PREPARATION OF THIN FILM TRANSPARENT
TIN OXIDE CONDUCTING CONTACTS

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ABSTRACT

Tin oxide, indium oxide and indium tin oxide (ITO) films are extensively used in applications where a high electrical conductivity and good optical transmission in the visible region are required. Highly conducting, transparent fluorine doped tin oxide films were prepared on glass substrates by spray pyrolysis employing $SnCl_2$ instead of the commonly used $SnCl_4$. A systematic study on the spray pyrolysis conditions, optical and electrical properties of the films obtained, the influence of air and vacuum annealing of the films on their properties and also surface topography studies are presented.

INTRODUCTION

Tin oxide (SnO_2), indium oxide (In_2O_3) and mixtures of the two, commonly called indium tin oxide (ITO) have their lowest electrical resistivity in the range of 10^{-8} ohm-cm [1]. The optical transmission of the layers is spectrally dependent. SnO_2 shows ultraviolet absorption for low wavelengths, its band gap being about 3.6 eV. It reflects to the extent of about 90% in the infrared region. These properties make SnO_2 or ITO films useful in applications where a high electrical conductivity, good optical transmission in the visible region and/or good reflective properties in the infrared region (or any combination of these properties) are required.

These oxide films have some advantages over metallic films since the former are stabler and harder and show greater adhesion of many substrates. Thin metallic films ($<$ 10 nm thick) though highly transparent are quite fragile, while the oxide films are not so.

High electrical conductivity, transmission in the visible region and reflective properties in the infrared region shown by SnO_2 and ITO films are useful in solar cell applications [2-6]. Their infrared reflective nature is useful in flat plate collector technology [7-9]. SnO_2 and ITO material find use in glazing units employed for increasing the thermal insulation of buildings [10,11]. They are also used as transparent heating systems in digital displays and light emitting devices.

The authors are interested in preparing highly conducting, transparent SnO_2 films on glass to produce a good ohmic substrate for photoactive layers of cadmium chalcogenides. Besides being useful as ohmic contacts, SnO_2 substrates facilitate fabrication of backwall illuminated photoelectrochemical (PEC) cells, because of their transparent nature to visible radiation. The backwall illuminated PEC cells suffer less attenuation as the light energy does not have to pass through the electrolyte solutions to reach the photoactive electrode. As an additional advantage, the infrared reflective properties of the SnO_2 films prevent the cell heating effects considerably.

These oxide films are known to have complex structures and films of high perfection are difficult to make. The physical properties of the films have been found to be strongly dependent on the conditions of preparation [1].

The methods of preparation include spray pyrolysis [12,14], chemical vapour deposition [15-18], sputtering methods [19-21] and thermal evaporation [22,23].

The present work was performed with spray pyrolysis on glass substrates. Conditions have been optimized for the production of satisfactory SnO_2 layers for use as conducting contacts for photoactive layers of cadmium chalcogenides.

Spray pyrolysis of SnO_2 is performed mainly by the use of tin chlorides. Undoped SnO_2 films show extrinsic conduction of the n-type which is caused by the presence of Sn^{2+} ions associated with oxygen vacancies. The residual Cl^- ions from the mode of preparation also act as electron donors. This unintentional doping usually occurs when tin chlorides are used in the preparation of the films. The extrinsic conduction of SnO_2 is thus a result of both. Electrical conductivity in the range of 10^2 to 10^3 ohm^{-1} cm^{-1} has been reported for undoped films [13].

Doping with Group V elements (for e.g. 1 mole percent of antimony) markedly increases the quasi-free electron concentration [13,24,25]. The pentavalent Sb atoms are assumed to go into Sn sites (Sb_{Sn}) giving rise to quasi-free electrons. However, high concentration of Sb ($\sim$ 20 mole %) has been found to raise the resistivity by ten orders of magnitude [13]. This is attributed to a loss in crystallinity, the films behaving like typical amorphous materials.

Fluorine too increases the quasi-free electron concentration in SnO_2. It is probably in a substitutional position as F_O [26]. The increase in carrier concentration is found to be in accordance with a controlled valency mechanism. Large quantities of fluorine have been reported to result in a decrease in conductivity [27].

The inclusion of chlorine impurity also accounts for the high electrical conductivity of SnO_2 films. Chlorine may be incorporated either substitutionally as Cl_O or interstitially, but only part of the chlorine incorporated supplies conduction electrons [28,29].

The use of $SnCl_4$ as the main substance employed in the spray pyrolysis preparation of SnO_2 films is wellknown. Relatively very little work on systematic spray pyrolysis experiments with $SnCl_2$ as the main ingredient is available. In this paper are presented the results on the suitability of employing $SnCl_2$ as the main

ingredient. Also doping with fluorine and a mixture of fluorine and chlorine is examined with $SnCl_2$. $SnCl_2$ has the advantage of being less expensive than $SnCl_4$. It is also less pungent and easier to handle and holds promise as a good substitute for $SnCl_4$ in the spray pyrolysis mode of preparation of SnO_2 films.

EXPERIMENTAL

The spray medium was mainly a dispersion of the ingredients $SnCl_2.2H_2O$ and $NH_4F.HF$ in rectified spirit. The spray nozzle was kept at a distance of 30 cm from the near end of the heater bearing the substrates. The temperature of the substrates was monitored by a thermocouple placed close to them.

The spray pyrolysis was conducted at 400°, 450° and 500°C and using different concentrations of the spray solution. Doping with fluorine (using ammonium bifluoride) and with a mixture of fluorine and chlorine (using ammonium bifluoride and ammonium chloride) was studied.

The surface resistances of the samples prepared at a temperature of 450°C were generally among the lowest and this temperature of deposition appears to be the best under the conditions of experiments presented here (i.e. considering the design and size of the hot chamber, nozzle size and distance between the nozzle and the heater).

RESULTS AND DISCUSSION

Figure 1 shows the variation of the resistivity of the films with the variation of the concentration of $SnCl_2$ in the spray solution with a constant amount of 1% $NH_4F.HF$ as the doping agent.
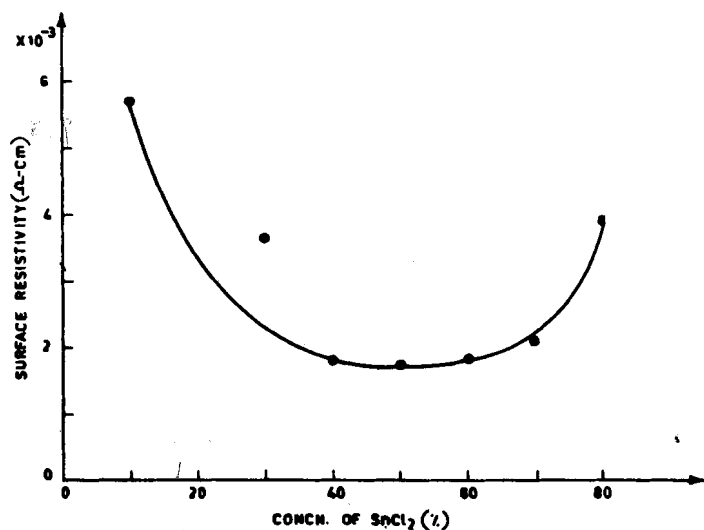
Fig. 1 : Film resistivity as a function of concentration of $SnCl_2$

In the region of 40-60% $SnCl_2$ with 1% $NH_4F.HF$ and at a substrate temperature of 450°C, resistivities as low as 1.8×10^{-3} ohm-cm of the films could be obtained. Figure 2 represents the same study with variation in surface resistance values.
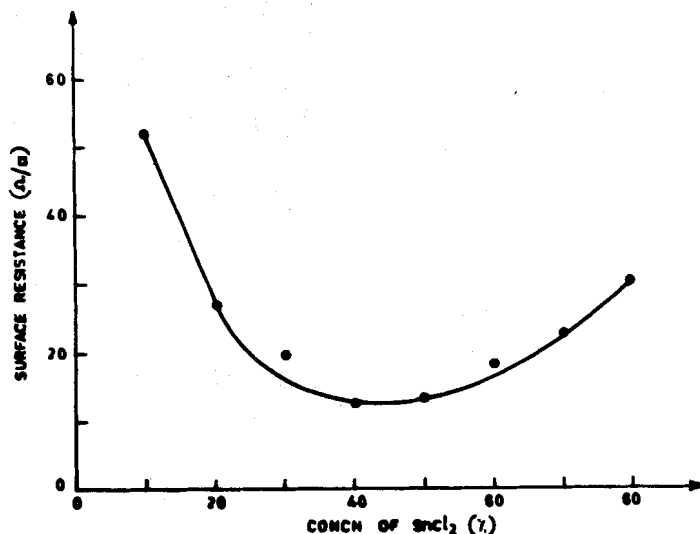
Fig. 2 : Variation of surface resistance of film with concentration of $SnCl_2$.

The lowest in the range of concentration of $SnCl_2$ which yields plates of low electrical resistance is about 40%. The effect of variation of the concentration of $NH_4F.HF$ in this concentration of $SnCl_2$ is shown in figure 3.

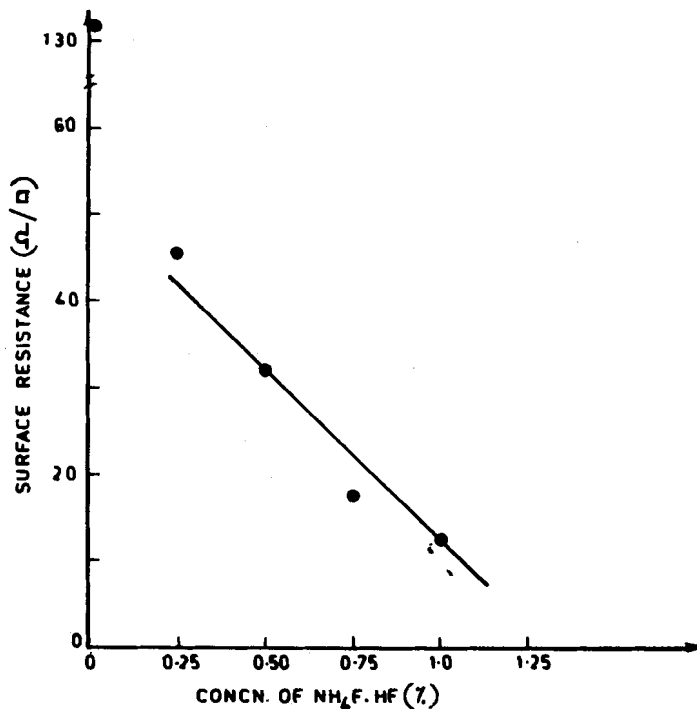*Fig. 3 : Effect of variation of concentration of $NH_4F.HF$ on surface resistance.*

The decrease in the surface resistance is remarkably proportional to the concentration of $NH_4F.HF$. Higher concentrations of $NH_4F.HF$ than about 1% are not practicable on account of the low solubility of $NH_4F.HF$.

It has been found that sequential deposition of the layer results in about 10% reduction of surface resistance. Thus, in a 30 spray run, cleaning the plates after every 10 sprays and continuing the deposition, yielded films with a lower surface resistance than those deposited by 30 sprays without break. This may be due to a higher thickness obtainable by sequential deposition as a result of a clean surface available for deposition at intervals. On a clean surface, the deposit is more adherent and the final cleaning operation before use removes less of the uppermost loose layer (loose because of the trapping of occasionally formed lumps of SnO_2) resulting in a higher thickness of the deposit and thereby ensuring a smaller resistivity.

High optical transmission is an important requirement for backwall illuminated electrodes and the SnO_2 contacts for the photoelectrode material should be highly transparent. The optical transparency of the layers has been studied with the concentration of $SnCl_2$ in the spray solution. Referring to figure 4, the transmission values follow the same pattern for different regions of the visible spectrum.
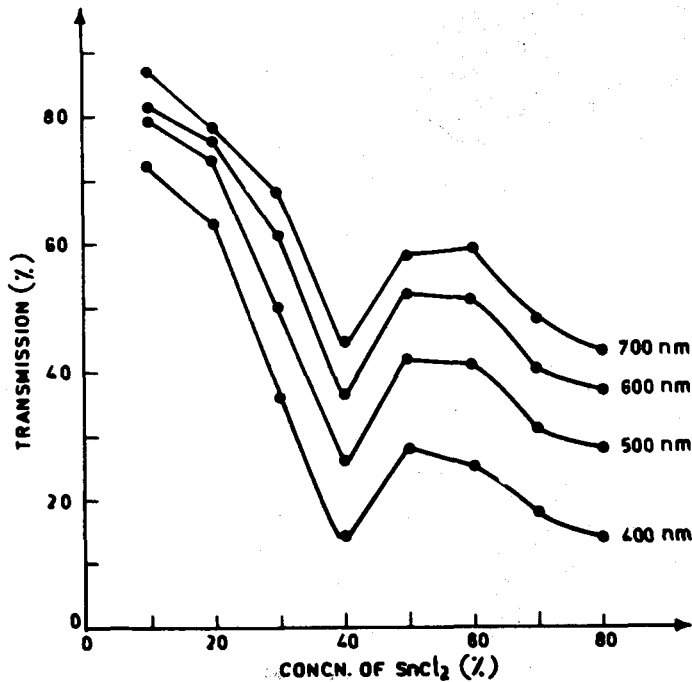

Fig. 4 : Transmission spectrum of films obtained with different $SnCl_2$ concentration

For reasonably good surface resistance values (12.5 ohm/sq to 16.9 ohm/sq), the maximum transmission values range from 44 to 58% for a wavelength of 700 nm, 36 to 52% for 600 nm and 26 to 42% for 500 nm.

Though optical transmission is high in SnO_2 obtained with low $SnCl_2$ contents in the spray solution fig. 4, the films show high electrical resistance. So, to obtain high transparency coupled with low surface resistances, a compromise has to be struck as regards the concentration of the $SnCl_2$ to be used in the spray solution. 40 to 50% of $SnCl_2$ appears to be a compromise, considering the requirements of transparency and electrical conductivity.

Figure 5 shows the effect of adding $NH_4F.HF$ to a solution of 40% $SnCl_2$ on the optical transmission of the layers.
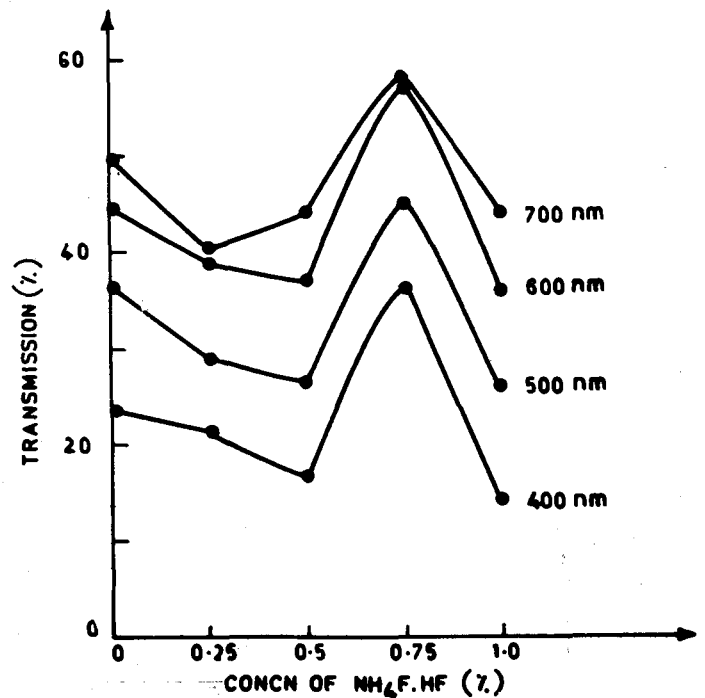

Fig. 5 : Transmission spectrum of films obtained by varying $NH_4F.HF$ concentration at 40%$SnCl_2$.

The transmission values reach a peak around a concentration of 0.75% $NH_4F.HF$. Figure 6 shows that slightly higher transmission can be obtained by adding NH_4Cl to a solution containing 40% $SnCl_2$ and 1% $NH_4F.HF$.

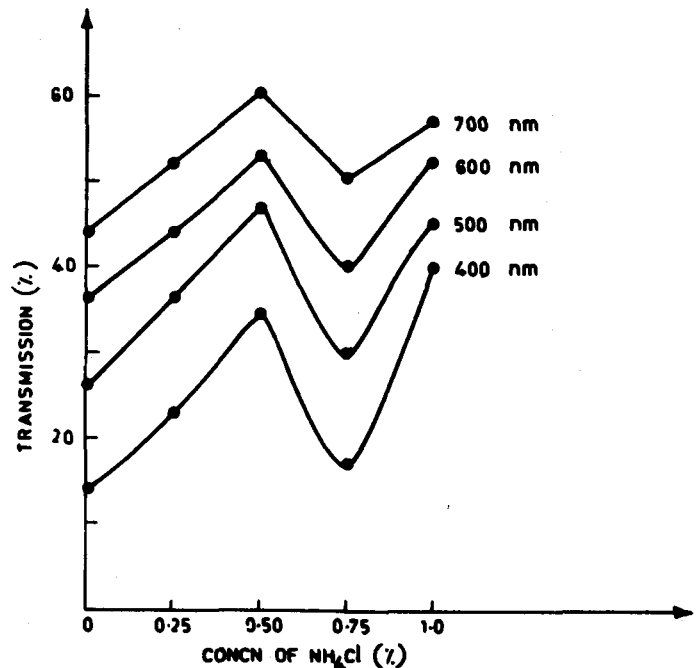

Fig. 6 : Transmission spectrum of films with variations in the concentration of NH_4Cl in the spray solution containing 40% $SnCl_2$ and 1% $NH_4F.HF$.

Though the two concentrations are not the best ones as regards transparency, they are the best ones if electrical conductivity is the preferred criterion, as for example, in a frontwall illuminated PEC cell.

It has been reported that Sb doped films of SnO_2 on air-annealing at 600°C have registered a decrease of resistivity by nine orders of magnitude during the first hour of heat treatment [13]. A decrease in resistivity has also been noted on heat-treatment of SnO_2 films at 400°C in air [30] and no explanation has been given for this behaviour. Contrary results have been obtained by the present authors on air annealing SnO_2 films doped with fluorine. Figure 7 shows the rising trend of the surface resistance of fluorine doped films with time of air-annealing at 400°C for different durations.
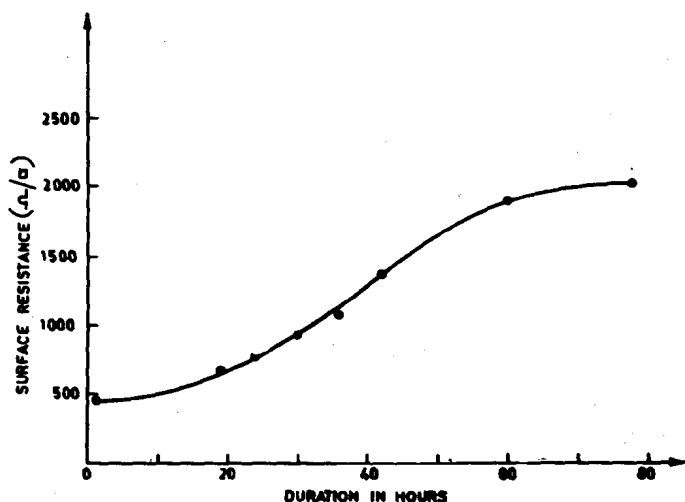
Fig. 7 : Effect of air annealing on surface resistance.

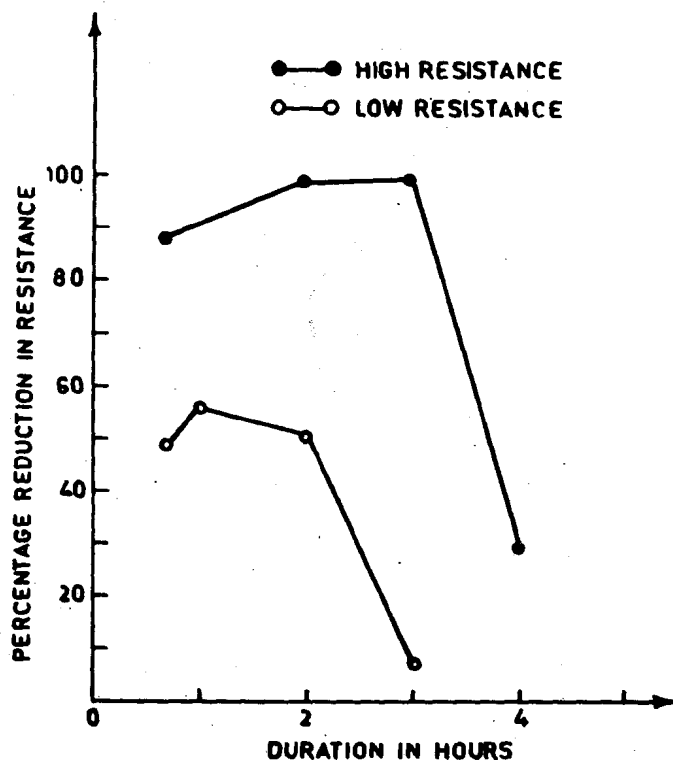with the duration of vacuum annealing at a temperature of 500°C around 2×10^{-5} torr.

Fig. 8 : Effect of vacuum annealing on surface resistance.

Through the increase is considerable, it is not by orders of magnitude. It can be visualized that heat-treatment in air has the inevitable effect of oxidation of the film, thereby removing the oxygen vacancies. Thus the SnO_2 films tend towards greater stoichiometry, which transition could explain the rise in the resistivity on heat-treatment in air. But the presence of fluorine as dopant ensures a reasonable conductivity of the films, the mechanism unaffected by air-annealing. Undoped SnO_2 films, when heat-treated in air have been shown to increase in resistance enormously [13].

It is wellknown that during annealing, there is a transition from the amorphous to the crystalline state; simultaneously there is an increase in grain size also. These are factors which reduce carrier scattering resulting in an increase in conductivity. The fact that there is no decresae but only an increase in resistivity on air annealing the SnO_2 films might also suggest that the films are already considerably crystalline in nature. The rise in the resistivity may therefore be attributed to O_2 incorporation (during air-annealing) in the SnO_2 material making it more stoichiometric.

When annealing is done in vacuum, the removal of chemisorbed oxygen takes place. SnO_2 is pushed to greater non-stoichiometric compositions which explains the reduction in resistivities as observed in the samples of the present study of vacuum annealing. Figure 8 shows the percentage reduction in surface resistance achieved

The curves show that the electrical resistance of the films decreases with the duration of annealing. The percentage reduction increases with time of annealing upto a certain point and then decreases. Removal of oxygen results in greater non-stoichiometry and higher conductivity. Vacuum annealing treatment is known to cause a transition to the crystalline state from the amorphous. The fraction of the material undergoing such transition will vary in direct proportion to the duration of annealing. The general continuous decrease in the resistance of the sample with the duration of annealing may be attributed to the progressive transition to crystallinity. The larger reduction in resistance in the initial stages may be the reason for the initial fast change, followed after a certain stage, to a slow change of the material in the interior. The reduction in electrical resistance by vacuum annealing is markedly seen in the case of high resistance films.

The dependence of surface resistance and optical transmission of the films on the temperature of formation are brought out in figures 9 & 10 respectively.
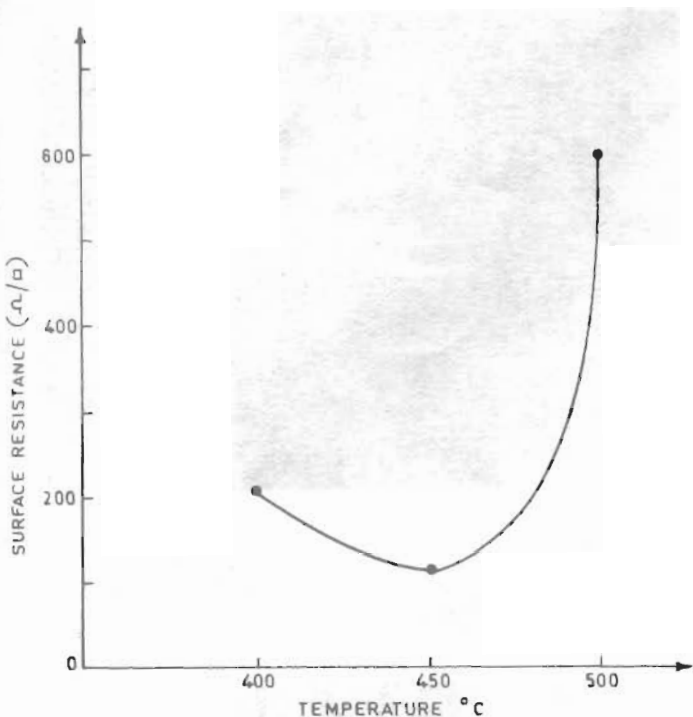
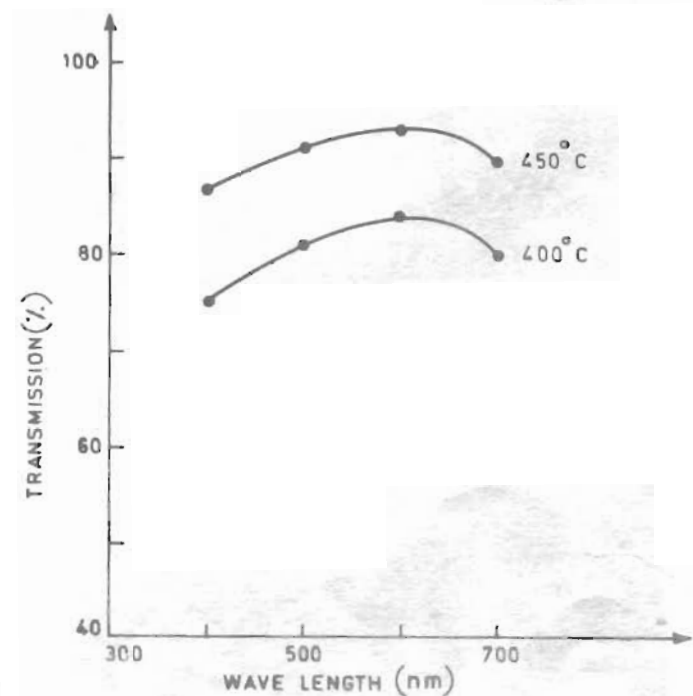Fig. 9 : Dependence of film resistance on temperature of formation.
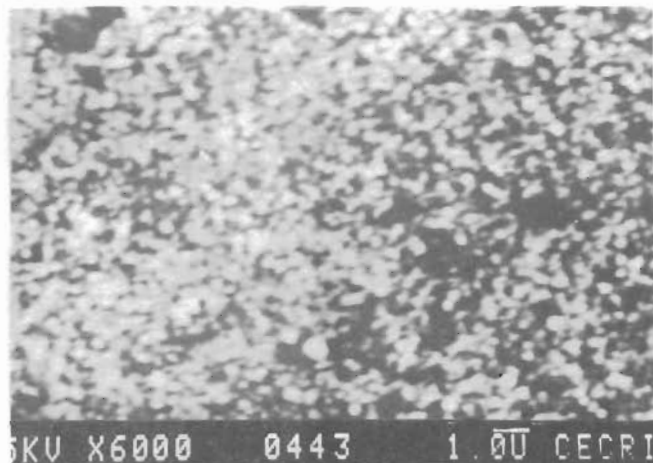

Fig. 10 : Transmission spectrum of film obtained at different temperatures.

Microscopic examination : A qualitative surface examination of the SnO₂ film was attempted by scanning electron microscopy (SEM).
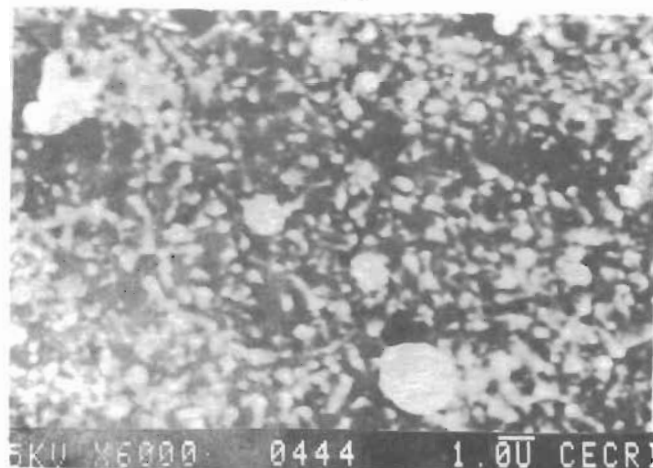
Surface morphology was observed by SEM at magnification upto 6000X in the secondary electron emissive mode. The SEM pictures are shown in figures 11 and 15.
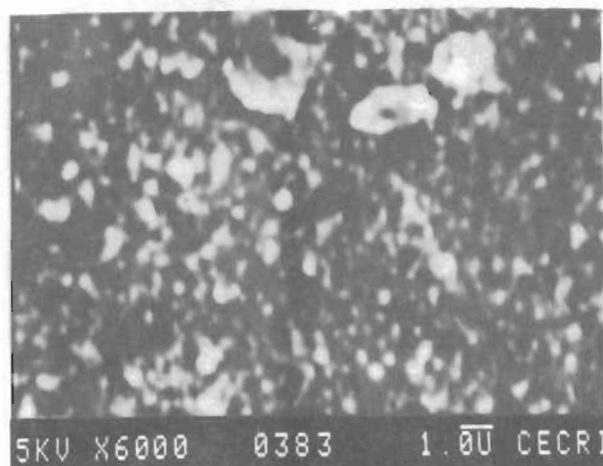
(a)

(b)

(c)

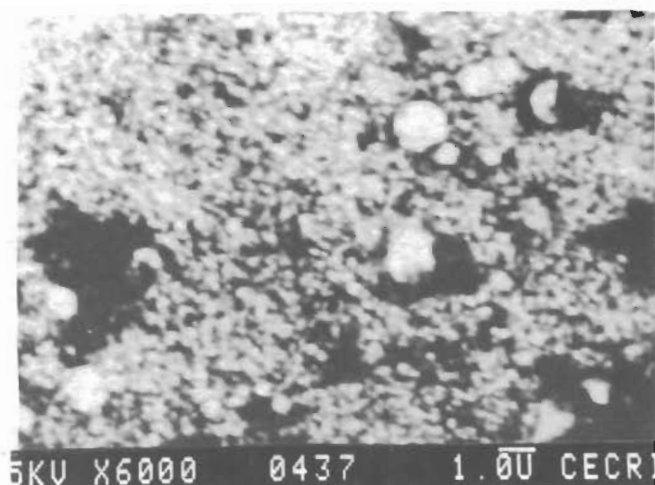Fig. 11 : SEM pictures of tin oxide films formed with (a) 40% SnCl₂, (b) 60% SnCl₂, (c) 80% SnCl₂ with an invariant concentration of 1% NH₄F.HF.
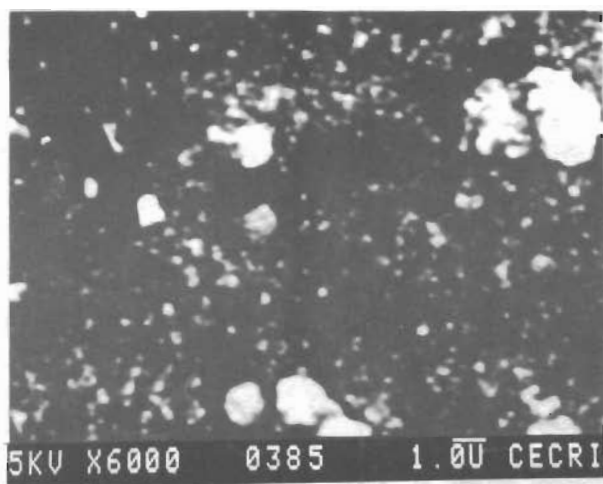
Fig. 12 : SEM picture of tin oxide film obtained with 40% SnCl₂ and P.5% NH₄F.HF.

13 (c)
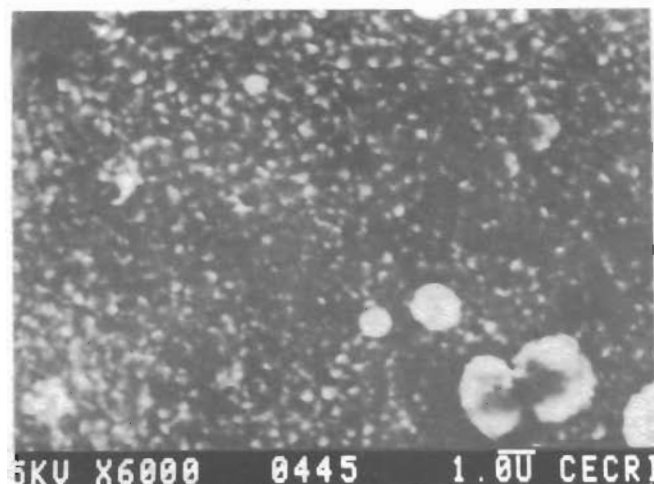
Fig. 13 : SEM picutres of tin oxide films formed with 40% SnCl₂ and 1% NH₄F.HF as invariants and (a) 0.25% NH₄Cl, (b) 0.75% NH₄Cl, (c) 1% NH₄Cl.
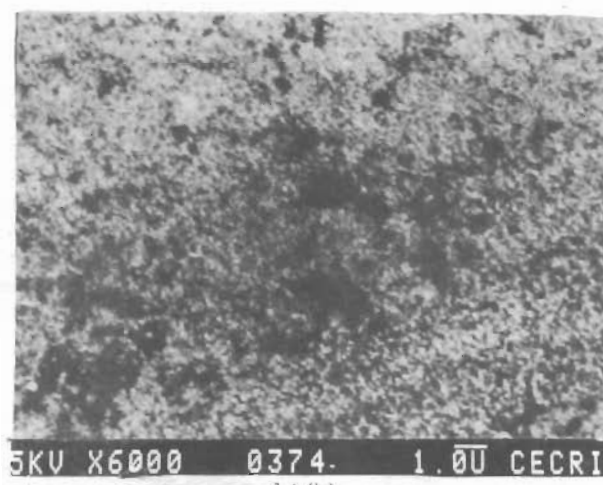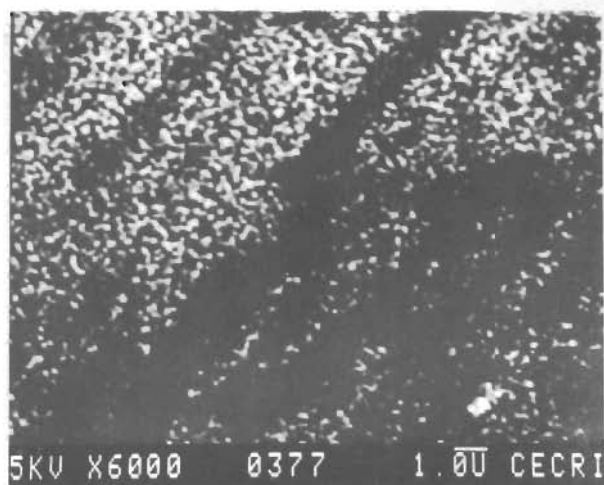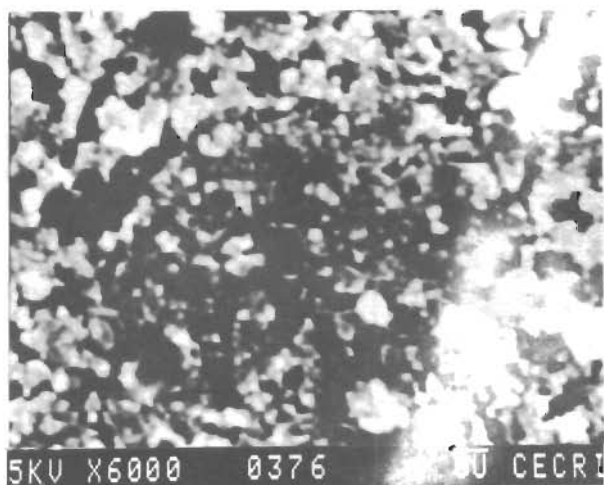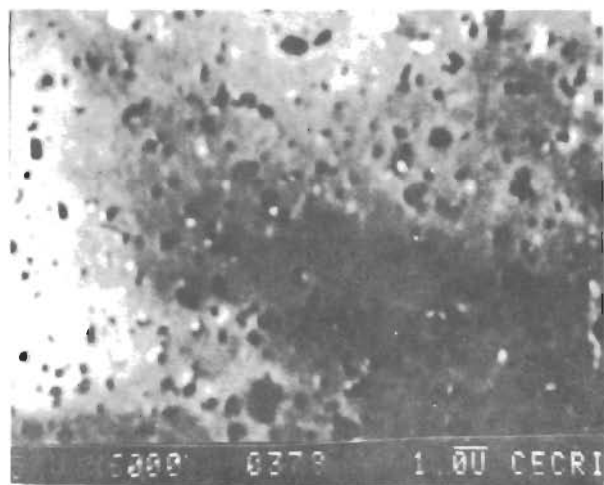

13 (a)
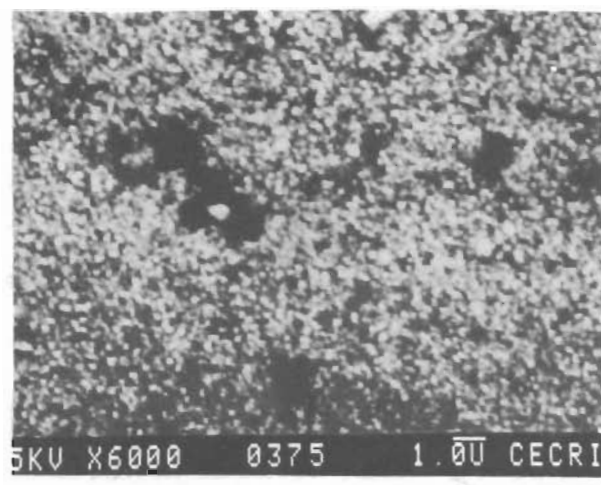
14 (a)
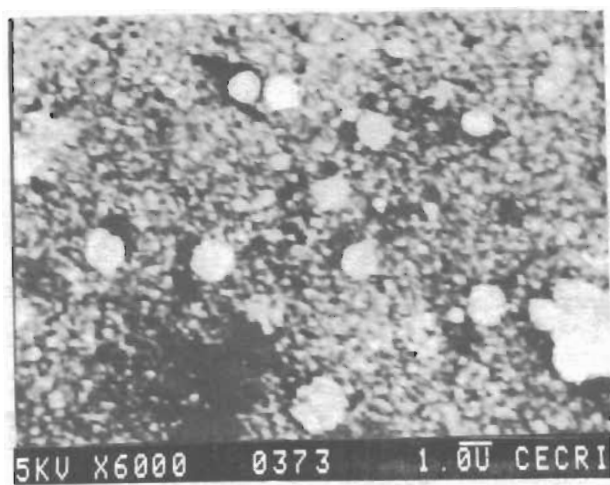
13 (b)

14 (b)

Fig. 14 : SEM pictures of tin oxide film subjected to air annealing (a) before air annealing (b) after air annealing

15 (a)

15 (b)

15 (c)

Fig. 15 : SEM pictures of tin oxide film subjected to air annealing (a) before annealing (b) after annealing in the case of low resistance films (c) after annealing in the case of high resistance films.

They reveal a fine grained surface. The bright spots in a few pictures are unknown non-conductive impurities included during the process of preparation of the films.

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