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Influence of Growth Temperature on Structure and Optical Properties of Tin Oxide Films by Spray Pyrolysis Method

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Tin oxide films (SnO_2) are prepared by the spray pyrolysis technique at different temperatures. The XRD measurement confirm that the thin films grown by this technique have good crystalline tetragonal rutile structures. The observations by scanning electron microscopy indicate that polycrystalline SnO_2 film surfaces were formed by pyramidal grains (200 nm 300 nm), The composition on the films was obtained by Auger electron spectroscopy (AES), which is identical to the analysis EDS. Characterization by UV-visible spectrophotometry of thin films showed that the films have an optical transmission above 80 % in the visible and the values of E_g were in the range 3.98-4.02 eV.

Keywords: SnO_2, Spray deposition, Auger electron spectroscopy (AES), Structural, Optical and electrical properties.

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1. INTRODUCTION

SnO_2 is an excellent transparent conductive oxide (TCO) widely used in optoelectronic devices [1-4]. It is especially suitable for the fabrication of thin film photovoltaic devices since it possess some remarkable properties such as a high transmittance in the visible range of the electromagnetic spectra, a low sheet resistance and a high chemical stability. Deposition can be carried out by different methods, such as sputtering [5], chemical vapor deposition [6-7], sol-gel [8-9] and spray pyrolysis [10-14]. His latter technique are considered as the most appropriate in many areas for the deposition of TCO layers, since it requires minimal costs to be implemented and allows obtaining films with high optical and electrical qualities. S. Hamzaoui and al. studied the effects of temperature in electrical and optical properties of SnO_2 [15] P.S. Patil and al. studied the effect of substrate temperature on structural, electrical and optical properties of sprayed tin oxide (SnO_2) thin films [16]. In present work the SnO_2 films were deposited by spray pyrolysis. The influence of the temperature substrate on the structural and optical properties the thin films is study.

2. EXPERIMENTAL

Thin films of SnO_2 were prepared using a home-made spray pyrolysis experimental. Tin chloride was used as the source for tin. Microscopic glass slides ($75 \times 25 \times 1$ mm^3) were used as substrates. 0.4 M of $SnCl2.2H_2O$ dissolved in 30 ml mixture of methanol, HCl and distilled water served as starting solution. The deposition time was 10 minutes for all depositions. The carrier gas flow rate was maintained at 10 l/min. The normalized distance between the spray nozzle and the substrate is 25 cm. The spray time interval was a 30 s. One of the dominant parameters in methods for depositing thin layers such spray that is the temperature of the substrate surface. The first study is focused on the influence of the temperature on the different properties of the deposit. The temperature range selected for this study is 350 °C to 450 °C with a pitch of 50 °C. The structural properties of this films were analyzed by a PHILIPS X'PERT PRO diffractometer with using Anode Material: Cu, K-Alpha 1 = 1.54060 Å, Generator Settings: 40 mA, 45 Kv. The XRD spectra were recorded in $2\theta/\theta$ continuous scanning mode over a 2θ range of 20°-100 with a scan speed of 0.8°/min and a step size of 0.02°. The surface morphology of the film was studied by a Field-Emission Environmental Scanning Electron Microscope Philips XL30 ESEM-FEG, operating at a voltage of 10 kV, with an EDS (Energy Dispersive Spectroscopy). The spectrum Auger obtunded by Perkin Elmer PHI 600 system. The optical measurements of SnO_2 thin films were carried out at room temperature using UV Spectrophotometer in the wavelength range of 300-1100 nm.

3. RESULTS AND DISCUSSION

3.1 Structural Characterization

Fig. 1 show XRD spectra of tin oxide deposited under different substrate temperatures. The comparison the spectra of the reference JCPDS file (card No 46-1088) confirmed the tetragonal rutile structure of our deposits. This structure is typical of deposits SnO_2. At 350 °C, more peaks are present with a preferred orientation in (200) and minority peaks according (110), (211) and (310). At 400 °C, the graph has the same aspect with a preferential orientation (200) with a greater intensity. In other words, the crystallinity of the samples increased by increasing the temperature [17].

The average particle size of SnO_2 is estimated from X-ray line broadening using the Debye-Scherrer equation [18]:

$$D = \frac{0.9\lambda}{\beta \cos\theta_{hkl}} \quad (1)$$

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where D is the grain size of crystallite, λ (= 1.54059 Å) the wavelength of X-rays used, β the broadening of diffraction line measured at half its maximum intensity in radians and θ is the angle of diffraction. We note that the values of the grain size change between 26 nm and 45 nm. The results are regrouped in the Table 1. When the substrate temperature is increasing, the grain size is increasing.

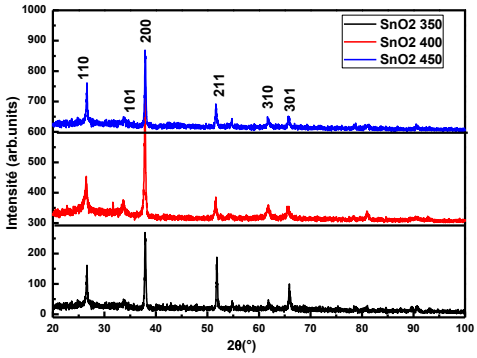

Fig. 1 – X-ray diffraction patterns taken from the spray SnO_2 films deposited at 350 °C, 400 °C and 450 °C

3.2 Morphological Characterization

The observations by scanning electron microscopy of the surface for pure SnO_2 different temperature are shown in Figure 2 (a-b-c). The grain diameter between range from several tens to hundreds of nanometer. However, grains whose size is around 500 nm are most. The films produced at temperatures 350 °C have spherical surface. The growth temperature has a strong influence on crystal growth mechanism. At high temperatures, 400 and 450 the particles are of pyramid shape.

The compositional analysis of SnO_2 thin film by energy dispersive X-ray analysis is shown in Fig. 2d. EDX spectrum confirmed the presence of Sn and O elements in the deposited films. The silicon signal possibly appears from the substrate [19].

3.3 Characterization by Auger Spectroscopy

Auger electron spectroscopy allows to characterize the surface atoms of thin films. Quantitative analysis involving the use of elemental sensitivity factors. The atomic concentration (C) of an element x in a sample is given by relation 5[20].

$$C_x = \frac{\frac{I_x}{S_x}}{\sum \frac{I_i}{S_i}}. \qquad (2)$$

Where I_x is the intensity of the Auger signal from the unknown specimen (I_i: peak-to-peak heights of transitions LVV oxygen and transitions LMM tin.) and Si is the relative sensitivity of pure element i.

The AES spectra from the SnO_2 thin film deposed at 400 °C are shown in Fig. 3. Spectrum (a) was recorded before Ar^+ sputtering, whereas (b) was taken after 8 min of sputtering times. The energy peaks are displaced towards the low energies about 7 eV with respect the

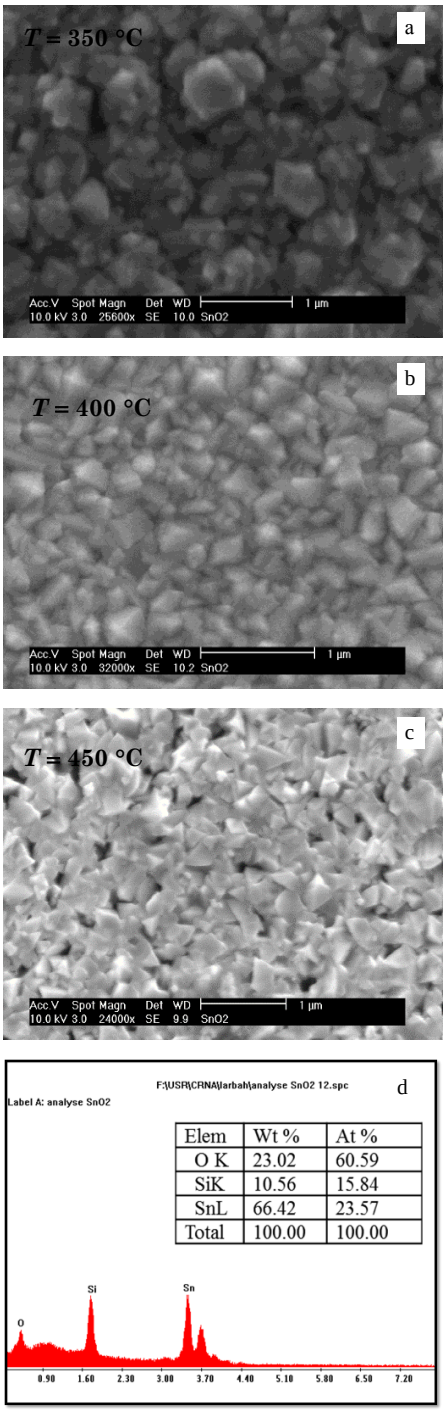

Fig. 2 – SEM micrographs of SnO_2 films deposited at a) 350 °C, b) 400 °C, c) 450 °C and d) analysis EDS

position of the recorded pikes on pure tin. The peaks are displaced due to changes in the energy electronic structure of tin atoms, to form chemical bonds with oxygen atoms. This energy shift shows the formation of SnO_2. We observe a good agreement between the EDS and analysis by Auger electron spectroscopy. The Fig. 4 present the profile of the SnO_2 thin film deposed at 400 °C. The Sn and O fractions are homogeneous within the explored depth, whereas the carbon concentration decreases, this result already obtained by other authors [21].

Table 1 – Structural parameters of SnO_2 thin films

T [°C]	(hkl)	FWHM [°2Th.]	d-spacing [Å]	Crystallite size [Å]	D_{Moy} [Å]
350	110	0.450	3.373	181	268
	200	0.238	2.375	353	
	211	0.329	1.771	268	
400	110	0.236	3.330	389	425
	200	0.214	2.361	449	
	211	0.229	1.760	437	
450	110	0.213	3.351	439	453
	200	0.236	2.370	402	
	211	0.196	1.768	519	

3.4 Optical Characterization

Fig. 5 presents the optical transmittance in the wavelength range (300-1100 nm) for the SnO_2 thin films deposited at T = 350 °C 400 and 450 °C. The optical transmission of the coatings increases with the growth temperature (Fig. 5). The films were transparent with transmittance of 80 % and exhibit a regular interference bands in the visible light for the films fabricated at substrate temperature 400 °C and 450 °C. This is a direct consequence of their being wide band gap Semiconductors (E_g > 3.6 eV)[22-23].

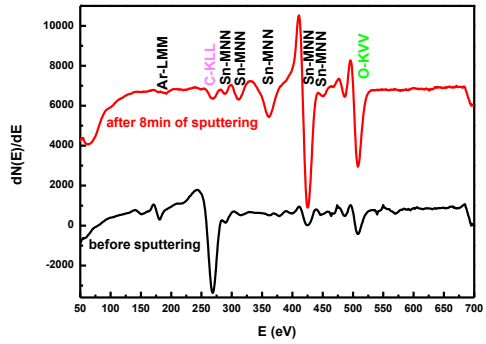

Fig. 3 – AES spectra of SnO_2 deposed at 400 °C (a) before Ar^+ sputtering and (b) after 8 min sputtering time

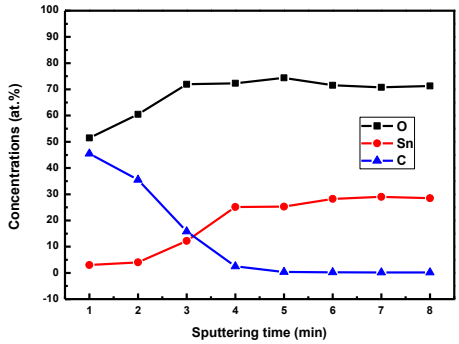

Fig. 4 – Concentration profile in the SnO_2 thin film deposed at 400 °C

To determinate gap energy of direct transition (E_g) of the SnO_2 thin films, optical method was used. In this method, the plots of $(\alpha h\nu)^2$ versus $(h\nu)$ for SnO_2 thin films at different temperatures are shown in Fig. 6. The linear intercept at the $(h\nu)$ axis gives the value of the direct band gap. The direct band gap varies from 3.98 to 4.02. These values are higher than the value of E_g = 3.57 eV reported for single crystal SnO_2 [22].

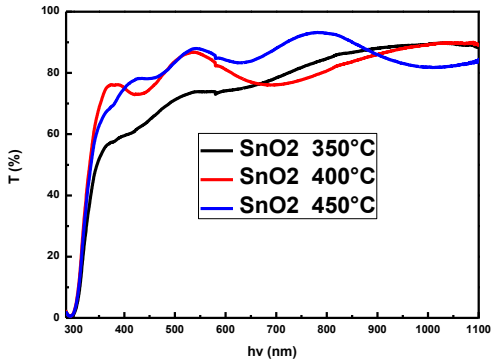

Fig. 5 – Transmittance spectra of SnO_2 thin films at different temperatures

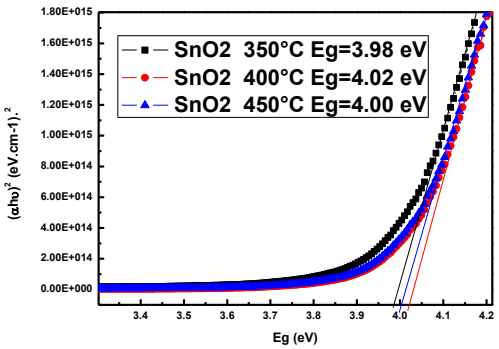

Fig. 6 – Graph of $(\alpha h\nu)^2$ versus $(h\nu)$ at different temperatures

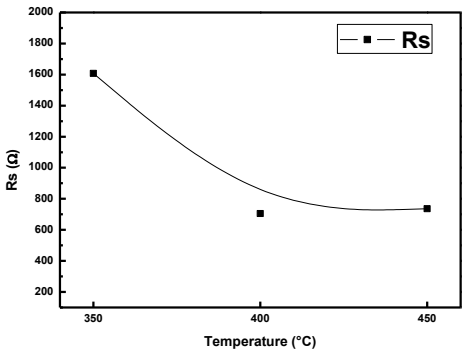

Fig. 7 – The variation in sheet resistance of SnO_2 thin films as a function of temperature

3.5 Characterization Electrical

The sheet resistance (R_s) measurements of the films were done via 4-point probe technique. As can be seen in Fig. 7 when the temperature decreases R_s of the thin

film decreases. The study of the influence of the temperature allowed to know the optimum deposition temperature. The selected optimal temperature is 400 °C because its have the lowest sheet resistance of 700 Ω and good transparency 80 %.

4. CONCLUSIONS

SnO_2 thin films were deposited by the spray pyrolysis method at different temperature on glass substrate. The XRD studies of the prepared films showed polycrystalline nature and tetragonal (rutile) phase, which prefer the orientation (200) for all temperature. Observation by SEM showed good crystallization of the SnO_2 starting from 400 °C. Analysis by Auger spectroscopy confirmed the film to be composed on tin and oxygen and the proportion rapprochement of concentration SnO_2. As we observe a good agreement between the chemical analysis and analysis by Auger electron spectroscopy. The average transmittance in the visible (400-800 nm) was over 80 %. The best sheet resistance obtained equal to 700 Ω/□ at 400 °C.

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