CHAPTER III

CHAPTER THREE

Deposition of films by spray pyrolysis technique

...

3.1 Introduction:

Much work has been done on the development and investigatior of semiconducting electrodes because of their potential application to photovoltaic conversion of solar energy. Several methods such as chemical vapour deposition(1,2), evaporation of solution on a substrate(3,4), chemical bath deposition technique(5) and spray pyrolysis (solution spraying)(6) are used to obtain semiconducting electrodes that can be used in photoelectrochemical cells.

In the present investigation, an attempt has been made to prepare films by spray pyrolysis method which has been developed by Chamberlin and Skarman for producing large area thin films by solution spraying technique. This method consists, basically, of spraying a solution on the hot substrates. The process of deposition of films by spray pyrolysis method is unique because all the elements are contained in the solution which is being sprayed. Neither the gas being used to operate the spray nozsle, the ambient atmosphere, the substrate nor any post treatment contributes to chemical composition of films, which is being deposited. Chamberlin and Skarman prepared CdS films using spray pyrolysis (S.P.) technique. In the present investigation an attempt has been made to prepare Bi_2O_3 films using spray pyrolysis technique. This technique is convenient and economical for the deposition of films on the hot substrate. The major advantage of spray pyrolysis is its ability to produce uniform and adhesive thin films.

3.2 Experimental Set-up:

Fig.3.1 shows typical experimental arrangement designed and constructed in our laboratory for the deposition of films. It consists of (i) spray nozzle (ii) rotor for spray nozzle (iii) speed controller for rotor (iv) liquid level monitor (v) air pressure control (vi) hot plate with controller and (vii) air tight metallic chamber. The glass spray nozzle, specially designed in our laboratory is rotated with the help of rotor whose speed can be controlled with the help of speed controller.

Atomization of spray is acheived with air compressor. The liquid spray rate was controlled by an air pressure applied to nozzle and height of liquid. Gas flow meter attached to mechanical value, measures air pressure and mechanical valve governs the air pressure applied to nozzle. The pressure on the liquid is maintained constant with the help of liquid level adjustment as shown in fig.3.1. The substrate heater employed has sufficient thermal capacity to raise and maintain a temperature up to 600°C. The temperature of substrate heater was controlled moderately with the help of temperature controller (Aplab 9601).

3.3 Dependence of the Spray rate:

The variation of solution spray rate with atomising air pressure and with the height of liquid is studied. It is found that the spray rate varies with air pressure and with height of solution(7). The spray rates, for different air pressures, are measured by keeping height of the solution constant. Solution level is measured with reference to the tip teep of nozzle. The spray rate increases with increase in an air pressure. However, it attains saturation at higher pressures. During film deposition air pressure is kept constant at a moderate value, because at lower air pressure droplets are not fine and uniform. At the higher pressures it is difficult to maintain the temperature of substrate heater. The spray rate increases with height of solution and remains constant above + 20 cm for that specific nozzle. Saturation height varies from nozzle to nozzle.

3.4 Deposition of Films:

3.4.1 Substrate Cleaning:

Careful cleaning of substrates is very important factor to obtain uniform and adhesive films. The microslides of size 3.8 cm X 1.13 cm X 0.1 cm, supplied by Bluestar, have been used as glass substrates. Initially glass substrates are cleaned by chromic acid and detergent " Teepol " solution. After that glass substrates are cleaned by double distilled water and finally dried in alcholic vapours. Such glass substrates have been used for the deposition of Bi_2O_3 films.

3.4.2 Preparation of Solution:

The 99% pure A R grade bismuth nitrate $[Bi(NO_3)_3\ 5H_2O]$, supplied by division of glaxo laboratories (India) Ltd., Bombay, is used for the preparation of Bi_2O_3 films. The measured quantity of bismuth nitrate is dissolved in very small quantity of nitric acid and required volume is made by addition of freshly prepared double distilled water. 0.1 M solution is prepared and used for deposition of films.

3.4.3 Deposition of Bi_2O_3 Films:

The films are prepared by spraying an aqucous solution (0.1 M) of bismuth nitrate on the heated substrates. Solution is sprayed by an atomizer spray nozzle and spray rate is controlled by mechanical value. Keeping nozzle fixed, the 100 C.C. solution of $Bi(NO_3)_3$ is sprayed at a fixed temperature 550°C. The height of solution was zero. Suitable air pressure was adjusted. After the solution is sprayed on the hot substrates, thermal decomposition of bismuth nitrate takes place as follows:

$$2\,Bi\,(NO_3)_3 \xrightarrow{\Delta\ (550^{\circ}C)} Bi_2O_3 + 6NO_3$$

Thus series of Bi_2O_3 films of uniform thickness are grown on the conducting and non conducting glass substrates. Films are allowed to cool slowly in the chamber itself on the substrate heater. The gases evolved during the decomposition of bismuth nitrate, are exhausted. Uniformity of the film depends on different parameters such as spray rate, solution concentration and substrate temperature.

3.4.4 Preparation of Bi_2S_3 Films:

Being low band gap semiconductor, Bi_2S_3 is attracted by many of researchers because it covers maximum span of solar spectrum. Hence in the present investigation an attempt has been made to prepare Bi_2S_3 films from Bi_2O_3 films by dipping later in to the solution of sodium sulphide $[Na_2S]$ (0.1 M) for five seconds. These films then, are rinsed by double distilled water and dried.

$$Bi_2O_3 + 3Na_2S + 3H_2O \rightarrow Bi_2S_3 + 6NaOH$$

3.5 Thickness of the Films:

Film thickness is an important parameter in the study of film properties such as conductivity, light transmittance, light absorption etc. Thus to characterise the film it is often necessary to measure the film thickness. Thickness is defined as the distance, perpandicular to the surface from a point on boundary surface, through the film, to other boundary surface. If the boundary surfaces are rough or non parrallel, the thickness is not well defined. The following methods have found widest application in the thickness measurement
(i) weighing (ii) stylus (iii) multiple beam interferometry
(iv) β - ray back - scattering (v) x-ray fluroscence.

Out of these methods weighing method is simpler and used for the measurement of thickness (> 2800°A) using the relation:

$$t = \frac{m}{A\ \rho_B} \qquad ---- \qquad (3.1)$$

where A - is area of film

ρ_B - is density of material in the bulk form which is 8.9 gm/cm^3 for Bi_2O_3 and 7.6 gm/cm^3 for Bi_2S_3.

-0-

Figure Captions:

3.1 Spray Pyrolysis technique for deposition of films.

1) Spray nozzle.
2) Substrate heater.
3) Temperature controller.
4) Mechanical valve.
5) Gas flow meter.
6) Rotor for spray nozzle.
7) Speed controller for rotor.
8) Exit to gases.
9) Liquid level adjustment.

...

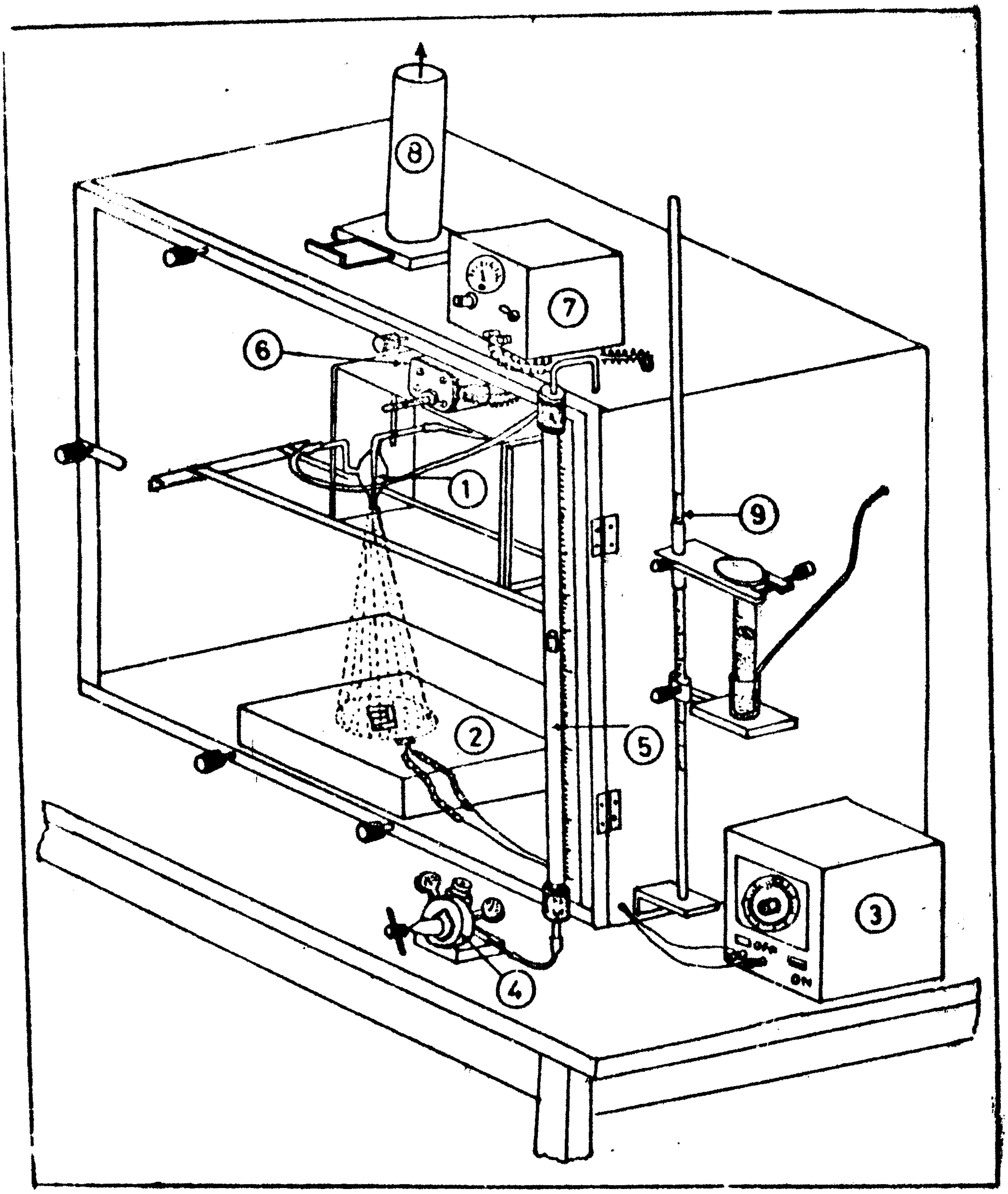

FIG. 3·1

References:

1. K.L.Hardi and A.J.Bard, Electrochem. Acta. 122, 739 (1975) 123, 1024 (1976).
2. K.L.Hardi and A.J.Bard, J.of Electrochem. Soc. 124, 215 (1977).
3. J.S.Curran and W.Gissler, J.of Electrochem. Soc. 126, 56 (1979).
4. D.Shub, A.Remenev and V.Vesclovski 11, 616 (1975).
5. N.R.Pawaskar, C.A.Menezes, and A.P.B. Sinha, J.Electrochem. Soc. 124 743 (1977).
6. R.R.Chamberlin and J.S.Skarman, This journal, 113 86 (1966).
7. M.D.Uplane and S.H.Pawar, Indian J.Pure & Applied Phy. submitted.

-000-