CHAPTER-III

Spray Pyrolysis Technique and Deposition of Mn - Oxide Films.

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3.1 Introduction

Several methods were used for depositioin of thin films /1-6/. The choice of the particular method depends on the several factors like material to be deposited, nature of the substrate, required film thickness, structure of the films, application of the film, area to be deposited, etc. The techniques for the deposition of thin films may be broadly classified as (a) physical methods:- vacuum evaporation, sputtering and evaporation by electron bombardment and (b) chemical methods :- Chemical vapour deposition, electrophoresis, chemical bath deposition, solution gas interface, electroplating, dip and dry and spray pyrolysis /7-8/.

The techniques like vacuum evaporation, sputtering and evaporation by electron bombardment have certain drawbacks and difficulties like careful and precise control of boat temperature to obtain the good stoichiometric films and to obtain the particular composition in the alloy films. Chemical methods are relatively economical and simple one as compared to physical methods. The chemical methods listed above have some drawbacks and advantages over the other methods. However, there is no ideal method to prepare thin films.

Among the chemical methods mentioned above, solution spraying technique is most popular today because of large number of conducting and semiconducting materials are prepared by this technique /9-14/. Also it has certain unique advantages over currently used chemical deposition techniques i.e. low cost, inexpensive, simplicity in assembly and operation.

Production of oxide films by spraying suitable solution on the preheated substrates is a convenient and economic one. The main advantage of spray pyrolysis technique is its ability to produce thin films with better uniformity, reproducibility and adherence over large surface areas.

In this technique, the choice of starting ingradients, composition of the starting solution spray rate and substrate temperature are needed to be optimized because these parameters determine the homogeneity and crystallinity of the film.

In this chapter the principle and mechanism of spray pyrolysis technique is given in Section 3.2. The Section 3.3 gives the details of fabrication and development of the spray pyrolysis setup. The procedure of deposition of Mn-oxide and SnO_2:F films are given in Section 3.4. The dependence of the spray rate on the pressure and height of the solution is also studied in Section 3.5 and general observations on the quality of the films are given at the end.

3.2 Spray Pyrolysis Technique : Principle and Mechanism :

Spray pyrolysis technique consists of a thermally stimulated chemical reactions between clusters of liquid or vapour atoms of different chemical species. According to the definition of thin film formation processes, spray-pyrolysis lies somewhere between a thin film and thick film techniques, depending on atom and cluster size. It involves spraying of a solution usually aqueous containing soluble salts of the constituent atoms of the desired compound on the preheated substrates. Every sprayed droplet reaching to the surface of hot substrate undergoes pyrolytic [endothermic] decomposition and forms a single crystallite or a cluster of crystallites as a product. The other volatile byproducts and excess solvent escape in vapour phase. The hot 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 a uniform and coherent film. The automization of the chemical solution into a spray of fine droplets is affected by the geometry of a spray nozzle with the help of carrier gas which may play an important role in pyrolytic reaction involved.

The spray pyrolysis setup consists of solution reservoir, filter, solution container, an air compressor, gas regulator (control volve), sprayer, heater, rotor, speed controller, spray chamber, temperature controller and exhauster.

The spray pattern, distribution of droplets and spray rate depend sensitively on geometry of nozzles. In the present work we have used the nozzle shown in fig. 3.3 which yields the uniform and reproducible films. Good quality (optical) and smooth films are obtained when both the size and momentum of the spray droplets are uniform. The liquid droplet tends to flatten out on impact on the substrate surface due to its momentum. The radially outward forces are balanced by the surface tension and thus droplets spread over the substrate in disc shaped structure. The disc geometry depends on the momentum and volume of the droplets and substrate temperature The random disc-by-disc growth exposed to a continuous flow of pressurized liquid droplets eliminates microscopic and macroscopic voids and cavities in the growing film. Thus spray deposited films are pinhole free even at 0.1 μm thickness provided the substrate temperature is sufficiently high for complete pyrolytic reaction. The microstructure and quality of the films depend on deposition conditions such as spray nozzle geometry, carrier gas pressure, liquid flow rate droplet velocities, temperature of substrate, kinetic and thermodynamics of the pyrolytic reactions and temperature profile during deposition process.

On thermal decomposition, the chemicals used for spray pyrolysis in a solution form should provide the species/

complexes to undergo a thermally activated chemical reaction to yield the desired thin film of a particular material. The remaining byproducts of the constituents of the chemicals including the solvent should be volatile at the deposition temperature. These conditions must be satisfied by the chemicals which produce required compound material. Different optimized deposition parameters are required to obtain comparatively reproducible films for different chemicals.

3.3 Experimental setup for Spray Pyrolysis Technique :

In the present investigation the spray pyrolysis technique is designed, developed in our laboratory is described in detail.

The schematic diagram and photograph of experimental setup is shown in fig. 3.1 and fig. 3.2. It consists of mainly i) spray nozzle ii) rotor for spray nozzle iii) speed controller for rotor iv) liquid level monitor v) gas flow meter and vi) substrate heater.

a) Spray nozzle

It is made up of a glass which is specially designed to spray the solution. The spray pattern, size distribution of droplets and spray rate sensitivity depend on the geometry of the nozzle. Out of a variety of nozzles, the nozzle which gives good quality (optical) films and suitable for our experimental setup is shown in fig. 3.3.

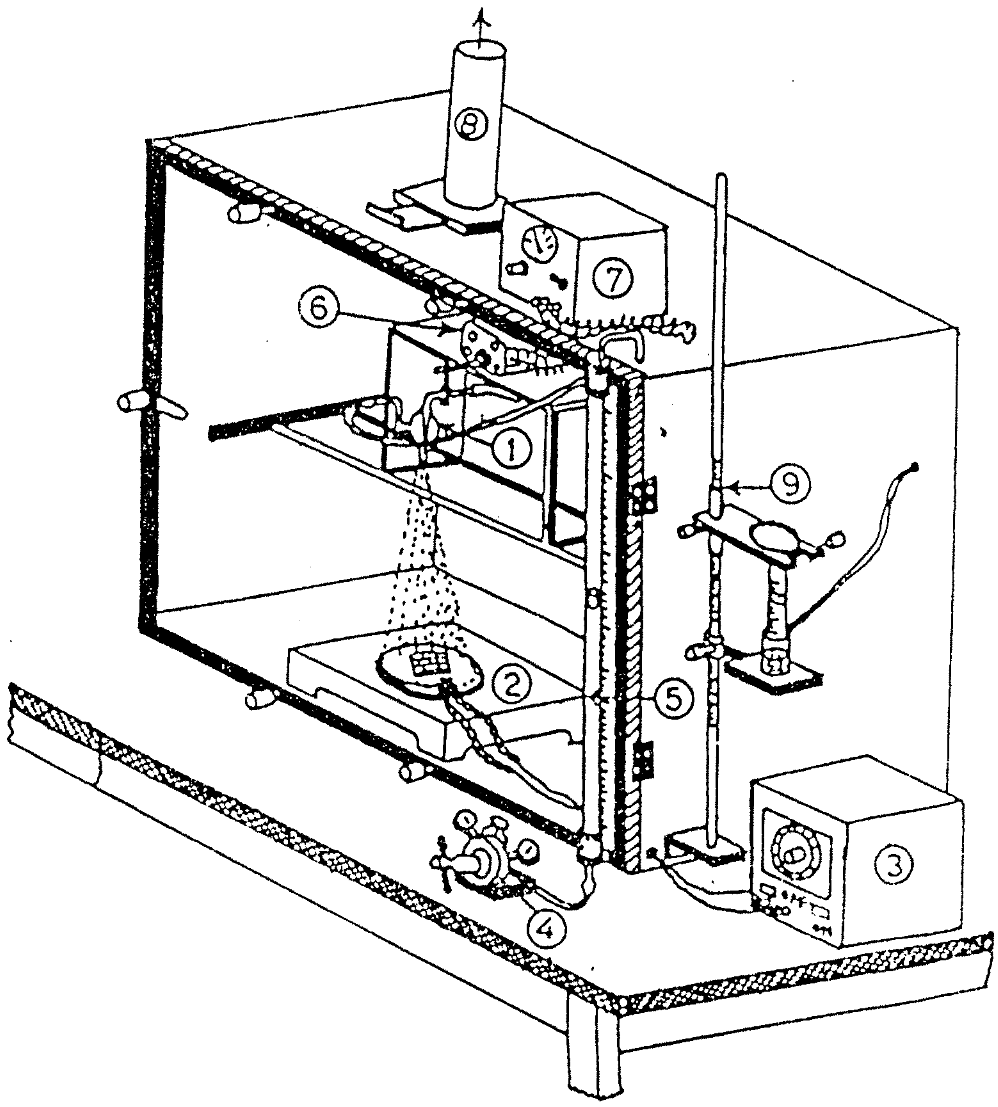

Fig. 3·1. The schematic diagram of experimental set-up for spray pyrolysis technique
1) Spray nozzle 2) Hot plate 3) Temperature controller 4) Gas valve 5) Flow meter
6) Roter 7) Speed controller 8) Exhaust
9) Liquid level adjustment.

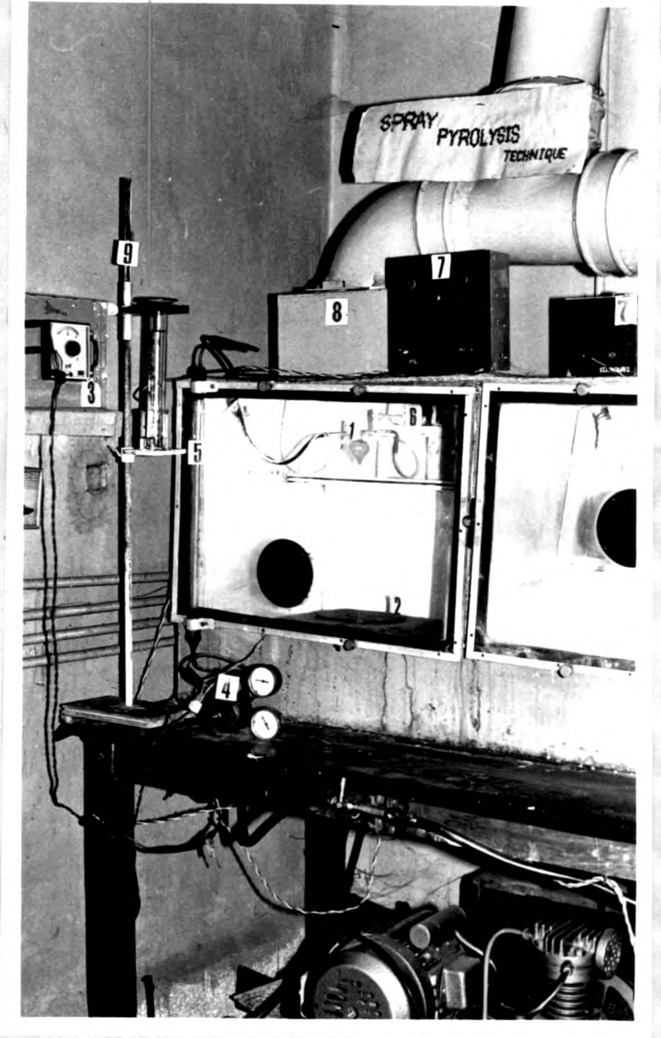

Fig. 3.2 Photograph of the spray-pyrolysis system.

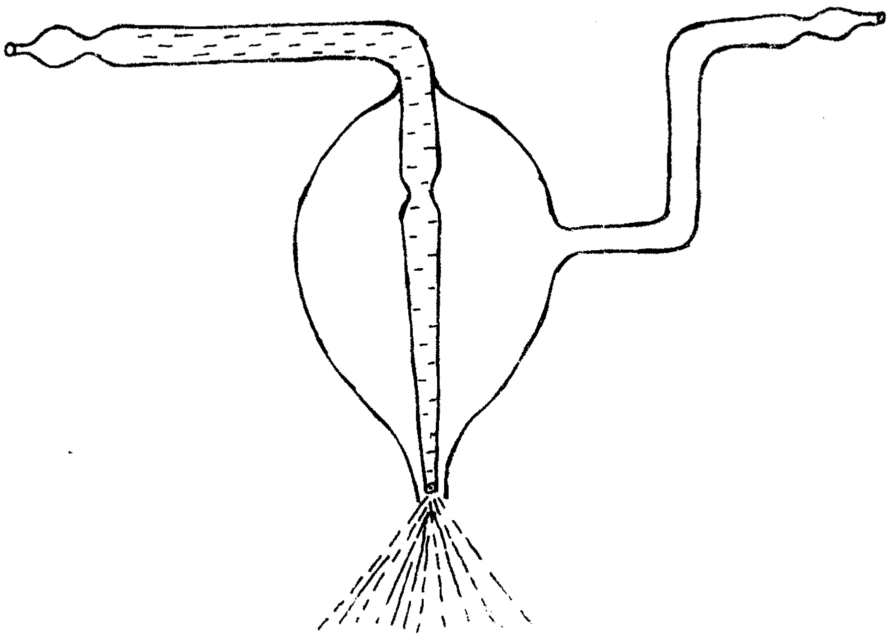

Fig. 3.3 Typical type of glass spray nozzle used for experimental setup.

It consists of mainly two parts 1) solution tube and 2) carrier gas tube. When pressure is applied through the carrier gas tube vacuum is created at the tip of the solution tube and solution is automatically suck through the solution tube and spraying is started.

b) Rotor for spray nozzle

The wiper motor [Mitsuba, made in Japan (12 V)] is used as a rotor to oscillate the nozzle. This helps to maintain the substrate temperature and to deposite uniform films. If the nozzle is in motion then uniform deposition over 7 to 8 inch distance is observed. If the nozzle is kept at a fixed vertical position then the temperature does not remain constant but falls down to a large extent. Hence, it is kept oscillating. Speed of the rotor is controlled by a speed controller circuit shown in fig. 3.4. Block A is a rectifying circuit and B is the well known complementary emitter follower circuit. The output voltage can be varied from 0-12 volts with the help of resistance R_1. The current capacity of the controller is 2 Ampere. Rate of oscillation of the spray nozzle is changed with the help of this circuit. One can determine the speed of the rotor by counting the number of oscillations per second.

c) Substrate heater

Substrate heater is specially designed to obtain the uniform temperature upto 600°C. The seven inch diameter porcellin base of electrical stove with 2000 W heating coil

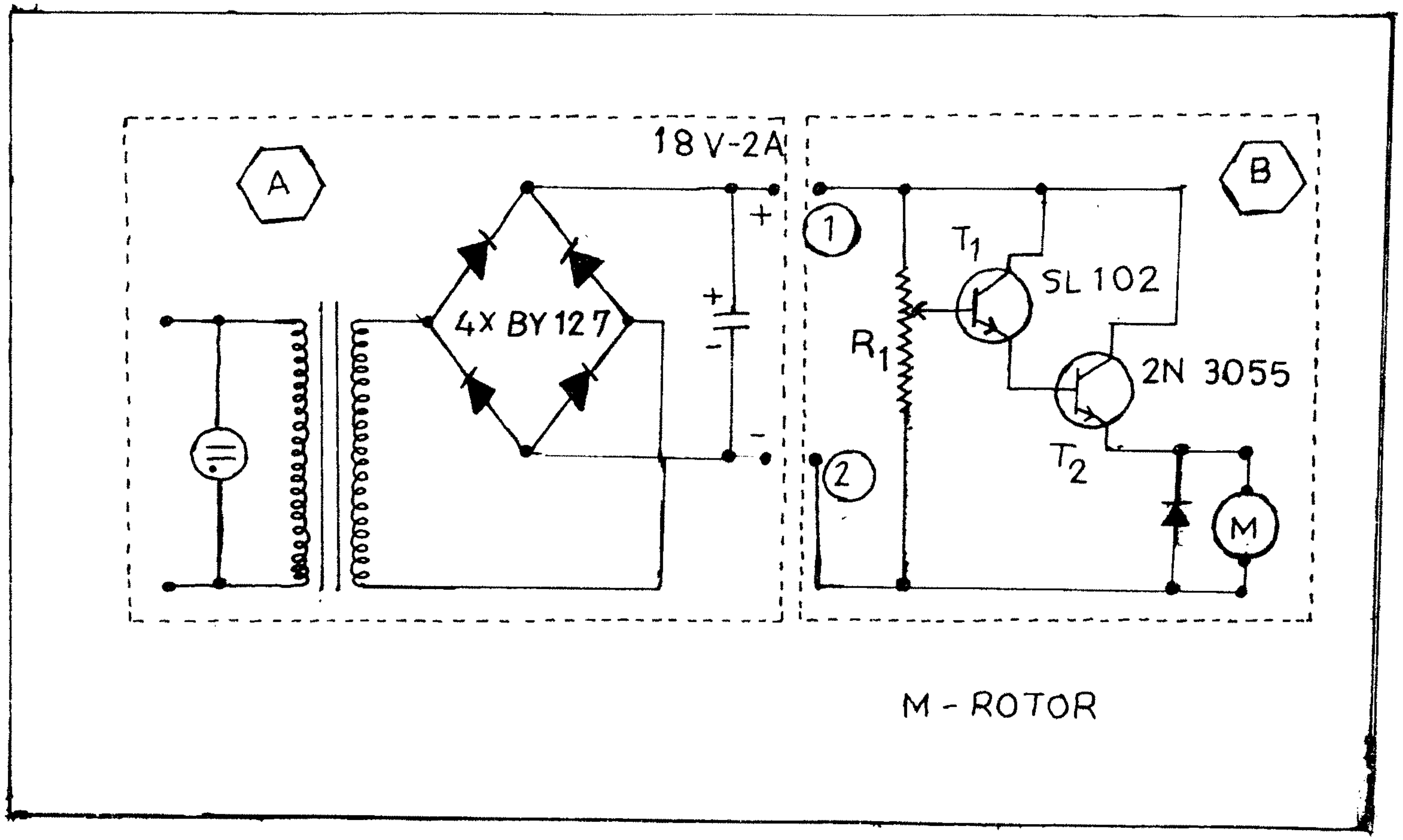

Fig. 3.4 Circuit diagram of the speed controller.

(20 gauge) was fixed in the fireclay to avoid the radiation losses. The whole assembly is then fixed in an aluminium frame. The iron plate of thickness 0.6 cm and diameter 18 cm was used as a hot plate to support the substrate. The Chromel-Alumel thermoccuple was fixed on the iron plate by using the screws and used to measure the temperature of the substrates. The temperature of the substrates was controlled with the Aplab temperature controller (Model-9601). The uniform temperature is observed at the centre of the iron plate.

d) Gas regulator

Gas regulator is a mechanical valve which is used to govern the air pressure from the compressor. As most of the film properties depend on the spray rate and ultimately spray rate is depending on the pressure of a gas. Therefore, one has to optimize the spray rate which is done with the help of a gas regulator. The variation in pressure is indicated by the gas flow meter. The gas flow meter consists of a glass tube of diameter 1.5 cm and of length 25 cm with the scale on back side. The rider inside the tube indicates any change in pressure by changing its steady position. The gas flow meter is fixed vertically on one side of the door of a chamber.

e) Gas exhauster

Since number of gases such as chlorine, fluorine and carbondioxide are evolved during spray which are very toxic in nature, it is necessary to remove these gases from the chamber as soon as they are evolved. This is done with an exhauster.

f) Liquid-level monitor

This is an arrangement which helps to maintain the flow of a spraying solution. It consists of a scaled iron rod of length 40 cm fixed in the wooden stand near gas flow meter. Two backelite stands are fixed on this rod which are used for support a beaker and the measuring cylinder which is hanged in the beaker. This arrangement maintains the constant gravity pressure. The change in height of the assembly changes the spray rate. It is explained in Section 3.4.

3.4 Procedure of Film Formation :

a) Substrate cleaning

In the thin film deposition process substrate cleaning is the important factor to get reproducible films as it affects smoothness, uniformity, adherence and porosity of the films. The substrate cleaning process depends upon the nature of the substrate, degree of cleanliness required and nature of contaminants to be removed. The common contaminates are grease, absorbed water, air-borne dust, lint, oil particles, etc.

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. The following process has been adopted generally for cleaning the glass and conducting glass substrates.

i) The substrates were washed with the detergent solution 'Teepol' and then with double distilled water.

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

iii) After that substrates were cleaned in distilled water separately.

iv) To remove the acidic contamination, substrates are kept in NaOH solution for few minutes.

v) Then substrates were again washed with distilled water, boiled for five minutes in distilled water and cleaned ultrasonically.

vi) Finally the substrates were dried in vapour of alcohol.

b) Preparation of solution

All the solutions were prepared in freshly prepared double distilled deionized water.

The chemicals used for preparation of Mn-oxide films and the conducting glasses are as given below:

i) A.R.Grade Manganese Chloride [$MnCl_2,4H_2O$] supplied by Chemco Fine Chemicals, Bombay.

ii) Stannic Chloride [$SnCl_4$, $5H_2O$] supplied by Loba-Cheme Inudstrial Company, Bombay.

iii) Ammonium Fluoride (NH_4F) supplied by Thomas Baker.

iv) Iso-propyl alcohol [$(CH_3)_2CHOH$] supplied by B.D.H. (India).

c) Deposition of conducting substrates (F.T.O.)

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 20 wt.% doping concentration of fluorine. From the above mixture 5 cc solution was taken and 20 cc of propen 2-01 (iso-propyl alcohol) was added. The final solution was sprayed through a glass nozzle with spray rate 6 cm^3/min. The substrate temperature was maintained at 550°C. And then the substrates allowed to cool at room temperature. These fluorine doped SnO_2 glasses are tested for their conducting nature by measuring their resistances. It is found that these conducting glasses have 10-20 Ω/cm^2 resi stance and near abot 90% transparency.

d) Deposition of Mn-oxide films

The solution prepared as mentioned above is used to deposit Mn-oxide films at different preparative parameters such as substrate temperature, concentration and spray rate. 120 cc of solution is used for spraying and both conducting and nonconducting substrates are used for deposition.

3.5 Optimization of Preparative Parameters :

3.5.1 Spray Rate

In spray pyrolysis technique it is found that the spray rate is varied with change in air pressure and height of the solution and are studied one by one.

i) Pressure dependent spray rate

The spray rate is measured by keeping height of the solution constant and by varying the air pressure. The solution level is kept at the height of the tip of the nozzle and is taken as a reference (zero) for solution height measurement. The variatioin of spray rate with pressure is shown in fig.3.5. It is seen that spray rate increases with increase in the air pressure and saturation is observed at higher pressure. Other effects are also observed with very high pressure that is the substrate temperature could not remain constant and the presence of residual gas molecules and other contaminations affect the characteristics of the film to a great extent. These molecules get incorporated in the vapour and hence in the film structure. If these gas molecules react chemically with the vapour atoms, the film formed may be of the resulting compounds and hence may have structure and properties totally different from that of the initial substance evaporated. Whereas at very low pressure instead of fine spray only large droplets of the solution falls directly on the substrates. Therefore, 2.5 kg/cm^2 pressure is revealed

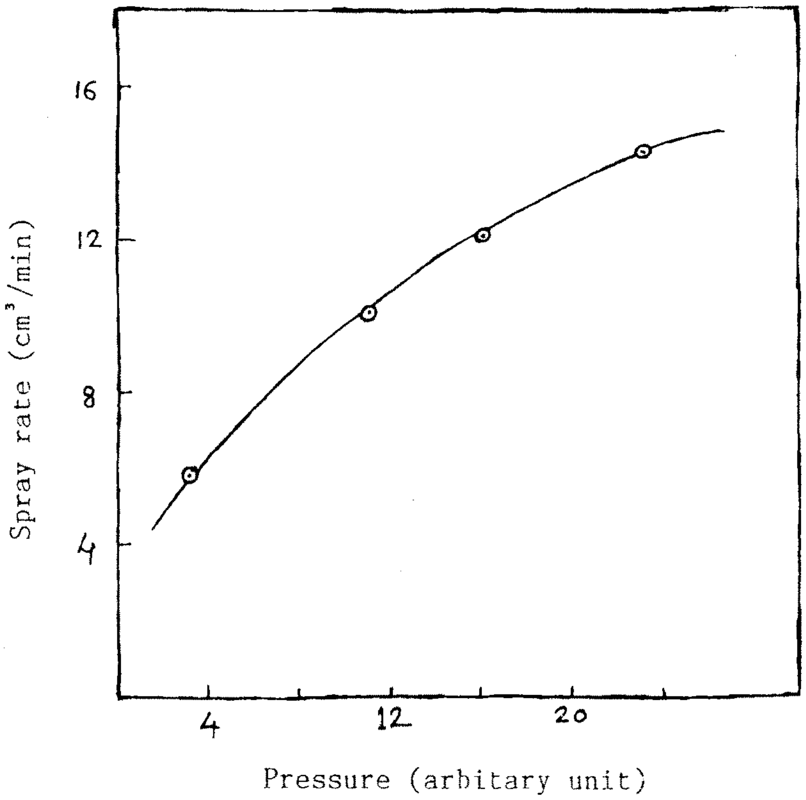

Fig. 3.5 Variation of spray rate with pressure.

as an observed optimum pressure of a carrier gas. The similar results have been observed by others /15/.

ii) Solution height dependent spray rate

The spray rate is varied by changing the height of the solution and these variations are shown in fig.3.6 (height of the solution below the tip of the nozzle is taken as -ve and above +ve). It is observed that the spray rate increases with height of the solution and remains constant above +16 cm The observed saturation in the spray rate is because of small bore of the spray nozzle and vary from nozzle to nozzle. The optimum spray rate is obtained 12 cc/min.

3.5.2 Substrate Temperature

Crystallinity and reproducibility of the film is affected by the change in substrate temperature. Therefore, the study of change in substrate temperature on growth of the film is of vital importance. Substrate temperature is changed from 250°C to 500°C. By observing electrical and optical properties of all films deposited on substrates having substrate temperature from 350°C to 450°C an optimum substrate temperature is revealed to be 400°C.

3.5.3 Concentration of Spraying Solution

Physical characteristics of a spray deposited films are also dependent on concentration of the spraying solution. Thus optimization of concentration of the spraying solution

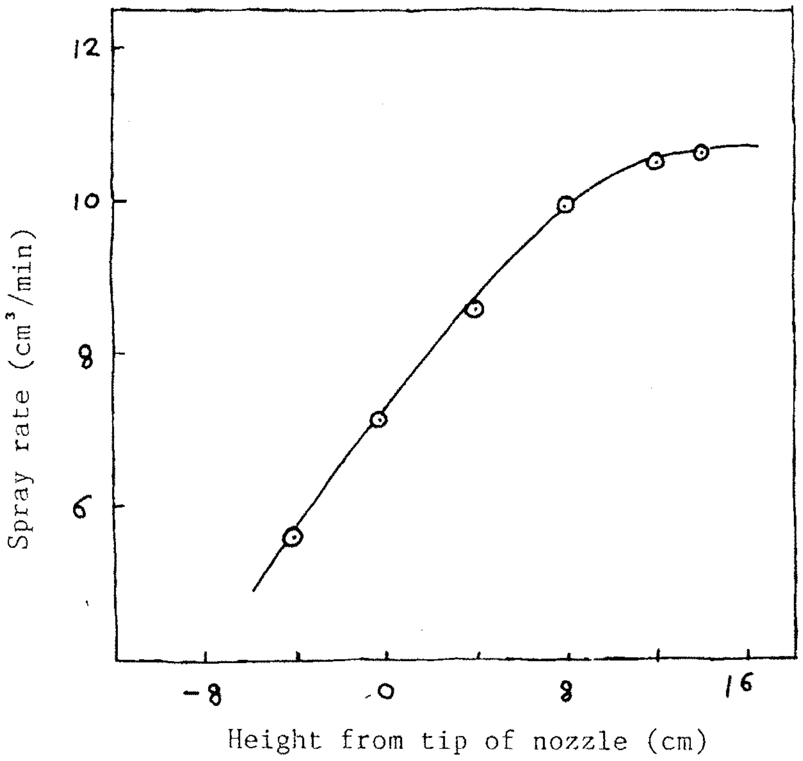

Fig. 3.6 Effect of height of the solution on spray rate.

is needed. In this study concentration of manganese chloride solution is varied from 0.1 M to 1 M. Physical appearance of the film is visualised with naked eyes. At very high concentration porous and nonuniform films are formed. At low concentration uniform films are formed but thickness of the same film is very small. It is found that at 0.25 M concentration non-porous, uniform and adhesive films of Mn-oxide can be formed.

3.6 General Observations :

Generally the oxides are formed at higher temperatures. Firstly 400°C temperature is selected as a substrate temperature. The $MnCl_2$ solution having 1 M, 0.5 M, 0.25 M and 0.1M concentratiion is sprayed with spray rate 12 cc/min on four different sets of conducting and non-conducting glass substrates kept at 400°C. For all concentrations sticky films are produced. But for 1M and 0.5 M concentrations films are porous and black-brown in colour. For 0.25 M and 0.1 M concentrations films are nonporous and reddish-brown in colour.

The study of transport properties [see Chapter V] shows that films prepared with 0.25 M concentration are more conductive. Thus 0.25 M concentration is taken for further study. This is in good agreement with the reported value /16/. For the selection of spray rate 0.25 M concentration solution is sprayed with the spray rates 6,8,10 and 12 cc/min. Only for 10 and 12 cc/min spray rates films are uniformly deposited on conducting as well as non-conducting glass substrates. But for 12 cc/min spray rate crystallinity is better as well as activation energy is in good agreement with the activation energy for Mn_2O_3 /17/. To fix the proper substrate temperature for better electrochemical effect $MnCl_2$ solution having 0.25 M concentration is sprayed with spray rate 12 cc/min, on the sets of conducting and non-conducting glass substrates which are maintained at 250,300,350,375,400,425 and 450°C. Films prepared at 250°C and 300°C substrate temperatures are faint brick colour and are not sticky. This may be attributed to incomplete decomposition of $MnCl_2$ to form Mn-oxide. Brown colour sticky films are formed at substrate temperatures 300, 375,400,425 and 450°C. At 450°C the films deposited on conducting glass are not uniform. Above 450°C i.e. at 475 and 500°C films do not form but few droplets are deposited. This may be attributed to increase in momentum, decrease in size of droplets and complete decomposition of $MnCl_2$ before reaching the glass substrate. For the films prepared at 400°C crystallinity is better and conductivity is more than the films which are deposited at 350,375 and 425°C substrate temperatures. Thus the films prepared at 400°C substrate temperature with 0.25 M concentration and 12 cc/min spraying rate may be useful for better study.

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