CHAPTER - III

DEPOSITION OF MOLYBDENUM OXIDE THIN FILMS

CHAPTER-III

DEPOSITION OF MOLYBDENUM OXIDE THIN FILMS

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 deposit thin films. Thin film deposition techniques can be broadly classified as follows :

Deposition Techniques

Physical	Chemical
1) Evaporation	1) Chemical vapour deposition
2) sputtering	2) Spray pyrolysis
	3) Electodeposition
	4) Anodization
	5) Solution Growth
	6) Screen printing
	7) Spin coating
	8) Sol-gel

The choice of the paticular method depends on several factors like material to be deposited, nature of 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 compound 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[3-6], CdSe [7-10], CdTe [7], $CuInS_2$ [11] $CuInSe_2$ [10-13], Bi_2CdS4 [14],Fe_2O_3 [15], WO_3 [16],CoO[17],NiO [18], ZnO [19] conducting substrates based on SnO_2 [20], In_2O_3 [21,22] etc. It is a simple and low cost technique for the preparation of semiconducting films for electrochromic 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 the 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 descibed. The procedure for MoO_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 to preheated substrates. Every sprayed droplet reaching to the surface of hot substrate undergoes pyrolytic (endothermic) decomposition and forms a single crystalline or cluster of crystallites as a product. The other volataile biproducts and solvent escape in the vapour phase. The substrate provides thermal energy for the thermal decompositon and subsequent recombination of the constituents species followed by sintering and recrysallization 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 the geometry of the spraying 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 lvel monitor, (d) Hot plate with temperature controlling arrangement, (e) Gas regulator valve and (f) Air tight metallic chamber.

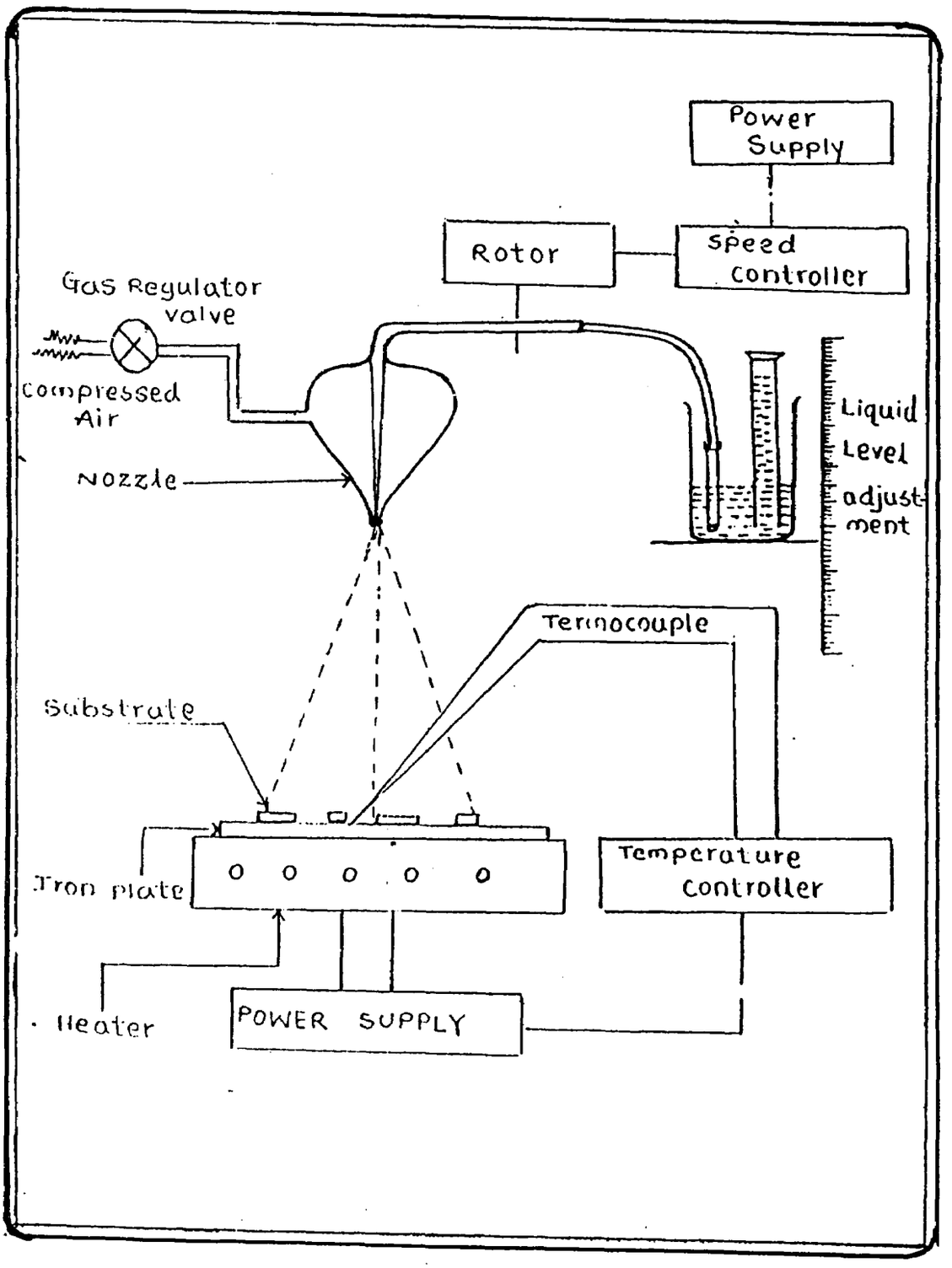

Fig.3.1 : A Typical Vertical Spray Pyrolysis Set up

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. 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.

b) Rotor For Spray Nozzle

An electric car wiper (12 V,2A) was used to rotate the spray nozzle along with 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 nozzle. The arrangement for the change in height of the solution form the liquid level monitor.

d) Hot Plate

The iron disc with diameter 16 cm and thickness 0.7 cm was supported on the electrical heater. Maximum temperature upto 600^{o}C can be obtained with the help of this arrangement Chromel-Alumel thermocouple was yused to measure the temperature of substrates and is fixed at the centre of the iron disc. The temperature of the host 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 substrate, degree of cleanliness requried and nature of contaminants to be removed. The common contaminants are grease, adsorpted water, air bome dust, link and oil particles.

Cleaning is the process of breaking of adsorption bonds between the substrate and 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 following 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 doubly distilled water.

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

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

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

v) Again the substrates were washed with doubly 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 g of ammonium fluoride was dissovled in it, to obtain the 40% doping concentration of fluorine. From the above mixture 10 cc solution was taken and 20 cc of propane 2-01 (iso-propyl alcohol) was added. The final solution was sprayed through the specially designed glass nozzle at the spray rate of 5 cc/min. The substrate temperature was maintained at 525^{o}C.

It was found that these conducting glasses have 10-50 ohm/□ sheet resistance and about 90% transparancy.

3.2.4 PREPARATION OF AMMONIUM MOLYBDATE SOLUTION

Appropriate weight of molybdenum trioxide powder (G.R. grade Loba Chimie, 99.5% pure) was taken using semimicrobalance so as to get the reqired concentration of solution. The weighed molybdenum trioxide powder was dissolved in ammonia solution. Thereby forming ammonium molybdate. The following reaction takes place.

$$MoO_3 + 2NH_3 + H_2O = (NH_4)_2MoO_3 \quad .....(3.1)$$

MoO_3 was completely dissolved , doubly distilled water was added, to get the desired quantity and concentration 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 MoO_3 Thin Films

a) Spray Rate

In this technique the spray rate depends mainly on the pressure of 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 (> 6 kg/cm^2), we obtained inferior quality

films due to lowering of substrate temperature, whereas at very low pressure (< 2 Kg/cm^2) instead of fine spray larger droplets of the solution falls directly on the substrate and films appear spongy. Hence, 2.5 Kg/cm^2 pressure was the optimum pressure of the carrier gas (air) and the corresponding spray rate was 2.5 cc/min.

b) Substrate Temperature

Substrate temperature was changed from 150°C to 450°C. It was observed that for the same spray rate at lower temperatures the films formed were spongy in appearance while at the higher temperatures the deposition rate was very slow. It is found that good quality thin films were obtained above 250°C substrate temperature. At the substrate temperatures 250°C and 300°C the films were amorphous and above 300°C the films were polycrysalline and the effect of substrate temperature on the structural, optical, electrical and electrochemical properties of the thin films is discussed in chapters IV and V.

c) Concentration of Spraying Solution

Physical and chemical characteristics of a spray deposited films are also depend on the concentration of the spraying solution. In the present study concentration of ammonium molybdate solution was 0.05 M.

3.3.2 Preparation of MoO_3 Films by Thermal Decomposition of Ammonium Molybdate Solution

MoO_3 powder was dissolved in ammonia solution thereby forming ammonium molybdate. The chemical reaction may be given as follows :

$$(NH_4)_2MoO_3 \longrightarrow MoO_3 + 2NH_3 \uparrow + H_2O \uparrow \quad ....(3.2)$$

This solution was then sprayed onto the preheated glass substrates maintained at different temperatures. The films were prepared by changing the substrate temperature from 250 to 450°C in steps of 50 and denoted by S_{250}, S_{300}, S_{350}, S_{400} and S_{450} where subscripts denote the substrate temperature of respective sample. It was noted that, the films deposited by the spray pyrolysis technique with all parameters optimized were uniform and adherent to the substrates used.

The molybdenum trioxide films, thus deposited on to the amorphous glass substrates were used for the electrical, optical and structural characterization . Those deposited on to F.T.O. coated glass substrates were utilized for the electrochromic characterisation.

REFERENCES

1) K.L.chopra and I.J.Kaur, 'Thin Film Device Applications' Plenum Press, New York, 1983

2) K.L.Chopra and S.R.Das, 'Thin Film Solar Cells', Plenum Press, New York, 1983.

3) R.R.Chamberlin and J.S.Skaraman, J.Electrochem.Soc. 113 (1966) 86.

4) R.Krishnakumar, V.Subramanium, Y.Ramprakash and A.S. Lakshmanan. Mat.Chem. and Phys. 15 (1987) 385.

5) Y.A.Ma and R.H.Bube, J.Electrochem. soc. 124 (1977) 1430.

6) M.Tusiki, H.Minoura, T.Nakamura and Y.Ueno, J.Appl. Electrochem. 8 (1978) 523.

7) S.N.Chen and J.McDonough, J.Electrochem. Soc., Extended Abstr 79-2 (1973) 1603.

8) J.F. Jordon, Proc. Int. Conf. Solar Electricity, CNES, Toulouse 57 (1976).

9) C.C.Tsou and J.R.Cleveland, J.Appl.Phys. 51 (1980) 455.

10) M.S.Tomar and F.J. Garcia, Prog. Crystal Growth Character 4 (1981) 221.

11) B.R.Pamplin and R.S.Feigelson, Thin Solid films, 60 (1979) 141.

12) C.W.Bates, K.F. Nelson, S.A.Raza, J.B.Mooney, J.M. Recktenwald, L.Macintosh and R.Lamoreaux, Thin Solid Films, 88 (1982) 279.

13) B.R.Pamplin and r.S.Feigelson, Mat.Res.Bull.,14 (1979) 1.

14) S.H.Pawar,S.P.Tamhankar and C.D.Lokhande, J. Electrochem. Soc. 132 (1985) 261.

15) P.S.Patil,R.D.Madhale,C.D.Lokhande and S.H.Pawar Indian J.Pure Appl.Phys. (1989) 227.

16) P.S.Patil and P.R.Patil Tr.J.Phys. 18 (1994) 1.

17) P.S.Patil,L.D.Kadam and C.D.Lokhande, Thin Solid Films (In Press).

18) P.S.Patil and L.D.Kadam Jr.J.Phys (Submitted).

19) L.Bahadur and J.P.Pandey, J.Electrochem. Soc. 137 (1990) 3755.