Effect of substrate temperature on the electrical and optical properties of reactively evaporated tin oxide thin films

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Transparent conducting thin films of tin oxide have been prepared by reactively evaporating pure tin in oxygen atmosphere under controlled conditions. Variation in parameters such as sheet resistance, activation energy, optical band gap with variation in substrate temperature (100 to 275°C) and annealing temperature (200 to 275°C) were studied. The electrical, optical and structural properties of these films were measured to characterize the films. It is found that the activation energy of the film is decreased with increase in substrate temperature. The lowest activation energy of 0.268 eV was obtained for a film, deposited at a substrate temperature of 275°C. The direct optical band gaps of the films at various substrate temperatures were determined and found to vary from 3.76 to 3.97eV. A conductivity of $1.8 \times 10^{-3} \Omega^{-1} \text{m}^{-1}$ and a transmittance of more than 85% in visible region was obtained in the optimized conditions. It is observed from the XRD results that the films are polycrystalline. From SEM photograph, the grain size of tin oxide thin film annealed for 30 min at 275°C is found to be 19.5 nm.

Keywords: Tin oxide, Electrical properties, Optical properties, Structural properties
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1 Introduction

Tin oxide is an $n$-type semiconductor that presents the unusual combination of high transparency in the visible region together with high electrical conductivity. Transparent conductors are widely used in electronic, opto-electronic and industrial devices such as solar cells, LEDs, heat mirrors, and laser damage resistant coatings. Tin oxide thin films can be prepared by different methods such as reactive evaporation, electron beam deposition, chemical vapour deposition (CVD), RF sputtering and spray pyrolysis. The early works in this field have been reviewed by Vossen\textsuperscript{1}, Jarzelski\textsuperscript{2} and Chopra\textsuperscript{3}.

In this paper, the effect of substrate temperature on electrical, optical and structural properties of tin oxide thin films prepared by reactive evaporation has been reported. Reactive deposition by evaporation of tin in an oxygen atmosphere is one of the simplest of these methods. We have chosen this technique because of the ease of preparation, high purity, quality and uniformity in thickness. Moreover, it does not cause radiation damage to the substrate.

2 Experimental Details

Tin oxide thin films have been prepared by reactively evaporating tin powder in oxygen atmosphere. A 12-inch vacuum coating unit (model 12A4) with a tantalum boat is used for the evaporation of tin powder. Spectroscopically pure (99.99%) tin is used as the source material. Initially the vacuum chamber is evacuated to a base pressure of $10^{-6} \text{ mbar}$. Thoroughly cleaned glass slides are used as the substrates on which a calibrated chromel-alumel thermocouple is attached. The coating chamber is equipped with a high tension (1.5 kV DC) anode which is positioned near the substrates. The chamber vacuum is reduced to the order of $10^{-2} \text{ mbar}$ by introducing pure argon gas through the needle valve and a glow discharge is established in the chamber. The substrates are subjected to this ionic bombardment for 5 minutes as the final cleaning before deposition. The substrate temperature is maintained at various desired temperatures between 75 and 300°C using a substrate heater and a thermocouple attached to a digital temperature indicator.

In another set of experimentation with constant substrate temperature and varying oxygen partial pressure, it was observed that oxygen partial pressure of $10^{-4} \text{ mbar}$ is required to obtain optically transparent films. With this background the oxygen partial pressure was fixed to be $10^{-3} \text{ mbar}$. The required oxygen was admitted to the chamber using the needle valve. The thickness of the film is monitored by a crystal thickness monitor and counter checked by the Tolansky’s multiple beam interference technique.
The rate of evaporation is controlled within the range 7-8 nm/min and the film thickness is approximately 150 nm. The samples were annealed in a muffle furnace for 30 min. The electrical conductivity of the samples was measured by means of a conductivity cell and a Keithley programmable electrometer (model no. 617). The ohmic contacts are made by pre-evaporated silver electrodes and silver paste. The conductivity measurements are carried out in a subsidiary vacuum of $10^{-3}$ mbar to eliminate the contamination of the film. A double beam spectrophotometer (Schimadzu 160A) is used for recording the UV/visible spectrum. XRD spectra of the samples are recorded by means of Schimadzu 610-X D, X-ray diffractometer.

3 Results and Discussion

3.1 Electrical properties

The sheet resistances of the films are measured before and after annealing using the standard four probe technique. The sheet resistance of a film of thickness 150 nm and deposited at 225°C dropped to a value of 80 kΩ/㎟ after annealing which had an initial sheet resistance of 131.5 kΩ/㎟. Similar behaviour was observed for films deposited at other substrate temperatures. The lowest sheet resistance was obtained for the film deposited at 275°C is 12 kΩ/㎟ which corresponds to a conductivity of $1.8 \times 10^{-3}$ Ωm.

Figure 1 shows the temperature dependence of the electrical conductivity of tin oxide thin films deposited at different substrate temperatures and annealed at a temperature of 300°C for 30 min. The data were measured as the temperature was decreased from 250°C to room temperature in the conductivity cell. From the Fermi level analysis of conductivity in a material with donor levels located at a distance $E$ below the bottom of the conduction band, a plot of $\ln \sigma$ versus $(1000/T)$ where $\sigma$ is the conductivity and $T$ is the temperature (in absolute scale), exhibits a straight-line region with a slope $(\Delta E/2k)$ indicating an activation energy of $\Delta E$. Below 250°C, the conductivity of tin oxide film exhibits an exponential behaviour with an activation energy of 0.268 eV for the film deposited at 275°C.

The activation energy obtained for the samples deposited at different substrate temperatures is shown in Fig. 1. The values are comparable to the values reported by others. The reduction in the activation energy of the film is obtained with increase in substrate temperature. This can be associated with the increase in grain size of the sample, which is caused due to higher substrate temperature. The structural studies carried out on these samples using the XRD reveal reorientation and enhancement of grain size, which corroborates this argument.

3.2 Optical properties

The UV-visible transmission spectra for tin oxide thin films of thickness 150 nm, deposited at different substrate temperatures and annealed at 300°C for 30 min are studied. Unannealed samples have a transmission of less than 40% in the visible range. It is observed that transmission varies significantly with annealing and with the variation of substrate temperature. An average transmittance of more than 85% is obtained for the annealed sample deposited at 275°C. The transmission curves in the visible region of the spectrum are shown in Fig. 2. The values are related to the uncoated substrates. Absorption coefficient $\alpha$ of tin oxide thin films at different
photon energies were calculated from the transmission data. The spectrum is analyzed by the theory of Bardeen et al.\textsuperscript{6} using the relation:

\[ \alpha = \alpha_0 (h\nu - E_g)^n \]

between the parabolic bands. In the case of direct transitions between parabolic bands, \( n = \frac{1}{2} \). The extrapolation of the straight-line portion of the plot of \( \alpha^2 \) versus \( h\nu \) to zero absorption gives the direct band gap of the films. The \( \alpha^2 \) versus \( h\nu \) plot for tin oxide thin films deposited at different substrate temperatures is given in Fig. 3. The direct band gap is found to increase with increase in substrate temperature. The values obtained are presented in Table 1. Increase in band gap may be attributed to the partial filling of the conduction band of tin oxide, resulting in a blocking of the lowest states. This widening of the optical band gap is termed as Burstein-Moss shift\textsuperscript{7}.

The shift is given by the relation.

\[ E_g = E_{go} + \Delta E_g^{BM} \]

where, \( E_{go} \) is the intrinsic band gap and \( \Delta E_g^{BM} \) is the Burstein-Moss shift. This shift is related to the carrier density as:

\[ \Delta E_g^{BM} = \frac{\pi^2 \hbar^2}{2m^*} \left( \frac{3N}{\pi} \right)^{2/3} \]

where \( m^* \) is the reduced effective mass, \( h \) is the Planck’s constant and \( N \) the carrier concentration. The values obtained for direct band gap are comparable to the values reported by others\textsuperscript{8}.

3.3 Structural properties

Tin oxide films are deposited at a substrate temperature 100°C with an oxygen partial pressure of \( 1 \times 10^{-4} \) mbar. They are then annealed in air at temperatures 200, 225, 250 and 275°C for 30 min. The grain size is calculated from Scherrer’s formula\textsuperscript{9}.

\[ D_{hkl} = \frac{0.9\lambda}{\beta_1 \cos \theta^{1/2}} \]

where \( \beta_1 \) is the full width at half maximum intensity (FWHM) at an angle 2\( \theta \). \( \lambda \) is the wavelength used (0.154056 nm). The variation in grain size with respect to the increase in annealing temperature is presented in Table 2.

When annealed, prominent peak is observed at \( 2\theta = 44.82^\circ \) for an annealing temperature of 200 and 225°C, which corresponds to reflection from (211) plane. For samples annealed at 250 and 275°C, main peak is observed at \( 2\theta = 29.76^\circ \), which corresponds to reflection from (101) plane, which leads to the conclusion that a structural change happens above an annealing temperature of 225°C. The XRD spectrum analysis shows that the films are polycrystalline in nature. The SEM photograph of tin oxide thin film annealed at 275°C is shown in Fig 4. The grain size estimated from SEM is 19.5 nm, which matches with the value obtained using XRD.

### Table 1—Variation of optical band gap with substrate temperature

<table>
<thead>
<tr>
<th>Substrate temperature (°C)</th>
<th>Direct band gap (eV)</th>
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<tbody>
<tr>
<td>200</td>
<td>3.76</td>
</tr>
<tr>
<td>225</td>
<td>3.81</td>
</tr>
<tr>
<td>250</td>
<td>3.86</td>
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<td>275</td>
<td>3.97</td>
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### Table 2—Variation of grain size with annealing temperature

<table>
<thead>
<tr>
<th>Annealing temperature (°C)</th>
<th>Grain size (nm)</th>
</tr>
</thead>
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<tr>
<td>200</td>
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<tr>
<td>225</td>
<td>8.37</td>
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<tr>
<td>250</td>
<td>12.71</td>
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<td>275</td>
<td>18.04</td>
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</table>
4 Conclusion

Reactively evaporated tin oxide thin films exhibit high electrical conductivity (1.8×10⁻³ Ω m) and a transmittance of more than 85% in the visible range. The activation energy is calculated to be 0.299 eV for a film of thickness 150 nm deposited at a substrate temperature of 225°C. High quality films with low sheet resistance and high transmittance were obtained by controlling the deposition parameters. The optical band gap is found to increase from 3.76 to 3.97 eV with increase in substrate temperature from 200 to 275°C. The grain size is found to increase with annealing temperature. XRD results show that the films are polycrystalline.

References