

Characterization of Aluminum-doped SnO₂ thin films obtained by spray pyrolysis method

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Abstract: Aluminum doped tin oxide SnO₂: Al thin films were deposited on glass substrates using spray pyrolysis method. The deposited films are a polycrystalline with a tetragonal rutile structure. The variation of lattice parameters *a* and *c* decreases as a function of Al concentration due to ionic radius of (Sn=0.71Å) and (Al=0.51Å). Crystallites sizes varied between 29.25 and 32.80 nm. Al the samples have a transmission raised between 92 and 95% in the visible range. The optical band gap energy was found to vary in the range of 3.68 - 3.85 eV. Electrical measurements revealed the increase of the electrical conductivity with Al content and show a maximum at 2% of the doping and then decreases due to decrease of the grain size. Following this study we can conclude that the Aluminum doped tin oxide developed by this technique can be used in gas sensors and photovoltaic cells.

Keywords: Tin oxide, XRD, Al content, spray pyrolysis; sensors

1. INTRODUCTION

In the past few years, an improvement in the research was observed on TCOs, like SnO₂ due to its remarkable physical properties and several applications in various domain like transparent conducting electrodes in solar cells [1], light emitting diodes, and gas sensors [2]. Many reaches have been used for photovoltaic application [3-5] due to high transparency in the visible region and good electrical conductivity. SnO₂ is a wide band gap semi-conductor with an energy of 3.6 eV at room temperature exhibiting n type electrical conductivity. In order to improve the physical properties, doping is necessary step. In SnO₂, doping is achieved by replacing Sn⁴⁺ atoms with atoms of higher valences element. Doping with selective elements helps to enhance the structural, electrical and optical properties of SnO₂ films. The efficiency of the doped element depends on difference on doping ionic radius and tin ionic radius.

Doping aluminum is chemically stable and have ionic radius (Al³⁺=0.51Å), ionic radius of tin (Sn⁴⁺=0.71Å) therefore it can be substituted into Sn lattice site and can contribute to improve the electrical conductivity. Several research have studied the physical properties of SnO₂:Al synthesized by various techniques like RF

magnetron sputtering [6] sol gel [7] spray pyrolysis [8], electron beam evaporation [9].

In our work the spray pyrolysis method is used to deposit the SnO₂:Al thin films, due to its low fabrication cost and its high deposit temperature on glass substrates [10-11].

The physical properties were investigated. Characterizations have been done by X-ray diffraction (XRD), UV-visible spectrophotometry and four-probe electrical measurements.

2. EXPERIMENTAL PROCEDURES

Doped tin oxide thin films have been deposited on glass substrates using a spray pyrolysis technique.

For the prepared of undoped SnO₂ precursor solution, we used 5g of tin chloride (SnCl₂·2H₂O) of 99.99% purity dissolved in 33 ml of methanol and 17 ml of distilled water to obtain a starting solution with a 0.44 mol/l concentration.

Doping of tin oxide thin films with Aluminum were prepared by adding the compound of Al (AlCl₃) in the starting solution with a atomic percentage [Al/Sn] = 0.2, 0.4, 0.6 and 0.8 at.% wt. Prior to the deposition, glass substrates were ultrasonically cleaned in acetone, and distilled water.

The resulting solution was sprayed onto the heated substrates at a constant temperature of 480°C measured using electronically

thermocouple positioned under the substrate. X-ray diffraction pattern of the thin films were measured using an X-ray diffractometer D8 Advance, Bruker with Cu radiation generated at 30 kV and 20 mA ($\text{CuK}\alpha = 1.542\text{\AA}$) as the X-ray source. The diffraction patterns were determined over a range of diffraction angle 2θ from 20 to 80.

We used the spectrophotometer (Shimadzu 3101PC) using UV-visible/NIR in the range of 300 and 900 nm, to measure the transmittance spectra and a four-point probe to get square resistance of the films.

3. RESULTS AND DISCUSSION

3.1. Structural properties

Figure.1 shows the XRD patterns of SnO_2 thin films with various Al doping ratios. For the un-doped SnO_2 film, it can be seen that all of them are polycrystalline; predominant diffraction peaks at $2\theta = 26.50^\circ$, 33.77° and 51.55° are presented in the XRD pattern, which correspond to the (110), (101) and (211) according to the JCPDS N^o.041-1445 peaks of the SnO_2 tetragonal rutile structure. Other diffraction peaks appeared with a low intensity corresponding to (200), (310) and (301), observed at 37.92° , 61.78° and 65.7° , which agrees well with the reported values [12].

The absence of Al diffraction peaks indicates that doping with Aluminum does not change the tetragonal structure of SnO_2 and proved in the deposited films, Al atoms substitutes well Sn atoms into the crystal lattice.

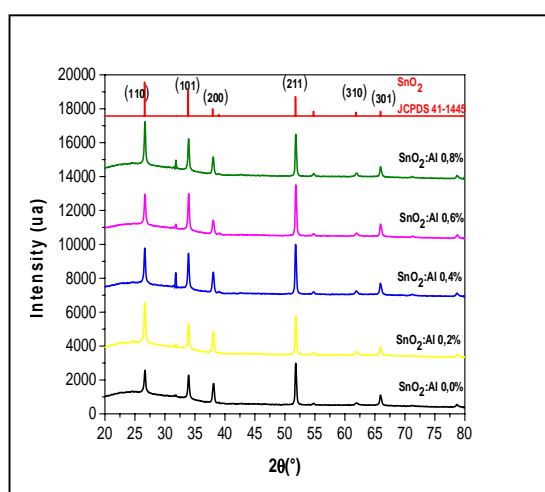


Fig.1. XRD diagram from un-doped and Al doped SnO_2 with different Al dopant concentration.

A slight increase in the intensity of the diffraction peak oriented (110), (101), (211) as function of Al concentration was observed which proves the influence of aluminum on the crystalline structure of the films. Crystallite size was determined using the Debye Scherer formula given by [13].

$$D = \frac{0.9}{\beta \cos \theta} \quad (1)$$

Where λ is the wavelength of the applied X-ray ($\lambda_{\text{Cu-K}\alpha 1} = 0.154046 \text{ nm}$), θ is Bragg's angle and β is the broadening of the diffraction peak measured at half its maximum intensity in radians.

Crystallites sizes of $\text{SnO}_2:\text{Al}$ thin films as a function of Al content (fig. 2), the grain sizes varied between 29.25 and 32.80 nm and it can be seen that Al doped has no influence on the grain sizes except for 2% of concentration, which probably due to the constraints in the film structure.

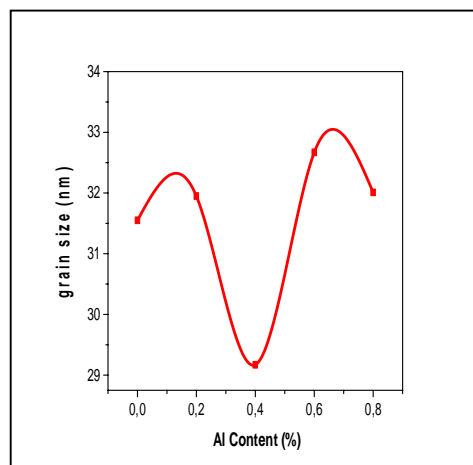


Fig. 2: Variation of the grain size as a function of Al dopant concentration.

Figure 3 presents the variation of the lattice parameters as a function of Al content. The lattice parameters a and c are calculated using the following equation [14]:

$$\frac{1}{d_{hkl}^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2} \quad (2)$$

Where h , k and l are the Miller indices. d_{hkl} is the lattice spacing. as shown in Fig. 3, the lattice parameter a and c decreases, from 4.755 Å and 3.188 Å to attend 4.712 Å and 3.178 Å respectively when Aluminum doping increase and the parameters reach the value which is close to that mentioned in the above SnO_2 ($a = 0.4737 \text{ nm}$, $c = 0.3185 \text{ nm}$ JCPDS card).

The decrease of lattices parameters a and c with the increase of Al concentration is due to ionic radius difference of aluminum ($r_{\text{Al}^{3+}} = 0.51 \text{ Å}$) and tin ($r_{\text{Sn}^{4+}} = 0.71 \text{ Å}$).

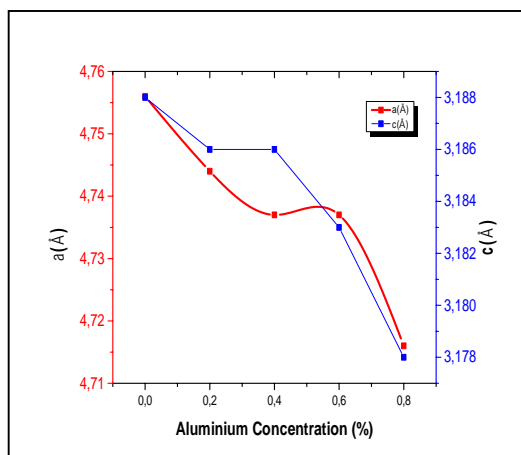


Fig. 3: Variation of lattices parameters a and c as a function of Al concentration.

3.2. Optical properties

Thin films of SnO₂: Al were deposited at various content of Aluminum doped 0.2; 0.4; 0.6 and 0.8% at a wavelength range of 300 nm – 900 nm. Figure 4 shows the transmittance spectrum in the visible region of SnO₂ doped Aluminum.

The films deposited with different concentration of aluminum were highly transparent more than 90% that vary between 92 and 95% depending on the dopant concentrations.

Transmission spectra reveal that the films have not the same transmittance this may be due to the difference in films structure. As can be seen, all the spectrums exhibit interference fringes.

The interference fringes are due to the multiple reflections at the two film edges, at the film/air and the film/substrate interfaces. This indicates that the film surface is smooth and uniform [15].

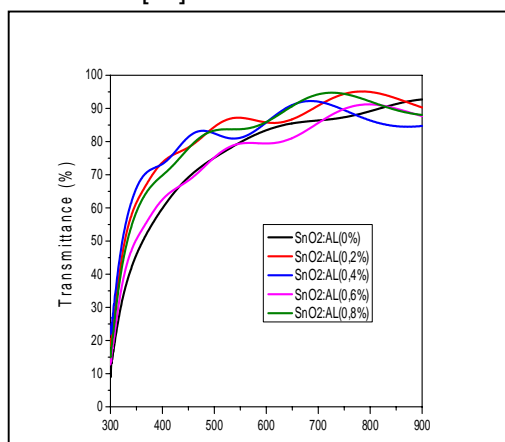


Fig. 4: Optical transmissionspectra of un-doped and Al doped tin oxide films with different Al dopants content

We have also determined the value of the direct optical band gap for doped and undoped SnO₂ thin films, from the optical absorption for direct energy band gap. The optical absorption coefficient, α is given by [16]:

$$\alpha h\nu = A(h\nu - E_g)^{\frac{1}{2}} \quad (3)$$

Where A is a constant depending on the material, α is the absorption coefficient, $h\nu$ is the photon energy and E_g is the band gap energy. E_g is determined by extrapolating the linear portion of the plotted curves (Fig.5) to zero absorption. The optical band gap is found to vary between 3.68 to 3.85 eV. There is a good accordance with literature where the value depending on the dopants and preparation method [14-17]

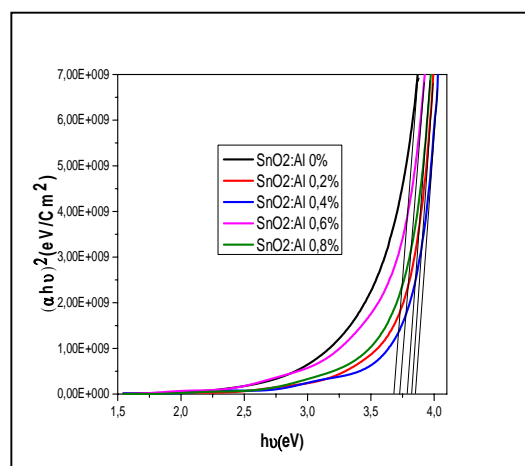


Fig. 5. Plot of $(\alpha h\nu)^2$ versus $h\nu$ of Aluminum doped tin oxide thin films.

3.3 Electrical properties

The introduction of dopants can cause increase in number of charge in lattice structure and therefore can modify the conductivity properties of the material [18]. The electrical conductivity at different Aluminum concentration was carried with square resistance measurement chows in fig.6.

The variation in conductivity as function of the doping concentration, in the case of weak incorporation of aluminum (< 2%), conductivity increase due to substitution of Al³⁺ atoms the Sn²⁺ site which creates free carrier.

Up to this doping concentration (> 2%) conductivity of the thin film decreases probably to the Al atoms occupy the interstitial positions leading to distortion of the

crystal structure which gives higher resistance. Structural variation causes changes in electrical properties.

A decrease in the crystallite size leads to an increase of grain boundary assimilated a potential barrier for the charges carriers in the polycrystalline materials and this causes an increase of electrical resistivity.

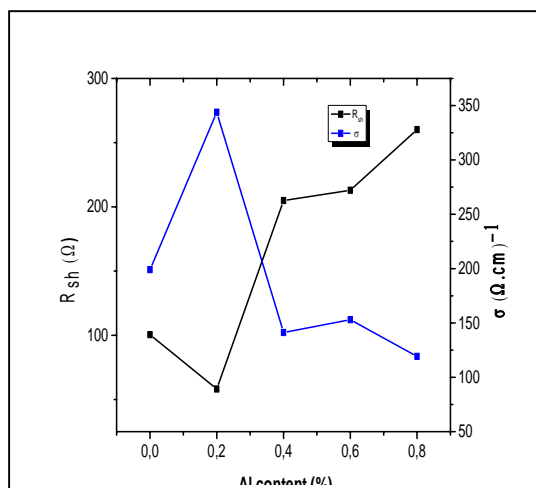


Fig. 6. Evolution of electrical Conductivity and Square resistance as a function of Al content.

4. CONCLUSION

We successfully deposited SnO₂:Al films using spray pyrolysis technique at different dopant concentration, to determine their effect on structural optical and electrical properties of the obtained films.

The deposited films crystallizes in the tetragonal rutile structure, with the absence of Al diffraction peaks and that doping with Aluminum does not change the tetragonal structure of SnO₂. Average crystalline size is about 30nm, and Al doped has no influence on the grain sizes except for 2% of concentration, which probably due the constraints. Films exhibit higher values of transmittance, with interferences fringes. Indicates that films have homogenous surface and the band gap varied from 3.68 to 3.85eV.

Electrical conductivity increase, with the increase of Aluminum dopants, and then decreases due to distortion of the crystal structure.

References

- [1] A.Lousa, S.Gimeno, J.Marti, Vacuum 45(1994) 1145.
- [2] I.Castro-Hurtado, J.Herran, G.G.Mandyo, E.Castano, Thin Solid Films 520(2012)4792

- [3] R. Tala-Ighil, Moumaour, M.S. Belkaid, A. Maallemi, K. Melhani, A. Iratni, Sol. Energy Mater. Sol. Cells 90 (2006) 1797.
- [4] M.K.I. Seneverathna, P.K.D.D.P. Pitigala, E.V.A. Premalal, K. Tennakone, G.R.A. Kumara, A. Konno, Sol. Energy Mater. Sol. Cells 91 (2007) 544.
- [5] Shadia J. Ikhmayies, Riyad N. Ahmad-Bitar, Sol. Energy Mater. Sol. Cells 94 (2010) 878.
- [6] F. Khan, M. Mehmood, A.M. Rana, M.T. Bhatti, A. Mahmood, Chin. Phys. Lett. 7 (2009) 077803
- [7] S. Wang, J. Huang, Y. Zhao, S. Wang, S. Wu, S. Zhang, W. Huang, Mater. Lett. 60 (2006) 1706
- [8] P. N. Onkundi, K. M. Munji, D. B. Bem and B. Muthoka, International Journal of Thin Films Science and Technology, 7, No. 1, 25-33 (2018)
- [9] J.C. Jiang, K. Lian, E.I. Meletis, Thin Solid Films 411(2002) 203.
- [10] A.R. Babar, S.S. Shinde, A.V. Moholkar, C.H. Bhosale, J.H. Kim, K.Y. Rajpure. Journal of Alloys and Compounds, 509, 3108, 2011.
- [11] C.E. Benouis, M. Benhaliliba, F. Yakuphanoglu, A.T. Silver, M.S. Aida and A.S. Juarez. Journal of Synthetic Metals, 161, 1509-1516, 2011.
- [12] Hyoun Woo Kim, Seung Hyun Shim, Chongmu Lee, Ceramics International 32 (2006) 943-946
- [13] S. Gupta, B. C. Yadav, P. K. Dwivedi, B. DAS University Lucknow-226025, U.P., India, (2012)
- [14] Soumia Belhamri, Nasr-Eddine Hamdadou, Communication Science & technology vol 18. January 2017 COST
- [15] K. S. Shamala, L. C. S. Murthy and K. Narasimha RAO, Bull. Mater. Sci., Vol. 27, No. 3, June 2004, pp. 295-301. Indian Academy of Sciences.
- [16] P. Sreedhara Reddy, G. Raghupathi Chetty, S. Uthanna, B. Srinivasulu Naidu, P. Jayarama Reddy, Solid State Commun. 77 (1991) 899.
- [17] Saadeddin, B. Pecquenard, J.P. Manaud, R. Decourt, C. Labrugere, T. Buffeteau, G. Campet, Applied Surface Science 253 (2007) 5240-5249
- [18] B. Correa-Lozano, C. Comninellis, A. de Battisti, Journal of Applied Electrochemistry, 26, p. 83, 1996.