CHAPTER-VIII

Some Studies on Mn - Oxide Films Prepared by Chemical Bath Technique.

CHAPTER - VIII

SOME STUDIES ON Mn-OXIDE FILMS PREPARED BY CHEMICAL BATH TECHNIQUE

8.1 Introduction :

Mn-oxide films can be prepared by chemical bath technique /1/, spray pyrolysis as well as by oxidation of vacuum deposited 4N purity manganese films /2,3/. The chemical bath method is relatively simple and convenient, in which variety of substrates like metal, semiconductor and insulator can be used. Film deposition by this method is slow process which allows for better stoichiometry and crystallinity than other methods. Hence in the present investigation Mn-oxide films were also prepared by chemical bath deposition technique.

The preparation of Mn-oxide films and the study of electrical and optical properties are presented in this chapter. Section 8.2.1 gives the details of fabrications and development of the chemical bath deposition setup and sections 8.3 and 8.4 give electrical properties and optical properties respectively.

8.2 Experimental :

The chemical bath technique which is designed and developed in our laboratory is described in detail.

8.2.1 Experimental setup for Chemical Bath Technique :

The schematic diagram of chemical bath deposition chamber is shown in fig.8.1. It consists of mainly a] dust proof chamber b] chemical bath c] substrate holder and d] constant temperature bath.

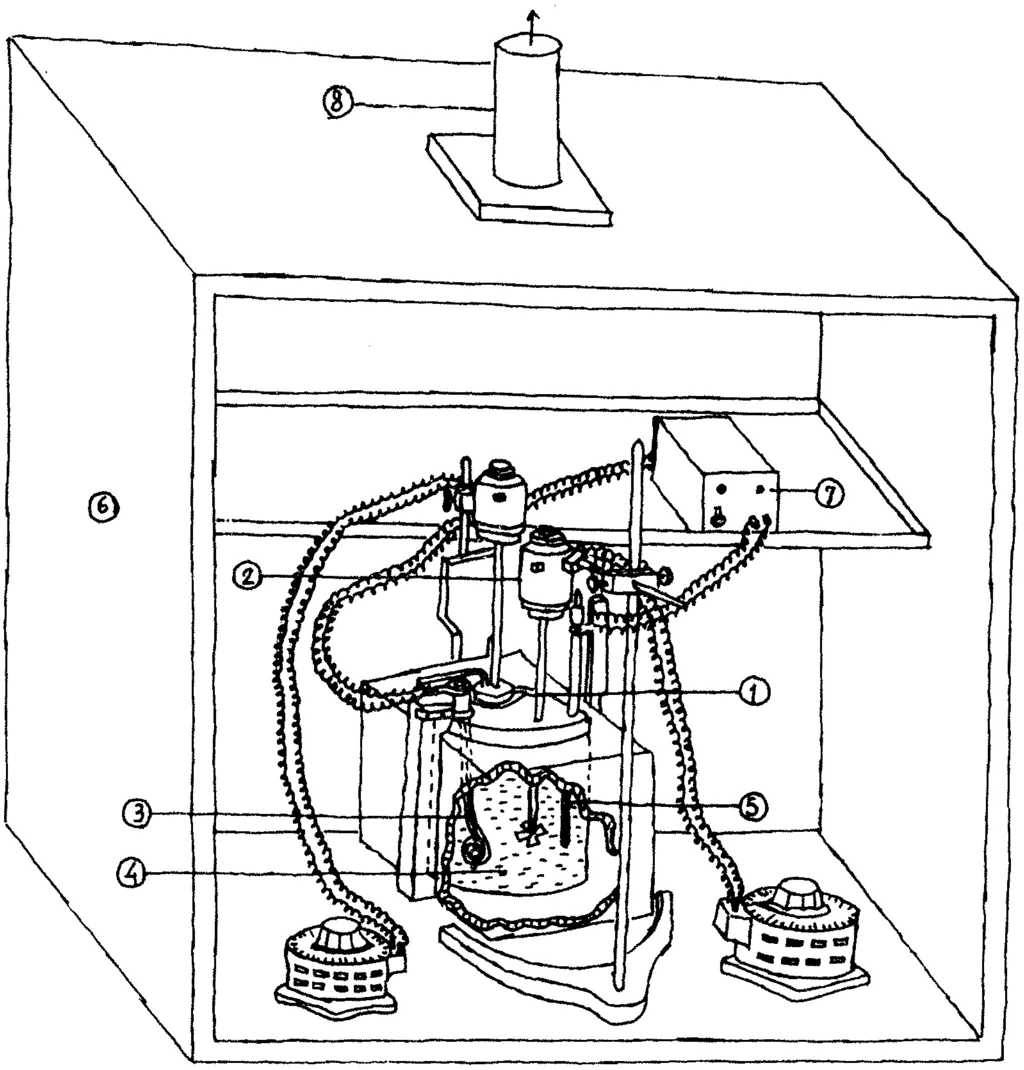

Fig. 8.1 Schematic diagram of chemical bath deposition chamber.

1) Chemical bath
2) Synchronous motors
3) Heater
4) Oil bath
5) Mercury contact thermometer
6) Dust proof chamber
7) Temperature controller
8) Exit for gases.

a] Dust proof chamber

A dust proof, clean metallic chamber of the size 1.1 x 0.8 x 1 meters was designed and constructed to avoid the contamination of the film due to dust particles. An outlet at the top of the chamber was fitted with exhaust fan to let the gases out.

b] Chemical bath

A corning beaker of 250 cc capacity acts as a chemical bath. It is filled with appropriate amount of reaction mixture of chemicals which are used to prepare Mn-oxide films. This reaction mixture along with the chemical bath was heated with the help of a constant temperature bath. The substrates were kept rotating in the chemical bath during film deposition.

c] Substrate holder

The quality of films produced in chemical bath deposition depends upon the geometry of the substrate. As the substrates at 90° gave uniform films, a substrate holder in which substrates make angle 90° with the diameter of the holder was used.

d] Constant temperature bath

Parafin oil was used for heating the reaction chamber in constant temperature bath. A cylindrical aluminium pot of 15 cm height and 7 cm diameter size was used as oil container which was kept in the wooden box to reduce the thermal losses. A 1000 watts heater was used to heat the oil and a synchronous motor was used to stirr the oil for maintaining uniform temperature. A mercury contact thermometer (Jumo, Germany make) with relay circuit was employed to control the oil bath temperature within ± 1°C.

8.2.2 Procedure of Film Formation

a] Substrate cleaning

Glass microslides (Blue star) of the size 75 x 10 x 1mm were used as the substrates. The following procedure was adopted for cleaning the glass substrates.

i) Substrates were boiled in chromic acid for five minutes and were washed with distilled water.

ii) Substrates were dipped in 'Teepol' detergent solution and again washed with distilled water.

iii) Substrates were cleaned with ultrasonic cleaner for 5 minutes and were exposed to alcohol vapours for some time.

iv) Substrates were kept immersed in double distilled water before use.

b] Preparation of Solutions

Chemicals used for preparing the Mn-oxide films were as follows:

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

ii) Ammonia solution supplied by B.D.H. (India) Laboratory reagent of sp.gr. 0.91.

iii) Ammonium chloride supplied by Glaxo Laboratories (India).

All solutions were prepared in double distilled water.

c] Deposition Procedure

100 cc of desired molar manganese chloride solution was taken into the 250 cc beaker and appropriate amount of ammonium chloride and liquor ammonia of concentrations 0.8 M and 0.28 M respectively were added at room temperature. The solution was continuously stirred during liquor ammonia addition. The pH of the solution was between 10.5 and 11. The reaction mixture was heated to 80°C in which substrates with constant speed, 110 rpm, were kept rotating. The substrates were taken out of the mixture after 30 minutes.

Films are also deposited at different substrate temperatures between 30°C and 90°C. The deposited films were washed with double distilled water to remove loosely bound Mn-oxide powder. The washed films were dried and preserved in a light proof desiccator.

8.2.3 Optimization of Preparative Parameters

There are variable preparative parameters in this method /4-6/. These are : (a) temperature of the chemical bath (b) deposition time (c) substrate holder geometry

(d) Speed of substrate rotation and (e) molar concentration of ingradiants. Out of these five parameters, deposition time, substrate holder geometry and speed of substrate rotation were kept fixed.

Temperature of the chemical bath :

Temperature of the chemical bath plays an important role in the film formation. In the chemical bath, there is no solid phase of manganese hydrous oxide present to enhance the decomposition of ammonium chloride. It is, therefore, expected that film formation will take place above certain temperature. Heating of the solution helps the decomposition of ammonium chloride and also provides kinetic energy to the ions, resulting in increased number of collosions and hence their combination to form Mn-oxide films. The films deposited at 80°C are found to be of uniform and maximum thickness.

Molar concentration :

Molar concentration of $MnCl_2$ and NH_4Cl was varied by keeping the other parameters fixed as mentioned above. Thin reflecting films were obtained with lower molar concentrations, while at higher concentrations thick and nonreflecting films were obtained.

By this process an adherent, mirror smooth and specularly reflecting films of brown coloured hydrous Mn_2O_3 were obtained from a bath of composition - $MnCl_2$ (0.02 M), NH_4Cl

(0.8 M), NH_3 (0.28 M) and the total volume = 200 cc. Films were annealed in vacuum at 250°C for one hour. A brief account of the chemistry of the reaction of formation of good quality Mn-oxide film is being given below.

8.3 Growth Mechanism of Mn-oxide films :

Ions of Mn^{2+} do not yield precipitate of $Mn(OH)_2$ as they are not sufficiently acidic to react with NH_3 solution. On the other hand in alkaline solutions Mn^{2+} ions are rapidly oxidized to Mn^{3+} ions by atmospheric oxygen and are acidic enough to yield precipitate of $Mn(OH)_3$ which is not defined compound but an indefinite hydrous oxide form Mn_2O_3, H_2O. Also the addition of alkali metal hydroxides to a solution of Mn^{2+} ions yields precipitate of $Mn(OH)_2$ which on air oxidation produces Mn_2O_3, xH_2O. The oxidation product of divalent manganese in basic solutions depends upon a number of factors such as concentration of solution, the oxidant, the temperature and period of oxidation. Mn_2O_3, xH_2O on drying at 100°C gives MnO(OH). On dehydration of Mn(OH) in vacuum at 250°C yields γ- Mn_2O_3.

The fraction of NH_4Cl in chemical bath is to reduce the rate of reaction resulting in thicker films. Thus the overall reaction is

$$Mn^{2+} \xrightarrow[\text{alkaline}]{\text{air}} Mn_2O_3, xH_2O \xrightarrow{100^\circ C} MnO(OH) \xrightarrow{250^\circ C} Mn_2O_3 .$$

The Mn-oxide films which were prepared by chemical bath method at different substrate temperatures were used to study electrical and optical properties. Also the annealing effect on optical properties were discussed.

8.4 Electrical Properties of Mn-oxide Films :

Experimental setups for the measurement of the dark conductivity and thermoelectric power are as described in Chapter-V.

Dark conductivity:

The dark conductivity of all the films is measured in the temperature range between 300°K and 450°K. The increase in conductance with rise in temperature indicates the semiconducting behaviour of Mn-oxide films. The fig. 8.2 gives the variation of log R with 1/T for the films which are deposited at different substrate temperatures. The values of activation energy calculated from the slopes of these plots are tabulated in table 8.1.

Fig. 8.3 shows the variation of conductivity with substrate temperature. The conductivity increases with the substrate temperature. It is maximum for 40°C substrate temperature and then decreases with increase in the substrate temperature. The maximum conductivity at 40°C substrate temperature may be attributed to better crystallinity.

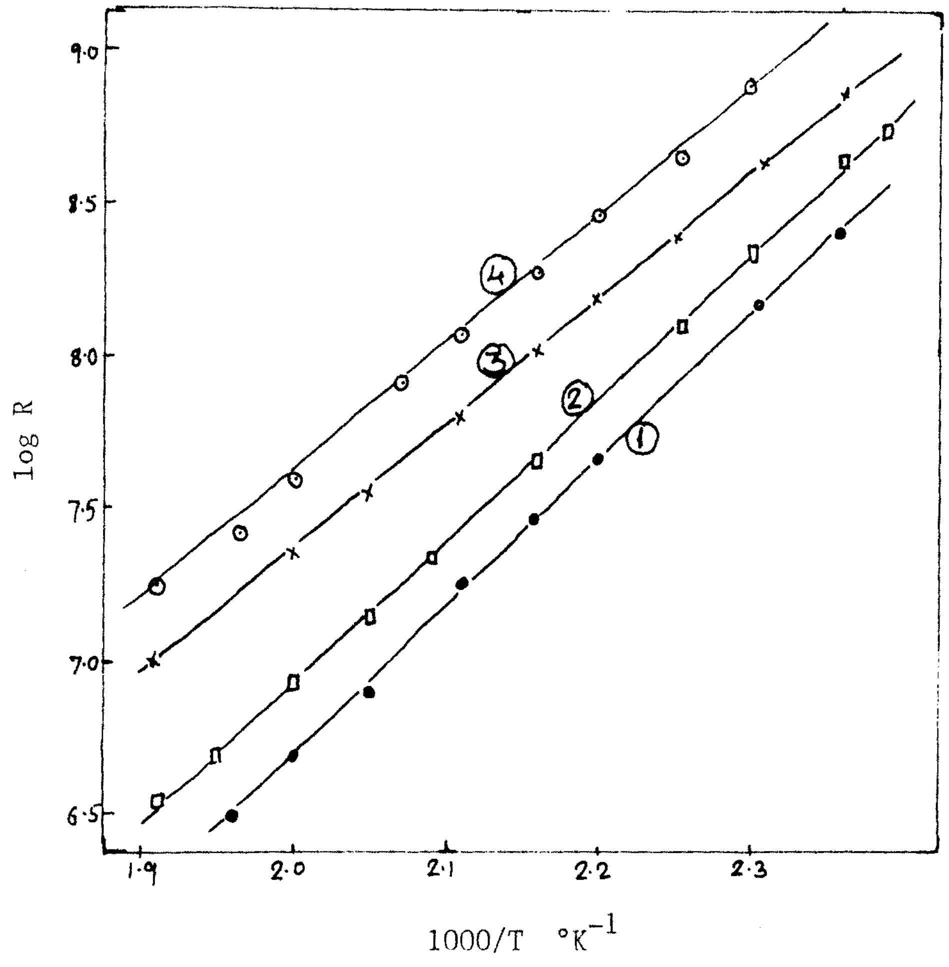

Fig. 8.2 Plots of log R versus 1000/T for Mn-oxide films deposited at different substrate temperature
(1) 40°C (2) 60°C (3) 50°C and (4) 80°C

Table No. 8.1

Activation Energy Chart

Substrate Temperature in °C	Activation energy in eV
30	0.83
40	0.83
50	0.69
60	0.75
70	0.70
80	0.68

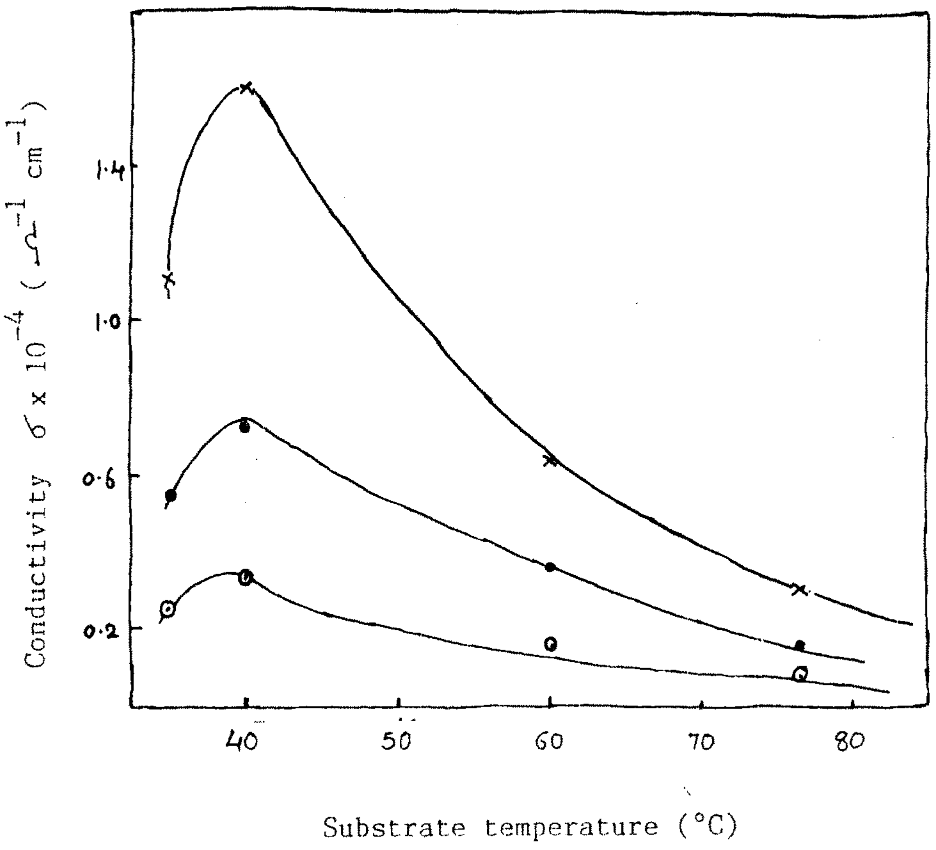

Fig. 8.3 Plot of conductivity versus substrate temperature.

Thermoelectric power :

The thermoelectric power is measured in dark as a function of temperature in the range between 300°K to 450°K for all samples. From the polarity of the thermo e.m.f. it is found that all the films studied are of p-types. It is seen that thermoelectric power increases with increase in mean temperature. This may be attributed to decrease in concentration of the free holes at higher temperatures as discussed in Chapter-V. The film deposited at 80°C substrate temperature has maximum thermoelectric power as compared to the films deposited at other substrate temperatures.

8.5 Optical Properties of Mn-oxide Films :

Optical density and transmission were measured with the help of monochromator (Spekol, Carl Zeiss Jena) in the wavelength range 7500 A° to 4300°A.

The absorption coefficient is evaluated from optical density (αt) which is found to be of the order of 10^3 to 10^4 cm^{-1}. Low values of absorption coefficient indicate indirect bandgap material. Band gap energy of Mn-oxide is determined from the plot of $\alpha^{\frac{1}{2}}$ versus $h\nu$. The nature of the plot is as shown in fig. 8.4. The bandgap energy is found to be of the order of 2.6 eV and is affected by substrate temperature but unaffected by annealing.

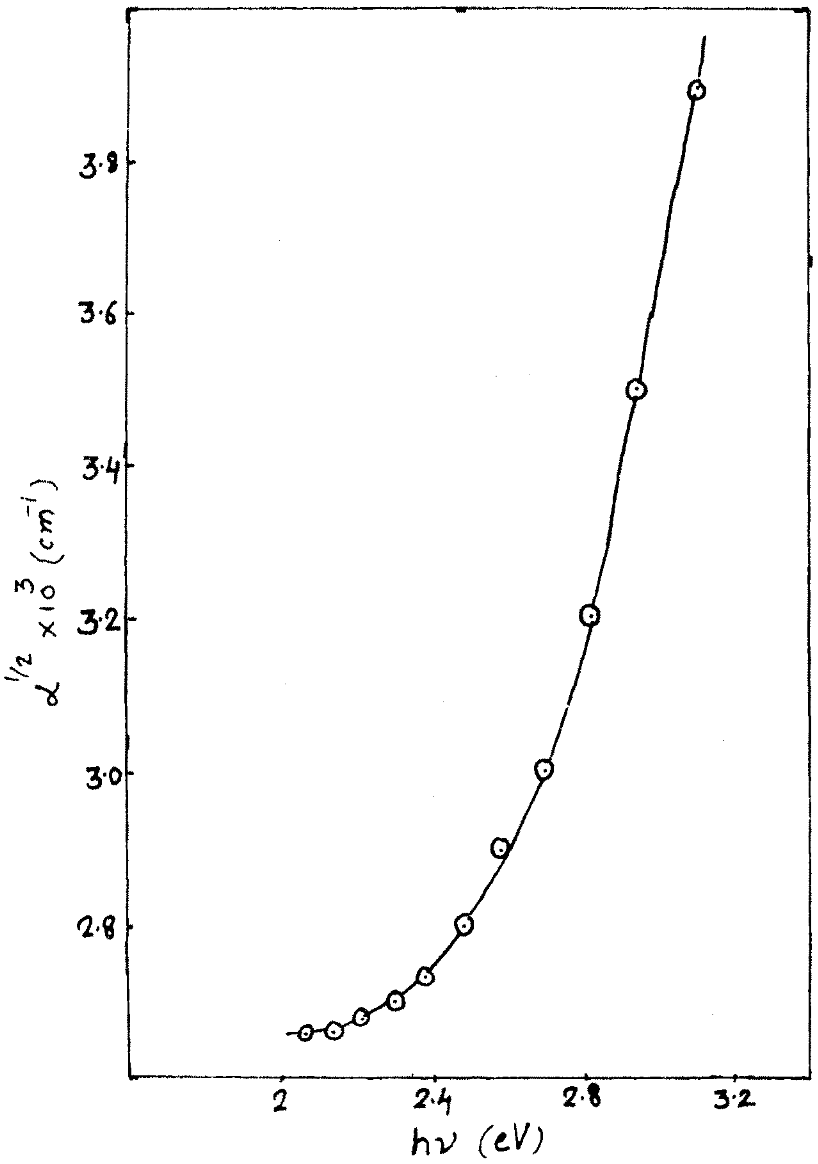

Fig. 8.4 $\alpha^{\frac{1}{2}}$ versus hν for a typical sample.

Fig. 8.5 shows the variation of transmission (T) with wavelength (λ) for the Mn-oxide films which are prepared at different substrate temperatures ranging from 30°C to 80°C. Beyond certain wavelength transmission remains nearly constant and below this wavelength transmission decreases with the decrease in wavelength for all the films except the film deposited at 30°C substrate temperature. For this film the transmission increases with the increase in wavelength. Due to the constancy of transmission beyond certain wavelength Mn-oxide films can be used as filters for radiations. Fig.8.6 shows the variation of transmission with wavelength for a particular film before and after annealing. After annealing the transmission slightly increases.

Thickness :

The film thickness of all the samples was measured by interference method /7/. Fig.8.7 shows the variation of thickness with substrate temperature. A straight line graph indicates the increase in thickness with increase in substrate temperature. This may be attributed to complete formation of Mn-oxide at higher substrate temperatures. At 30°C and 40°C substrate temperatures the graph shows slight deviation from the straight line. This may be due to incomplete reaction of these substrate temperatures. At 80°C substrate temperature the thickness of the film is maximum. Hence this substrate temperature is proper temperature for film deposition.

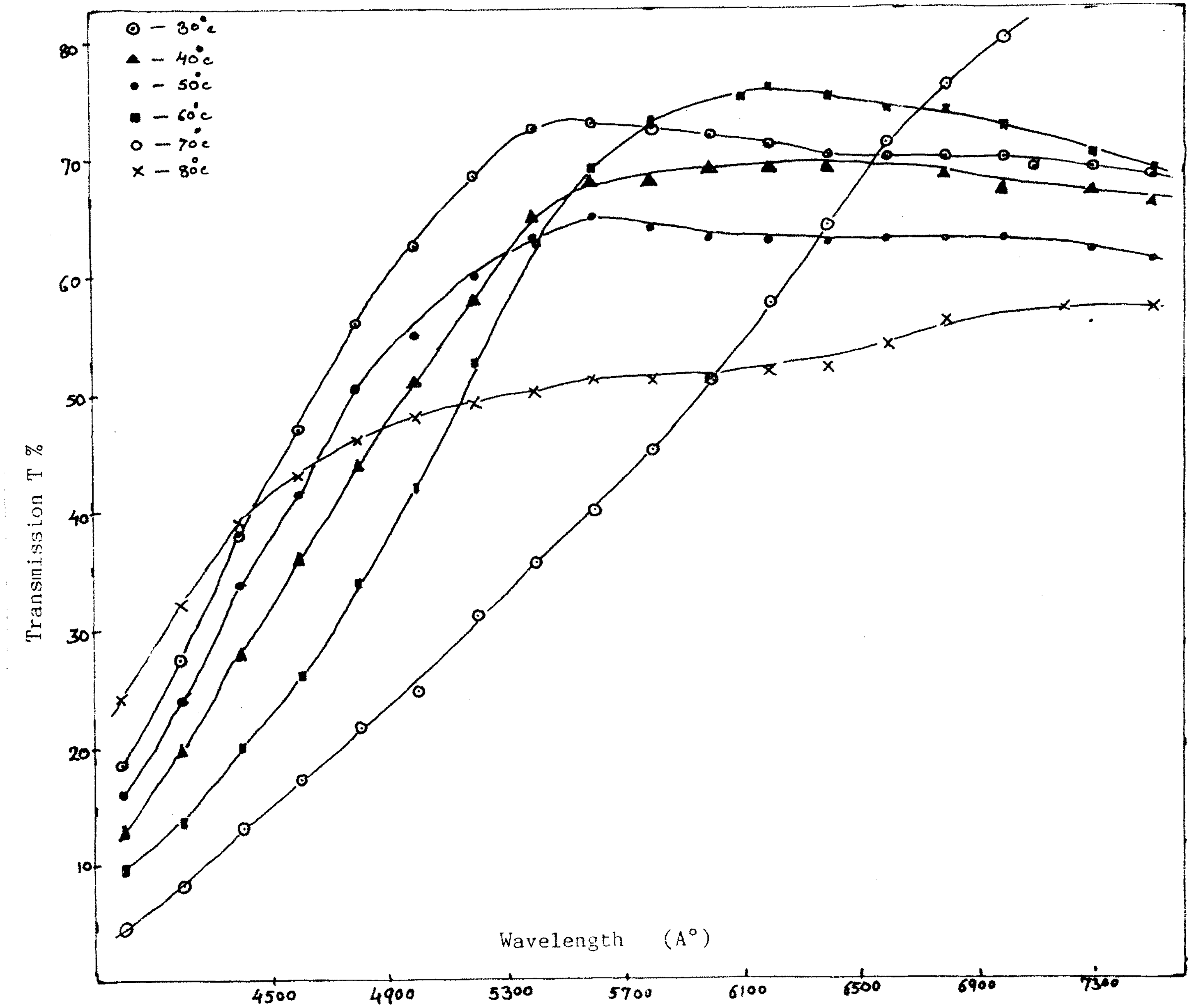

Fig. 8.5 Variation of transmission with wavelength for Mn-oxide films deposited at different substrate temperature.

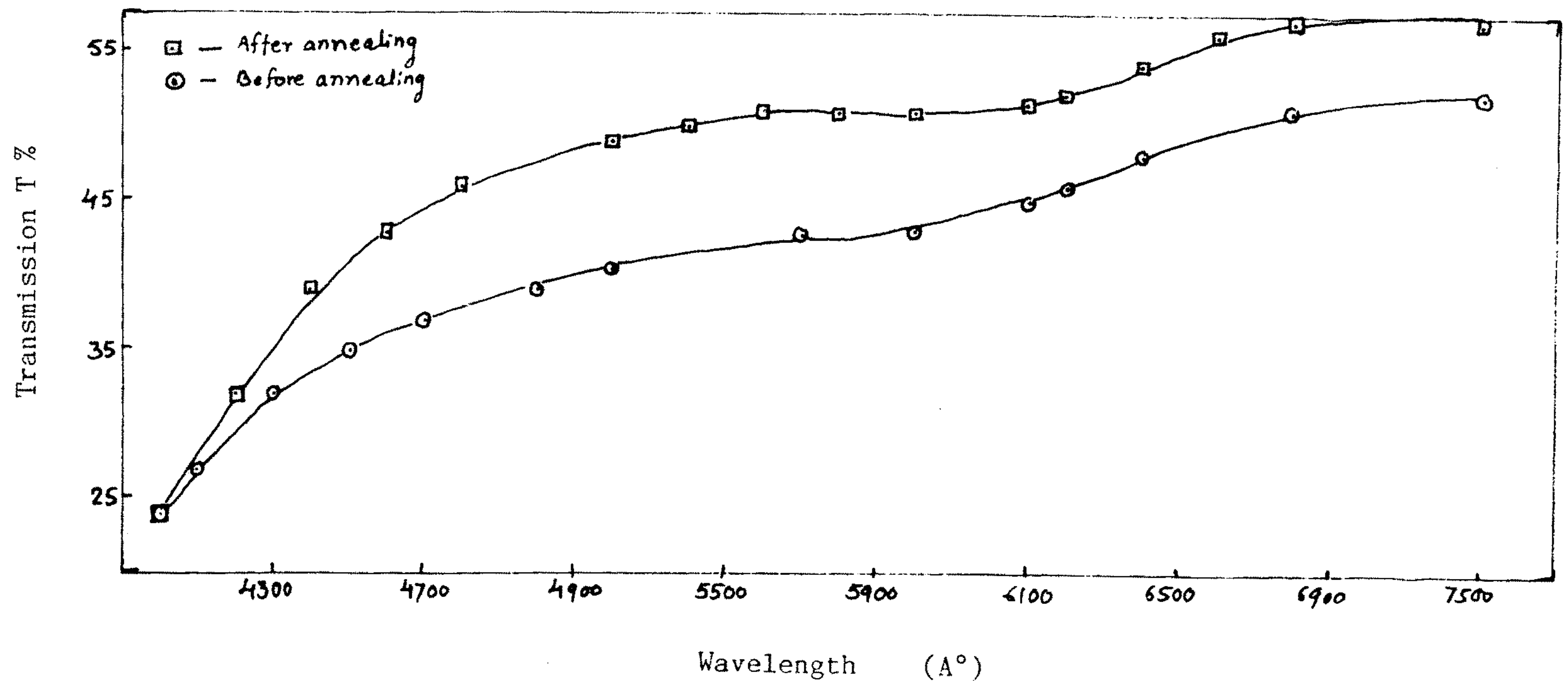

Fig. 8.6 Variation of transmission with wavelength for a typical sample before and after annealing.

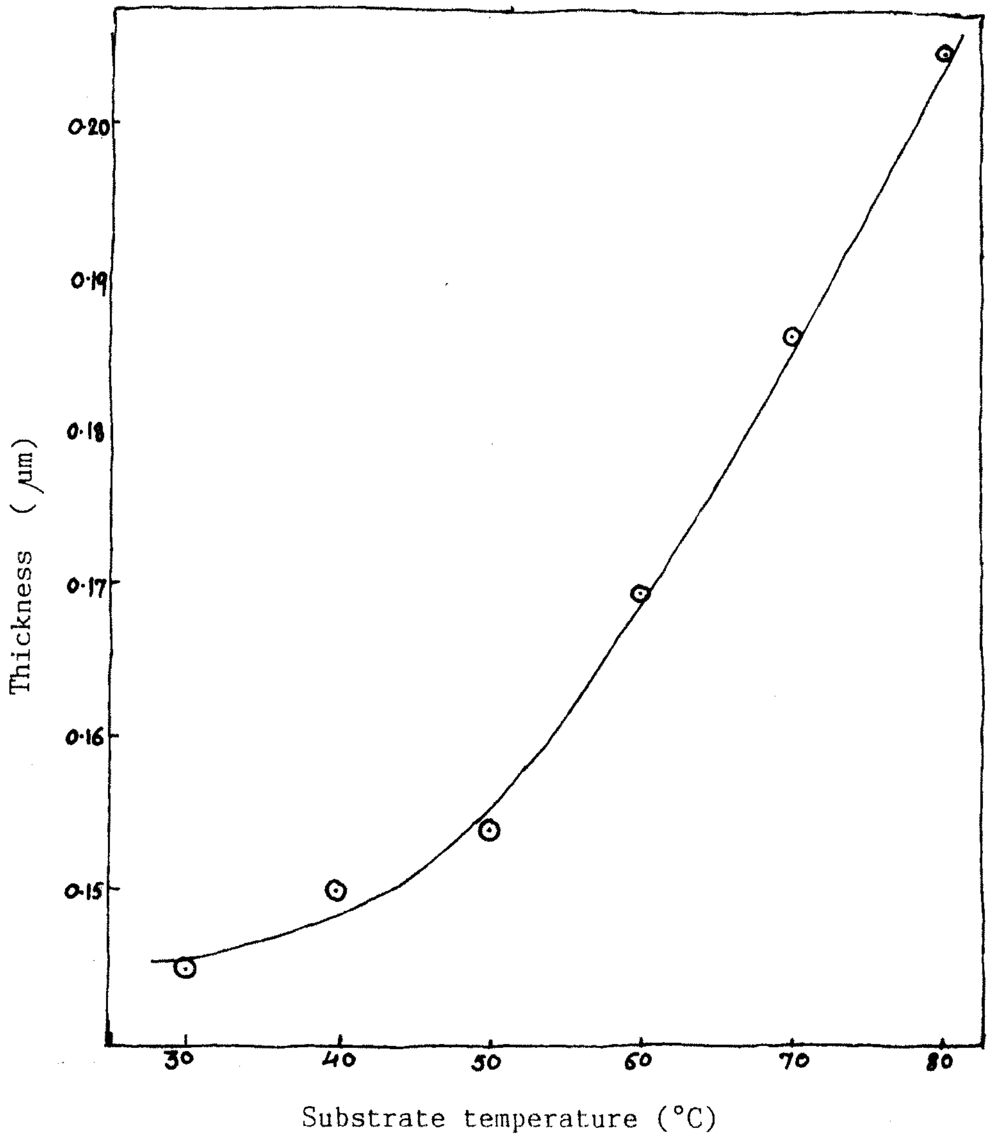

Fig. 8.7 Plot of Thickness versus substrate temperature.

The Mn-oxide films deposited by chemical bath method with optimised preparative parameters are tested for electrochemical characterization by using carbon as counter electrode and different electrolytes in aqueous and non-aqueous solvents. These include ferri-ferrocynide, ferrous-ferric chloride polysulfide, hydroquinone, formaldehyde and ferrocene in DMSO. For aqueous electrolytes KCl solution and NaOH solution are used as a supporting electrolyte. The film corrodes in all electrolytes and shows very poor response in NaOH + K_4/K_3 $Fe(CN)_6$ electrolyte due to poor junction formation caused by very low thickness of the film. Hence these films are not found suitable for their applications in ECPV cells.

REFERENCES

1. I. Kaur, Ph.D.Thesis, Bombay Univ., Bombay.
2. A.K.Raturi, R.Thangaraj, A.K.Sharma, B.B.Tripathi and O.P. Agnihotri, Thin Solid Films, 91, 55-64 (1982).
3. Manju Sen H.D.Banerjee and D.R.Rao, Proceedings of National Solar Energy Convention, 8.014 (1982).
4. A.G.Shikalgar, Ph.D.Thesis, Shivaji Univ. Kolhapur (1979).
5. B.B.Bargale, Ph.D.Thesis, Shivaji Univ. Kolhapur (1978)
6. C.D.Lokhande, Ph.D.Thesis, Shivaji Univ. Kolhapur (1983).
7. Mrs. Mitra, Ph.D.Thesis, Poona Univ. Pune (1974).