Characterization of Pure and Antimony Doped SnO_2 Thin Films Prepared by the Sol-Gel Technique

Novinrooz, Abdoljavad*+; Sarabadani, Parvin; Garousi, Javad
Ion Beam Application Division, NRCAM, P.O. Box 31485 - 498, Karaj, I.R. IRAN

ABSTRACT: *Pure and antimony doped SnO_2 thin films have been prepared by the sol-gel dip coating technique on glass substrate using starting material $SnCl_2.2H_2O$ as a host and $SbCl_3$ as a dopant. Our experimental results revealed that, the quality of the coated films on the glass depends on process parameters. The effect of annealing temperature, dipping numbers and the dopant concentration on the structural and electrical properties were investigated. Duration of coating and dragging speed for each sample were 3 minutes and 90cm/min respectively. The films Characterization was carried out by X-ray diffraction pattern (XRD) and scanning electron microscopy (SEM). The XRD results showed the amorphous structure of deposited sample at 350°C. Beyond this temperature (350°C), the preferred plane with a random textured shifts to (101). By addition of 25g/lit antimony at 550°C, the preferred plane shifts to (200). The electrical properties were determined by four point probes technique. Addition of 25g/lit antimony at 550°C was reduced the resistivity of the SnO_2 films to 0.94×10^{-4} (Ωcm).*

KEY WORDS: *Deposition process, Tin oxide, Sol- gel, Dip coating, Electrical properties, Structural properties, Antimony doped tin oxide.*

INTRODUCTION

Semiconducting thin films of SnO_2 is usually "n" type and transparent in visible range which can be conductive by contribution of some elements such as antimony, molybdenum [1,2]. Tin oxide is an interesting metal oxide which is widely studied by many research groups for different purposes like solar cells, display panels, transparent electrodes, and gas sensors [3,4].

Due to vast utilization of SnO_2 films in different fields of science and technology, many reports are devoted to the preparation and fabrication of these films by different techniques like chemical vapor deposition (CVD) [5], spray pyrolysis [6,7], sputtering [8] and sol gel [9]. Among them, the sol gel method has certain privileges [9,10] namely: (i) ability to obtain ultra fine films, (ii) easy coating at large area on non flat and complex shaped substrates, (iii) low cost and simple with no sophisticated equipments, (iv) films obtained in both thin and thick form with high porosity area, there by offering improvement in device fabrication. Most significant advantage of sol gel is the films are obtained under low temperature process and preparation parameters are easily controlled which leads to high

* To whom correspondence should be addressed.
+ E-mail: anovin@aeoi.org.ir
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quality SnO_2 layers.

Sol gel method is substantially involved in two processes, namely hydrolysis and condensation. The first is fulfilled by reaction taken between water and metal alkoxides as follows:

$$Sn(C_2H_5O)_4 + 4H_2O \overset{\text{Hydrolysis}}{\rightleftharpoons} Sn(OH)_4 + 4C_2H_5OH$$

In hydrolysis process, alkoxy groups are substituted by hydroxide groups leading to the formation of the colloidal particles into the sol solution. The second process is accomplished under the following reaction:

$$2\,Sn(OH)_4 \overset{\text{Condensation}}{\rightleftharpoons} 2\,SnO_2 + 4\,H_2O$$

Here two hydrolyzed molecules link together and liberate water. As the reaction proceeds, the number of Sn-O-Sn bonds increase by the polymerization which produces a macroscopic gel. In sol gel method solution or sol is used for coating. There are three kind of methods for applying sols to the substrate: dip coating, spin coating and laminar flow coating. In dip coating the substrate is immersed in a dipping solution and is drawn up vertically. The solution dragged by the substrate is solidified into a gel. In spin coating an amount of solution is dropped on the rotating substrate and the solution propagates outwards on the substrate, covering it. The sol film formed becomes solidified as gel film. In laminar flow method a substrate is coated in an upside–down position. The coating solution is pumped into a slot applicator tube and flows out to the surface through the slot, forming a continues liquid films so that a narrow meniscus created between it and the applicator tube. As the applicator is moved horizontally relative to the substrate, a liquid film is left on the substrate. In all these methods films formed after evaporation of the solvents. Between these three methods, dip coating requires less equipment and manpower, has fewer complexities. In present work, however, dip coating process was employed.

Most of workers have used alkoxides [11,12] and non alkoxides such as carbonates, nitrates, acetates, chlorides and etc as a starting material [1,13]. Although alkoxides obtained good quality films, but their materials are expensive and difficult to control process. A challenging task of present work is therefore, to prepare tin alkoxide for achieving high quality SnO_2 films, using low cost starting materials. It is known that addition of some donors like Sb, F, Mo have remarkable effects on electrical and optical behavior of SnO_2 films [14]. Incorporation of antimony dopant in SnO_2 matrix was studied. As the quality of the films depended on process parameters, therefore, the effect of annealing temperature, dipping number and concentration of dopant on the SnO_2 microstructure and electrical properties were investigated. It will be discussed in proceeding that SnO_2 crystalline structure remain the same after antimony addition, but electrical resistivity changes.

EXPERIMENTAL

Instrumentation

The crystallity and morphology of species were analyzed using X-ray diffraction pattern (XL-30) and Scanning electron microscopy (PW-1800 model) respectively. The electrical resistivity was measured by means of a four point probes.

Preparation of undoped and doped tin oxide solutions

Undoped SnO_2 solution is prepared by dissolving of 4.2 g of $SnCl_2.2H_2O$ salt (>99% supplied by Aldrich company) in 50 ml of pure ethanol. The mixture was stirred and refluxed at 80°C for two hours under nitrogen ambient in tightly covered balloons. A white tin alkoxide powder was obtained after heating of solution at 80°C under vacuum condition. This powder was dissolved, stirred and refluxed in 25 ml pure ethanol for two hours at 50°C under nitrogen atmosphere. For the species containing antimony, the antimony alkoxides powder with different concentrations of antimony chloride, were prepared by the same process explained above, and then, subjected to the similar process of dissolving in ethanol, stirring and refluxing in nitrogen ambient and dissolved in 25 ml ethanol, then they are added to the solution containing pure SnO_2. Finally, samples were obtained by deposition the films on to the glass substrates for two hours duration at 50 °C and dried them by IR lamp (~100°C). The influence of Sb concentration and effect of heat treatment at 350 °C to 600 °C under pure oxygen ambient, on the properties of SnO_2 films was investigated.

Dipping Process

Deposition of SnO_2 films is carried out using a dip coating system with an arrangement is showed in Fig. 1.

The main parts of apparatus consist of: 1-Plexiglas chamber 2-hygrometer 3-solution container 4- motor and gearbox 5- pulley 6-substrate.

Plexiglas chamber was used to control the atmosphere and to prevent undesired air convection effect around the film during the pulling. The relative humidity (%RH) was measured by hygrometer and the speed of pulling of substrate was controlled by pulley.

The glass substrates with dimensions (26×76×3) mm were cleaned by alcohol and acetone before dipping into the sol solution. The dipping time 3 minutes and dragging speed of 90cm/min were kept constant throughout the experiments. Because of deterioration effect of humidity on the deposited films, the dipping process is carried out under argon ambient.

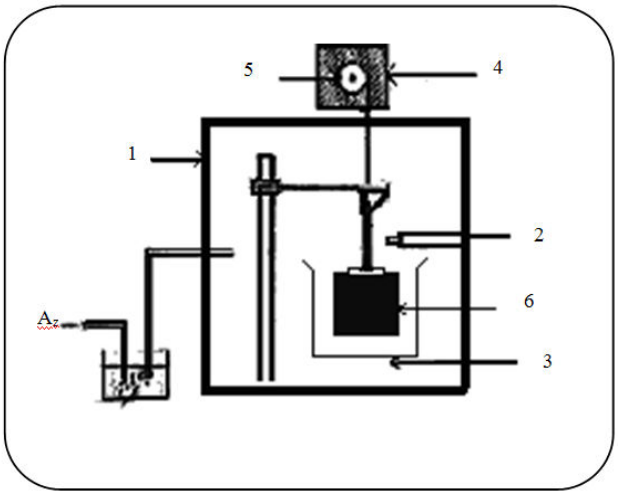

Fig. 1: Schematic diagram of dip-coating equipment.

RESULTS AND DISCUSSION

X-ray diffraction

X-ray diffraction pattern (XRD) of SnO_2 films prepared from the pure alkoxide solution with five dipping number and annealed at different temperatures is shown in Fig. 2. According to this figure, the film is amorphous at 350°C and only a wide band at 2θ ranges between 20° to 30° is present. It is evident, that the crystallity of SnO_2 films, increases with annealing temperature from 450°C to 550°C. For the temperature beyond 550 °C, a degradation of the crystallity was observed.

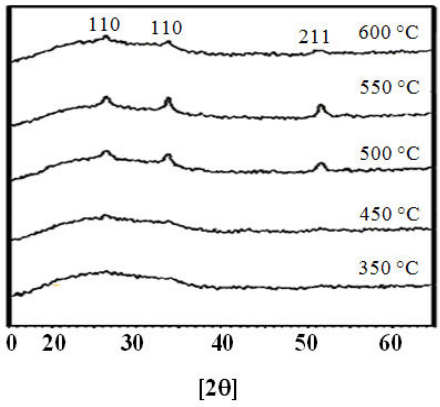

Fig. 2: XRD Pattern of dip coated undoped film at 5 dips and heated at : 350 °C , 450 °C , 500 °C , 550 °C and 600 °C.

In addition, EDX (Energy dispersive X-ray) analysis is given in table 1, demonstrates an increase of silicon impurity incoming from glass substrate into the films at 600°C. It is therefore supposed that film impurity may associate in the structural defects.

The effect of annealing temperature on the film thickness exhibited in Fig. 3.

Decrease in thickness due to increase in temperature corresponds fairly with more densification and clustered grains formation. The explanation is however, supplemented by the results obtained from SEM studies given in proceeding section.

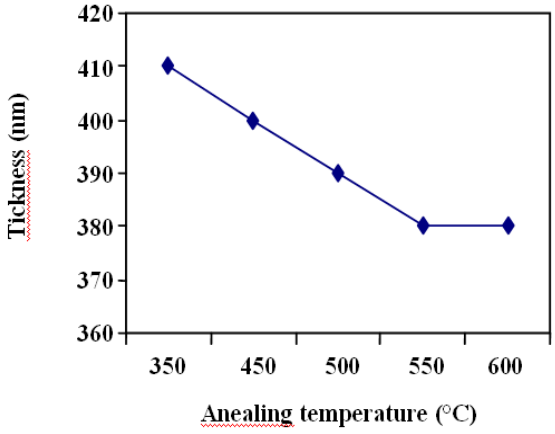

Fig. 3: Variation of film thickness as a function annealing temperature for the SnO_2 films prepared with five dipping numbers (at constant speed of 90 cm/min).

The Fig. 4 (a) represents the amorphous nature of films after one dip. This is quite reasonable, because, evaporation of solvent and weak dissolution of tin alkoxide produces pores on the films during initial dipping process [13,15]. When dipping number is increased Fig. 4 (b, c), the XRD peaks up-grate, such that

Table 1: EDX analysis of undoped SnO_2 film at different temperatures.

Temperature (°C)	25	350	450	500	550	600
% Si	0.01	5.02	5.09	5.15	5.30	12.64

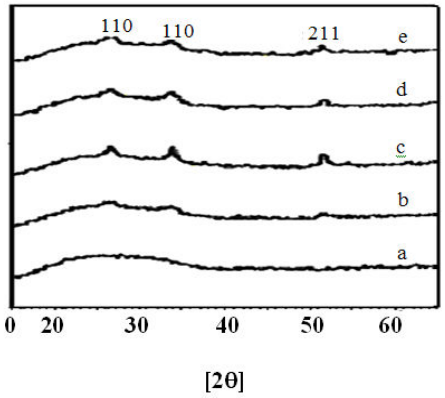

Fig. 4: XRD Pattern of dip coated undoped SnO_2 film at 550 °C: (a) one dip, (b) three dips, (c) five dips, (d) seven dips, (e) ten dips.

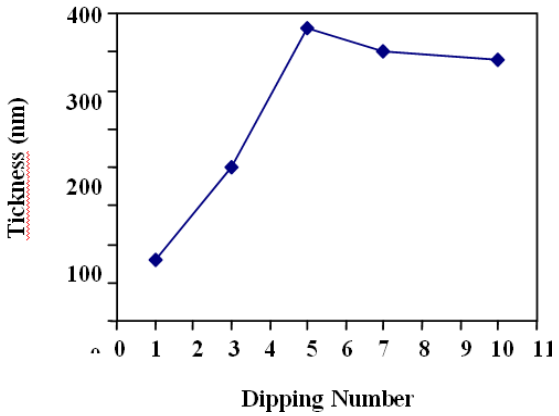

Fig.5: Variation of film thickness as a function of dipping number (at 550 °C and constant speed of 90 cm/min).

at 5 dips they become higher and sharper, it is to say that, the successive dipping can fill up the pores and enhance the nucleation of the SnO_2 grains. But, at 7 and 10 dipping times shown in Figs. 4(e,d), the crystalline structure suffers deterioration. Taking all these observations in to the account, it can decline that, in our studies 5 dips suggest better performance.

Since, in literature survey, more than 5 dips are reported, it may, therefore, refer this work as a significant and remarkable process in film preparation by sol-gel dipping technique. Furthermore, the thickness of the films is also affected by dipping number, the status is given in Fig. 5. Initially thickness value increases as dipping numbers increase and reaches to maximum value with respect to 5 dips. But, beyond this value (5 dips), it decreases. A reason for this is that, the adhesion energy of upper layer to previous layer weakens so that, it collapse to sol solution, and hence thickness of the film decreases.

MICROSTRUCTURAL

Effect of annealing temperature

SEM pictures of undoped SnO_2 films prepared from sol-solution of tin alkoxide on the glass substrate annealed at different temperatures are given in Fig. 6. For all the films, the dipping number was taken fix at 5 dips. As we had discussed in preceding section, the amorphous feature of films at 350°C is seen in Fig. 6a. It is obvious from the micrographs that by increasing temperature, grains are gradually grown up, such that well adherent film with tight bonded grains built up at 550°C as shown in Fig. 6d. At 600°C (Fig. 6e) films are deteriorated and no proper crystal structure is observed. This is also justifies our argument about XRD results obtained from SnO_2 samples under the same circumstances.

EFFECT OF DIPPING NUMBER

Fig.7 demonstrates the influence of dipping number on the microstructure of SnO_2 films. From Figs. 7 (a,b,c) it is recognized that dipping number up to 5 dips, results more packed and homogenous films. Where as, the density and homogeneity of the deposited SnO_2 films appear to decrease at 7 and 10 dips, as shown in Figs.7 (d,e). Once again, the X-ray results discussed previously justify our argument. It can be generally concluded that five numbers of dipping and 550°C post annealed temperature are the useful processing parameters, leading to the formation of desired undoped SnO_2 films.

Effect of antimony

The SEM micrographs of Sb-doped SnO_2 films prepared at 5 dips and 550°C post annealed temperature but at different Sb concentration are given in Fig. 8.

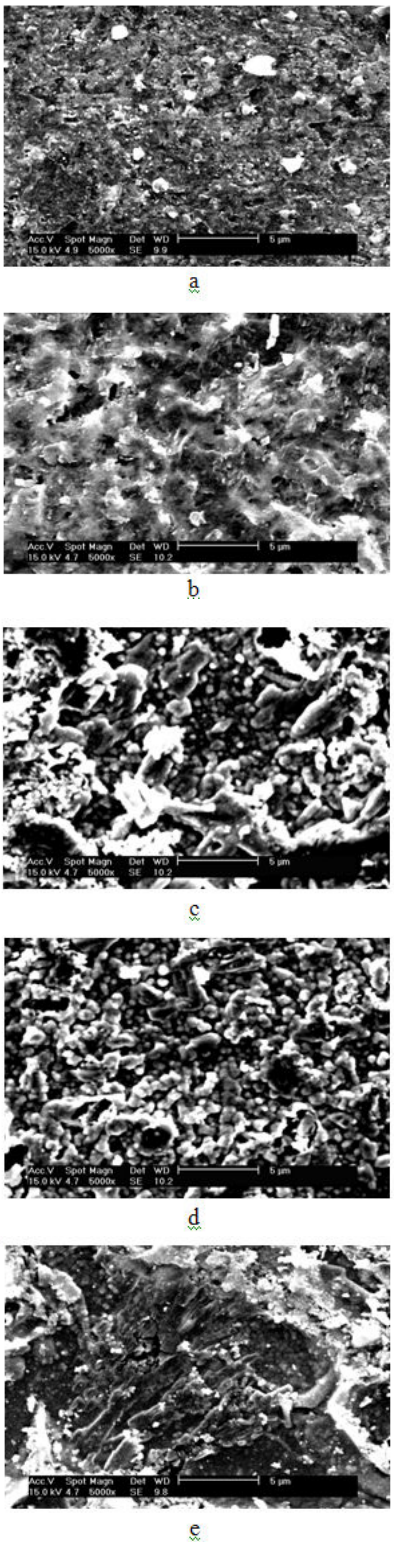

Fig. 6: SEM images of SnO_2 films prepared 5 dips and processing at different annealing temperature: a)350 °C , b)450 °C , c)500 °C , d) 550 °C , e)600 °C.

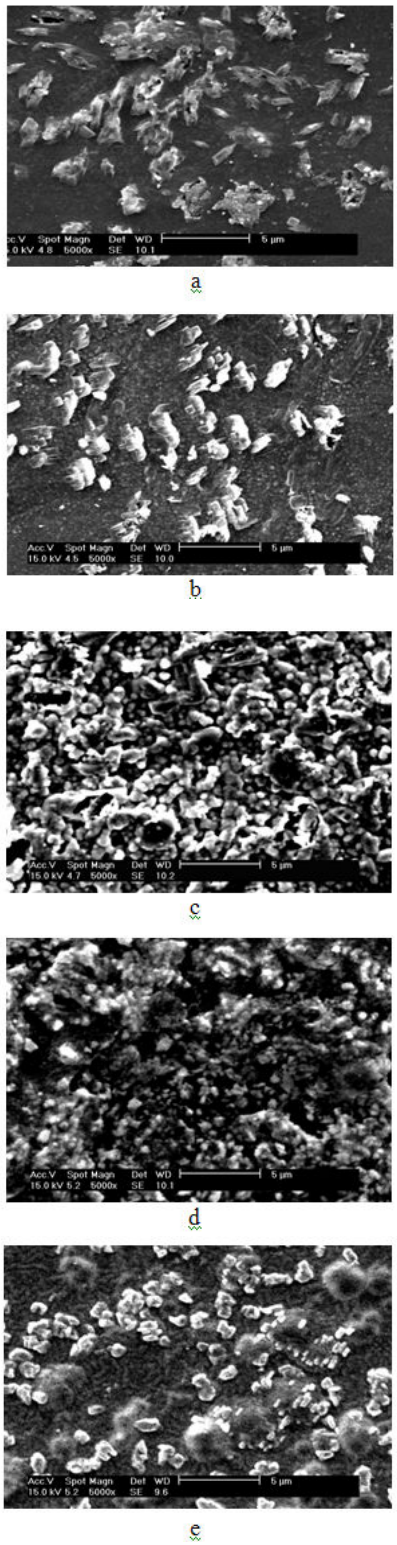

Fig. 7: SEM images of SnO_2 films prepared through different number of dipping at 550 ° C: (a) one dip, (b) three dips, (c) five dips, (d) seven dips, (e) ten dips.

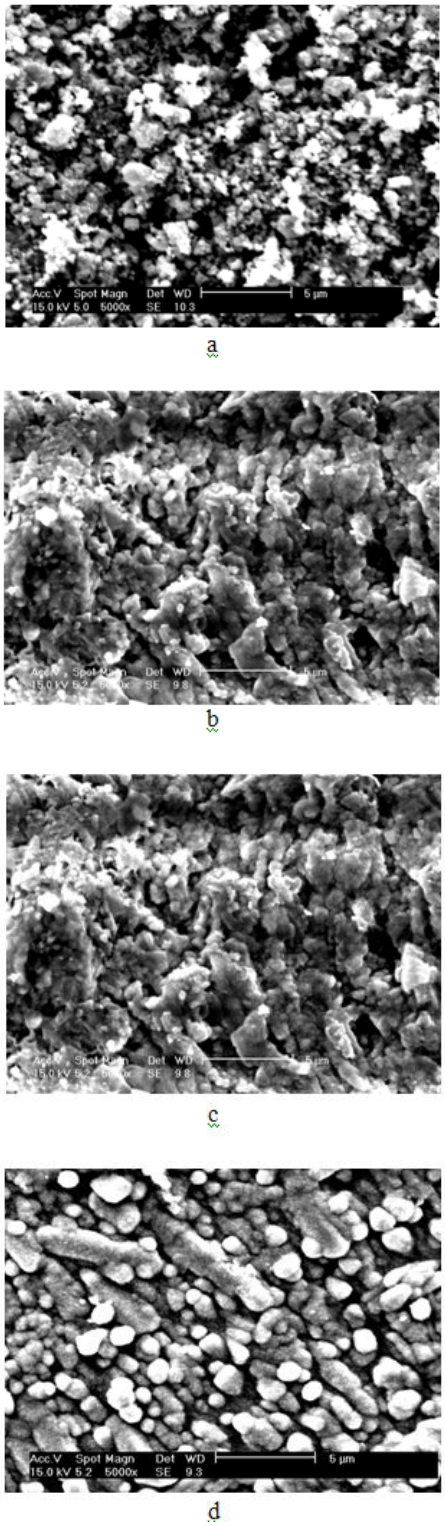

Fig. 8: SEM images dip coated doped SnO_2 ***film with different antimony concentrations (g/lit) at 5 dips and 550 °C : a) 8.52 , b)17.04 , c)25.6 , d)34.12.***

When the concentration of Sb in the SnO_2 matrix increased to 34.12 g/lit cauliflower feature is transformed to well defined grains structure (Fig. 8d). This, however is related to the optimum condition of the film formation.

Fig. 9 shows the XRD patters of the Sb-doped SnO_2 films at different antimony concentration. The poly-crystalline SnO_2 film with tetragonal structure is present in all the samples. An interesting point in this figure is the presence of the (200) texture, which had not been already observed in undoped SnO_2 samples. A reason for this event, may be at proper dopant concentration, Sb^{+5} changes to large ionic reduce Sb^{+3} [14] where they fill up the vacancies of SnO_2 lattice during heat treatment at 550°C. As shown in Fig. 9, (200) plane along with other plans are enhanced by increasing of antimony concentrations .

ELECTRICAL PROPERTIES

Electrical property is a strong tool to assess crystalline film (like metal oxide) behaviors, considering grain sizes and boundaries. Ordered domain with a rather large grain sizes (in other word, the center to center distance between neighboring grain) is a great interest. With this intention, we carried out a set of experiments under different circumstances to study the film characteristics. Fig.10 represents our results of investigations on the resistivity with respect to dipping number of the species annealed at 550 °C. It is evident from the figure that lower resistivity, or high electrical conductivity corresponds to five dipping number. That is to say, SnO_2 films posses well packed grains with less grain boundaries. This result is in a good agreement with our interpretation given in effect of dipping number section.

The Similar feature is noticed from Fig. 11 where, the measured resistivity values are ploted with respect to annealing temperature. The lower resistivity value is measured at 550°C. As discussed earlier, at this temperature, the grain density and particle size is higher than other temperatures and therefore film defect is less. It is supposed that the electrical properties of conducting films are strongly affected by crystal sizes and crystal defects [16]. Thus, the results have proven to be acceptable.

Fig.12 shows the SnO_2 films resistivity as a function of antimony concentrations at 550 °C and five dipping numbers. Resitivity values continuously decrease with Sb

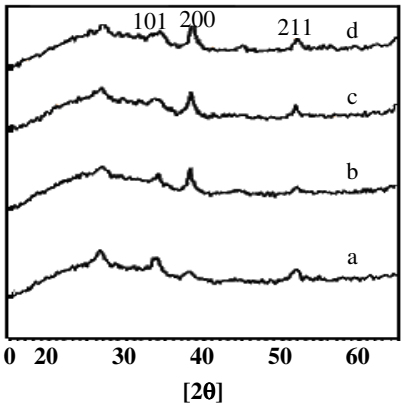

Fig.9: X-ray diffractograms of doped SnO_2 films prepared at 5 dips and 550℃ annealing temperatures with different antimony concentrations(g/lit): a)8.52, b) 17.04, c) 25.6, d) 34.12.

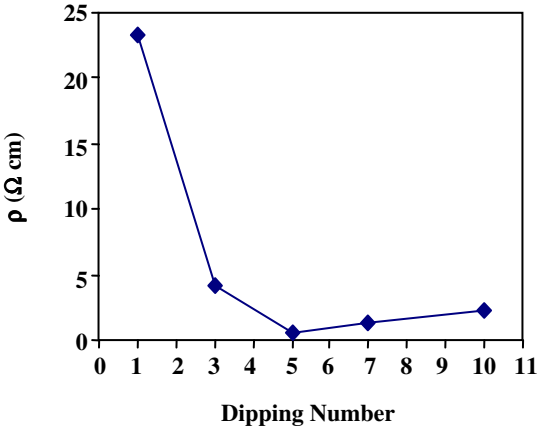

Fig. 10: Variation of undoped SnO_2 film resistivity as a Function of dipping number at 550 °C.

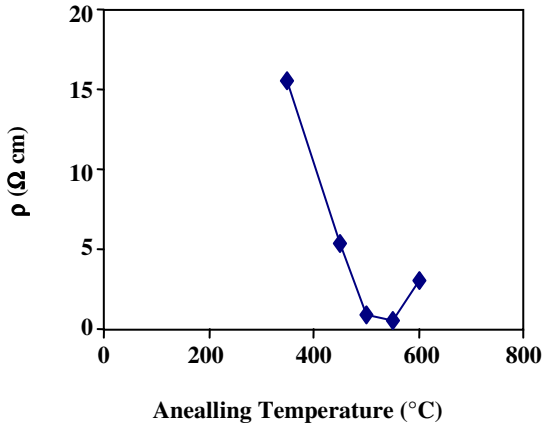

Fig. 11: Variation of undoped SnO_2 film resistivity as a function of annealing temperature with 5 dips.

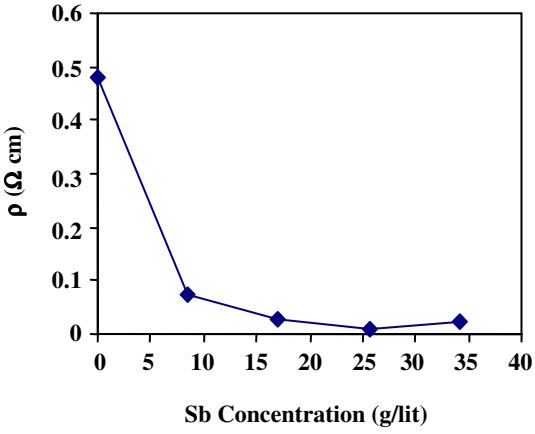

Fig. 12: The variation of resistivity as a function of antimony Concentration.

concentrations up to 25 g/lit, but for higher concentrations (> 25g/lit), it tends to increase.

That is to say, by introduction of antimony in sol solution, Sb^{+5} would be available, in the media such that, the appropriate Sb concentration (ie 25 g/lit) leads augmentation of electrons as majority carriers. This suggests higher conductivity or lower resistivity. But at concentration more than 25g/lit, antimony changes in the form of Sb^{+3}, where the free electron number diminishes in the solution and consequently resistivity increases [1].

CONCLUSIONS

Thin films of pure and antimony doped SnO_2 were prepared by employing sol-gel dip coating technique. Deposition time and dragging speed of species were kept fix to 3 minutes and 90cm/min respectively through out the experiments.

In the conclusion one can say that the following results were obtained under experimental conditions:

1- The XRD and SEM results analysis of undoped and Sb-doped SnO_2 species revealed that, the five successive dipping number of each 3 minutes duration would be sufficient for the desirable characteristics. Unlike the other groups that refer to more than 5 dips, this result could be remarked in terms of cost reduction process.

2- The low resistivity (or high conductivity) of 0.94×10^{-4} (Ωcm) was obtained under oxygen ambient at 550 °C and 25.6 g/lit Sb concentration.

3- (200) plan of reflection was appeared only in the

Sb doped samples. The intensity and sharpness of the peak were depended on Sb concentration.

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