CHAPTER 3

TRANSPARENT CONDUCTING TIN DIOXIDE FILMS BY A NOVEL CVD TECHNIQUE

*3.1. Introduction :

There are some semiconducting oxides where simultaneous occurance of high optical transparency in the visible region and high electrical conduction is observed. Such semi conducting oxides are called transparent conducting oxides or transparent conductors (TCO). These are obtained by creating electron degeneracy in a wide band gap oxide by controllably introducing non-stoichiometry and/or appropriate dopants. Several oxides in the thin film form, prepared by various deposition techniques are transparent conductors. Major application of these is in electronic and opto-electronic devices, such as transparent heating elements, transparent electrodes for solar cells, and different display devices. Widely studied transparent conductors are Tin Dioxide doped with Sb, F or As, Indium Oxide, Tin doped indium oxide, Zinc oxide, Indium doped

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Zinc Oxide and Cadmium stannate. Other materials, which may be used include oxides of bismuth, molybdenum, titanium, tungsten, rhodium and rhenium, sodium tungstate and zinc stannate.

In the family of semi conducting oxides that have been used as transparent conductors, tin dioxide is one of the most prominent members. Both undoped and doped SnO_2 films can be used for various practical applications [1,2]. Undoped tin oxide films are anion deficient, where oxygen vacancies are created by chemical reduction. A similar or better effect is obtained by introducing dopants like Sb, In, Cd, P, in the cation sites or F or Cl in the anion sites. The essential requirement for the dopants are that the ionic radii of the dopants must be of the same size or smaller than the ion it replaces and that no compounds or solid solutions of dopant oxide with host oxide are formed. If the dopant ion is too large, it will capture the interstitial site instead of the substitutional, and will act as a scattering site rather than as a source of charge carriers [1]. Depending on all these conditions only the above mentioned dopants are generally used.

A large variety of methods that have been used to deposit conducting tin dioxide films are hydrolysis of chlorides, spray pyrolysis, reactive evaporation and sputtering, screen printing, doctor-blade, vapour transport

and glow discharge of organotin compounds. The fabrication and properties of transparent conducting oxide films have recently been reviewed by Chopra et al [2].

Here we describe an extremely simple method for the deposition of undoped and Sb-doped conducting tin dioxide films. This novel technique utilizes the hydrolysis of $SnCl_4$ on the surface of a hot substrate, which is also the basis of the familiar spray pyrolysis and chemical vapour deposition processes. But unlike other methods, it does not require any specialized sophisticated experimental setup, and hence can be carried out in any laboratory. In most of the methods mentioned earlier, $SnCl_4$ is taken as the starting material for hydrolysis. In the present technique, however, the starting material is the easily available material $SnCl_2, 2H_2O$, which, as described below, is decomposed to yield $SnCl_4$ in situ.

3.2. Deposition Technique

A paste is made by dissolving $SnCl_2, 2H_2O$ crystals in a minimum amount of distilled water. As a rough guide, 10 gms of $SnCl_2, 2H_2O$ require 3 to 5 drops of distilled water. In the case of doping, the requisite amount of dopant $SbCl_3$ is dissolved in a minimum amount of HCl and is then added to the paste. [It may be mentioned here that direct

addition of $SbCl_3$ to the undoped paste produces a chalky white precipitate, a compound presumably of insoluble hydroxides, and useful films cannot be produced from this material [7]. The paste is then allowed to stand for 1-3 days. When nearly dry, the mass is throughly stirred mechanically, and with the help of paint brush a band approximately 3 mm wide is applied near one end of the substrate [Fig.3.1].

The substrate is heated using the arrangement shown in Fig.3.1(a). The simple set up requires a heater and an arrangement for holding the substrate. The substrate is kept initially in a position where only the portion of the substrate over which the film is to be deposited receives direct radiation from the heater. After some time, when the substrate has attained the required substrate temperature ($\approx 400^{\circ}C$), it is raised to its final position, so that the $SnCl_2$ 'band' now also receives heat.

The $SnCl_2$ mass first becomes dry, then melts into a glassy form and finally swells and starts into 'spit'. Simultaneously, white fumes are given off and seen to deposit the SnO_2 film where they come into contact with the substrate. The thickness of the film being deposited can be visually monitored by looking at the reflection from the substrate and observing the interference colours. It is essential to control the air current (by properly placed shields), which is the carrier gas in this case,

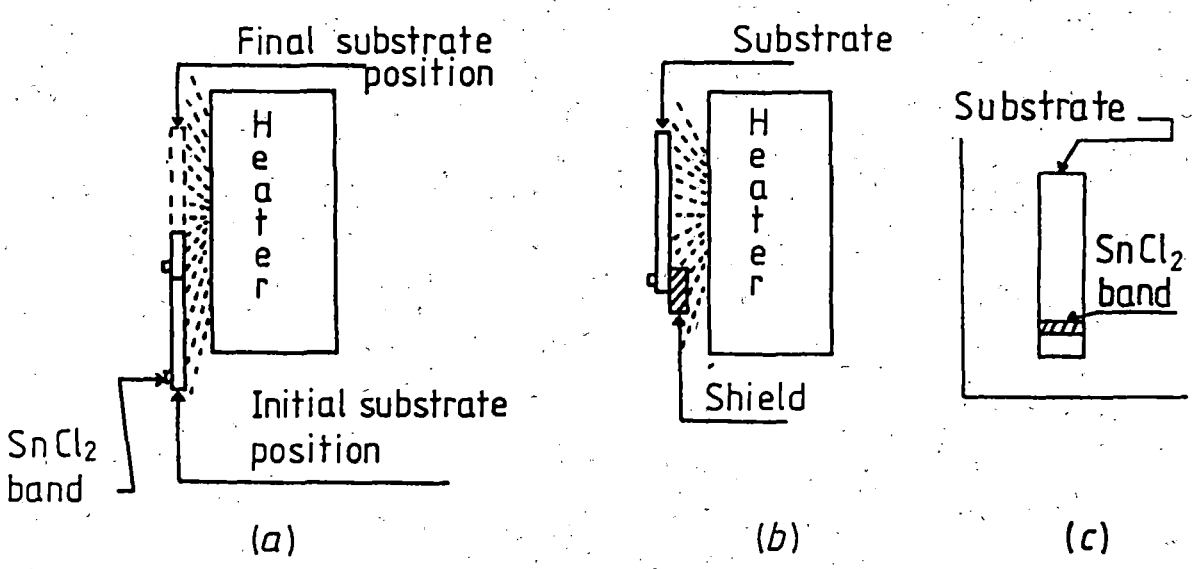

Fig. 3.1. Arrangements for the deposition of SnO_2 films. Figure (c) shows the location of the $SnCl_2$ band with respect to the substrate.

for better uniformity of the film. Uniformity can be improved by slightly rocking the substrate at the time of film deposition. Finally, by painting another 'band' parallel to and at a distance $\approx$ 8 cm from the first one with the substrate turned arround, and repeating the whole process of deposition it is possible to deposit a reasonably uniform film of approximate area 5 x 2.5 cm.

Essentially similar results are obtained if the substrate is positioned to receive direct radiation from the heater, while the region with the $SnCl_2$ 'band' is shielded from the heater by a metallic strip [Fig.3.1(b)]. In this case, no repositioning of the substrate is necessary as the shielding ensures that the substrate is already at the required temperature before the $SnCl_2$ paste starts to decompose.

Results reported here were obtained for films deposited using the arrangement described earlier [Fig.3.1(a)].

It was found that the best films in terms of conductivity, optical transmission, and resistance to peeling -off and acids were obtained for a substrate temperature of the order of 400°C. Films prepared at lower temperatures ($\lesssim$ 300°C) have a relatively higher resistivity, whereas films prepared at higher temperatures ($\sim$ 500°C) tend to peel off easily.

In an attempt to understand the chemistry of the film-forming process, an amount of $SnCl_2$ paste was strongly heated in a closed flask and the vapours given off condensed and collected. The condensate was chemically analysed and found to consist of $SnCl_4$, HCl and H_2O. A separate chemical analysis showed that $SnCl_2$ paste itself contains Sn mostly in the Sn^{II} state.

It is well known [3] that, in the presence of oxygen, an aqueous solution of $SnCl_2$ becomes turbid on account of the following reaction

$$6\ SnCl_2 + 2\ H_2O \rightleftharpoons 2\ SnCl_4 + 4\ Sn(OH)Cl.$$

It is suggested that, at room temperature this reaction is relatively slow, but proceeds rapidly on heating, as during the film deposition process. Thus $SnCl_4$ vapour, which is one of the reaction products, is hydrolyzed to produce the film on contact with the hot substrate, the necessary moisture coming from the starting material itself as also from the atmosphere.

With the help of this technique, it is also possible to deposit SnO_2 on a set of 5 to 10 painted substrates at a time, if a heater having a sufficiently large area is available. A number of substrates can thus be coated by a batch process to save deposition time per substrate.

The paste remains in usable condition for a month or two. If it dries up, then it is necessary to add again a few drops of distilled water for further use.

3.3. Results

3.3.1. Thickness

By varying the amount of starting material in the painted band and the deposition time, films of various thicknesses, ranging from 100-5000A^{o}, as ascertained from the interference colours [1] can be obtained.

The films are smooth over a length $\approx$ 5 cm from the position of the $SnCl_2$ band. Initially the thickness is not uniform, the layer being thicker nearer the band, as expected. But by repeating the process, with another band $\approx$ 8 cm away from the first one and the substrate turned arround, as described earlier, uniformity can be improved. Thus a region of 3-5 cm long having a fairly uniform thickness can be obtained with the help of this technique.

3.3.2. Microstructural Details

3.3.2(i) X-ray Diffraction (XRD)

Fig.3.2 shows an x-ray diffraction pattern of a typical SnO_2 film with CuK_α radiation. The diffractogram suggests that the film is polycrystalline in nature. The crystal structure is found to be in accordance with the usual tetragonal form of SnO_2, which has a unit cell having dimensions, a = 4.74A°, C = 3.19A°.

(ii) Scanning Electron Microscopy (SEM)

The surface topography as studied by a scanning electron microscope is shown in Fig.3.3. The grain size is seen to be $\approx .2\,\mu m$.

3.3.3. Optical Transmission

Typical optical transmission versus wavelength data for the films of various sheet resistances are shown in Fig.3.4(a) and 3.4(b) for undoped and Sb-doped (2 at %) SnO_2 films. Optical transmission data were obtained by a SHIMADZU UV-240 doublebeam spectrophotometer (air reference). Films of average optical transmission 70-90% could be routinely obtained by this method. However, optical transmission values show a wide scatter in the

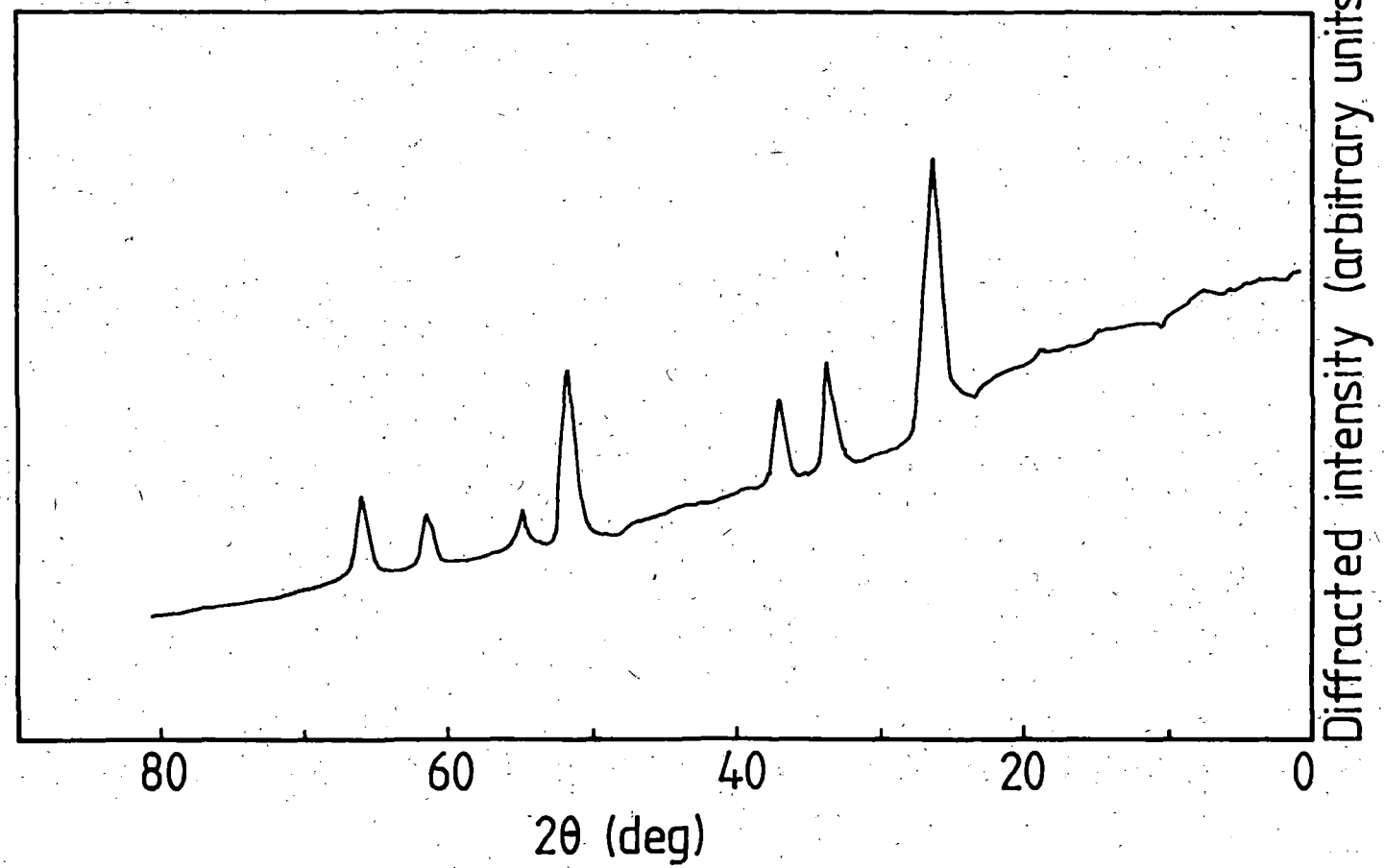

Fig.3.2. An X-ray diffractogram of a typical SnO_2 film.

Fig.3.3 A scanning electron micrograph of a typical SnO_2 film.

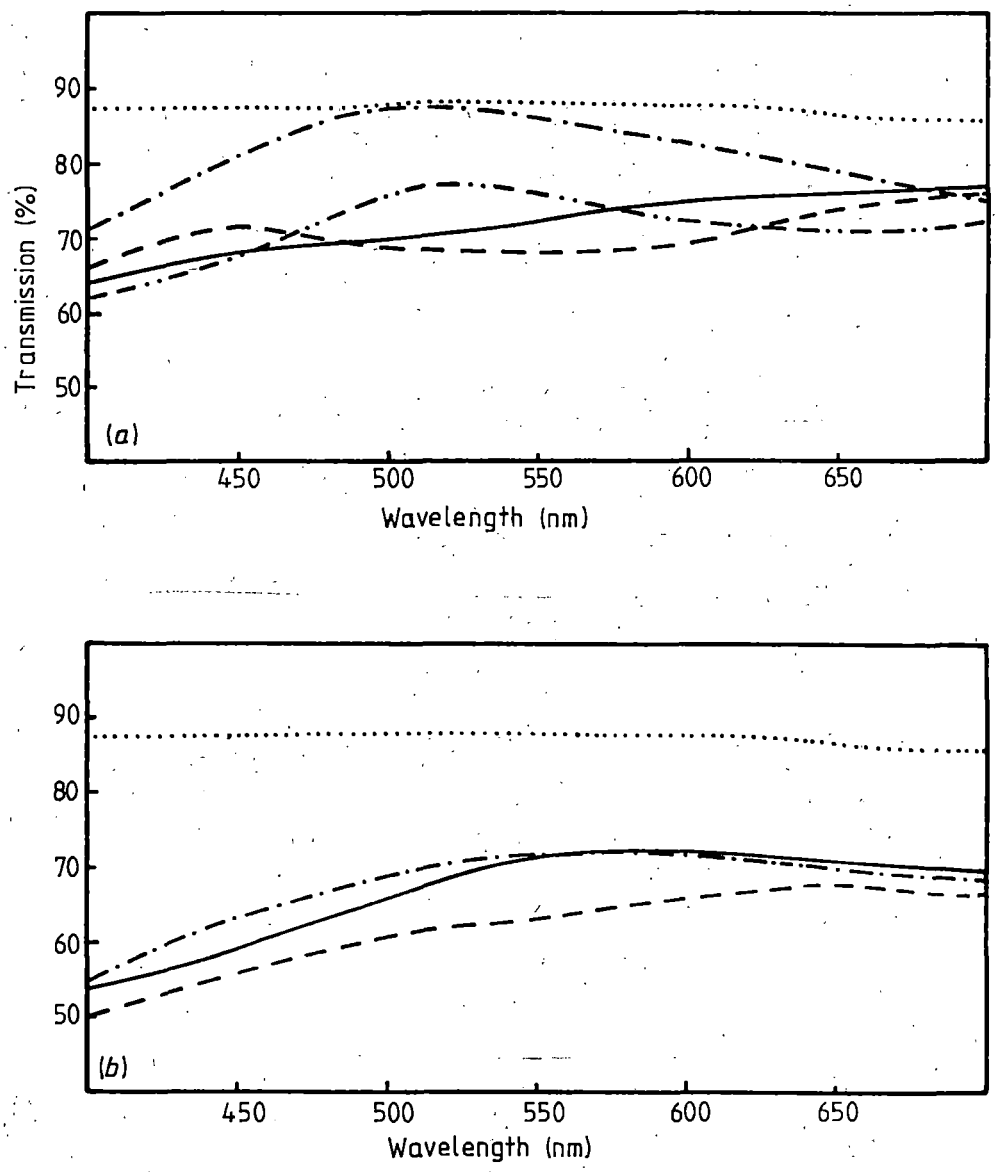

Fig. 3.4. Optical transmission versus wavelength for typical SnO_2 films of various sheet resistance (a) Undoped: (- - - -), 475 Ω/□ (-·-·-·-·-), 670 Ω/□; (———), 860 Ω/□; (·-·-·-), 1400 Ω/□; (·····), bare substrate. (b) Sb-doped (2 at.%): (- - - -), 110 Ω/□; (-·-·-·-), 550 Ω/□ (———), 870 Ω/□; (·····), bare substrate.

case of undoped films. This is due to the variable oxygen content in the resulting undoped films. This fact is also reflected in the conductivity data mentioned later (Fig. 3.6).

3.3.4. Electrical Measurement

Films of various sheet resistances from 100-5000 ohms/square could be obtained by varying the starting material, proportion of dopant, deposition time and substrate temperature. In Fig.3.5 is shown the sheet resistance - thickness relationship for undoped and 2 at. % Sb-doped films at various substrate temperatures. The sheet resistances of the films were measured by standard four-probe method. The resistivity of the Sb-doped (2 at %) films prepared at 400°C by this technique is estimated to be $\lesssim 5 \times 10^{-3}$ ohm-cm, which is comparable with the sheet resistance value $\sim 2 \times 10^{-3}$ ohm-cm of spray-pyrolysed SnO_2:Sb films [2]. Relation between the sheet resistivity and optical transmission of undoped SnO_2 and Sb-doped (2 at %) SnO_2 also bare glass (for reference) is shown in Fig.3.6. The sheet resistance values show a wide scatter in the case of undoped films prepared by the present technique. It therefore appears that the amount of anion (oxygen) deficiency is difficult to control by this method.

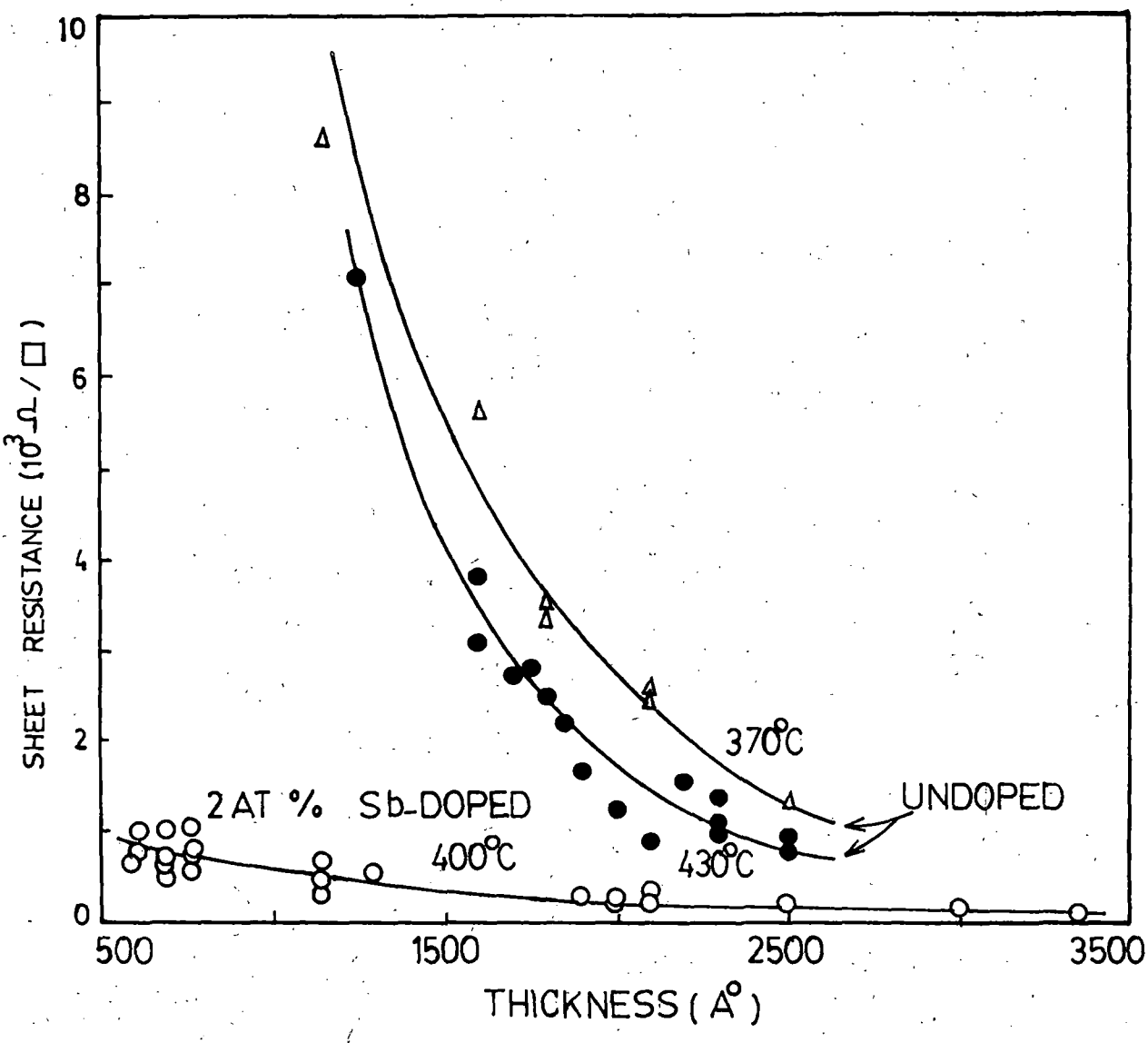

Fig. 3.5. Sheet resistance—thickness relationship for undoped and 2 at.% Sb-doped SnO_2 films prepared at various substrate temperatures: 370°C, 430°C and 400°C.

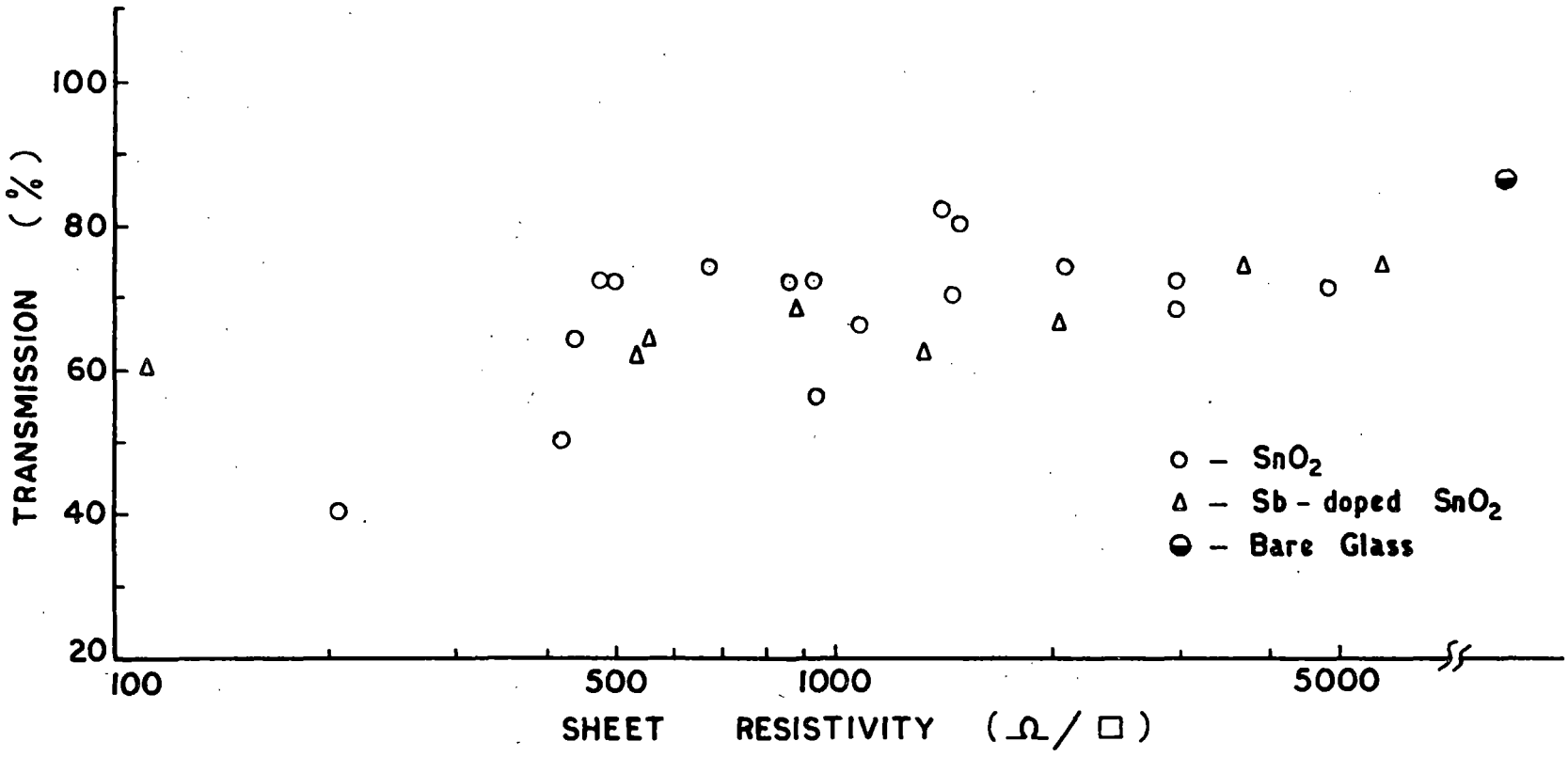

Fig. 3.6. Average(between 400 nm-700 nm) Optical transmission —— Sheet resistance relation for undoped and Sb-doped (2 at.%) SnO_2 film on soda-glass substrate.

3.4. Conclusions

The method discussed above is a very simple and low-cost one. With the help of this technique, one can deposit transparent conducting SnO_2 films in any laboratory without using any specialized experimental set up. Another advantage is the use of the low cost laboratory grade $SnCl_2$, $2H_2O$ as the starting material. Thus an uniform coverage of about 5 x 2.5 cm is obtainable by this technique, which should make it useful in various device applications.

3.5. Comparison of the Dip Technique for producing SnO_2 films with the present method.

Both the present method as well as the dip technique, are very simple and low-cost methods for the deposition of SnO_2 films. But with the help of dip technique, it is difficult to get low resistivity films. As the chemical analysis results show (art.3.2), when the liquid film containing $SnCl_2$ is heated in a high temperature furnace, the major portion of $SnCl_4$ evaporates, leaving the hydrates of SnO and SnO_2 and traces of $SnCl_4$. Hydrates of SnO and SnO_2 are highly insulating in nature and only the residual amount of $SnCl_4$ is converted into the conducting SnO_2. So the resulting film is semi-insulating in electrical

properties and its resistivity value ranges from 4.5×10^{-1} ohm-cm to 4.5×10^{2} ohm-cm.

The major portion of $SnCl_4$ vapour, which escapes from the substrate in the case of dip technique, is used in the present method to hydrolyze on the hot substrate surface. As a result, semi-conducting SnO_2 films are obtained, whose sheet resistance lie in the range 100-5000 ohms/square for a thickness of $1000A^{o}$, which corresponds to a resistivity value $\sim 4.5 \times 10^{-3}$ ohm-cm — 2.2×10^{-1} ohm-cm.

These two techniques together can produce SnO_2 films having a wide range of sheet resistance from about 100 ohms/square to 10^{7} ohms/square.

References

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