confirms that the deposited films are of SnO_2 with cassiterite tetragonal structure. The (1 1 0) is the most intense peak which is observed for all samples, other peaks assigned as (1 0 1), (2 0 0), (2 1 1), (3 1 0) and (3 0 1) were also observed. The reflection intensities for each peak contains information being related to the preferential or random growth of polycrystalline thin films investigated by calculating the texture coefficient TC (*hkl*) for the planes using the following Eq. (1) [15].

$$TC_{(hkl)} = \frac{I_{(hkl)}}{\frac{1}{N}\sum I_{(hkl)}} \quad (1)$$

where, $I_{(hkl)}$ is the measured intensity of X-ray reflection, and N is the number of reflections observed in the XRD pattern. The calculated TC values are presented in Table 1. The variation of the texture coefficient with solution concentration for each peak has been depicted.

Fig. 3 a sample which has randomly oriented crystallite presents TC (*hkl*) = 1. The larger this value, the larger the abundance of crystallites oriented at the (hkl) direction [16]. In this study, TC values of (1 1 0) peaks for all samples are larger than unity. In all films, TC values for (1 1 0) are relatively higher than those of other planes, TC values of (1 1 0) peak continuously decrease and increase of (1 0 1) and (2 1 1) peaks with solution concentration. This confirms reorientation with increasing solution concentration.