CHEMICAL VAPOUR DEPOSITED SEMICONDUCTING TIN OXIDE THIN FILMS : EFFECT OF VARIATIONS IN PROCESS PARAMETERS ON FILM CONDUCTIVITY

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ABSTRACT

Effect of vartiatons in process parameters such as impurity doping concentration, substrate temperature, substrate material, film thickness, etc., on the surface resistivity and bulk conductivity of semiconducting tin oxide thin films (deposited by the chemical vapour deposition method) have been investigated.

Key words: Tin oxide, thin films, CVD films.

1. INTRODUCTION

Thin films of semiconducting tin oxide are known to have a number of applications in various technologies [1–3], such as the high stability resistors, transparent electrodes for certain semiconductor and liquid crystal devices, transparent heating elements for Aeroplane and automobile windshields, etc. Thin films of semiconducting tin oxide are deposited either by the chemical vapour deposition method [4–7] or by the vacuum sputtering technology [8–11]. Pure and stoichiometric tin oxide is an insulator. Thin films of tin oxide can be made semiconducting either by introducing nonstoichiometry by creating slightly reducing conditions during their deposition, or by doping the material with suitable impurities such as Sb, P, Bi, etc.

We have deposited thin films of semiconducting tin oxide by the chemical vapour deposition (CVD) technique [12] and have studied the effect of variations in various process parameters on the electrical characteristics of such films.

2. EXPERIMENTAL

As mentioned ealier, the samples were prepared by the C.V.D. technique, using the chemical reaction of hydrolysis of tin chloride on the

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surface of the hot ceramic substrates. Two types of substrate materials were employed in the present work, *viz.*, glass (microslides) and unglazed porcelain. The deposition of the film was carried out at three different substrate temperatures (*viz.*, 450, 500 and 550° C) in case of the glass samples; and at five different substrate temperatures (*viz.*, 450, 500, 550, 700 and 800° C) in case of the porcelain samples.

The substrates were first cleaned with acids, soap, water, organic solvents and distilled water and dried and then heated in a small electric furnace to the desired substrate temperature. The substrate temperature was maintained within ± 10° C with the help of a thermocouple and a Philips on-off type solid state temperature controller.

The deposition of the film was then carried out by spraying the desired solution of tin chloride (A.R., Renal, Hungary) (doped with the appropriate concentration of Sb impurity ions) on the surface of the hot substrate, when a thin film of tin oxide gets deposited on the surface of the hot substrate by the hydrolysis of tin chloride.

In case of glass samples, five different antimony doping concentrations (*viz.*, 1, 2, 4, 8 and 15 at %) were used for each of the three substrate temperatures, while in case of porcelain samples, the deposition was carried out at five different substrate temperatures but using only one type of impurity doping concentration (2 at %).

For each impurity ion concentration and in case of each substrate temperature and material, five film samples were prepared with varying values of film thickness, in order to obatin five different surface resistivity values, varying in the range from about 25 ohms to 25,000 ohms per square.

The chemical nature of the films deposited by this technique has been analysed by A.Ya. Kuznetsov [1] and has been reported to be SnO_2. The average film thickness of our tin oxide films was calculated from the knowledge of the weight of the film and the area of the substrate. The weighings were carried out on a SARTORIUS 2604 single pan semimicro balance with the accuracy of ± 0·01 mg, and the corresponding accuracy in the film thickness values for our samples was ± 15 Å. (Uniformity of film thickness was checked by reflection spectrum).

After deposition, the samples were annealed in an electric oven at 150 ± 1° C for 75 hours for stabilisation of the film resistivity by the thermal annealing; and contacts were then made by electroplating nickel metal at the desired positions and then soldering the leads on to this nickel.

The measurements of electrical resistance values of the samples were carried out using a OSAW wheatstones bridge and the values of surface resistivity and bulk conductivity for each sample, were calculated from the knowledge of the area of the sample and film thickness value for the respective sample.

3. RESULTS AND DISCUSSION

3.1. *Effect of Film Thickness*

If the bulk conductivity of a material is independent of film thickness (even when the material is deposited as a thin film), then the surface resistivity 'ρ_s' of the thin film of such a material should exhibit an inverse proportionality with the thickness of the film 't'. Consequently, the plots of log ρ_s *versus* log 't' for all such materials should exhibit parallel straight lines with slopes equal to unity (Fig. 1 dotted line).

A typical experimental plot of log ρ_s *versus* log 't' is shown in Fig. 1, which exhibits such a linear relationship between log ρ_s and log t, but with a slope differing from unity. This indicates that the surface resistivity 'ρ_s' of the films is related with the film thickness 't' by a 'power law' relation ship—

$$\rho_s = \frac{k}{t^m} \tag{1}$$

where 'k' and 'm' are constants.

When the magnitude of 'm' equals '1' this equation represents the standard relationship of inverse proportionality. But on the other hand when the magnitude of $m \neq 1$, the relatoinship indicates that the bulk conductivity 'σ_v' of the material is dependent upon the film thickness. Further, the magnitude of 'm' indicates the extent or degree of such dependence of 'σ_v' as a function of the film thickness.

The phenomenon of the variation in bulk conductivity as a function of film thickness can possibly be explained as follows. During our previous studies on the effect of 'Thermal Annealing' on the surface resistivity of the tin oxide thin films, reported earlier [13], we had found that the initial deposition of the C.V.D. tin oxide films is associated with a

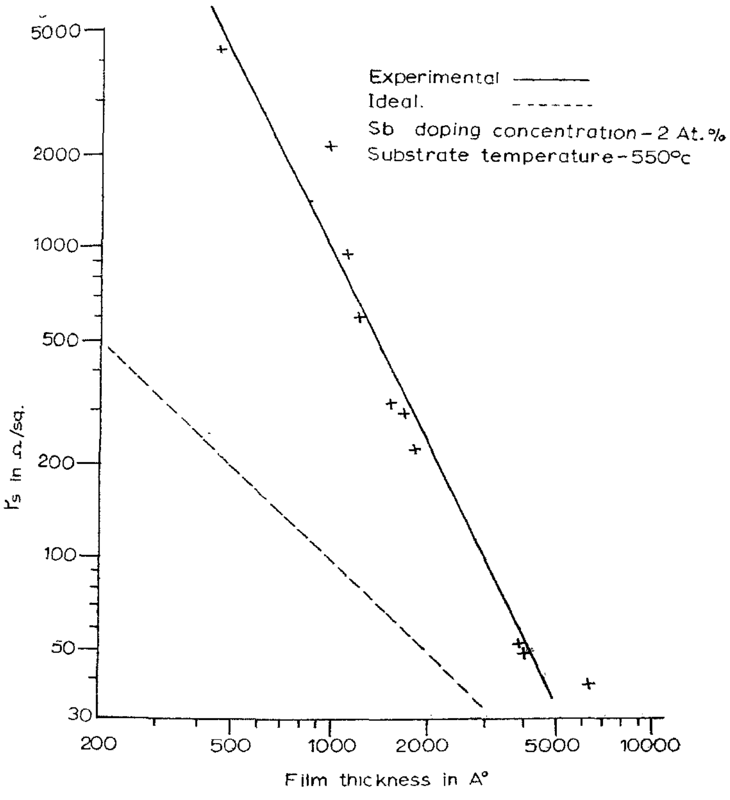

FIG. 1. A typical plot depicting the variation in surface resistivity 'ρ_s' as a function of the film thickness 't'.

higher density of lattice defects and that this lattice defect density gradually decreases with film thickness until the magnitude of the film thickness exceeds about 1000 Å, when the lattice defect density reaches a certain minimum magnitude depending upon the various process parameters. Any further increase in the film thickness is then associated with this minimum density of lattice defects which remains constant for a given set of process parameters such as substrate temperature, substrate material, composition of the spraying solution, etc. When seen in the light of this phenomenon, it follows that the bulk conductivity of the CVD tin oxide thin films should exhibit a dependence on the film thickness during the initial stages of the deposition and then reach to an apparent constant magnitude at very high film thickness values. The plots of log σ_v *versus* log t for our samples do indicate such a behaviour. (Fig. 2).

It may also be noted here that, even though the lattice defect density might assume an apparently constant magnitude above a film thickness of about 1000 to 2000 Å, this phenomenon can become apparent in the measured values of 'σ_v' only after a much higher film thickness, (Fig. 2) because the experimentally measured values of 'σ_v' actually represent only the average magnitude of 'σ_v' corresponding to the entire thickness of the deposited film.

3.2 *Effect of Substrate Temperature and Material*

From the typical plots of log ρ_s *versus* log t (Fig. 3) it can be seen that for a given doping concentration, substrate material and film thickness, the surface resistivity of the film decreases with the substrate temperature, *i.e.*, the bulk conductivity of the film increases with the substrate temperature which is in keeping with the normal expectations.

The plots of bulk conductivity 'σ_v' as a function of substrate temperature 'T' for a given film thickness magnitude, shown in Fig. 4, indicates that the bulk conductivity of the film material increases (almost linearly) with the increase in the substrate temperature. Further, one can also see that this effect of substrate temperature on the bulk conductivity of the film material is more pronounced at lower antimony doping concentration (1 at %). Therefore, it appears that, in case of the heavily doped films, the bulk conductivity is less affected by the variations in the substrate temperature as compaed with the case of the lightly doped films.

As mentioned in section 3.1, the magnitude of the exponent 'm' corresponding to a plot of log ρ_s *versus* log t, represents the degree of the dependence of 'σ_v' as a function of the film thickness. The magnitudes of 'm' corresponding to each of our spraying compositions and also corresponding to each substrate temperature and material are given in Table I. It can be seen from Table I that in case of the glass samples the magnitude of 'm' is initially high and decreases along with the substrate temperature.

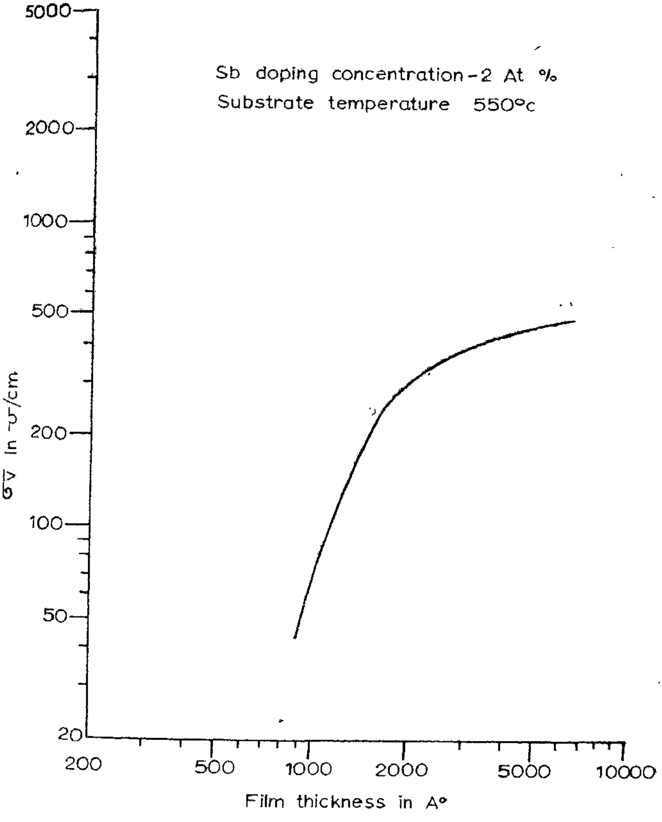

FIG. 2. A typical plot dipicting the variations in bulk conductivity 'σ_v' as a function of the film thickness 't'

It can also be seen that the magnitude of 'm' also decreases with the antimony doping concentration. Now, a higher magnitude of 'm' represents higher rate of variations in the lattice defect density with the increase in the film thickness and *vice versa*. Therefore, it can be infered from this

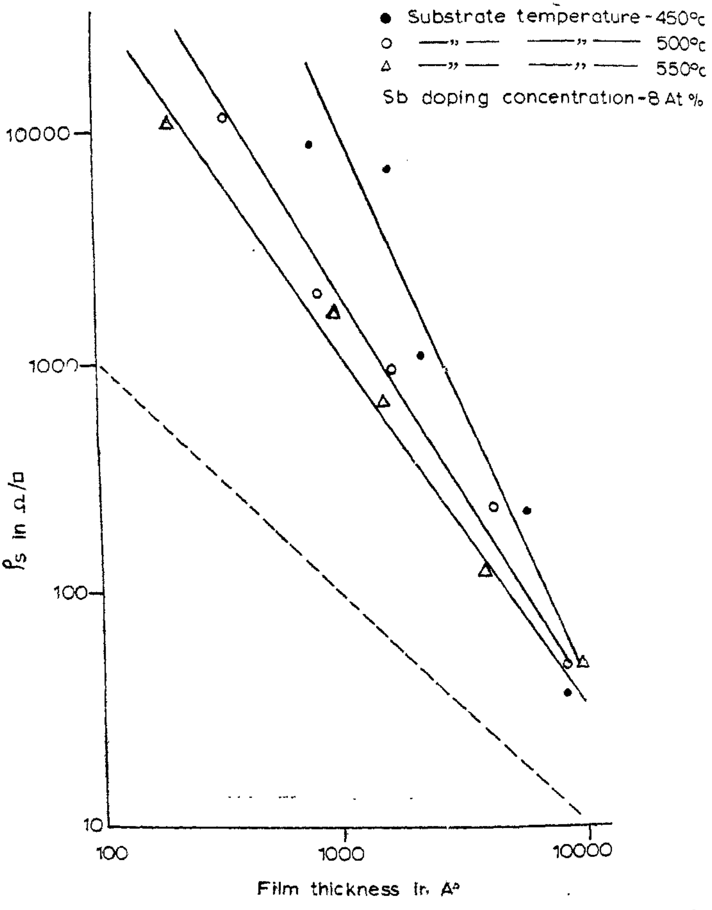

FIG. 3. Variations in surface resistivity 'ρ_s' as a function of filmthickness 't' at various substrate temperatures.

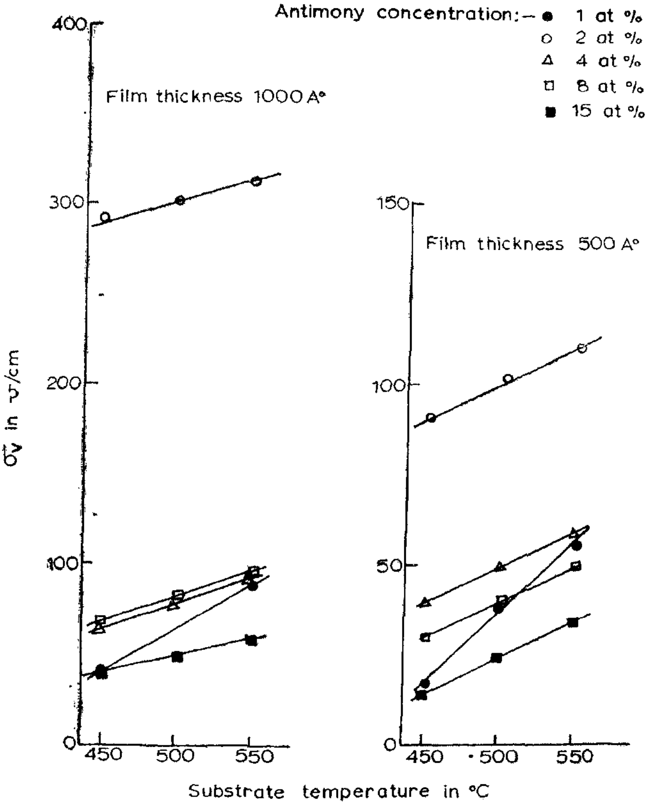

FIG. 4. Variations in bulk conductivity 'σ_T' as a function of the substrate temperature 'T'

datum presented in Table I, that the deposition at lower substrate temperatures is associated with higher lattice defect density in the initial stages of deposition and further that the increase in the antimony dopping concentration also helps to decrease the lattice defect density at lower substrate temperatures. At higher substrate temperature (550° C), however, the

TABLE I

Magnitudes of the exponent 'm' at various substrate temperatures and doping concentration

Substrate material	At % antimony	Substrate Temperature in ° C 450	500	550	700	800
	1	2·38	1·33	1·48		
Glass	2	2·67	2·08	1·48		
	4	2·16	1·94	1·52		
	8	2·04	1·60	1·46		
	15	2·0	1·47	1·40		
Unglazed porcelain	2	1·60	1·46	1·43	1·12	1·00

magnitude of '*m*' is already low and the effect of antimony doping concentration is therefore only marginal.

Further in case of the unglazed porcelain substrates, the magnitude of '*m*' is comparatively smaller even at lower substrate temperatures, and it almost approaches the ideal value of unity at around 800° C substrate temperature. This effect might be assigned to be due to the fact that the surface of the unglazed porcelain is crystalline in nature as compared with the amorphous nature of the glass substrates. The crystalline nature of the surface of the substrate material might be helpful in reducing the initial high magnitude of the lattice dislocation density and consequently reduces the variations in the bulk conductivity of the tin oxide films as a function of the film thickness.

3.3 *Effect of Antimony Doping Concentration and the Source of Antimony Ions*

Tin oxide is known to be a wide band semiconductor with a high band gap level [1, 4, 5, 7, 14, 15]. Pure and stoichiometric tin oxide therefore behaves like an insulator. However, when the material is doped with pentavalent ions such as Sb and P, it becomes an '*n*' type semiconductor and the electrical conductivity of the material increases with the antimony doping concentration. The presence of these foreign donor ions in the lattice, however, also act as scattering centres for the charge carriers [7]. At very high donor levels, therefore, the scattering centre density also increases and the mobility of electrons decreases, thus resulting in the reduction of electrical conductivity. The material therefore exhibits a maxima in the bulk conductivity at a doping ion concentration level of around (4 at %) and any further increase in the doping concentration only leads to a decrease in the conductivity of the material.

The plots of σ_v as a function of antimony doping concentration for a given film thickness and substrate temperature for our samples are shown in Fig. 5. It can be seen from Fig. 5 that in case of our samples the composition with (2 at %) of antimony ion concentration gives the highest conductivity. Except for this shift in the antimony ion concentration corresponding to the highest conductivity composition, the general trends represented by the plots in Fig. 5 are in agreement with the results of the previous workers.

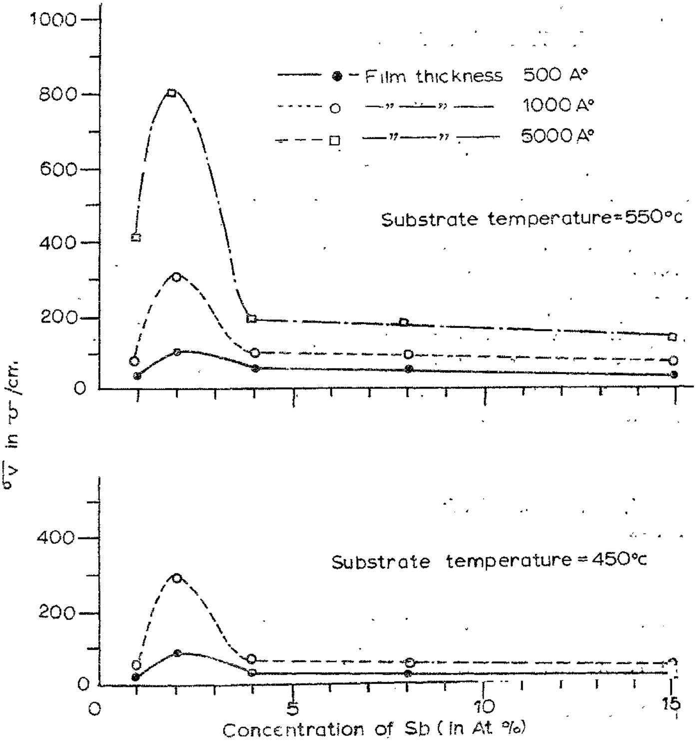

FIG. 5. Variations in the bulk conductivity 'σ_v' as a function of the antimony doping concentration.

We have used Sb_2O_3 dissolved in HCl as the source of antimony ions, while the previous workers have used antimony chloride as the source of antimony ions. We therefore prepared two compositions corresponding to 2 and 4 at % of antimony ions, using antimony chloride as the source of antimony and found that in such a case the 4 at % composition did give higher electrical conductivity. Therefore, this shift in the antimony ion concentration corresponding to the highest conductivity composition seems to arise from the possibility of formation and presence of some oxychlorides of antimony when Sb_2O_3 is dissolved in HCl and this might result in some changes in the distribution of final oxidation states of the antimony ions.

4. CONCLUSIONS

The bulk conductivity of semiconducting CVD tin oxide thin films was found to vary as a function of film thickness. This behaviour has been attributed to the variation in the lattice defect density during the deposition of the film. The bulk conductivity of the films was also found to increase with the substrate temperature. Crystalline nature of the surface of the substrate material probably reduces these variations in bulk conductivity as a function of the film thickness. Higher substrate temperature and higher antimony doping concentration also seem to help in reducing these variations in the bulk conductivity as a function of film thickness. The bulk conductivity of the films reaches a maximum value at a critical antimony doping concentration and this critical value was found to vary with the nature of the source of antimony.

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