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Influence of annealing time on structural and electrical properties of Sb doped SnO_2 films

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Abstract - *Nanocrystalline 14 at % Sb-doped SnO_2 films have been synthesized by a sol-gel method, to use them as solar cells electrodes. In this paper, we present a study of the annealing time of the films versus the increase of the particle size (varying from 6 nm to 19 nm) established by Scherer's equation. We have also followed electrical resistance evolution with annealing temperature and time. An optimum value of 222 Ω/; was measured on a sample annealed at 500 °C for 2 h. The crystalline structure of the films was characterized and phases identified by X ray diffraction in grazing incidence. Their thickness has been measured by spectroscopic ellipsometry around 200 nm.*

Résumé – *Les couches minces nanocristallines de SnO_2 dopées à 14 % at Sb ont été synthétisées par la méthode Sol-Gel, dans le but de les utiliser comme électrode dans les cellules solaires. Dans le présent article, nous présentons l'effet du temps de recuit sur la taille des grains. La taille des grains est déterminée par l'équation de Scherer et varie de 6 nm à 19 nm. Nous avons, également, étudié l'évolution de la résistance de ces couches en fonction de la température et du temps de recuit. La valeur optimum est de 222 Ω/;, elle a été mesurée pour le cas d'un échantillon recuit à 500°C pendant 2 heures. La structure cristallographique des films a été caractérisée par la diffraction des rayons X (DRX) en incidence rasante. Les épaisseurs de ces films ont été mesurées par ellipsomètrie, elles sont de l'ordre de 200 nm.*

Key words: Solar cell - SnO_2 – Sb - X Ray Diffraction – Nanocrystal – Nanostructure - Photovoltaic device - Electrical properties – Annealing - Thin layers.

1. INTRODUCTION

Tin dioxide SnO_2 is a wide gap semiconductor efficiently used as transparent conducting oxide (TCO) when doped with atoms such as antimony. TCOs are the object of several researches to improve their transparencies in visible range and their electrical conductivities. They are used as transparent electrodes, or as hetero junction for microelectronic applications or as gas sensors. These films are known for their chemical [1, 2] and mechanical high stabilities [2, 3], except their interaction with oxygen atoms at high temperatures [4] SnO_2 layers can be deposited using various methods: sputtering [5], pulsed excimer laser ablation deposition (PLAD) [6], chemical vapour deposition (CVD) [7, 8], pyrolysis [9-12], and, more recently by sol-gel process [13-15]. We have chosen the sol -gel method which is of easy use and makes possible to deposit thin and even ultra thin layers on various substrates of different shapes. The dip-coating technique has been developed during the last decade for the deposition of many oxide compounds. This method presents the following major advantages: an easy treatment of large and complex–shaped substrates, the possibility of high-purity starting materials, homogeneous doping and a low-cost process.

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The present paper exhibits the influence of the annealing time and temperature on the crystallinity as well as on electrical properties of SnO_2 layers doped with antimony at a ratio of about 14 % [13]. The relative humidity ratio was about 25 % [15]. Grain size is strongly linked to the annealing conditions (times and temperatures). For Sb-doped SnO_2 films the resistances are between 222 Ω/; to1633 Ω/; for an annealing of 500 °C and between 252 Ω/; to 1472 Ω/; for an annealing of 600 °C.

2. EXPERIMENTAL PROCEDURE

2.1 Powder and sol preparation

Powder has been prepared from $SnCl_2$, H_2O mixed to a volume of absolute ethanol. This solution is dried and stirred at 80 °C for 2 hours first in a closed container which is then opened up to obtain a powder. This powder has been used for first X-ray analysis. It can be dissolved in ethanol under stirring for two hours in order to prepare the solution used for film deposition.

2.2 Deposition of the films

Deposition of the films from the solution (sol) was performed using dip-coating described in ref. [14, 15]. The substrates were cleaned glass plates, and then emerged in ultrasonic bath during 5 minutes and finally rinsed by ethanol. They were dipped into the solution and then slowly withdrawn from the bath at a constant speed equal to 80 mm/min. The relative humidity (RH) ratio in the atmosphere near the meniscus is continuously controlled and is between 20 % and 30 %. Films were first dried at low temperature (100 °C) during 15 min and heat treated at 300 °C during 15 min at constant flow of pure and dry oxygen gas, the corresponding thickness is of the order of 250 nm for five dipping.

Samples are heat treated at 500 °C and 600 °C for different times: 1h, 1h30, 2h and 2h30 in a constant flow of pure and dry oxygen gas flow. The experimental conditions selected in this paper are similar to those used by other authors [14, 15].Terrier [15] in its PHD thesis studies the effect of humidity on the quality of SnO_2 layers and the effect of the various Sb concentrations on the electric properties.We chose the temperature of 500 °C – 600 °C temperature range because, according to Chatelon [14], 500 °C is the temperature of a complete crystallization of the obtained layer. The ratio of crystallization and the size of crystallites according to the temperature were studied by Chatelon [14]. Szczuko *et al.* [16] have studied the variation of crystallites size in depending on doping element and concentration.

We processed 5 layers of Sb doped SnO_2 to get a sufficiently thick deposit for photovoltaic solar cells nanocrystalline application and also to improve the electric properties. We varied the annealing time and study the influence of this time on the grains size and on the resistances values of these layers.

3. MEASUREMENTS

Sample's X-ray diffraction in grazing incidence (XRD) was carried out using Cu K_α (Drom-3m diffractometer) because layers deposited have thicknesses lower than 1µm. The diffraction angles used vary from 20° to 70°. The detector displacement speed is 0.05 °/min. Thicknesses of films were measured by ellipsometric spectrometry performed on a Jobin Yvon UVISEL.

The phases obtained of the SnO_2 powder and those obtained of layers, were analyzed by X-Ray Diffraction (XRD) method (θ -2θ).

The spectrum represented on Figure 1 was recorded on the synthesized SnO_2 powder. It shows the characteristic diffraction peaks of the SnO_2 compound. The SnO_2 powder obtained is therefore crystallized.

Figure 2 shows the X-ray diffraction at grazing incidence, corresponding to the samples annealing at 500 °C for 1h, 1h30, 2h and 2h30, respectively.

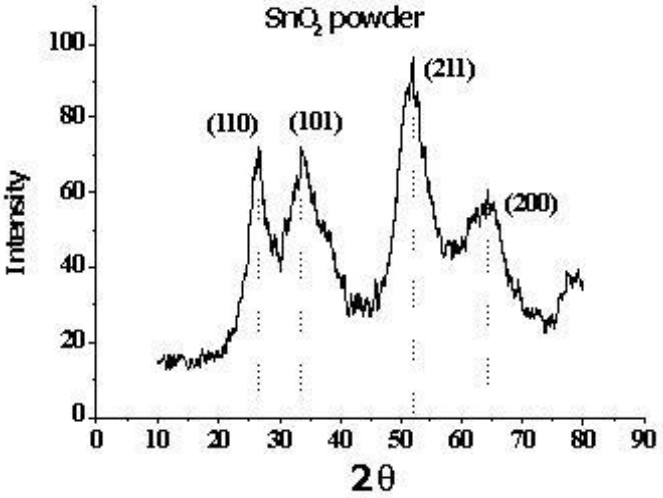

Fig. 1: X-ray pattern obtained on SnO_2 powder

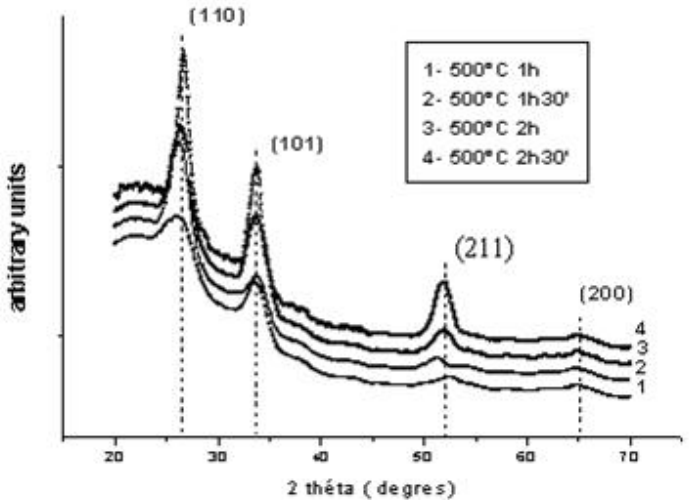

Fig. 2: X-ray diffraction at grazing incidence of Sb-doped SnO_2 films annealed at 500 °C during different times (1h, 1h30min, 2h, 2h30min)

The spectra shows peaks at 26.60°, 33.89°, 52.41° and 65° angles are characteristic of the diffraction lines (110), (101), (211) and (200) respectively, of the tetragonal Sb-doped SnO_2 phase [12, 17-19]. Tsumachima *et al.* [20] found no trace of any other crystalline phase but cassiterite in diffraction pattern of thin of SnO_2 film containing up to 30 % at Sb and heated at 600 °C.

More the annealing time or the temperature increases more the peaks of the SnO_2 structure are intense and straight. That corresponds to the grain size enlargement of SnO_2 nanocrystals.

Four other samples were annealed at 600 °C for the same durations.Figure 3 shows the x-ray diffraction pattern of the four samples, obtained in the same experimental conditions than the previous one. The same behavior is noted versus annealing duration. or two hours and half of annealing, the bump characteristic of amorphous phase decreases appreciably to evolve to intense and fine peaks indexed (110) and (101).

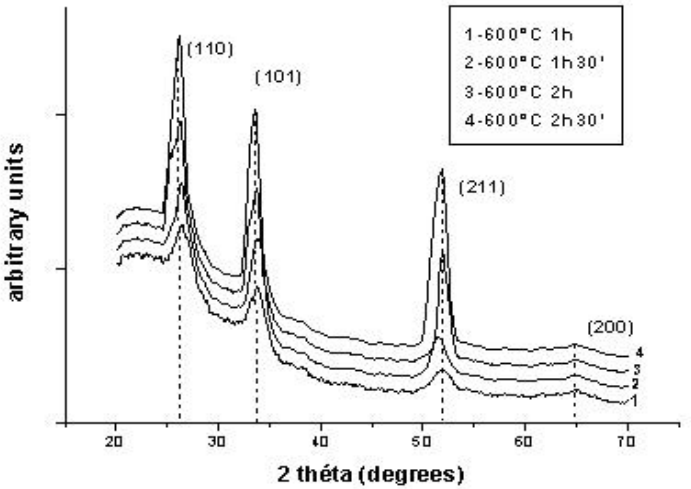

Fig. 3: X-ray diffraction in grazing incidence of Sb doped SnO_2 films annealed at 600°C during different times (1h, 1h30mn, 2h, 2h30mn)

3.1 Determination of crystallites size

To obtain the complete crystallization of our thin layers, the annealing temperatures 500 °C and 600 °C have been chosen [14]. We estimate the crystallites size, by using Scherer's equation, which represents the average diameter of crystallites in the absence of significant residual stresses.

$$T = \frac{K\lambda}{\beta\cos(\theta)} \quad (1)$$

where T is the size of crystallites in nm, λ is the X-ray wavelength (0.154 nm in our case), β is the Full Width at Half Maximum (FWHM) of the most intense peak (i.e. (110)) [21], K is the Scherer's constant equal to 0.9 [22].

According to these calculations we note that for the annealing temperature 500 °C (resp. 600 °C), the size of the grains varies between 6 nm and 15 nm (resp. from 10 nm to 19 nm) in direct relationship to annealing time (see **Table 1**).

The average size of crystallites for the temperatures higher than 400 °C, increases with the temperature. We obtain thus a significant growth of the size when the temperature increases.

For the annealing temperature 600 °C and for all heat treatment durations, the size of the grains is more important than for 500 °C, which is also the case in Sb doped SnO_2 nanocrystalline layers used for gas-sensors [23].

Table 1: Influence of the temperature and annealing time on the crystallite size T (nm)

	500°C				**600°C**			
Annealing time	1h	1h30	2h	2h30	1h	1h30	2h	2h30
Full Width at Half Maximum FWHM β (°)	2.71	2.04	1.98	1.18	1.57	1.30	1.25	1.004
the crystallite size T (nm)	6	7.8	8.1	15.1	10.6	13.3	14.4	18.5

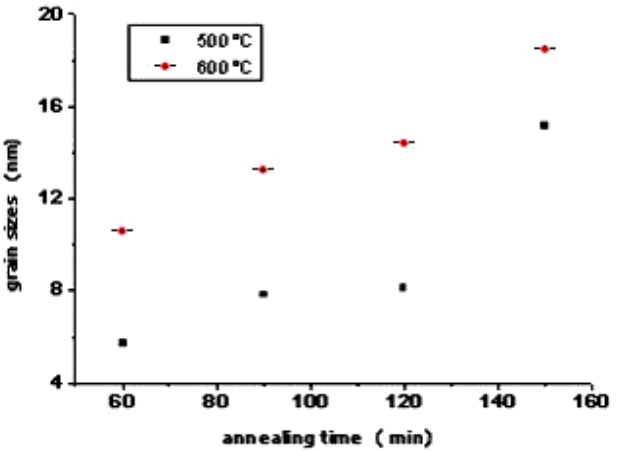

Fig. 4: Relation between the size of crystallites and the temperature (500°C et 600°C) and the annealing time (1h, 1h30mn, 2h, 2h30mn)

3.2 Resistances of the thin layers

Figure 5 shows the values of the resistances of the thin layers, measured by the four points method, versus the annealing duration. The shape of the curves for the temperatures 500°C and 600°C is similar. For the temperature of annealing of 500°C (resp. 600°C), we note that for an annealing duration of 1 hour the value of resistance is 1633 Ω/; (resp. 694 Ω/;), for 1h30mn 694 Ω/; (resp. 480 Ω/;) and for 2h it reaches 222 Ω/; (resp.252 Ω/;) and for 2h30 it increases to 282 Ω/; (resp.1472 Ω/;). This latter is more important than measured for the annealing time of 2h at 500°C. Terrier [15] showed that the value of the resistance of the layers of 14 % Sb doped SnO_2 500 nm thick, reheated at 500 °C during 30mn is 150 Ω/;.

Electric resistances of the Sb-doped SnO_2 layers depend on the following parameters: the Sb doping ratio, thicknesses of the layers, temperatures and times of annealing.

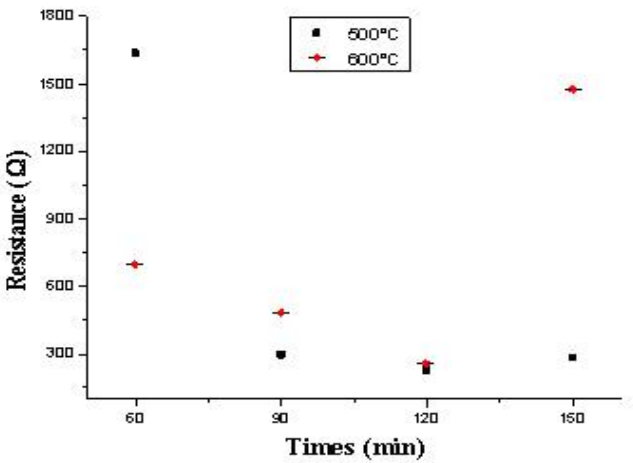

Fig. 5: Resistance (Ω/;) of films for various temperature (500°C et 600°C) and different annealing time (1h, 1h30mn, 2h, 2h30mn)..

The values of resistances for annealing at 500 °C are generally lower than for annealing at 600 °C. We can note that the difference between these two values decreases when the time of annealing increases. When the annealing time reached 2h30mn, the two values of resistance for

the two temperatures increase but the increase in resistance to 600 °C is very important. Indeed, it passes from 252 Ω/; for 2h to 1472 Ω/; for 2h30mn. To optimize the operation of the photovoltaic nanocrystalline solar cells, when we use these results, we will choose the thermal treatment at the temperature of 500°C and 2h for the annealing time. The resistance value is lowest, corresponding to a more important electrical current. The resistances values as well as the electrical current are in relation to the grain size of SnO_2 the sizes of the crystalline grains contribute in determining the electrical resistance of the material.

The thin film structure obtained is porous. If this surface is spread out, there will be an active surface. This latter depends on the size and the depth of crystallites formed. More this surface is important more the electrical current which circulates will be important and more electric resistance is low. When this surface (activates) decreases the electrical current decreases and electric resistance increases consequently.

The grain size is a significant factor for resistance values. The active surfaces (spread out) of our thin layers are directly related to the size of crystallites. We noted, that during the increase in the annealing temperature and times, the average diameter of crystallites increases, therefore the spread out surface of the layer formed by these nanocrystallites decreases, also, and when crystallites formed reach certain cuts limit for annealing 2 hours, its 8 nm for annealing at 500°C and 14 nm for annealing at 600°C, this spread out (active) surface increases and the value of the resistance of the layers decrease consequently.

The minimal resistance is equal at 222 Ω/;, it is gotten for a size of grain 8 nm that is gotten for annealing at 500°C during 2 hours.

4. CONCLUSION

We have deposited by this method antimony 14% (Sb) doped SnO_2 layers. Initially, we synthesized the powder of SnO_2. The characterization by X-ray diffraction indeed showed that this powder is crystallized. The thin layers characterization by X-ray diffraction with grazing incidence shows the crystalline character of these from a heat treatment temperature of 500 °C. The size of the grains varies with annealing temperature and influences the values of resistances We notice that the size of crystallites is in direct relationship with the increase of the temperature and the time of annealing, more the temperature is high more the size of the grains is important and more the annealing duration is important more the grain is large.

The studying method used for the electrical characterization of the layers is the four points. Considering the potential photovoltaic applications, the layers of Sb-doped SnO_2 present a minimum of resistance of about 222 Ω/;, for an annealing at 500 °C during 2 hours.

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