CHAPTER II

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DEPOSITION OF THE FILMS

2.1 Introduction :

There are several methods used for deposition of thin films[1-6] which can be employed as photoelectrodes in photoelectrochemical cells. Depending on the material to be deposited, nature of the substrate, thickness of the film, the method can be chosen. The important methods used for the depositions can be broadly classified as :

(a) Physical Methods

i) Vacuum evaporation
ii) Sputtering
iii) Evaporation by electron bombardment

(b) Chemical Methods

i) Chemical vapour deposition
ii) Chemical bath deposition
iii) Solution-gas interface technique
iv) Spray pyrolysis technique

The techniques like vacuum evaporation and sputtering have certain drawbacks and difficulties though these can be employed to deposit many compounds. The chemical methods listed above also have some drawbacks but these methods are relatively economical and easier one as compared to physical methods. In order to obtain the particular composition in alloys films and for obtaining good stoichiometric films a careful and precise control of the temperature is required, which is achieved by spray pyrolysis technique.

2.2 Spray Pyrolysis Technique :

Now a days, solution spray technique is the most popular technique, among the chemical methods. In the present study an attempt has been made to prepare molybdenum sulphide film by spray pyrolysis method. This method was first developed by Chamberlin and Skarman for obtaining large area thin film The method consists of spraying a solution on the hot substrates. The advantage of the spray pyrolysis method is great ease with which films can be prepared by a simple mixture of the components in the appropriate ratio. The important merits of the spray pyrolysis method are ability t produce uniform and adhesive thin films, suitable and economical for the deposition of films on the hot substrate. The spray pyrolysis technique is designed and developed in our laboratory.

2.2.1 Experimental set-up

The schematic diagram of the experimental set-up for the spray pyrolysis technique is shown in fig.2.1. It mainly consists of i) spray nozzle ii) rotor for spray nozzle iii) speed controller for rotor iv) liquid level monitor v) gas flow meter vi) substrate heater.

(i) Spray Nozzle

The geometry of the nozzle affects so many factors such as distribution of droplets, spray pattern and spray rate sensitivity. A number of nozzles have, therefore, been designed and fabricated for spraying. A typical nozzle is shown in the fig.2.2. Solution tube and carrier gas tube are two important parts of the nozzle. A vacuum is created at the tip of the solution tube when pressure is applied through the carrier gas tube. Due to this vacuum, solution is automatically sucked from the solution tube and spray starts.

(ii) Rotor for Spray Nozzle

The wiper motor [mitsuba, made in Japan (12 V)] is used as a rotor to oscillate the nozzle. Oscillations are adjusted so as to maintain constant substrate temperature and to deposit uniform films.

(iii) Speed Controller for Rotor

The rate of oscillations of a nozzle is controlled by the speed controller.

(iv) Liquid Level Monitor

With the help of this arrangement a regular flow of the solution is obtained. A measuring cylinder is hanged in a beaker and the spray rate can be easily measured with the help of this assembly. The increase or decrease in height of the assembly changes spray rate.

(v) Gas Flow Meter

It consists of a graduated glass tube containing a rider. The rider indicates any change in pressure by changing its position. The air pressure from the compressor is controlled by mechanical valve and variation in pressure is indicated by gas flow meter.

(vi) Substrate Heater

The procellin base of electrical stove (7 inch in diameter) with 2000 W heating coil is fixed in the fireclay. The iron plate of thickness 0.6 cm and diameter 18 cm is used as a hot plate to support the substrate. The chromel-Alumel thermo-couple is fixed on the iron plate and is used to measure the temperature of the substrate. The Aplab temperature controller (Model-9601) is used to control the temperature of the substrate. The substrates are kept at the center of the iron plate during deposition since uniform temperature is observed at the center of the iron plate.

2.2.2 Dependence of the spray rate on pressure and height of the solution

It is observed that the spray rate inflect with atomising air pressure and with the height of the solution.

(i) Pressure Dependent Spray Rate :

The spray rates, for different air pressures, are measured by keeping height of the solution constant. The solution level is kept at the height of the tip of the nozzle and this is taken as reference (zero) for solution height measurements. It is seen that the spray rate increases with increase in the air pressure and saturation is observed at higher pressure. During film deposition air pressure is kept constant at a moderate value. At lower air pressures droplets are not fine and uniform whereas at the higher pressures it is impossible to maintain constant and uniform temperature of the substrate heater. The major effects of a fast spraying rate are stacking faults, dislocations and vacancies in the films. Increase in spray rate also causes a decrease in grain size. Sensitivity of the film properties depend mainly on spray rate.

(ii) Solution Height Dependent Spray Rate

The pressure is kept constant and the effect of the height of the solution on the spray rate is studied [height of the solution below the tip of the nozzle is taken as -ve and above is taken as +ve]. It is noticed that spray rate increases with height of the solution and remains constant above + 20 cm. The observed saturation in the spray rate is because of limitation of the spray nozzle and it varies from nozzle to nozzle.

2.3 Substrate Cleaning :

To obtain uniform, adhesive and reproducible films, the substrates must be cleaned carefully. The microslides of size 3.8 cm x 1.13 cm x 0.1 cm, supplied by Blue star, are used as glass substrates. The common contaminants are grease, dust, oil particles etc. The following procedure is generally adopted for cleaning the glass substrate.

1) The substrates are washed with the detergent solution Teepol.
2) Such washed substrates are boiled in chromic acid for few minutes.
3) After this, these substrates are cleaned in double distilled water.
4) To remove the acidic contamination, substrates are kept in NaOH solution for a few minutes.
5) The substrates are again washed with double distilled water and cleaned ultrasonically.
6) Finally the substrates are dried in vapour of alcohol.

2.4 Preparation of Films :

All the films were prepared by spraying an equimolar (0.05 M) aqueous solutions of ammonium heptamolybdate and thiourea in appropriate volume ratio in order to obtain the Mo : S ratio 1 : 2. Weighed quantity (6.179 gm) of ammonium heptamolybdate is dissolved in 100 c.c. of double distilled water to obtain 0.05 M solution and 1.903 gm of thiourea in 500 c.c. of double distilled water to achieve the same concentration. Two solutions were mixed thoroughly and a final mixture was sprayed through a glass nozzle. The solution was sprayed by an atomizer spray nozzle and the liquid spray rate was controlled by a flow meter and the air pressure applied to the nozzle. The air compressor was used to atomize the spray. The spray rate was fixed at 8 c.c./min and controlled by mechanical valve. The gases evolved during the decomposition are exhausted. The films were allowed to cool slowly on substrate heater in the chamber itself. The substrate temperature was varied and controlled from 250°C to 400°C in the interval of 25°C with the help of temperature controller (Aplab 9601).

2.5 Thickness of the Films :

In the study of the film properties such as conductivity, light absorption, transmission, film thickness is an important parameter. Thus to characterise the film it is necessary to measure the film thickness. The following methods have found widest application in the thickness measurements :
(i) Weighing (ii) Stylus (iii) Multiple beam interferometry (iv) X-ray fluorescence.

Out of these methods, weighing method is simpler and is used for the measurement of thickness using the relation

$$t = \frac{W}{A \times \rho_m}$$

where

i) A = area of the film

ii) W = weight of the film

iii) ρ_m = density of the material in the bulk form which is 4.8 gm/cm^3.

Figure Captions

2.1 The schematic diagram of the spray pyrolysis technique.

2.2 A diagram of typical spray nozzle.

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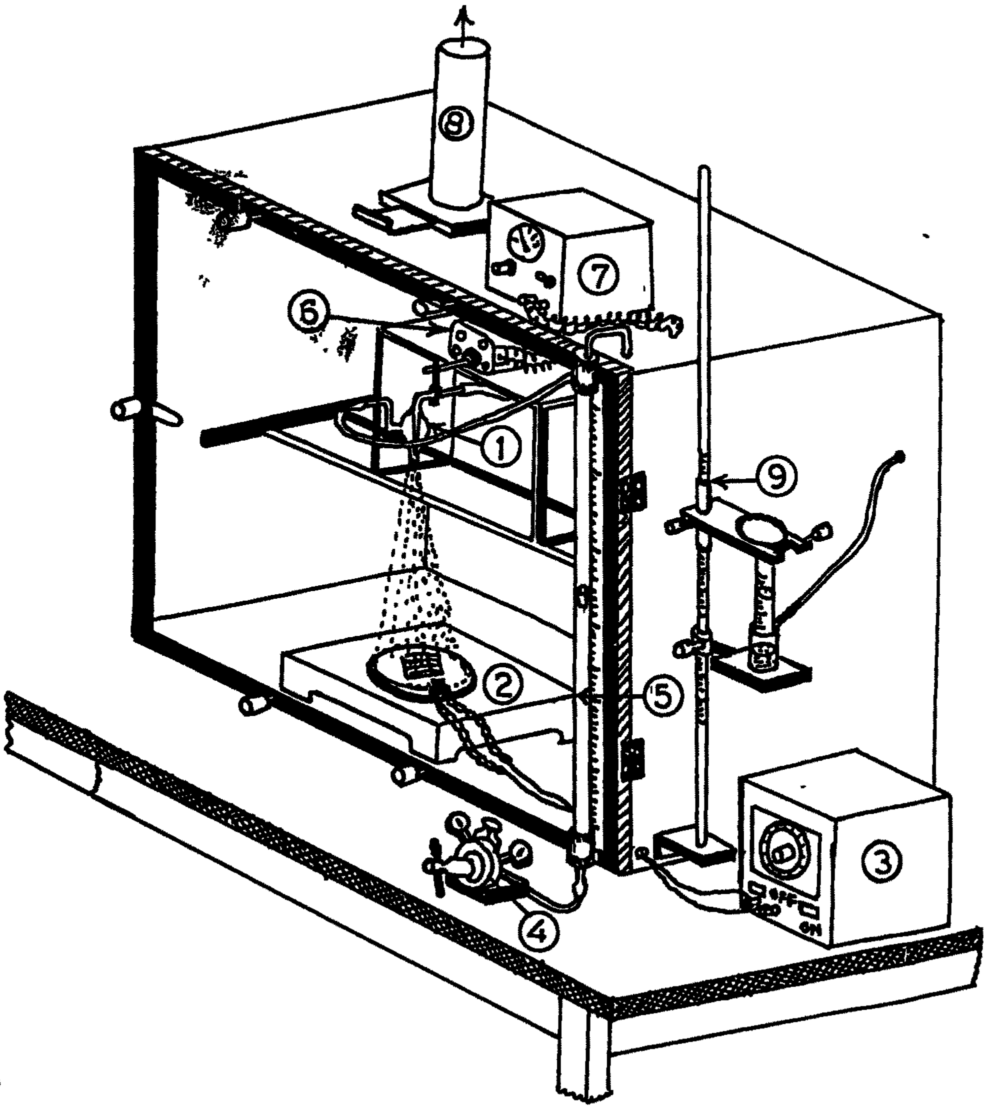

Fig. 2.1 : The schematic diagram of experimental set-up for spray pyrolysis technique
1) Spray nozzle 2) Hot plate 3) Temperature controller 4) Gas valve 5) Flow meter
6) Roter 7) Speed controller 8) Exhaust
9) Liquid level adjustment.

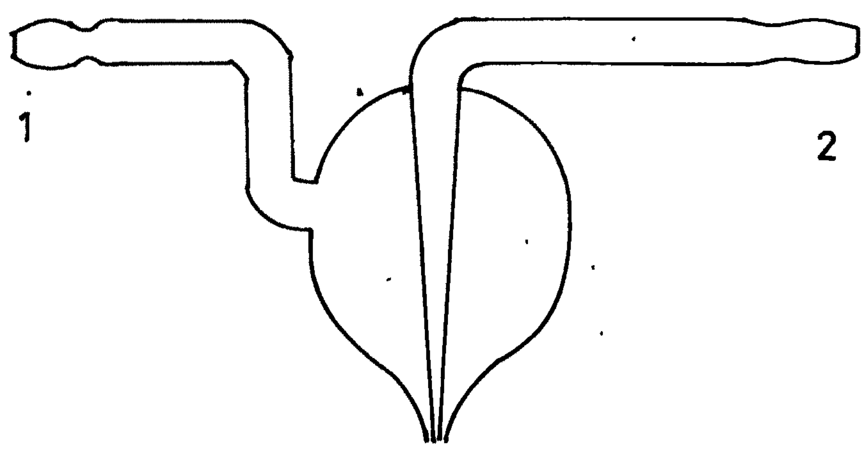

Fig. 2.2

1 - Carrier gas tube

2 - Solution tube