Effect of annealing on properties of transparent conducting tin oxide films deposited by thermal evaporation

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The surface morphology, structural characteristics and optical properties of the transparent conducting SnO$_2$ films deposited by vapour deposition of SnCl$_2$·2H$_2$O on heated glass substrate have been evaluated by X-ray diffraction, scanning electron microscopy, EDAX analysis and spectro-photometric examination. The ‘as deposited’ films of tin oxide were found to be polycrystalline, adhesive and pin hole free. After annealing at a higher temperature, these films exhibited an improved crystalline surface morphology and also displayed random perforations having a dendrite structure. It is found that heat treatment of the ‘as deposited’ tin oxide films results in conversion of the SnO component into SnO$_2$ phase which resulted in a better transparency, larger crystallite size and reduced film thickness due to diffusion of tin into the matrix of the glass substrate thereby making the film more suitable for device applications. The increased porosity of ‘annealed’ films provides more surface area for use as sensors and also makes them less likely to fracture when used as high temperature electrodes.

Keywords: Transparent conducting coating, Thermal evaporation, Annealing, SnO$_2$, Optical spectra, XRD, SEM, EDAX

1 Introduction
Thin films of metallic oxides like tin oxide, indium tin oxide (ITO), and zinc oxide exhibit electrical conductivity while being transparent in the visible region of the spectrum. Such transparent conductive oxides (TCO) coatings find wide spread use in electro-optical devices where the transparency of electrical contacts is a vital requirement for device operation. Of these, the tin oxide based films have the unique characteristics of inertness, stability and mechanical hardness and are widely used in fabrication of devices such as gas sensors, electroluminescent displays, solar cells, protective coatings, touch-sensitive switches and other applications. Transparent conducting films of tin oxide are usually prepared by sputtering, spray-pyrolysis, sol-gel technique, vacuum evaporation and chemical vapour deposition (CVD). The structural, electrical and optical properties of these films vary with the method used in their preparation and are also influenced by doping as well as by the formation of complexes involving oxygen. In fact, disproportion of SnO, SnO$_2$, Sn$_2$O$_3$, SnO$_{1-x}$ etc co-existing in the matrix of the film.

Since SnO (band gap 2.5-3.0 eV) is a $p$-type semiconductor while SnO$_2$ (band gap 3.8 eV) exhibits $n$-type conductivity, the composite film would be non-stoichiometric and in-homogeneous. In addition, the barriers formed at the boundaries of the heterogeneous regions of the film would make its electrical properties more complex. On the other hand, films deposited by chemical methods show strong non-stoichiometry and therefore, necessitate subsequent heat treatment to increase their crystallinity, surface morphology, transparency, electrical conductivity, stability and adhesion of the films.

2 Experimental Details
In the present work, transparent conducting films of tin oxide were deposited by thermal evaporation of SnCl$_2$·2H$_2$O on to a heated glass substrate. A crucible containing about 5 g of SnCl$_2$·2H$_2$O was kept at a temperature of about 200°C inside an electrically heated tubular furnace while the glass substrate was placed at a temperature of about 300°C inside the tubular furnace whose both ends were open to the atmosphere and the temperature profile therein peaked at the middle of the furnace length, decreasing
symmetrically towards both ends. A very light draft of air into the crucible end of the tubular furnace drifted the evaporated SnCl$_2$.2H$_2$O on to the glass substrate whence the oxidized tin vapours got deposited on it. The thickness of the deposited films was about 1030 nm. To ensure that the tin oxide coating is mostly deposited as SnO$_2$, the substrate was annealed in air at a temperature of about 450°C for 15 min to facilitate conversion of any residual phases like SnO$_{1-x}$ into SnO$_2$ and to improve the crystalline size, optical transparency and electrical conductivity. These films were evaluated by Hitachi spectrophotometer model U-3400, Scanning electron microscope with EDAX analysis, X-ray diffraction and four probe method for the above characteristics.

3 Experimental Results

The transmission and absorption spectra of the ‘as deposited’ and the ‘annealed’ films are shown in Fig. 1. It is seen that annealing slightly increases the transmission while the absorption is somewhat decreased. However, the absorption edge becomes sharper and its tangent gives the value of band gap as 3.81 eV. The values of refractive index and the extinction coefficient of the films were determined by using Manifacier’s envelop method$^{21}$ where the refractive index \( n(\lambda) \) at any wavelength \( \lambda \) is given by:

\[
n(\lambda) = \left[ N + \left( N^2 - n_0^2 n_1^2 \right)^{1/2} \right]^{1/2} \]

where \( N = \{ (n_0^2+n_1^2)/2 \} + 2n_0n_1[(T_{\text{max}}T_{\text{min}})/(T_{\text{max}}+T_{\text{min}})] \), \( T_{\text{max}} \) and \( T_{\text{min}} \) being the values of film transparencies as represented by the envelop of the extrema in the percentage transmission curves as shown Fig. 1(a), \( n_0 \) and \( n_1 \) being the refractive indices of air and the glass substrate, respectively. From the different values of \( N \) and \( n(\lambda) \) at different wavelengths, the thickness \( t \) of the film was determined by the relation$^{22}$:

\[
t = (M \lambda_1 \lambda_2)/\{2[n(\lambda_1) \lambda_2-n(\lambda_2) \lambda_1] \}
\]

where \( M \) is the number of oscillations between two extrema corresponding to wavelength \( \lambda_1 \) and \( \lambda_2 \) in the transmission curve.

From the value of \( t \), the extinction coefficient \( k \) can be calculated from:

\[
k = (-\lambda/4\pi) \ln P
\]

where

\[
P = (n+n_0)(n_1+n)\{1-(T_{\text{max}}/T_{\text{min}})^{1/2}\}/(n-n_0)(n_1-n) \times \{1+(T_{\text{max}}/T_{\text{min}})^{1/2}\}
\]

The wavelength dependence of refractive index and extinction coefficient of the ‘as deposited’ and ‘annealed’ films as calculated from the aforesaid expression are shown in Fig. 2. It is seen that both the refractive index as well the extinction coefficient of the film are increased as a result of annealing. The thickness of the ‘as deposited’ film decreased from about 1030 to 441 nm after annealing. These results point towards the re-crystallization, oxidization and diffusion of tin from the deposited film into glass matrix. Since inhomogeneties and defects drastically influence the optical properties of thin films$^{16,17}$, the effect of different phases of oxidation and re-crystallization of tin oxide on the film properties can vary divergently$^{13}$ and cannot be explained in terms of any one factor. It is known that optical properties of tin oxide conducting films are also affected by the characteristic at the glass-SnO$_2$ interface$^{23}$. This is seen by the change in the values of

![Fig. 1 — Effect of heat treatment on wavelength dependence of transmission (a) and absorption (b) spectra of SnO$_2$ films. The graphical tangent in Fig. (b) intercepts the X-axes at 325 nm which correspond to a band gap of 3.81 eV](image-url)
refractive index and the extinction coefficient in Fig. 2(a and b) where annealing would alter the film-glass interface due to re-crystallization, more complete oxidation and the diffusion of tin into glass.

The X-ray diffraction patterns of the ‘as deposited’ and the ‘annealed’ of SnO$_2$ films are shown in Fig. 3. These XRDs show that in the case of ‘as deposited’ films, the peaks corresponding to the (110), (211) and (220) planes of SnO$_2$ are very weak as compared to the intensity of the SnO(110) plane. However, after annealing the XRD show that the crystalline phase of SnO$_2$ is greatly enhanced as seen by the peaks corresponding to the (110), (101), (200), (211), (220), (310) and (301) planes while the peaks depicting the SnO planes are greatly reduced. The conversion of intermediate oxides into dioxide is also confirmed by EDAX studies which depict the Energy-dispersive X-ray spectroscopy result for the ‘as deposited’ and the ‘annealed’ tin oxide films as shown in Fig. 4. The peaks corresponding to the constituent elements oxygen and tin, respectively show that the concentration of the oxygen component relative to that of tin is increased in the annealed films due to the more complete oxidation of the oxide complexes.$^{12,20}$ It is also expected that annealing would increase the crystallite size too.$^{12}$ The mean grain size of the
films was determined from the half maximum width of the XRD peak using the classical Debye-Scherrer formula:

\[ d = \frac{0.9 \lambda}{\beta \cos \theta} \]

As expected, the high temperature annealing did increase the grain size from 35.98 to 69.96 nm.

The Scanning Electron Micrographs of the ‘as deposited’ and the ‘annealed’ films are shown in Fig. 5(a and b), respectively. It is seen that non-uniformity and surface roughness characterize the surface morphology of the ‘as deposited’ films. After annealing, the surface is seen to have become markedly more smooth and uniform. The enlarged view of these SEM micrographs is shown in Fig. 5(c and d), respectively where the contrast between the surface morphologies of the ‘as deposited’ and the ‘annealed’ films is better visualized. The salient feature of the ‘annealed’ film is the porosity of the dendrite structure which intrinsically provides a larger surface area and increased resilience and flexibility to the film to withstand the strains produced by its differential thermal extension with respect to the substrate. It is also observed that the increased porosity of the annealed films as revealed by the magnified scanning electron micrographs in Fig. 5 would increase the refractive index of the films. The structural measurement on the tin oxide films suggests that the excess tin atoms located in interstitial positions of the \( \text{SnO}_2 \) lattice. The deviation from the stoichiometry would, thus, strongly affect the optical transmittance of the films and also change the values of their refractive indices.

The temperature dependence of sheet resistivity of the deposited film is shown in Fig. 6. It is seen that after annealing, the resistivity increased by almost

![Fig. 5 — SEM micrographs of SnO\(_2\) films at different magnification](image-url)
five folds. The annealing converts tin oxide into its predominantly SnO\(_2\) phase which is a larger band gap material and would increase the transparency and also the resistivity of the film. Moreover, annealing would result into greater diffusion of tin into the glass substrate thereby making the tin oxide layer thinner which would further increase its electric resistivity. The contribution of contact barrier at the boundaries of the different phases of tin oxides would also contribute towards the electrical resistivity in an unspecified manner\(^8\). The scenario becomes more complex when the semiconductor aspect of the increase in carriers with increasing temperature and the temperature dependence of mobility are also taken into account. Thus, any type of temperature dependence can be expected in the properties of tin oxide films and no specific reason can be ascribed for the phenomenon as shown in Fig. 6 where the resistance of the films first seen increase and then followed different pattern for the ’as deposited’ and the ’annealed’ films.

4 Conclusions

Analysis of the aforesaid results suggests that tin oxide films deposited by thermal evaporation of SnCl\(_2\)\(\cdot\)2H\(_2\)O are essentially polycrystalline, non-stoichiometric and inhomogeneous due to simultaneous existence of the multiple phases of tin oxide having the chemical composition varying between SnO\(_{1+x}\) and SnO\(_{2-x}\). Annealing these films at about 450°C improved the crystalline surface morphology, increased grain size and also displayed random perforations having a dendrite structure. Heat treatment of the ’as deposited’ tin oxide films also results in conversion of the SnO component into SnO\(_2\) phase which resulted in a better transparency, larger crystallite size, and reduced film thickness due to diffusion of tin into the matrix of the glass substrate thereby, making the film more suitable for device applications. The increased porosity of ’annealed’ films provides more surface area for use as sensors and also makes them less likely to fracture when used as high temperature electrodes.

References