 Preparation and Characterization of SnO₂ Thin Film Coating using rf-Plasma Enhanced Reactive Thermal Evaporation

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Abstract
Due to high transparency and electrical conductivity, the transparent conductive glass applied in very large area like gas sensor, LCD, image storage device. It is also use in field of solar cell for both Si solar cell and Dye sensitized solar cell. Radio Frequency Plasma enhanced Reactive Thermal Evaporation method is used to fabricate the transparent conductive glass by coating of tin oxide on transparent glass. In this study on attempt has been made for SnO₂ thin film coating using rf-PERTE with variation of oxygen partial pressure of 8×10⁻⁴ mbar, 6×10⁻⁴ mbar, 4×10⁻⁴ mbar, with tin oxide boat voltage of 16 V, 20V, 24V and deposition time of tin oxide on the glass subtract 3 min, 10 min, 20 min and compare resistivity with commercial available ITO. The resistivity observed for thin film coated on lab and commercially available Indium coated ITO were 82.63 Ω/cm² and 1.191 Ω/cm² respectively.

Keywords: Conducting Glass, DSSC, Thin layer coating.

Nomenclature

| Symbol  | Description       |
|---------|-------------------|
| ρ       | Resistivity       |
| ρ₀      | Microscopic Resistivity |
| Rₛ      | Sheet resistance  |

1. Introduction
The transparent conductive glass by the coating of tin oxide semiconductor layer serves high transparency, highly electrical conductive and ability to withstand at higher temperature [1-2]. Film of conductive tin oxide on glass subtract is used mostly for low-E glass window for energy conservation due to their durability [3]. Use of transparent conductive glass is not resist to environment research laboratory but they are widely applied to gas sensor, LCD, heat mirrors, low emissivity windows, image storage device, light emitting device [1],[4]. Tin oxide thin films are also used as window layer in Si solar cell because of their low resistivity and high transmittance. For Si solar cell transparent conductive glass serves an effective

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coupling of light into the solar cell by refractive index matching and an efficient trapping of light scattered in the solar cell at the rough transparent conductive glass/silicon interface [5]. Now the transparent conductive glass widely used in dye sensitized solar cell owing to its transparency as well as conductivity characteristics [6-10]. Conductivity to transparent glass can be applied by various methods like thermal evaporation, chemical vapor deposition, spray pyrolysis, electron beam evaporation, reactive evaporation, thermal oxidation and radio frequency plasma reactive thermal evaporation [11-15]. Radio frequency plasma with the absence of any post deposition heat treatment decrease the production cost [16].

In this paper transparent conductive glass is fabricated by coating of tin oxide on transparent glass substrate by radio frequency plasma enhanced reactive thermal evaporation. Effect on resistivity is seen in experiment by varying partial pressure of oxygen, tin oxide temperature and coating time.

2. Materials and Methods

The rf-PERTE (radio frequency Plasma Enhanced Reactive Thermal Evaporation) technique was used to obtain transparent conductive oxide glasses. The apparatus present at FCIPT, Gandhinagar is a high vacuum system (10^{-6} mbar). A rotary pump, a roughing valve and a diffusion pump are part of the whole system to attain the required pressure. The deposition of the metal (in this case tin) is an evaporation process. The metal is kept in molybdenum boats (tungsten also used) in such a way that the substrates (glass / polymer) are placed above them. Provided are heaters for the substrates as well as the molybdenum boats for an effective evaporation. The system is first initiated for generating the desired pressure. A chevrol baffle is used for attaining a high vacuum of 10^{-6} torr. Once the pressure is attained, an rf supply is connected to the system. After this, the desired gas (oxygen) is released slowly. This results in decreasing the pressure. Plasma is generated at pressure range of 10^{-1} to 10^{-2} mbar. Thus, the pressure is to be decreased to that range to generate plasma.

Once the plasma is generated, the pressure is then increased by manipulating the gas valve and set at the desired process pressure. At this pressure, the boats are heated and the evaporation starts. Within a specific deposition time, the metal gets deposited on the substrate (heated / unheated). After removing the substrates, the conductivity is measured with the help of a multimeter. The parameters can then be set accordingly.

![Fig.1. Configuration of a basic vacuum system](image-url)
3. Results and Discussion

The conductive glass characteristics can be found by simply measuring the resistance across the TCO glass. A multimeter gives varying results due to its limitations. To have better results, the four point probe method has been used. The apparatus consists of 4 probes with the ends making a contact with the silicon wafers (in this case TCO glass substrate). Figure 3 shows a schematic of a 4 point probe apparatus. The values of Current and Voltage can thus be calculated. Fixing any one value, the other is to be varied and thus one can calculate the resistivity of the selected substrate. Table 1 shows the substrate characteristics of different conducting glasses and the parameters to identify them. Sheet Resistance is also calculated as many applications take it to be a deciding factor. The calculation is shown in the Appendix A.

The conductive glasses synthesized by rf PERTE method can be analysed with naked eyes too. The characteristics as mentioned above can thus be optimized. Fig 4 shows different Tin Oxide Thin films deposited on Glass substrates. It is not necessary that a thin transparent film, as shown in 4(c), be highly conductive. The SnO$_2$ formation needs to be optimized. Although being highly transmitting, the conductive layer is a thin one which is undesired. Unlike this in fig 4(a), a thick film is deposited giving better conductivity. But, the transmission which is less than 30% is not desired for its application. Since TCOs play a crucial part in transmitting the solar rays, the transparency of the glass is of much importance. Fig 4(b) shows a much desired sample of a SnO$_2$ thin film deposited on a glass substrate. The conductivity is optimized and so is the transmittance. A yellow layer seen by naked eyes proves to be synthesis of a much desired thick film without compromising on the transparency.

Once the Substrates are being synthesized it is very important to know the transmittance. To test the same, special holders were fabricated to fit in a UV spectrophotometer. These holders were made to attach a small piece of the substrates with the help of a 2-sided gum tape. The reference initially was a bare glass substrate. It was found that mostly all the samples fell in the range of 80 -90% transmittance with the wavelength range being from 290-1100 nm. Fig 5 shows the comparisons of the transmittance of different substrates including a polymer substrate. The minor oscillation observed in the ITO substrate symbolizes the fact that the film is thick and also that it has a good transmittance.
Table 1. Substrate Characteristics

| Sr no | P_b (10^-4 mbar) | P_o (10^-4 mbar) | P_p (10^-4 mbar) | Boat Volt (V) | Dep time (min) | ρ (Ω/cm) | R (Ω/cm^2) |
|-------|------------------|------------------|------------------|--------------|---------------|---------|----------|
| 1.    | 2.5              | 8                | 7.75             | 16           | 3             | 13.424  | 111.86   |
| 2.    | 2                | 8                | 7.8              | 16           | 10            | 48.39   | 403.25   |
| 3.    | 1.5              | 6                | 5.85             | 16           | 10            | 15.94   | 132.83   |
| 4.    | 2                | 4                | 3.8              | 16           | 10            | 134.11  | 1.11×10^5 |
| 5.    | 1.5              | 8                | 7.85             | 16           | 20            | 39.56   | 329.6    |
| 6.    | 1.5              | 8                | 7.75             | 16           | 20            | 9.916   | 82.63    |
| 7.    | 1.5              | 8                | 7.75             | 24           | 10            | 21.52   | 179.3    |
| 8.    | 0.1              | 8                | 7.99             | 20           | 10            | 18.46   | 153.8    |
| 9.    | 1.5              | 8                | 7.85             | 20           | 20            | 15.18   | 126.5    |
| 10.   | COMMERCIALLY AVAILABLE ITO FILM | 0.143 | 1.191 |

Fig. 3. Schematic of a 4 point probe method
Fig. 4. Images of SnO$_2$ deposited on Glass Substrates (a) conductive but thick film (b) Conductive and thin film (c) conductive but very thin film

Fig. 5. UV spectra of the substrates
4. Conclusion

At constant boat voltage and partial pressure the increase in deposition time decreases resistivity. Further, at constant bolt voltage and deposition time the resistivity inversely proportional to partial pressure. Similarly at constant partial pressure and deposition time the resistivity inversely proportional to boat voltage. Therefore optimized results for more transitivity and minimal resistivity observed at partial pressure of $7.75 \times 10^{-4}$ mbar, bolt voltage of 16 V and deposition time of 20 min. However the comparison of results proves that poor efficiency of thin layer coating of SnO₂ compare with commercially available ITO in the market. This might be because of lab thin layer coating is done with only SnO₂, while commercially available ITOs are coated with indium doped SnO₂.

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Appendix A.

Four point probe calculation:

\[
\rho = \frac{\rho_0}{G_7 \times \left(\frac{W}{S}\right)}
\]

Where,

\[\rho = \text{resistivity}\]
\[\rho_0 = \frac{V}{I \times \left(2 \times \Pi \times S\right)}\]
\[S = 2 \text{ mm (Distance between two probes)}\]
\[W = 1.2 \text{ mm (width of sample)}\]
\[G_7 \times \left(\frac{W}{S}\right) = \text{correction factor.}\]

Now, for a sample with \(I = 1.8 \text{ mA and } V=1.93 \text{ V}\)
\[\rho = \frac{1.93 \times 2 \times \Pi \times 2}{1.8} = 13.47 \text{ mm V / mA}\]
\[
G_2 = \left( \frac{W}{S} \right) = \frac{2 \times 2 \times \log_e^2}{1.2} = 1.0034
\]

\[
\rho = \frac{13.47}{1.0034} = 13.424 \ \Omega \text{cm}
\]

\[t = 0.12 \text{ cm (thickness of the sample)}\]

Sheet resistance \(R_s = \frac{\rho}{t}\)

\[R_s = 111.86 \ \Omega / \text{cm}^2\]