Some properties of indium-tin oxide films

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Abstract. Thin films of indium-tin oxide have been deposited by DC diode sputtering from an indium-tin alloy target in an argon, hydrogen and oxygen atmosphere. Films with sheet resistance of 11 ohms/square and 80% light transmission have been obtained. The effect of cathode composition and gas mixture on sheet resistance and optical transmission properties of the films have been studied.

Keywords. Indium-tin oxide films; optical properties of thin films; reactive evaporation.

1. Introduction

Transparent conducting thin films have generally been obtained by vapour phase deposition of compound. In recent years, interest has been shown in thin films of indium oxide doped with tin (ITO) deposited by sputtering (Aitchson 1954, Vossen 1971, Rupprecht 1954, Muller 1968, Radhakrishna and Ramakrishna Rao 1973, Fraser and Cook 1972). These films have been deposited by R F Sputtering—both reactively and passively—from premixed targets which are in the form of either oxides or metals. The ITO films are of great interest in view of their characteristics like high light transmission (more than 80% in the visible region) low sheet resistance (less than 11 ohms per square) low temperature coefficient of resistance and high infrared reflectivity. These characteristics make indium-tin oxide films very useful for applications like optical device electrodes, transparent heating elements and infrared reflectors.

This paper reports our investigations on diode sputtered films of indium doped with tin in a reactive atmosphere. The influence of gas composition and target composition on sheet resistance and optical properties of the films have been reported.

2. Sputtering procedure

The indium oxide films were DC sputtered (diode-reactive) from a metal alloy target of tin and indium in Ar, H₂ and O₂ gas mixture. The target composition was varied and the resistance measurements were made. The films with lowest resistance values were obtained from a cathode composition of indium with 5.6% tin by weight. The

target was prepared by melting the alloy in a graphite crucible (high purity metals of 99.9% were employed) in air. The outermost oxide layer was skimmed off before the alloy solidified. This alloy target was fixed to the water cooled cathode holder.

The sputtering vacuum system consisted of a 4" diffusion pump giving an ultimate vacuum of 1×10^{-5} torr. The details of sputtering system has been described elsewhere (Radhakrishna and Ramakrishna Rao 1973).

The technique of sputtering was to evacuate the chamber to better than 1×10^{-5} torr and then introducing argon, oxygen and hydrogen through three different needle valves to the required pressure. The constant pressure in the chamber is maintained by controlling gas input and throttling the high vacuum valve. The amount of gas bled was controlled by counting the number of bubbles of each gas passed through silicon oil. For all the experiments, except for the study of effect of gas composition, the gas composition of 50% argon, 25% oxygen and 25% hydrogen by volume was employed. This composition was arrived at after studying the effect of gas composition on the sheet resistance and optical transmission of the films. A gas pressure of 0.01 torr was maintained inside the bell jar throughout sputtering.

Glass slides of 25mm $\times$ 25mm were used as substrates. These substrates were cleaned by the detergent teepol and rinsed in water. Finally 'breath figure test' was employed for checking the cleanliness of the substrates. The substrates were water cooled at ambient temperature during some trials and heated to 120°C during other trials.

After admitting the gas, and stabilising the pressure of the gas mixture at 0.01 torr, high voltage of 1000 volts was applied to the cathode and anode. Voltage was adjusted to get a current density of 3.0 mA/cm². Pre-sputtering was done with the shutter closed for about 5 min to activate the cathode.

Thickness of these films were measured by multiple beam interferometer and by transmission interference pattern. The error in thickness measurement was found to be ± 50 Å.

Electrical measurements were made by using four probe technique (Valdes 1954). Optical measurements were carried out using Unicam Spectrophotometer SP-700.

3. Results

The effect of gas composition (relative proportions of argon, oxygen and hydrogen) on the electrical and optical properties was studied. The experimental data for three different compositions are presented in table 1 and represented in figure 1.

The analysis of the data shown in table 1 indicates that the composition of 50% Ar, 25% O₂ and 25% H₂ by volume gives best results regarding the low electrical resistance and high transmission. The sputtering time is 40-45 min for the lowest sheet resistance, reported. The current density is 3mA/cm². The other compositions give either low sheet resistance with poor transmission or high transmission with high sheet resistance. The lower the oxygen content in the chamber, the greater the metallic nature of the film due to insufficient oxygen to form oxides. The addition of H₂ enables the formation of hydride of metals which increases the conductivity of the films. The transmission curve shown in figure 4 gives neutral transmission in the visible region for the films made from a cathode of indium with 5.6% tin by weight, in an atmosphere of 50% Ar, 25% O₂ and 25% H₂. The measurements were also carried out on substrates which were heated to 100°C before sputtering. At the

Cathode composition INDIIUM With 5.6 % TIN by weight.

□—□ — 50% Ar, 30% O₂, 20% H₂x—x — 75% Ar, 10% O₂, 15% H₂o—o — 50% Ar, 25% O₂, 25% H₂

Figure 1. Variation of sheet resistance with thickness of the film at various gas compositions.

Table 1. Electrical and optical properties of indium-tin oxide films in argon, oxygen and hydrogen gas mixtures.

Gas composition (by Vol.)	Thickness in Å	Resistance in Ohm/Square	T% at 5500 Å
50% Ar, 30% O ₂ , 20% H ₂	500	240	90
	1251	215.3	84
	3250	220	80
	3846	215.3	80
	4110	180	78
75% Ar, 10% O ₂ , 15% H ₂	1700	100	0
	3452	57	0
	4350	40	0
	6000	9	0
	7200	9	0
50% Ar, 25% O ₂ , 25% H ₂	1100	90.63	88
	2300	79.3	88
	2900	68	87
	4300	42	83
	5300	23	80
	6000	11	80

Gas composition 50% Ar, 25% O₂, 25% H₂

Substrate temperature - 28°C

Current density - 3.0 ma/cm²

Sputtering time - 45 minutes.

Figure 2. Thickness vs sheet resistance of the film at different temperatures.

end of the sputtering the substrate recorded a temperature of 120°C, and the resistance measurements were done at room temperature. The results are tabulated in table 3 and represented in figure 2 which shows the values of sheet resistance of films with the substrate temperature at 120°C and 28°C. It is observed that the effect of increase in temperature is to decrease the sheet resistance which is in agreement with the reported values (Molzen 1975). It also confirms the observations of Hecq (1974) who have carried out similar investigations on the films deposited on the substrates at 40°C and 200°C. The prolonged heating due to sputtering of the substrate and high current density make the glass slide warp. Hence higher substrate temperatures were not used in this investigation. However, both the graphs follow the same pattern, i.e. the sheet resistance decreases as the film thickness is increased.

Table 2. Sheet resistance of films with different cathode compositions

Composition of cathode with tin % by weight	Sheet resistance Ohms/Square
0	906
2	57
5.6	23
13.6	91

The dependence of sheet resistance of the film on the chemical composition of the cathode was studied. Four cathodes having the composition of, pure indium (99.9%), indium with 2%, 5.6% and 13.6% tin by weight were employed in this investigation. Figure 3 is the graphical representation of the sheet resistance versus cathode composition of the film. These films were analysed by mass spectrometer which gave the actual values of composition. They were sputtered in the gas mixture of 50% Ar, 25% O₂ and 25% H₂. The chemical composition of 5.6% tin by weight in indium has given the lowest resistance with an optical transmission of more than 80%. Hecq *et al* (1974) reported that the best results were obtained for powder-mixture of In₂O₃ and SnO₂ when indium and tin were in the ratio 9:1 (atomic). The behaviour of the composition curve reported by us and Hecq *et al* is similar even though the starting materials are different.

4. Stability of films

These films are hard and can be cleaned with acids and alkalis. No reduction in

Figure 3. Percentage composition of tin in indium vs sheet resistance.

Table 3. Resistance measurements recorded at 120°C

Thickness Å	Sheet resistance Ohms/Square at 120°C	Transmission %
510	100	80
2012	56	80
3500	23	80

Gas composition 50 % Ar, 25 % O₂, 25 % H₂

Cathode composition INDIUM With 5.6 % TIN by weight.

Figure 4. Transmission curve of an indium oxide film. (Thickness of the film = 6000 Å).

resistance of these films was found even after dipping for 30 min in strong acids and alkalis like HNO₃, H₂SO₄, NaOH and KOH. These films could be etched by making the film as cathode and using platinum anode in HCl electrolyte.

5. Conclusion

Indium oxide films of low sheet resistance of 11 ohms/square with transparency of 80% could be produced with gas composition of argon, oxygen and hydrogen from a target consisting of 5.6% tin in indium matrix by weight. Higher substrate temperature and post deposition heat treatment will further improve the properties of the film.

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