C H A P T E R -III

DEPOSITON OF TUNGSTEN OXIDE THIN FILMS (EXPERIMENTAL)

CHAPTER-III

EXPERIMENTAL

3.1 INTRODUCTION :

Modern day technology requires several types of thin films for a variety of applications [1,2].There are various techniques by which one can deposite thin films. Thin film deposition techniques can be broadly classified as follows,

Deposition Techniques

Physical

1) Evaporation
2) Sputtering

Chemical

1) Chemical Vapour Deposition
2) Spray Pyrolysis
3) Electrodeposition
4) Anodization
5) Solution Growth
6) Screen Printing.

The choice of the perticular method depends on the several factors like material to be deposited, nature of the substrate, required film thickness, structure of the film, application of the film etc. Among the methods mentioned above, solution spraying method is most popular today because of large number of conducting and semiconducting materials are prepared by this technique. The compounds in the thin film form on a variety of substrates (glass, ceramic or metallic) have been prepared by this technique, the more common examples being CdS [3 to 6)], CdSe [7 to 10], CdTe [7], ,$CuInS_2$ [11], $CuInSe_2$ [10-13], $Bi_2 CdS_4$ [14], conducting substrates based on SnO_2 [15] In_2O_3 [16,17], etc. It is a simple and low cost technique for the preparation of semiconducting film for solid liquid junctiion solar cells. It has capability to produce large area of high quality adherent films of uniform thickness.

Doping of the semiconductor film is simple, since it is accomplished by mere addition of the dopant to the spray solution. It is easy to prepare the film of any composition by simply mixing the components in appropriate ratios. However, this technique needs the optimization of different preparative parameters such as substrate temperature, quantity of the solution to be sprayed, concentration of the solution, spray rate etc. as they affect the quality of films and also reflects on the film properties.

In this chapter a method used for preparation of fluorine doped tin oxide (F.T.O) coated glass substrates on amorphous glass substrates by using conventional '$SnCl_4$' solution and 'NH_4F' solution is described. The procedure of WO_3 film formation and optimization of preparative parameters for its deposition is also discussed.

3.2 EXPERIMENTAL :

3.2.1 SPRAY PYROLYSIS TECHNIQUE :

Spray pyrolysis technique consists of a thermally stimulated chemical reactions between clusters of liquid or vapour atoms of different chemical species. It involves spraying of a solution usually aqueous containing soluble salts of the constituent atoms of the desired compound on the preheated substrate. Every sprayed droplet reaching to the surface of hot substrate undergoes pyrolytic (endothermic) decomposition and forms a single crystallite or cluster of crystallites as a product. The other volatile biproducts and solvent escape in vapour phase. The substrate provides thermal energy for the thermal decomposition and subsequent recombination of the constituent species followed by sintering and recrystallization of the clusters of crystallites and thereby resulting in coherent film. The atomization of the spraying solution into a spray of fine droplets also depends on geometry of spray nozzle and pressure of a carrier gas.

The schematic diagram of the spray pyrolysis technique is shown in Fig.3.1. It consists of mainly (a) Spray nozzle, (b) Rotor for spray nozzle with speed controller, (c) Liquid level monitor, (d) Hot plate with temperature controlling arrangement, (e) Gas regulator valve and (f) Air tight metallic chamber.

a) **Spray nozzle :**

It is made up of a glass and consists of the inner solution tube surrounded by the gas tube through which carrier gas flows (Fig.3.1). With the application of pressure to the carrier gas, the vacuum is created at the tip of the nozzle and the solution is automatically suck in the solution tube and the spray starts.

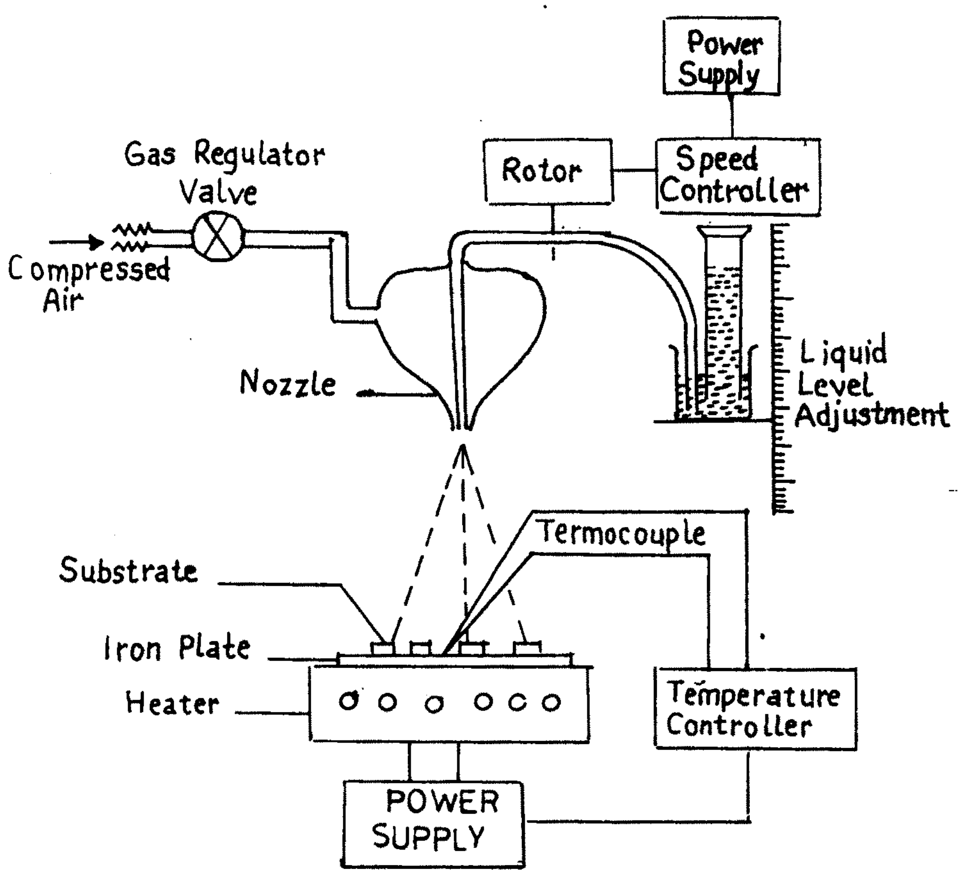

Fig.3.1 : Schematic diagram of the spray pyrolysis Technique

b) **Rotor for spray nozzle :**

An electric car wiper (12V,2A) was used to rotate the spray nozzle along with the speed controller.

c) **Liquid level monitor :**

The spray rate, at a fixed air pressure, depends upon height of the solution measured with reference to the tip of the nnozzle. The arrangement for the change in height of the solution forms the liquid level monitor.

d) **Hot plate :**

The iron disc with thickness 0.7 cm and diameter 16 cm was suupported on the electrical heater. Maximum temperature upto $500^{\circ}C$ can be obtained with the help of this arrangement. Chromel-Alumel thermocouple was used to measure the temperature of substrates and is fixed at the centre of the iron disc. The temperature of the hot plate was monitored with the temperature controller model, 9601 (Aplab make).

e) **Gas regulator valve :**

The gas regulator valve was used to control the pressure of the gas. A corning glass tube of length 25 cm and diameter 1.5 cm is converted in to gas flow meter.

f) **Air tight metallic chamber :**

Since number of toxic gases are evolved during the spray it is necessary to fix the spraying unit in an air tight metallic chamber. An outlet of the chamber is fitted to exhaust to remove the gases evolved during the deposition.

3.2.2 SUBSTRATE CLEANING :

Cleanliness of the substrate, for the thin film deposition, is one of the most important factors for obtaining the reproducibility of the properties. It also affects the adherence, smoothness, brightness and uniformity of the film. The technique to be adopted for cleaning depends upon the nature of the substrate, degree of cleanliness required and nature of contaminants to be removed. The common contaminants are grease, adsorbed water, air-bome dust, lint and oil particles.

Cleaning is the process of breaking of adsorption bonds between the substrate and the contaminants without damaging the substrate. There are many methods to supply energy for breaking such bonds, such as heating, bombarding by ions, chemical action and scrubbing. For obtaining good results, the folloowing cleaning procedure was carried out for glass substrates.

i) The glass substrates were first washed with the neutral detergent solution 'Labolene' and then with the double distilled water.

ii) These substrates were boiled in chromic acid for few minutes.

iii) Then, each substrate was cleaned with double distilled water separately.

iv) NaOH treatment was given to these substrates to remove any acidic contamination.

v) Again the substrates were washed with double distilled water and boiled in double distilled water for some time.

vi) Lastly, substrates were ultrasonically cleaned.

vii) Drying of the substrates was done in the vapour of alcohol with the help of special stand kept in a steel box which will be heated for few minutes.

3.2.3 Preparation of F.T.O. coated glass substrates :

100 cc of 2 M stannic chloride solution was prepared in double distilled water and 14.285 gm of ammonium fluoride was dissolved in it, to obtain the 40% doping concentration of fluorine. From the above mixture 5 cc solution was taken and 20 cc of propane 2 -ol (iso-propylalcohol) was added. The final solution was sprayed through the specially designed glass nozzle at the spray rate of 6 cc/min. The substrate temperature was maintained at 550^{o}C. It was found that these conducting glasses have 20-30 ohm/cm^{2} sheet resistance and about 90% transparency.

3.2.4 Preparation of Ammonium tungstate solution :
Appropriate weight of tungsten trioxide powder(LR grade,The British Drug House Ltd.) was taken using semimicrobalance so as to get the required concentrated solution. Concentrated ammonia solution is diluted in double distilled water in the ratio 1:10. The weighed tungsten

trioxide powder was then dissolved in diluted hot ammonia solution. After WO_3 was completely dissolved in ammonia solution, doubly distilled water was added, to get the required quantity of the solution. This solution was taken as starting solution to be sprayed on to the hot substrates.

3. 3 RESULTS AND DISCUSSION :

3.3 .1 Optimization of preparative parameters for WO_3 thin films :

a) Spray rate :

In this technique the spray rate depends mainly on the pressure of the compressed gas. If the pressure of carrier gas is increased, the spray rate also increases at the constant height of the solution level and at very high pressure spray rate remains almost constant. With very high air pressures (> 6Kg/cm^2) we obtained inferior quality films due to lowering of substrate temperature; whereas at very low pressure (< 4 Kg/cm^2) instead of fine spray larger droplets of the solution falls directly on the substrate and films appear spongy. Hence, 5 Kg/cm^2 pressure was the optimum pressure of the carrier gas(air) and the corresponding spray rate was 25 cc/min.

b) Substrate temperature :

Substrate temperature was changed from 150°C to 400°C. It was observed that for the same spray rate at lower substrate temperatures the films formed were spongy in appearence while at the higher substrate temperatures the deposition rate was very slow. It is found that good quality thin films were obtained at 250 ± 5^{o}C substrate temperature.

c) **Concentration of spraying solution :**

Physical and chemical characteristics of a spray deposited films are also depend on the concentration of thce spraying solution. In the present study concentration of ammonium tungstate solution was varied from 0.01 M to 0.05 M and the effect of concentration of the spraying solution on the structural, optical and electrical properties of the thin films prepared is discussed in Chapter IV.

3.3.2 Preparation of WO_3 films by thermal decomposition of Sprayed ammonium tungstate :

WO_3 powder was dissolved in hot ammonia solution thereby forming ammonium tungstate. The chemical reaction may be given as follows,

$$WO_3 + 2NH_3 + H_2O \longrightarrow (NH_4)_2\ WO_4.$$

This solution was then sprayed onto the glass substrates at optimised temperature of 250^{o} C. As ammonium tungstate is unisolated from aqueous solution, it, as it is, gets deposited onto the substrate. These films were then heated at 550^{o} C for 6 hrs. inorder to decompose the tungstate and to get WO_3 films [18] as per the following chemical reaction.

$$(NH_4)_2\ WO_4 \xrightarrow[\text{at } 550^{o}C]{\text{heated}} WO_3 + H_2O\uparrow + 2NH_3\uparrow.$$

The films were prepared by changing the concentration of ammonium tungstate solution from 0.01 M to 0.05 M. It was noted that, the films deposited by the spray pyrolysis technique with all parameters optimised, were uniform and adherent to the substrates used.

The tungsten oxide films, thus deposited on to the amorphous glass substrates were used for the electrical, optical and structural characterizations. Those deposited on to F.T.O coated glass substrates were utilized for the photoelectrochemical characterization.

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