Synthesis of Tin Oxide Thin Film and Effect of Number of Coating on Transmittance and Film Thickness

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This paper studies the synthesis of semiconducting tin oxide thin film on a glass substrate by dip coating method using Tin(II) chloride as precursor and methanol as solvent. The optical properties were studied by Elco-UV/VIS Spectrophotometer, Model- SL-159. The thickness of the film has been calculated from the interference pattern of the transmission spectrum (wavelength Vs. transmission curve) for each coat. It is concluded that thickness of the thin film increases nearly linearly with the number of coating. The effect of multiple applications on transmittance is also studied.

1. Introduction

The research and development on thin film technology have been increasing rapidly over the past two decades due to their vast applications in almost all fields of science and technology. Tin Oxide is a tetragonal rutile n-type semiconductor having high band gap energy (≈3.6 eV) [1]. It is more transparent in the region of visible spectrum due to high band gap and having high electrical conductivity due to free electrons in oxygen vacancy holes. Due to the above reasons and large surface area on thin films, tin oxide and dopped tin oxide thin films are used in lithium battery [2], gas sensors for environmental monitoring [3], photovoltaic cells [4], transistors [5], transparent conducting electrodes [6], and substrates for electro deposition [7,8].

A survey of literature reveals that there are many techniques employed for the synthesis of tin oxide thin film. They includes spray pyrolysis [9-11], sol-gel [12], physical vapor deposition [13], electron gun evaporation [14], pulse laser deposition [15], R.F. sputtering [16-18], and chemical vapor deposition [19]. Among all the above methods Sol-gel technique play a vital role due to many advantages such as: (a) one can synthesize thin or thick film with a high porosity area which improves the efficiency of sensor; (b) one can modify the composition with uniformly dispersed dopants and modifiers; (c) easy control on film thickness; (d) superb homogeneity; (e) ability to coat large area and complex shape; (f) equipments can be assembled at low cost; (g) low temperature in processing. Generally there are three methods that are used in the sol-gel technique. These are spin coating, dip coating and spray coating. In this study, dip coating method is applied. Starting from Tin(II) Chloride, which is preferred due to low cost as precursor, methanol as solvent and glacial acetic acid as chelating agent, a transparent solution was prepared and SnO_2 thin film was synthesized on a glass substrate (Corning 7059) by novel sol-gel dip coating technique. This is the better choice of sol-gel method than the alkoxide or Tin(IV) chloride due to the cost factor and availability. The main purpose of this presentation is to measure the thickness of thin film using the interference fringes of the transmission spectrum for each coat. The interference fringes are obtained by the equipment ELCO UV/VIS spectrophotometer (Model–SL-159) in the wavelength range 350nm to 1000nm. The effect of the number of coatings on thickness and transmittance was also analyzed.

2. Experimental Details

2.1. Procedure

In a conical flask, 2gms of anhydrous tin(II) chloride ($SnCl_2$) was dissolved in 80ml of methanol (CH_3OH) with 2gms glacial acetic acid(CH_3COOH). The solution was continuously stirred by a magnetic stirrer for 45 minutes at NTP to get a clear homogeneous solution. Before coating on the glass substrate of dimension 76.2x25.4x1.2mm (Corning 7059), the substrates were thoroughly cleaned with cleaning liquid soap and then with acetone to remove organic particles on the surface and then washed with distilled water. To prevent local hydrolysis, the substrates were then soaked with TEA diluted isopropyle alcohol for 10 minutes and then dried.

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Now the substrate was fixed in between the two jaws of a fixture connected with an inextensible cord wound around a pulley with a handle (to hold) of diameter 6.4cm. The cord length was so adjusted that the pulley will be rotated completely only once and by that time the substrate would have dipped 75% of its length roughly 60cm inside the prepared solution. The pulley was rotated by hand slowly such that it took nearly 1 minute to complete one rotation, that is, with a speed of nearly 20cm/minute. After dipping once, the pulley was rotated reversely for one complete rotation with the same speed. Here we have maintained the speed of dipping and withdrawal same to get uniform thickness. We would like to mention that since it was operated by hand, the speed might not be uniform but precautions were taken to make the speed nearly uniform. However, this method can be improvised by using gears and electric motor to make the speed constant.

Now the coated glass substrate was taken out from the jaws and dried at 150^0C in a furnace for 1hr to remove the other products. Then, the substrate was heat treated at 500^0C for about 15 minutes.

The above procedure was repeated for a number of times to get the desired thickness (1^{st} substrate one times, 2^{nd} substrate two times, 3^{rd} substrate three times, …, 8^{th} substrate eight times). In this dipping process there will be two sided coat on the substrate. To make successive coat, one side coat was removed by means of a sharp edge. While removing the coat, precautions were taken so that the other side coat would not be disturbed at all. Then, finally the heat treatment was carried out on each substrate at 600^0C for 75 minutes in a muffler furnace in air.

2.2. Optical characterization

Optical characterization was studied for transmission percentage versus wavelength curve, which was plotted from the data obtained from transmission spectrum analysis of the film by ELCO UV/VIS spectrophotometer Model- SL 157. Since thickness of the substrate is very large as compared with the thickness of the thin film, the effect of glass plate is to be considered. Therefore, to eliminate this effect, we choose a reference glass plate of same type as that of substrate. From Fig. 1 it is clear that the surface quality and homogeneity of the thin film is excellent.

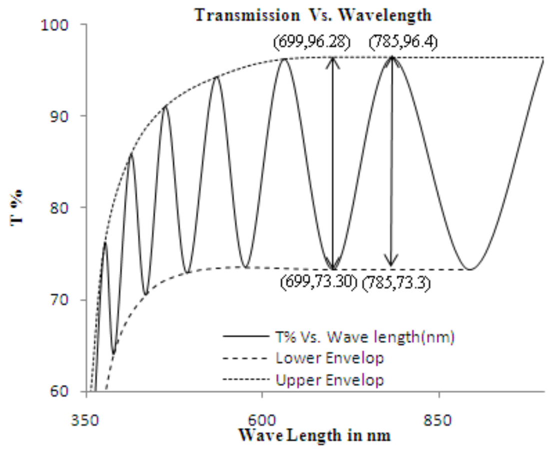

Fig.1: Transmission - wavelength (nm) curve in the wavelength range 350nm-1000nm.

2.3. Theory of thickness measurement

In this study, the refractive index and the thickness of the film were calculated using the envelop method developed by Manifacier et al. [20].

Now, the formula for refractive index of the thin film is

$$n = \left\{N + \left(N^2 - \mu^2\right)^{1/2}\right\}^{1/2} \tag{1}$$

Where,

$$N = 2\mu\frac{T_u - T_l}{T_u T_l} + \frac{\mu^2 + 1}{2} \tag{2}$$

If n_1 and n_2 be the refractive index of the thin film at maxima and corresponding minima, where the phase difference is π and φ_1, φ_2 be the phase angle at maxima and minima, then from equation $\varphi = \frac{4\pi n d}{\lambda}$

we have $\varphi_1 = \frac{4\pi n_1 d}{\lambda_1}$

and $\varphi_2 = \frac{4\pi n_2 d}{\lambda_2}$ and also $\varphi_1 - \varphi_2 = \pi$

$$\text{So, } \pi = \frac{4\pi n_1 d}{\lambda_1} - \frac{4\pi n_2 d}{\lambda_2} = 4\pi d\frac{(n_1\lambda_2 - n_2\lambda_1)}{\lambda_1\lambda_2}$$

$$\Rightarrow d = \left|\frac{\lambda_1\lambda_2}{4(n_1\lambda_2 - n_2\lambda_1)}\right| \tag{3}$$

However, if we consider two consecutive maxima whose phase difference is 2π, then

$$d = \left| \frac{\lambda_1 \lambda_2}{2(n_1\lambda_2 - n_2\lambda_1)} \right| \quad (4)$$

In this paper, we have used Eqn. (11) to find the width of the thin film.

3. Result and Discussion

3.1. Measurement of thickness

Here, we have mathematically calculated the thickness of 8th film.

From Fig. 1, for maxima

λ_1= 785 nm, T_u = 96.40%, T_l = 73.3% and μ = 1.53

Then, $N_1 = 2\mu \times \frac{T_u - T_l}{T_u \times T_l} + \frac{\mu^2+1}{2} = 1.68045$

and, $n_1 = \left\{ N_1 + \left(N_1^2 - \mu^2\right)^{1/2} \right\}^{1/2} = 1.54125.$

From Fig. 1, for minima

λ_2= 699 nm, T_u = 96.28%, T_l = 73.3% and also μ = 1.53.

Then, $N_2 = 2\mu \times \frac{T_u - T_l}{T_u \times T_l} + \frac{\mu^2+1}{2} = 1.68041$

and, $n_2 = \left\{ N_2 + \left(N_2^2 - \mu^2\right)^{1/2} \right\}^{1/2} = 1.54120.$

Using the relation, $d = \left| \frac{\lambda_1 \lambda_2}{4(n_1\lambda_2 - n_2\lambda_1)} \right|$

we have d = 1035.24 nm.

3.2. Film thickness versus number of coatings

After each coating the sample was studied for its optical characterization. From the transmission versus wavelength graph, the thickness is measured by the above mentioned formula. The thickness for each coat is shown in the Table 1.

Table 1: Number of coating versus thickness.

No. of Coating	Film thickness (nm)	No. of Coating	Film thickness (nm)
1	123.25	5	632.89
2	255.15	6	769.73
3	378.10	7	898.92
4	504.23	8	1035.24

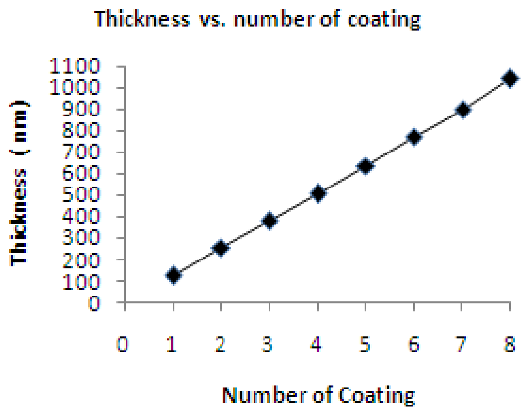

Fig.2: Thickness versus number of coatings.

Table 1 shows how the thickness of a thin film varies with number of coatings. Fig. 2 shows the graph between number of coatings and thickness. The curve is nearly linear. It indicates that for each coat thickness increases approximately by 125-130nm.

3.3. Transmission % vs number of coating

Fig. 3 shows the variation of transmittance with the number of coatings. Here, we have plotted the curve of transmittance versus wavelength for even number of coatings (2nd , 4th , 6th and 8th). From the figure, it is clear that as the thickness increases the percentage of transmission decreases.

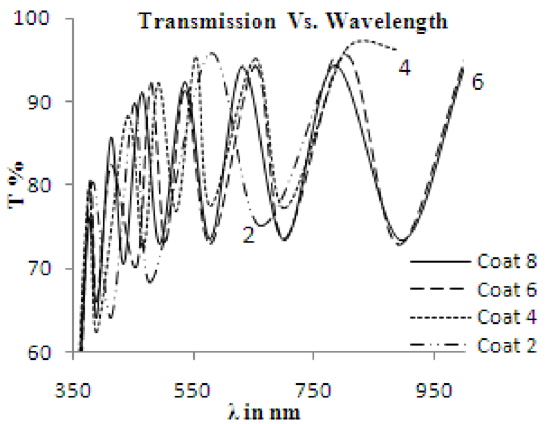

Fig.3: T % versus number of coatings.

4. Conclusion

Tin oxide (SnO_2) films were synthesized on glass plate by sol-gel (dip coating) method. Both the refractive index and the thin film thickness were determined from their transmittance spectra in the UV-VIS region using the envelop method. It was observed that the film thickness increases nearly 125-130 nm for each coat. The transmittance of the film was measured with number of applications. It was observed that transmittance decreases as the number of coatings increases and transmission value were more than 70% at wave length greater than 450nm in all cases.

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