7.1 INTRODUCTION

Antimony doped tin oxide thin films (Sn0₂:Sb/ATO) are of great technological interest, owing to their specific and combined electrical, optical and chemical properties. The ATO is an n-type and wide band gap semiconductor and has special properties viz., high transmittance in the visible and high reflectivity in the infrared region [1], excellent electrical conductivity [2, 3], greater carrier mobility [4, 5] and good mechanical stability [4, 5]. Due to these interesting characteristics, it finds application in solar cells [6] as transparent and protective electrodes [1, 7, 8], flat plate collectors and spectral selective windows [1, 8], sensors for gas detection [9, 10], photo thermal converters [11] and providing thermal insulation for houses [11].

Since the properties of the ATO films strongly depend on the method of preparation and growth parameters [5, 11], several techniques such as chemical vapour deposition [12], Photo CVD and Thermal CVD [13], APCVD [14], Sputtering and related methods [5, 11, 15], Spray Pyrolysis [1 - 11, 16 - 24] and thermal evaporation [11] have been successfully tried to produce device quality films. An increasing interest towards sol-gel synthesis [25 - 27] of the Sn0₂ based thin films has been observed due to many advantages of this technique such as increased capability, low cost technological equipment, low heating necessary for oxide films with highly controlled porosity nature [28].

An attempt has been made to prepare sol-gel spin coated ATO films for solar cell application. The material and opto-electronic properties of the ATO films depend critically on the spin coating preparation parameters. So, it is intended to prepare and characterize ATO thin films by spin coating method via sol-gel route.
and to optimize the various coating parameters in order to get uniform, reproducible, transparent and device quality films.

7.2 PREPARATION OF SOL-GEL

The sol was prepared by dissolving 13 grams (0.037 mole) of tin chloride (SnCl$_4$ 5FI,0) in 100 ml of ethyl alcohol. Ammonium tri chloride (SbCl$_3$) was then added into the solution for antimony doping. The amounts of SbCl$_3$ added were 0.0011, 0.0016, 0.021, 0.026 and 0.031 mole respectively. These doping amounts would correspond to 2.6, 3.9, 5.2, 6.5 and 7.8 mol % of Sb in SnO$_2$, respectively. Solubility of the solute in the solution can be improved by the addition of 5 ml of 0.1 normal concentrated hydrochloric acid as a catalyst [29], The solution was stirred well and refluxed for one hour at 60°C. The solutions were cooled in the ambient atmosphere and then aged in a beaker at room temperature, for gelation. The rheological behaviour of the prepared sol was studied by the density and viscosity measurements.

7.3 FIXING OF GELLATION TIME

The viscosity and density variation of the sol with aging time, for the sol prepared with a dopant concentration 5.2 mole % of Sb in SnO$_2$, at room temperature is shown in the Fig.7.1. The viscosity and density curves show a slow raise inially and after three days, the viscosity and density breaks off the base line and saturated after the seventh day. From the figure, it is evident that both viscosity and density abruptly increase between the third and seventh day of aging. The physical observation of the solution during the entire period shows increasing cloudy nature of the solution.

Between 4$^{th}$ and 6$^{th}$ days of aging, based on the discussions proposed in chapters 5 and 6, good and uniform coating could be obtained. So it can be inferred that the optimum coating period of the sol solution, so as to obtain good quality films, a time " $t_{1/2}$ " can be adopted, which is found to be 5 days and this is regarded
Fig. 7.1 Variation of viscosity and density of ATO sol solution
as the optimum time for the sol solution, for the preparation Sb doped Sn0₂ films in the present work.

7.4 OPTIMIZATION OF TURN TABLE SPIN RATE

The spin rate has been optimized by measuring film thickness and resistivity to obtain quality films. For this purpose, to start with ATO thin films were spin coated with a fixed dopant concentration of 5.2 mole % of Sb in Sn0₂, heated 400°C. Their thickness and resistivity were measured for different spin rate with different number of coatings and are shown in Fig.7.2 and Fig.7.3 respectively. Heating was done for 5 minutes for each coatings. Films prepared at a low spin rate of 2000 rpm are thick and highly non-uniform and show resistivity.

If the spin rate is gradually increased upto 3000 rpm, the luster and uniformity of the film are improved with a reduction in island information, film thickness and resistivity. This may be due to the enhanced outward flow and thinning of the sol, leading to better crystalline films. At the spin rate 3500 rpm, uniform films without islands are formed.

When the spin rate is increased above 3500 rpm, the degree of centrifugal force acting on the sol is enormous and this affects sol viscosity and wettability, which causes aggressive thinning of the sol with islands and discontinuities. At the same time, resistivity is found to be increasing with spin rate.

The thickness profile shown in Fig.7.2 indicates a gradual fall in film thickness between 2000 and 3500 rpm and film thickness becomes constant beyond 3500 rpm. The resistivity profile shown in Fig.7.3 shows a fall in resistivity at 3500 rpm. and then raises.

The above observations indicate that the optimum spin rate of the turntable could be fixed at 3500 rpm, to get optimum film thickness and good electrical properties for the spin coated ATO films.
Fig. 7.2 Variation of film thickness with turn table spin rate

Fig. 7.3 Variation of resistivity with turn table spin rate
7.5 OPTIMIZATION OF SPIN TIME

Spin time influences film thickness and uniformity, which changes the resistivity and also the optical and surface morphological properties.

Variation of film thickness with spin time for different number of coating is shown in the Fig.7.4. It shows a fall in film thickness up to 10 seconds and becomes constant above 10 seconds.

Fig.7.5 shows a reduction in resistivity with the increase in spin time, reaching a minimum at the spin time 10 seconds and then increases with the spin time. Hence in the present work the spin duration is fixed at 10 seconds for the development of FTO thin films.

7.6 OPTIMIZATION OF NUMBER OF COATINGS FOR SPIN COATED Sn0₂:Sb FILMS

In the spin coating technique, the desired film thickness could be achieved by making trails with many number of coatings. As the number of times coating is formed, the thickness increases linearly as shown in Fig.7.4. However, if the film crosses some critical thickness, there will be material loss as well as properties impairment also happens. Hence, XRD studies, electrical and optical studies are conducted to fix the optimum number of coatings to produce quality Sn0₂:Sb films.

Figure 7.6 shows the XRD pattern of Sn0₂:Sb films formed using different number of coatings. The temperature is maintained at 400°C and Sb doping as 5.2 mol %. The crystalline nature of the films increases with increased coating number upto 8 and then reduces. All the films show XRD peaks with orientations (110), (101), (200), (211) and (301). The films are oriented along (110) direction as its peak intensity is higher for all number of coatings. These planes confirm the formation of Sn0₂ : Sb films with tetragonal rutile structure. The lattice constant a and c values are 4.71Å and c = 3.16Å° respectively. The grain size variation and texture coefficient changes against number of coatings are given Fig. 7.7a and
Fig. 7.4 Variation of film thickness with spin time

Fig. 7.5 Variation of resistivity with spin time of the ATO thinfilms
Fig. 7.6 X Ray Diffraction pattern of ATO thin films spin coated with different number of coatings.
Fig. 7.7a Variation of mean grain size with number of coating of ATO thin films

Mean grain size (nm)

Number of coating

Fig. 7.7b Variation of texture coefficient with number of coating

Texture coefficient

Number of coating

(110) orientation
(101) orientation
(200) orientation
(211) orientation
(301) orientation
Fig.7.7b respectively. Films formed with 8 number of coatings have larger grain size (~90 nm) and texture coefficient (1.7) is observed for the (110) orientation.

The electrical properties like $\rho$, $n$, $\mu$ are studied for SnO$_2$:Sb films prepared for different number of coatings and are shown in Fig.7.8a, Fig.7.8b and Fig.7.8c respectively. For films developed using 8 number of coatings, $\rho$ value is 0.005 $\Omega$-cm, $n$ value is $4.8 \times 10^{20}$ cm$^{-3}$ and $\mu$ value is 18.26 cm$^2$/Vs.

Optical transmission studies (Fig.7.9a) show an average of 85 to 94 % transmittance in the wavelength region 300 – 700 nm. It is found maximum for 8 number of coatings. Above 8 number of coatings the transmission started reducing. The bandgap values, observed from the $\alpha^2$ Vs $h\nu$ curves (Fig.7.9b), are 2.8, 3.4, 3.8, 3.6 and 3.2 eV for the SnO$_2$:Sb films prepared at 4, 6, 8, 10, and 12 number of coatings respectively. Highest bandgap value is observed for the films developed with 8 number of coatings.

7.7 OPTIMIZATION OF HEATING TEMPERATURE

After optimizing the number of coatings as 8, the temperature of heat treatment should be optimized precisely by varying the temperature widely from 350°C to 475°C. The tentative Sb doping concentration is fixed as 5.2 mol %.

Figure (7.10) shows the XRD patterns of SnO$_2$:Sb films heated at temperature 350, 375, 400, 425, 450 and 475°C. At all temperatures, the preferential orientation is observed along (110) direction only. The peak intensities are found increasing upto 400°C and then decreases except for (101) peak which increases on heating temperature. The presence of intense peaks at (110), (101), (200), (211) and (301) shows the polycrystalline nature and tetragonal rutile structure for the SnO$_2$:Sb films. The films heated at 400°C shows well developed peaks with highest intensity. The a and c values are found to be 4.7368Å and 3.1836Å respectively which are in close agreement with the standard values. The c/a value of 0.6721 confirms the tetragonal structure and monophase SnO$_2$:Sb films. Mean grain size and texture coefficient values calculated for the (101) peak
Fig. 7.8a Variation of resistivity with number of coatings of the ATO thin film heat treated at 400°C

Fig. 7.8b Variation of carrier concentration with number of coatings of the ATO thin films heat treated at 400°C

Fig. 7.8c Variation of carrier mobility with number of coatings of ATO thin films heat treated at 400°C
Fig. 7.9a Transmission spectra of ATO thin film spin coated at different number of coatings.

Fig. 7.9b Variation of square of the absorption coefficient with photon energy of the FTO thin films.
Fig. 7.10 X Ray Diffraction pattern of ATO thin films heat treated at different temperatures
are the maximum at the heating temperature of 400°C as seen from Fig.7.1 la and Fig.7.11 b respectively.

The electrical properties of the Sn0₂:Sb films heated at different temperatures are shown in Fig.7.12a, Fig.7.12b and Fig.7.12c for p, n and p respectively. Minimum p value of 0.03 ohm-cm, maximum p value of 11 cm²/Vs are observed for the Sn0₂:Sb films heated at 400°C. Figure 7.13 gives the plot of transmission through the film against wavelength in the range 300 - 700 nm for Sn0₂:Sb heated at different temperatures. Films heated at 400°C have greater than 85% transmission in the visible light range. It decreases as heat treatment temperature of the films increase. Such effect of heating on transmission can be visualized by the fact that the grains of the films grow and reduce light transmission. After the surface uniformity becomes low with porosity which can also reduce the transmission due to scattering effect. From these results, the heating temperature for making Sn0₂:Sb films are fixed as 400°C to obtain device quality surface morphology.

7.8 OPTIMIZATION OF DOPANT CONCENTRATION

In order to optimize the dopant concentration, sol samples of different mole % of Sb in Sn0₂, viz., 2.6, 3.9, 5.2, 6.5 and 7.8 respectively were prepared and spin coated followed by different heat treatment temperatures of 375°C, 400°C and 425°C and 400°C with the optimum number of coatings as 10 and their properties were investigated and reported.

7.8.1 VISUAL OBSERVATIONS OF Sn0₂ : Sb FILMS

Films coated with lower dopant concentrations up to 3.9 mole % of Sb showed improved luster quality. When the mole % of Sb corresponds to 5.2 %, the films had excellent luster with a mixture of dominant colours blue, violet and green which may be due to light interference and good film thickness as well as uniformity. When the dopant concentration was increased above 5.2 mole % of Sb
Fig. 7.11a Variation of mean grain size with heat treatment temperature

Fig. 7.11b Variation of texture coefficient with heat treatment temperature of ATO thin films
Fig. 7.12a Variation of resistivity with heat treatment temperature of ATO thin films

Fig. 7.12b Variation of carrier concentration with heat treatment temperature of ATO thin films

Fig. 7.12c Variation of carrier mobility with heat treatment temperature of ATO thin films
Fig. 7.13 Transmission spectra of ATO thin film spin coated at different heat treatment temperature.
milky white patches begin to appear on the film surface and this whiteness gradually spreads with the increase in dopant concentration. Virola and Niinisto [30] have reported the appearance of bluish colour for the ATO films when doped above the optimum level and this blue colouration was more intense at the higher doping level. For the vacuum evaporated SnO₂ thin films, Wendell Spence [31] have reported yellow-brown colour after the initial heat treatment in vacuum and became yellow after heat treatment in air. The milky white layer formation at higher dopant concentration (mole % of Sb in SnO₂ above 5.2) tends to decrease the optical transmittance substantially.

7.8.2 STRUCTURAL VARIATIONS WITH Sb-DOPING CONCENTRATION

Figure 7.14 shows the X-ray diffractrogram of ATO thin films, spin coated at different dopant concentration. XRD patterns are broad and confirm the tetragonal rutile structure of tin oxide and no phase other than this is found. All the films show a nanocrystalline nature with preferred orientation along the (110) plane. Other orientations such as (101), (200), (211) and (301) are also observed comparatively with lower intensities. As the dopant concentration is increased from 2.6 to 3.9 at %, the peak intensity and sharpness of all these orientation gradually increases with preferred growth along (110) plane. The spin coated film at 5.2 mol % shows the prominent (110) peak with highest peak intensity. The other planes (101), (200), (211) and (301) are also found to have higher intensity count with increased sharpness. Above this dopant concentration (6.5 mol % and 7.8 mol %) the peak intensity and sharpness gradually decreases for all the planes but the preferred orientation is retained along the (110) plane.

These intensity variations of all the orientations with the dopant concentration may be attributed to the occupation of antimony atoms in substitution for tin. The decline in the peak intensity and sharpness at higher antimony concentration (above 5.2 mol %) may be due to the deterioration of the film lattice.
Fig. 7.14 X Ray Diffraction pattern of ATO thin films spin coated at different dopant concentration
and tending to loose their crystallinity. The extent of preferred orientation along (110) of these polycrystalline films seems to govern its electrical properties, which suggests that at lower doping levels the resistivity is more dependent on dopant concentration where as at higher doping levels the preferred orientation governs the resistivity.

With the increase in Sb dopant concentration, fine displacement of the peak position for all the orientations is observed. The lattice constant value a and c are found to decrease with the increase in dopant concentration. For the [Sb]/[Sn] ratio of 5.2 at %, a and c values are found as 4.7368Å, 3.1836Å respectively, which are well in agreement with the standard JCPDS data (No. 41 - 1445) for SnO₂ powder specimen. The c/a ratio is found to be constant for all the dopant ratios, which shows that the tetragonal rutile structure is retained at all antimony doping concentrations.

The average grain size variation with Sb concentration is shown in Fig.7.15. The increase in grain size up to the doping level 5.2 mol % is due to the heterogeneous nucleation and related to the well developed XRD peaks. Which results in crystallites with smaller size. The average grain size is found to vary between 50 nm and 92 nm for the entire range of dopant concentration and a maximum value of 92 nm is observed at the optimum doping level of 5.2 mol %.

The texture coefficients of the three prominent peaks at (110), (101) and (211) are evaluated and their variation with dopant concentration is shown in Fig.7.16. From the figure it is seen that TC(110) increases initially with doping, becomes maximum at 5.2 mol % and then reduces. The intensity of the (110) plane is associated with the increased number of grains along the (110) plane.

7.8.3 ELECTRICAL PROPERTIES OF SnO₂:Sb FILMS

Electrical parameters like resistivity (p), carrier concentration (n) and mobility (fi) of SnO₂:Sb films with different doping level like 2.6, 3.9, 5.2, 6.5 and 7.2% of Sb are studied. The number of coatings used is 8 and the heat treatment
Fig. 7.15 Variation of mean grain size with the dopant concentration of ATO thin films

Fig. 7.16 Variation of texture coefficient with dopant concentration of ATO thin films
temperature is kept constant at 400°C. Figure 7.17a, b and c show the variation of ρ, n and μ values with respect to Sb doping concentration. It is observed that the SnO₂:Sb films prepared at 5.2 mol % of Sb show lower resistivity, higher n and μ values. This can be discussed in the light of lattice behaviour of controlled valence oxides. When Sb exactly sits in the Sn sites, the resistivity decreases upto an optimum doping level of Sb. In the present study, it is 5.2%. This doping effect is due to a controlled valence mechanism usually observed in a controlled valence oxides crystal lattice as: Sn_{(1-x)}^{4+}Sb_x^{5+}O_x O_2^{2-}. When the Sb doping concentration increases to 7.8 mol %, the unsubstantiated Sb atoms go to interstitial positions there by determining the crystal lattice and morphology. This reduces the electrical properties.

7.8.4 VARIATION OF OPTICAL PROPERTIES WITH Sb DOPING

Optical properties were studied by measuring the transmission between 300 and 700 nm, for different Sb doping SnO₂ films prepared by the spin coating technique (Fig.7.18). The overall transmission increases with doping concentration. 5.2 mol % Sb doped SnO₂ films exhibit an average transmission of 85 - 92% whose resistivity value is about 0.005 ohm-cm. The high ‘n’ values (≈4.8 x 10²⁰/cm³) is the reason for high transmission due to highly ordered crystalline lattice. The decrease in transmission in 7.8 mol % Sb doped films may be due to the low mobility and coarse surface of the films in such high doping levels.

Figure 7.19 shows the variation of α² against photon energy (hv), which is a straight line, indicating that the direct transition is the dominant process in optical absorption. The energy gap found are 2.85, 3.4, 4.1, 3.2 and 3.0 eV for the Sb doping of 2.6, 3.9, 5.2, 6.5 and 7.8 mol % respectively. The absorption edge shift from 2.85 eV to 4.1 eV can be attributed to the Moss-Bustein shift for Sb doping, which occurs due to filling up of low lying energy levels by the conductor electrons. Such a large shift in absorption edge confirms the wide band nature of SnO₂:Sb films prepared in the present study. The figure of merit ΦTC calculation
Fig. 7.17a Variation of resistivity with dopant concentration of the ATO thin films

Fig. 7.17b Variation of Carrier concentration with dopant concentration of the ATO thin films

Fig. 7.17c Variation of Carrier mobility with dopant concentration of the ATO thin films
Fig. 7.18 Transmission spectra of ATO thin films spin coated with different dopant concentration.

Fig. 7.19 Variation of $\alpha^2$ with Photon energy for the ATO thin films spin coated with different dopant.
The surface topography of the Sb doping SnO\textsubscript{2} films with 3.9\%, 5.2\% and 6.5\% are shown in AFM (Fig.7.21a, b and c) respectively. Both the two dimensional and three dimensional picture are shown. With increased antimony concentration upto 5.2\%, the morphology of the SnO\textsubscript{2}:Sb surface becomes smooth. Above this optimum level, the surface becomes course and uneven. From the three dimensional pictures, the grain size are found to be maximum for the SnO\textsubscript{2}:Sb films prepared with 5.2\% Sb at the optimized spin conditions. A closure view of the SnO\textsubscript{2}:Sb film prepared at the optimal conditions with 5.2 \% Sb is shown as 1000 nm x 1000 nm area (Fig.7.22). The uniformity of the surface and the grains are evident which confirm that device quality films can be easily obtained by the spin coating techniques.

**7.9 SUMMARY AND CONCLUSION**

Sb doped SnO\textsubscript{2} films have been prepared by spin coating techniques under the optimized conditions. At an optimum doping of 5.2 mol \% of Sb, SnO\textsubscript{2}:Sb films with lowest resistivity, higher transmission, very good crystallinity and highly uniform characteristics are obtained with 8 successive coatings and heated at 400\degree C.
Fig. 7.20 Variation of figure of merit with wavelength for ATO thin films spin coated with different dopant concentration.
Fig. 7.21 AFM pictures of SnO$_2$:Sb films doped with (a) 3.9%, (b) 5.2 and (c) 6.5% Sb.
Fig. 7.22 AFM picture of 1000 nm x 1000 nm area
SnO$_2$:Sb (5.2\%Sb) film
REFERENCE


