PREPARATION OF THIN FILM TRANSPARENT TIN OXIDE CONDUCTING CONTACTS

R KRISHNAKUMAR, A S LAKSHMANAN, K RÄMAKRISHNAN, V SUBRAMANIAN AND C V SURYANARAYANA
Central Electrochemical Research Institute, Karaikudi-623 006

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 SnCl₂ instead of the commonly used SnCl₄. 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 (SnO₂), indium oxide (In₂O₃) 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. SnO₂ 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 SnO₂ 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 SnO₂ and ITO films are useful in solar cell applications [2-6]. Their infrared reflective nature is useful in flat plate collector technology [7-9]. SnO₂ 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 SnO₂ films on glass to produce a good ohmic substrate for photoactive layers of cadmium chalcogenides. Besides being useful as ohmic contacts, SnO₂ 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 SnO₂ 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 SnO₂ layers for use as conducting contacts for photoactive layers of cadmium chalcogenides.

Spray pyrolysis of SnO₂ is performed mainly by the use of tin chlorides. Undoped SnO₂ films show extrinsic conduction of the n-type which is caused by the presence of Sn²⁺ 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 SnO₂ is thus a result of both. Electrical conductivity in the range of 10² to 10⁴ 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 (Sn₅₋₃p), giving rise to quasi-free electrons. However, high concentration of Sb (~ 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 SnO₂. It is probably in an substitutional position as F₀ [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 SnO₂ films. Chlorine may be incorporated either substitutionally as Cl₋₃ or interstitially, but only part of the chlorine incorporated supplies conduction electrons [28,29].

The use of SnCl₂ as the main substance employed in the spray pyrolysis preparation of SnO₂ films is wellknown. Relatively very little work on systematic spray pyrolysis experiments with SnCl₂ as the main ingredient is available. In this paper are presented the results on the suitability of employing SnCl₂ as the main...
ingredient. Also doping with fluorine and a mixture of fluorine and chlorine is examined with SnCl₂. SnCl₂ has the advantage of being less expensive than SnCl₄. It is also less pungent and easier to handle and holds promise as a good substitute for SnCl₄ in the spray pyrolysis mode of preparation of SnO₂ films.

**EXPERIMENTAL**

The spray medium was mainly a dispersion of the ingredients SnCl₂.2H₂O and NH₄F.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 SnCl₂ in the spray solution with a constant amount of 1% NH₄F.HF as the doping agent.

![Fig. 1: Film resistivity as a function of concentration of SnCl₂](image1)

In the region of 40-60% SnCl₂, with 1% NH₄F.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 SnCl₂](image2)

The lowest in the range of concentration of SnCl₂ which yields plates of low electrical resistance is about 40%. The effect of variation of the concentration of NH₄F.HF in this concentration of SnCl₂ is shown in figure 3.

![Fig. 3: Effect of variation of concentration of NH₄F.HF on surface resistance](image3)

The decrease in the surface resistance is remarkably proportional to the concentration of NH₄F.HF. Higher concentrations of NH₄F.HF than about 1% are not practicable on account of the low solubility of NH₄F.HF.

186 — Bulletin of Electrochemistry 1 (2) Mar-Apr 1985
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 SnO₂) 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 SnO₂ contacts for the photoelectrode material should be highly transparent. The optical transparency of the layers has been studied with the concentration of SnCl₂ in the spray solution. Referring to figure 4, the transmission values follow the same pattern for different regions of the visible spectrum.

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 SnO₂ obtained with low SnCl₂ 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 SnCl₂ to be used in the spray solution. 40 to 50% of SnCl₂ appears to be a compromise, considering the requirements of transparency and electrical conductivity.

Figure 5 shows the effect of adding NH₄F·HF to a solution of 40% SnCl₂ on the optical transmission of the layers.

The transmission values reach a peak around a concentration of 0.75% NH₄F·HF. Figure 6 shows that slightly higher transmission can be obtained by adding NH₄Cl to a solution containing 40% SnCl₂ and 1% NH₄F·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 front-wall 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.](image)

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

![Fig. 8: Effect of vacuum annealing on surface resistance.](image)

The curves show that the electrical resistance of the films decreases with the duration of annealing. The percentage reduction increases with time of annealing up to 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.
Surface morphology was observed by SEM at magnification up to 6000X in the secondary electron emission mode. The SEM pictures are shown in figures 11 and 12.

Microscopic examination: A qualitative surface examination of the $\text{SnO}_2$ film was attempted by scanning electron microscopy (SEM).

**Fig. 9:** Dependence of film resistance on temperature of formation.

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

**Fig. 11:** SEM pictures of tin oxide films formed with (a) 40% SnCl$_2$, (b) 83% SnCl$_2$, (c) 80% SnCl$_2$ with an invariant concentration of 1% NH$_4$OH.
Preparation of thin film transparent tin oxide conducting contacts

Fig. 12: SEM picture of tin oxide films obtained with 40% SnCl₂ and 5.5% NH₄F-HF.

Fig. 13: SEM pictures of tin oxide films formed with 40% SnCl₂ and 1% NH₄F-HF as environment and (a) 0.75% NH₄Cl, (b) 0.25% NH₄Cl, (c) 1% NiCl₃.

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

ACKNOWLEDGEMENT: The authors thank Mr Y Mahadeva Iyer and Mr K R Ramakrishnan for providing the SEM photographs and the Director, Central Electrochemical Research Institute, for encouragement and permission to publish this work.

REFERENCES