CHAPTER - III

THIN FILM DEPOSITION AND CHARACTERIZATION TECHNIQUES

3.1 DESCRIPTION OF THE DEPOSITION TECHNIQUE (SPRAY PYROLYSIS)

3.2 CHARACTERIZATION TECHNIQUES

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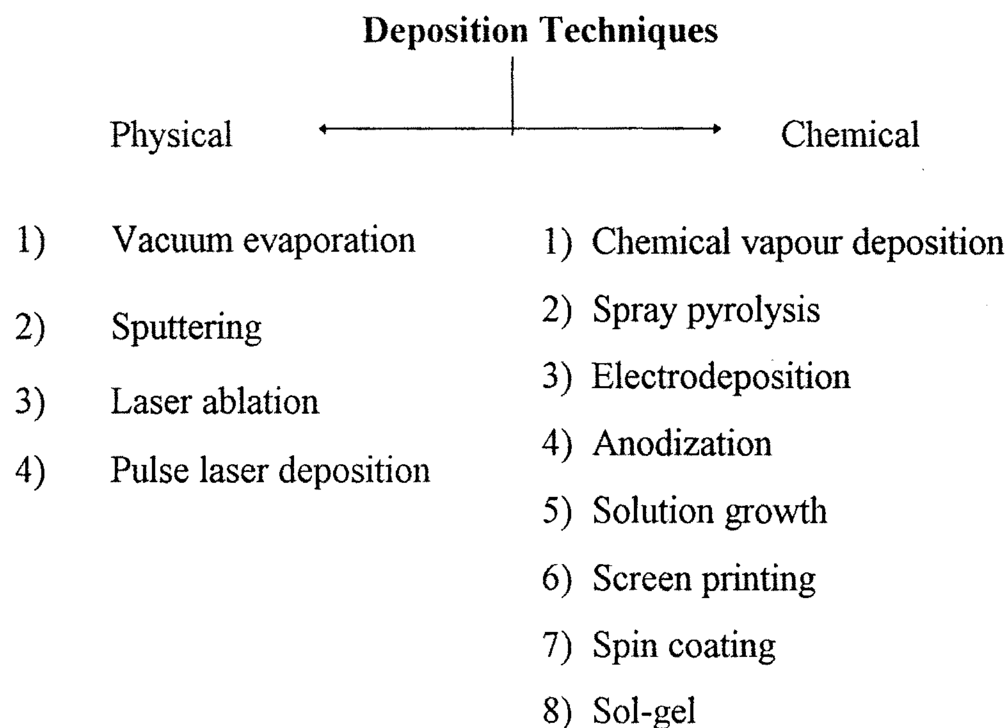
3.1 DESCRIPTION OF THE SPRAY PYROLYSIS TECHNIQUE

3.1.1 Introduction

Modern day technology requires several types (metallic, semiconducting, insulating) of thin films for a variety of applications [1,2]. There are various techniques by which one can deposit good quality thin films. Thin film deposition techniques can be broadly classified as follows :



The choice of the particular 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, spray pyrolysis method is most popular today because large number of insulating, conducting and semiconducting materials can be prepared by this technique. Compounds in the thin film form, on a variety of substrates (glass, ceramic or metallic) have been prepared by this technique. Many studies have been conducted over about three decades on spray pyrolysis processing and preparation of thin films. The mechanism of thin film formation and influence of variables on film formation process has been comprehensively reviewed in the literature [3]. Recently the versatility of the spray pyrolysis technique has been demonstrated by reviewing the wide range of materials that have been deposited using this technique [4]. Due to the simplicity of the apparatus and the good productivity of this technique on a large scale, it offered a most attractive way for the formation of thin films of metal oxides [4-12], metallic spinel type oxides [13-16], binary chalcogenides [17-22], ternary chalcogenides [23,24], superconducting oxides [25-28] etc.

Spray pyrolysis technique has a number of advantages :

1) It offers an extremely easy way to dope films with virtually any element in any proportion, by merely adding it in some form to the spray solution.

2) Unlike closed vapor deposition method, spray pyrolysis does not require high quality targets and/ or substrates or does not require

vacuum at any stage, which is a great advantage if the technique is to be scaled up for industrial applications.

3) The deposition rate and the thickness of the films can be easily controlled over a wide range by changing the spray parameters, thus eliminating the major drawbacks of chemical methods such as sol-gel, which produce films of limited thickness.

4) Operating at moderate temperatures (100 – 500^{0}C), spray pyrolysis can produce films on less robust materials.

5) Unlike high power methods such as radio frequency magnetron sputtering (RFMS), it does not cause local over-heating that can be detrimental for materials to be deposited. There are virtually no restrictions on substrate material, dimensions or its surface profile.

6) By changing composition of the spray solution during the spray process, it can be used to make layered films and films having composition gradients throughout the thickness.

7) It is believed that reliable fundamental kinetic data are more likely to be obtained on particularly well-characterized film surfaces, provided the films are quite compact, uniform and that no side effects from the substrates occur. Spray pyrolysis offers such an opportunity.

3.1.2 The Spray Pyrolysis Technique :

Spray pyrolysis technique consists of a thermally stimulated chemical reaction between clusters of liquid or vapour atoms of different chemical species. It involves spraying of a solution (either non-aqueous or aqueous) containing soluble salts of the constituent atoms of the desired compound on to preheated substrates. Every sprayed droplet undergoes pyrolytic (endothermic) decomposition and forms a single crystalline or cluster of crystallites as a product. The other volatile by-products and solvent escape in the vapour phase. The substrates provide thermal energy for the thermal decomposition and subsequent recombination of the constituent species, followed by sintering and crystallization of the clusters of crystallites and thereby resulting in coherent film. The atomization of the spray solution into a spray of fine droplets depends on the geometry of the spraying nozzle and pressure of a carrier gas. The properties of thin films, depend upon the anion to cation ratio, spray rate, substrate temperature, ambient atmosphere, carrier gas, droplet size and also on the cooling rate after deposition.

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 level monitor, (d) hot plate with temperature controlling arrangement, (e) gas regulator valve and (f) air tight metallic chamber.

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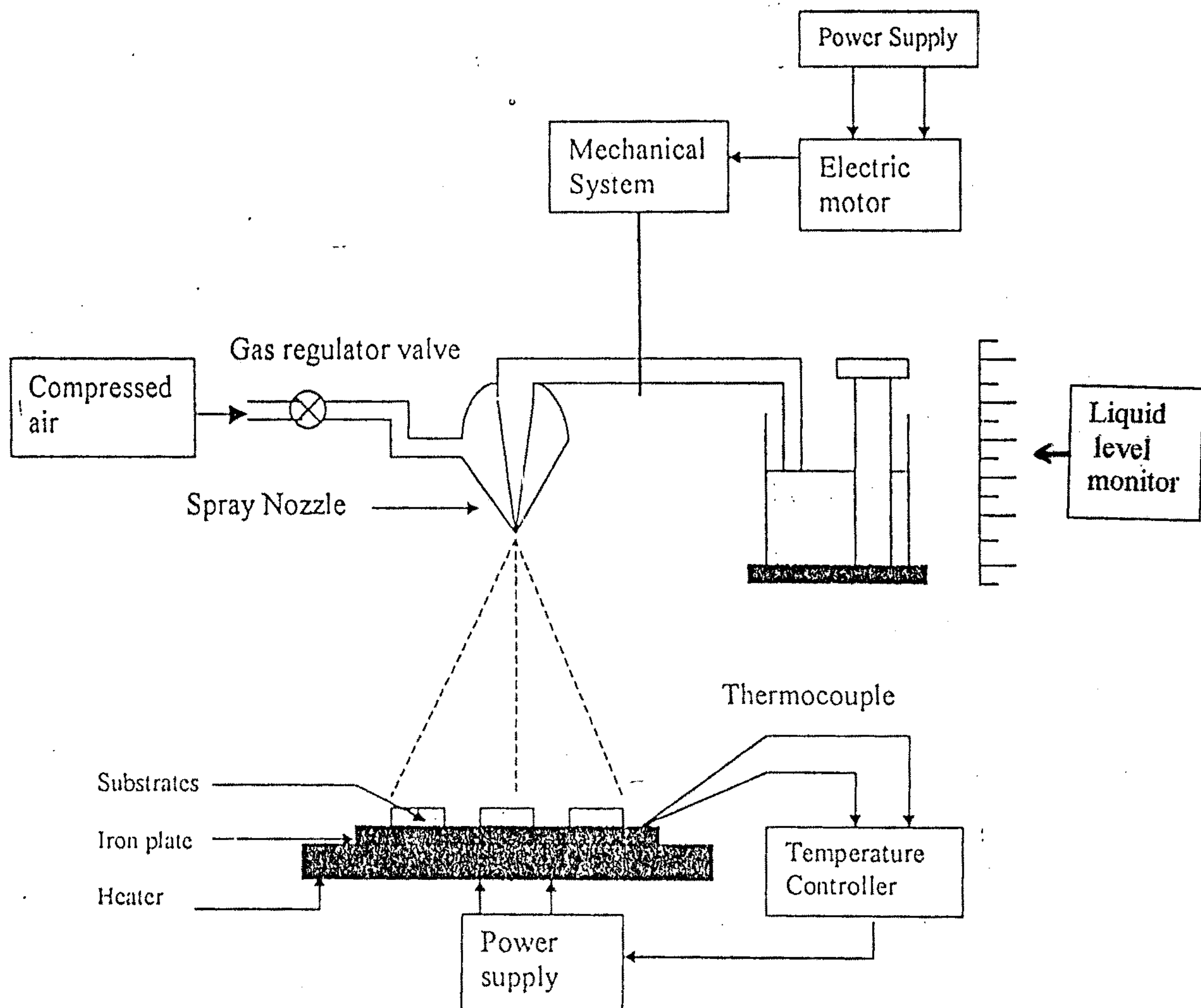


Figure 3.1 Schematic diagram of spray pyrolysis system.

change in height of the solution, forms liquid level monitor.

(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, a vacuum is created at the tip of the nozzle and the solution is automatically sucked and the spray starts.

(b) Rotor for spray nozzle :

8085- microprocessor- based dc motor is used to generate the to-and-fro motion of the nozzle.

(c) Liquid level monitor :

The spray rate, at a fixed pressure, depends on the height of the solution, measured with reference to the tip of the nozzle and the arrangement for change in height of the solution, forms liquid level monitor.

(d) Hot plate :

The iron disc, with diameter 16cm and thickness 0.7cm, was supported on the electric heater (2000 W). Maximum temperature upto 600^0C can be obtained with this arrangement. Chromel-alumel thermocouple was used to measure the temperature of the substrates and is fixed at the center of the iron disc. The temperature of the hot

plate was monitored with 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 25cm and a diameter of 1.5 cm was converted into a gas flow meter.

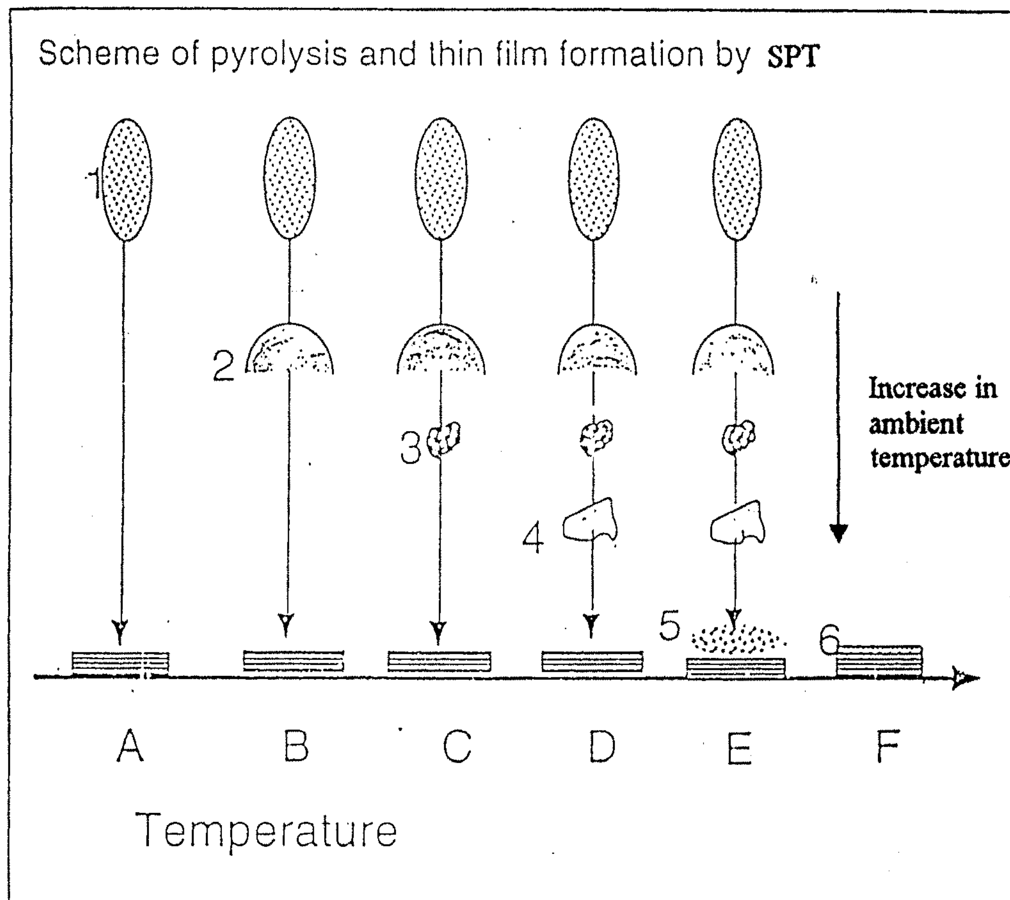
(f) Air tight metallic chamber :

Since number of toxic gases are evolved during the spray, it is necessary to fix the spraying unit in an airtight metallic chamber. An outlet of the chamber was fitted to exhaust to remove the gases evolved during spray deposition.

3.1.3 The Scheme of Pyrolysis and Formation of Thin Films :

In spray pyrolysis, precursor solution is atomized through a nozzle. The nozzle converts the solution into small droplets, known as aerosols. These aerosols are allowed to incident onto the preheated substrates. The pyrolytic decomposition of the aerosols depends on substrate temperature. Various steps during pyrolysis of aerosols are depicted in figure 3.2 and are summarized in this section.

1) In the first step, an aqueous precursor solution is converted into aerosols (droplets) by spray nozzle.



1. Droplet of aqueous solution of cupric acetate.
2. Solvent (methanol) evaporation.
3. Precipitate formation.
4. Pyrolysis of the precipitate.
5. Nucleation and growth of metal oxide thin film.
6. Formation of continuous metal oxide thin layer.

Fig. 3.2 Scheme of pyrolysis and thin film formation by the spray pyrolysis technique.

2) Solvent (methanol) evaporation takes place in the second step at about 280^0C.

3) In this step, vaporization of the solvent leads to precipitate formation as the droplets/ aerosols approach the substrate.

4) Pyrolysis of the precipitate occurs in succession before the precipitate reaches the substrate; this constitutes step 4.

5) In step 5, when the precipitate reaches the substrate, nucleation and growth of metal oxide thin films on the substrate surface takes place.

6) finally, growth of the nuclei leads to the formation of continuous thin layer of metal oxide (step 6).

3.2 CHARACTERIZATION TECHNIQUES

3.2.1 Introduction :

This section focusses on the theoretical aspects of various characterization techniques used for studying the properties of thin film materials. X-ray diffraction (XRD), optical absorption, electrical resistivity measurements, thermoelectric power (TEP), DTA/ TGA analysis of powder, Fourier transform infrared spectroscopy (FTIR) has been discussed. These techniques are used for structural, electrical and optical characterization of copper oxide thin films. The electrochemical techniques like cyclic-voltammetry (CV) and chronoamperometry (CA) have also been discussed.

3.2.2 Thickness Measurement :

Film thickness is an important parameter in the study of the film properties. Amongst different methods of measuring the film thickness, the weight difference method is simple and convenient and thickness 't' is measured using the relation,

$$t = \Delta m / A.\rho_b \qquad \ldots (3.1)$$

Where 'Δm' is the mass of the film deposited on area 'A' of the substrate and ρ_b is the density of the material in the bulk form. The mass 'Δm' of the film has been measured by using a one pan microbalance.

3.2.3 X-ray diffraction technique (XRD) :

A given substance always produces a characteristic diffraction pattern, whether that substance is present in the pure state or as one constituent of a mixture of substances. This fact is the basis for the diffraction method of chemical analysis. Qualitative and quantitative analyses are also possible, because the intensities of the diffraction lines due to one phase of a mixture depend on the proportion of that phase in the specimen. Detailed treatments of chemical analysis by X-ray diffraction are given by Klug and Alexander [29].

The crystallographic features are studied by using XRD. The XRD technique based on monochromatic radiation is generally more

important because the d-spacing of the planes can be deduced from the observed diffraction angles. The phenomenon of X-ray diffraction can be considered as a reflection of X-rays from the crystallographic planes of the material and is governed by Bragg's equation,

$$2d \sin \theta = n\lambda \qquad \ldots (3.2)$$

where 'd' is the lattice (inter-planar) spacing, λ is the wavelength of monochromatic X-rays, n is the order of diffraction and θ is the diffraction angle.

For thin films, the powder technique in conjunction with diffractometer is most commonly used. In this instrument the diffracted radiation is detected by the counter tube, which moves along the angular range of reflections. The intensities are recorded on a computer system. The 'd' values are calculated using the relation 3.2 for known values of θ, λ and n. The X-ray diffraction data thus obtained is printed in tabular form on paper and is compared with JCPDS (Joint Committee on Powder Diffraction Standards) data card to identify the unknown material. This X-ray diffraction data can also be used to determine dimensions of the unit cell, crystal structure and crystallinity.

3.2.4 Optical Absorption :

The equilibrium situation in semiconductor can be disturbed by generation of carriers due to optical photon absorption. Optical photon incident on any material may be reflected, transmitted or absorbed. The phenomena of radiation absorption in a material is altogether considered to be due to 1) inner shell electrons, 2) valence band electrons, 3) free carriers including holes as well as electrons and 4) electrons bound to localized impurity centers or defects of some type. In study of the fundamental properties of some semiconductors, the absorption by the second type of electrons is of great importance, In an ideal semiconductor, at absolute zero temperature, the valence band would be completely full of electrons, so that electron could not be excited to a higher energy state from the valence band. Absorption of quanta of sufficient energy tends to transfer the electrons from valence band to conduction band.

There are two types of optical transitions that can occur at the fundamental edge of the crystalline semiconductor, direct and indirect. The direct inter-band optical transition involves a vertical transition of electrons from the valence band to the conduction band such that there is no change in the momentum of the electrons and energy is conserved as shown in figure 3.3(a). Hence a wave vector k for electron remains

unchanged in E-k space. For simple parabolic bands and for direct transition absorption coefficient $\propto$ is [31]

$$\propto = \frac{\propto_o (h\nu - E_g)^n}{h\nu} \qquad \ldots (3.3)$$

Where Eg is the separation between bottom of the conduction band and top of the valence band, $h\nu$ is the photon energy, n is constant and is equal to 1/2 or 3/2 depending on whether transition is allowed or forbidden and $\propto_o$ is a constant depending upon the transition probability for direct transition. For allowed direct transitions n = ½ and allowed indirect transition n=2. Thus if the plot of $(\propto h\nu)^2$ against $h\nu$ is linear then the transition is direct allowed. The band gap energy 'Eg' is determined by extrapolating the linear portion of the curve to the energy axis at $\propto = 0$. In indirect interband transitions the wave vector k for electron changes in the E-k space, situation is shown in figure 3.3 (b).

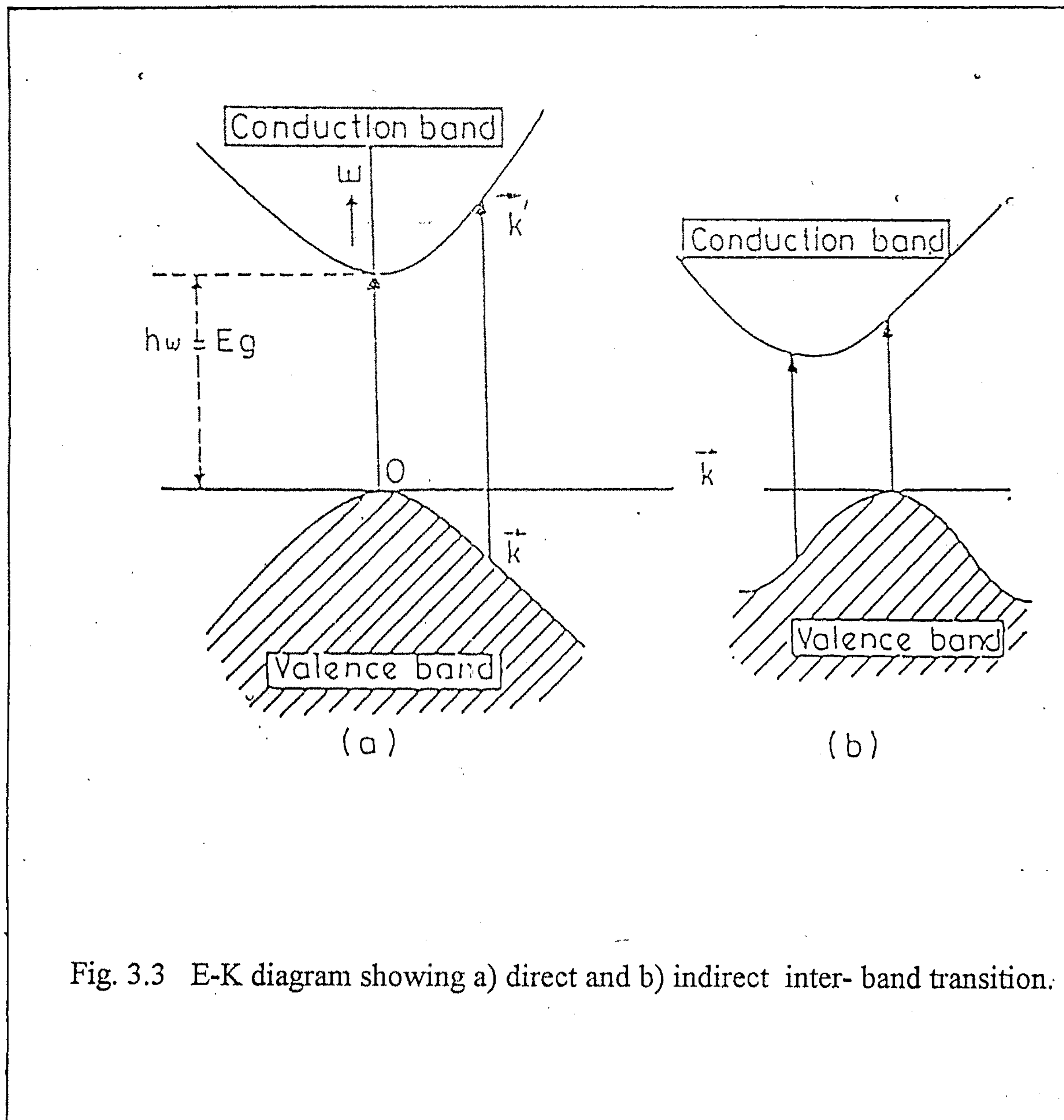


Fig. 3.3 E-K diagram showing a) direct and b) indirect inter- band transition.

3.2.5 Transport Properties

3.2.5.1 Electrical resistivity :

The use of thin films as resistors, contacts and interconnections has lead to extensive study of conductivity, its temperature dependence, the effect of thermal processing stability and so on. Investigations of the critical resistivity as a highly structure sensitive properties makes it possible to gain insight into the structural and electrical properties of the metal film which is important from both the theoretical and practical point of view.

The contact techniques are most widely used for the measurement of resistivity. These techniques include two-point probe, four-point probe and the spreading resistance methods. The two-point probe method is simple and easy to use. In this technique, a constant voltage V, is applied between two fixed position probes of separation d and a current passing through the samples of known dimensions (cross section area 'A') is measured with an appropriate current meter. For uniform sample resistivity is given by,

$$\rho = (A/I)\ (V/d) \qquad \text{... (3.4)}$$

In the case of semiconducting thin films, the resistivity decreases with increase in temperature. The thermal activation energies E_a are calculated by using conductivity relation [30].

$$\rho = \rho_o \exp [-E_a / kT] \qquad \ldots (3.5)$$

where symbols have their usual meaning. The slope of the log (ρ) versus 1/ T leads to the estimation of activation energy.

3.2.5.2 Thermoelectric power (TEP) :

It is well known that if a metal is connected at its two ends with a second metal and one of the junctions is heated, a voltage is developed across the open ends of the second metal. If some metal contacts are applied to the two ends of a semiconductor rod and if one junction is maintained at higher temperature than the other, a potential difference is developed between the two electrodes. This thermoelectric or Seebeck voltage is produced partly because,

1) The majority carriers in the semiconductor diffuse from hot to cold junction, thus giving a potential difference between the ends of the specimen. This voltage builds upto a value such that the return current just balances the diffusion current when a steady state is reached.

2) Other part, which contributes to the thermoelectric voltage, is the potential difference between the metal and semiconductor, which occurs at two junctions.

In a semiconductor, if the charge carriers are predominantly electrons, the cold junction becomes negatively charged and if the

charge carriers are positive holes, the cold junction becomes positively charged. The magnitude of the developed voltage is proportional to the difference in temperature between the hot and the cold junction, if the temperature is small. From the sign of the thermoelectric voltage it is thus possible to deduce whether a given specimen exhibits n – or p-type conductivity.

The thermoelectric power (TEP) which is defined as the ratio of thermally generated voltage to the temperature difference across the semiconductor, gives the information about the type of carriers in the semiconductors.

3.2.6 DTA/ TGA Analysis of Powder

(a) Differential Thermal Analysis (DTA):

Differential Thermal analysis (DTA) though often considered an adjunct to TGA, is in fact far more versatile and yield data of a considerable more temperature between a substance and a reference material against either time or temperature [of sample (T_s) or reference (T_f) or furnace (T_F)] as the two specimens are subjected to identical temperature regimes in an environment heated or cooled at a controlled rate.

DTA curve consists of an exothermic and endothermic peaks. Both the shape and size of the peak may furnish good information about the nature of the test sample. Generally a sharp endothermic

peak gives an idea of changes in crystallinity or fusion process whereas broad exotherms signify dehydration reactions. In most of the cases physical changes give rise to endothermic curves whereas chemical reactions (particularly those of an oxide nature) gives rise to exothermic peaks.

The origin of the temperature difference in the sample (ΔT) lies in the energy difference between the products and the reactants and between the two peaks of a substance. This energy difference is manifested as enthalpy changes either exothermic or endothermic. The DTA curve would be parallel to the temperature axis till the sample undergoes any physical or chemical change of state. However, as soon as the sample has reached temperature of change of state, the additional heat flux reaching the sample will not increase the sample temperature at the same rate as that of the reference and the differential signal appears as the peak. The differential signal would return to the base line only after the change of state of the sample is completed and temperature becomes equal to that of the reference material.

(b) Thermo Gravimetric Analysis (TGA) :

It is a technique whereby the weight of a substance in an environment heated or cooled at a controlled rate is recorded continuously as a function of temperature or time. In this technique, the sample is heated in an environment whose temperature is changing

in a predetermined manner, generally at a linear rate. A plot (TG) of weight change versus temperature represents results of this technique. Weight loss for various stages such as removal of water, decomposition of materials, etc. is indicated directly on TG covers. Much more information can be obtained from TG curve. From how much weight is lost by heating the sample at given temperature, one can determine the composition of a compound, decomposition temperature and can also understand the reaction involved in its decomposition. The shape of the TG curve depends on which type of instrument is used, instrumental effect and characteristics of the sample such as weight, particle size, compactness and purity of the sample. If a substance is being heated at a fast heating rate, the temperature of decomposition will be slightly higher than that obtained at a slower rate of heating. The decomposition temperature also depends on the furnace atmosphere (air, nitrogen, etc.).

3.2.7 Fourier Transform Infrared Spectroscopy (FTIR):

Electromagnetic radiations in which wavelength lies in the range of 1 micron to 1mm are termed as infrared, which lie between the visible and microwave region. Usually wavelength used in IR spectroscopy ranges from 2.5 to 25 micron or 4000 to 400 wave number 9wave per cm). FTIR is one of the most powerful analytical techniques, which offers the possibility of chemical identification. It

provides useful information about the structure of the molecule. The technique is based upon the simple fact that a chemical substance shows marked selective absorption in the IR region. After absorption of IR radiations, the molecule of a chemical substance vibrates at many rates of vibration, giving rise to close packed absorption bands, called an IR absorption spectrum, which may extend over a wide range of wavelength.

Band intensities in the IR spectrum may be expressed either as transmittance (T) or absorption (A). The band position in an IR spectrum may be expressed by the wave number ($\nu = 1/\lambda$), whose unit is cm^{-1}. Various bands will be present in IR spectrum, which will correspond to the characteristic functional groups and bonds present in a chemical substance is a fingerprint for its identification. A molecule absorbs radiation when the natural frequency of vibration (stretching or bending) of some part of a molecule (i.e. atoms or a group of atoms containing it) is the same as the frequency of the incident radiation.

Studies of the relation between structure and electromagnetic response of material are useful in understanding their properties. The vibration in electronic and magnetic dipole spectra can give information about the position and valence of the ions in the crystal lattice. The bands in the region 300-700 cm^{-1} are assigned to the fundamental vibration of the ions of the crystal lattice.

Usually sample is prepared by using KBr powder in the form of pellet for solid compound, which is transparent to IR radiations.

3.2.8 Electrochemical Characterization :

Electroanalytical techniques are concerned with the interplay between electricity and chemistry, namely the measurements of electrical quantities, such as current, potential and charge and their relationship to chemical parameters. Electrochemical processes take place at the electrode solution interface. The distinction between various electroanalytical techniques reflects the type of electrical signal used for quantitation. The measurement requires at least two electrodes (conductors) and a contacting sample (electrolyte solution), which constitute the electrochemical cell. The electrode surface is thus a junction between an ionic conductor and an electronic conductor. One of the two electrodes responds to the target analyte (s) and is thus termed the working electrode. The second one, termed the reference electrode, is of constant potential.

3.2.8.1 Cyclic voltammetry (CV) :

Cyclic voltammetry is the most widely used technique for acquiring qualitative information about electrochemical reactions. Cyclic voltammetry consists of scanning linearly the potential of a stationary working electrode (in an unstirred solution), using a triangular potential waveform. Depending on the information sought,

single or multiple cycles can be used. During the potential sweep, the potentiostat measures the current resulting from the applied potential. The resulting plot of the current versus potential is termed a cyclic voltammogram.

Figure 3.4 illustrates the expected response of a reversible redox couple during a single potential cycle. The characteristic peaks in the CV are caused by the formation of the diffusion layer near the electrode surface. These can be best understood by carefully examining the concentration – profiles during the potential sweep. For example, figure 3.5 illustrates four concentration gradients for the reactant and product at different times corresponding to (A) the initial potential value, (B) and (D) the formal potential of the couple (during forward and reverse scan) and (C) the achievement of zero reactant surface concentration. Note that the continuous change in the surface concentration is coupled with an expansion of the diffusion layer thickness. The resulting current peaks thus reflect the continuous change of the concentration gradient with the time. Hence, the increase to the peak current corresponds to the achievement of diffusion control, while the current drop (beyond the peak) exhibits a $t^{-1/2}$ dependence (independent of the applied potential).

This technique has been widely used to study the intercalation and deintercalation processes in the electrochromic materials.

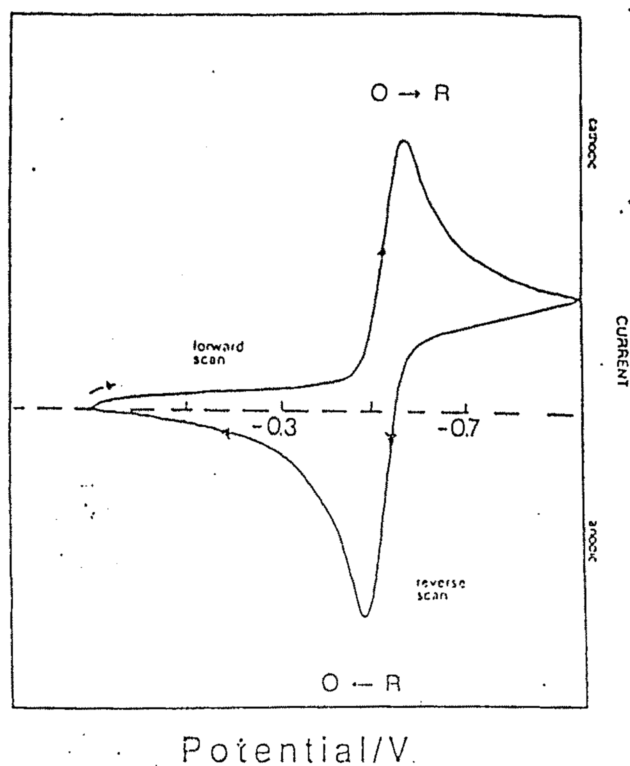


Fig. 3.4 Typical cyclic voltammogram for a reversible $O + ne^{-} = R$ redox process.

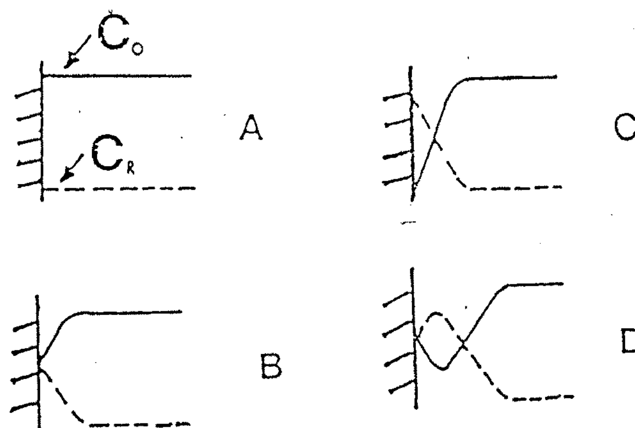


Fig. 3.5 Concentration distribution of the oxidized and reduced forms of the redox couple at different times during a CV experiment corresponding to (A) the initial potential, (B) and (D) the formal potential of the couple during the forward and reverse scans, respectively, and (C) the achievement of a zero reactant surface concentration.

3.2.8.2 Chronoamperometry (CA) –

CA involves stepping the potential of the working electrode (WE) from a value at which no faradaic reaction occurs to a potential at which the surface concentration of the electroactive species become effectively zero (figure 3.6A). The resulting current –time)(I-t) dependence is monitored. As mass transport under these conditions is solely by diffusion, the I-t curve reflects the change in the concentration gradient in the vicinity of the surface, with depletion of the reactant and hence decreased slope of the concentration profile as time progresses (figure 3.6B). Accordingly, the current decays with the time (Figure 3.6C) as given by Cotterll equation,

$$I(t) = nFA\, CD^{1/2} / \pi^{1/2}\, t^{1/2} = kt^{-1/2} \qquad \ldots (3.6)$$

Such an $it^{1/2}$ constancy is often termed "Cotterll behaviour."

This technique has been widely used to investigate the diffusion coefficient, the response times and amount of charge intercalated into the copper oxide thin films. This technique is helpful in studying the intercalation/ deintercalation kinetics in electrochromic cell systems.

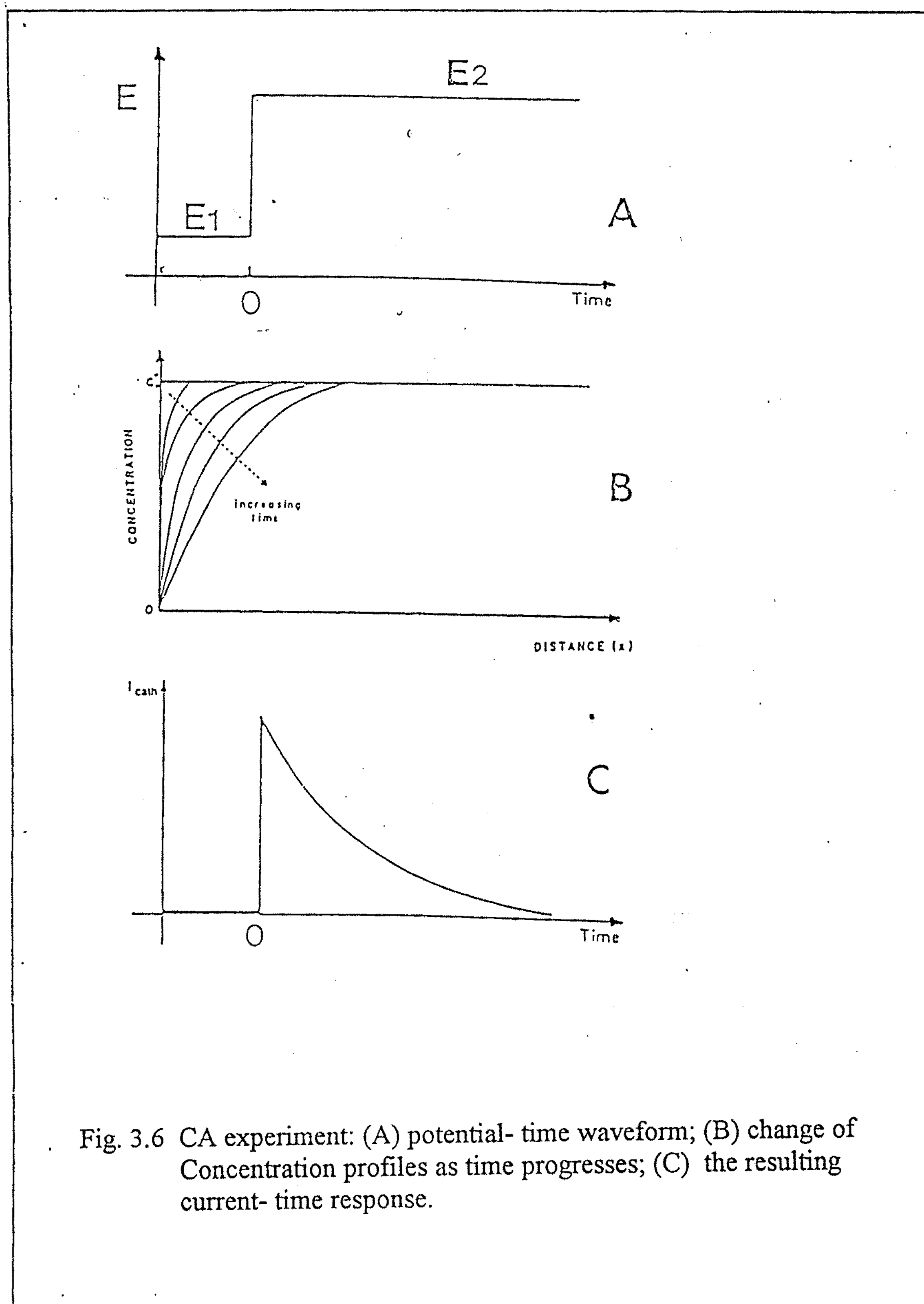


Fig. 3.6 CA experiment: (A) potential- time waveform; (B) change of Concentration profiles as time progresses; (C) the resulting current- time response.

3.3 EXPERIMENTAL PROCEDURE

3.3.1 Substrate cleaning :

In thin film deposition process, substrate cleaning is the important factor. It affects the adherence, smoothness and uniformity of the film. The technique to be adopted for cleaning depends on nature of substrates, degree of cleanliness required and nature of contaminants to be removed. The common contaminants are grease, adsorbed water, air borne dust, lint and oil particles. Cleanliness is the process of breaking the bonds between substrates and contaminants without damaging the substrates. Following cleaning procedure was used for the glass substrates.

1) The substrates were first washed with the neutral detergent solution 'labolene^n and then with the double distilled water.
2) The substrates were boiled in a chromic acid for few minutes.
3) NaOH treatment was given to remove the acidic contaminants.
4) The substrates were again washed with double distilled water.
5) Lastly, substrates were ultrasonically cleaned.
6) Drying of the substrates was done in the vapours of the alcohol.

3.3.2 Preparation of F.T.O. Coated Glass Substrates :

A 100 c.c. of 2M stannic chloride solution was prepared in double distilled water and 14.285 gm of ammonium flouride was

dissolved in it, to obtain 40% doping concentration of fluorine. From the above mixture, 10 c.c. solution was taken and 20 c.c. of propane 2-ol (iso-propanol) was added. The final solution was sprayed through the specially designed glass nozzle at the rate of 5 c.c./ min. The substrates were kept at 525^0C. It was found that these conducting glasses have 10-50 Ω/cm^2 sheet resistance and about 90% transparency.

3.3.3 Preparation of Cupric Acetate Solution :

The 1.9965 gm of cupric acetate $(CH_3COO)_2\ Cu.H_2O$ powder was dissolved in 1000ml of methanol. This 0.01 N cupric acetate solution was taken as a starting solution to be sprayed onto the hot substrates.

3.3.4 Optimization of preparative parameters :

In order to obtain copper oxide thin films with desired properties the preparative parameters like solution concentration, spray rate, nozzle to substrate distance and air pressure are optimized and values are given in table 3.1. The substrate temperature was maintained at 250, 300 and 350^0C.

Table 3.1

Optimized preparative parameters for copper oxide thin films

Sr. No.	Preparative parameter	Range studied	Optimized values
1.	Solution concentration	0.5 - 0.001 M	0.01 M
2.	Solution quantity	10 - 50 cc	30 cc
3.	Spray rate	5 - 10 cc/min	6 cc/min.
4.	Nozzle substrate distance	22-28 cm	25 cm
5.	Air pressure	0.5 - 3 kg/cm^2	1 kg/cm^2

Several preliminary experiments were performed to decide the rudimentary range of variables.

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