

A decorative border consisting of a repeating pattern of stylized leaves or floral motifs, arranged in a rectangular frame around the central text.

CHAPTER- III

THIN FILM DEPOSITION AND CHARACTERISATION TECHNIQUES

CHAPTER – III

THIN FILM DEPOSITION AND CHARACTERIZATION TECHNIQUES

3.1 Description of the deposition technique (Spray pyrolysis)

3.2 Characterization techniques

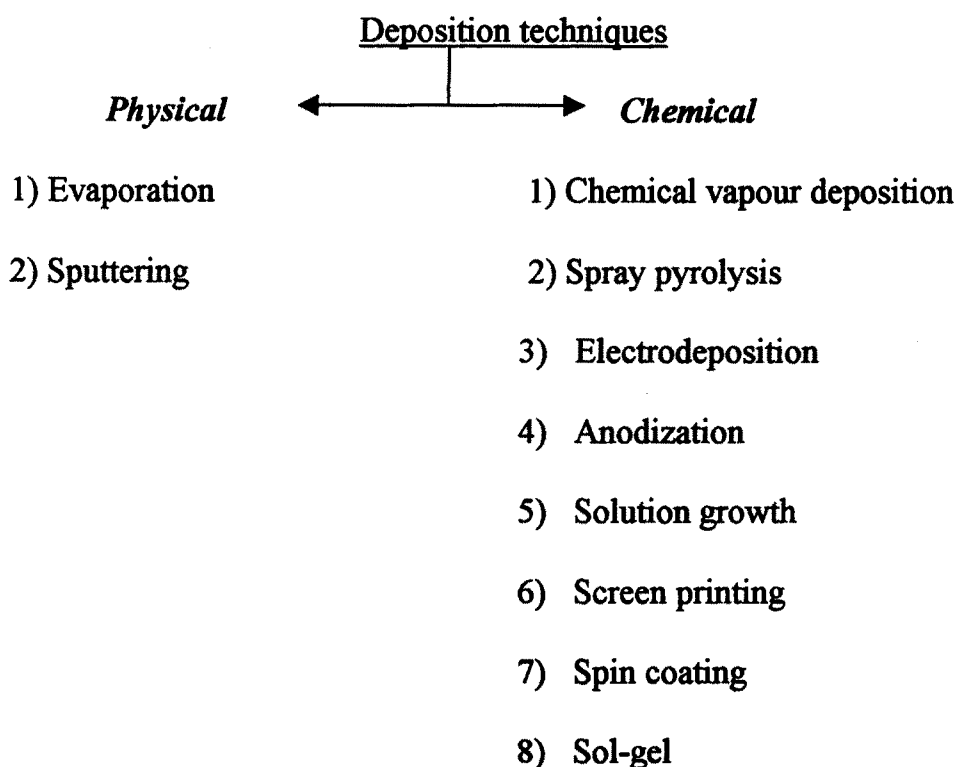
3.3 Experimental procedure

3.4 References

3.1 Description of the Spray pyrolysis technique

3.1.1 Introduction

Modern day technology requires several types of thin films for a variety of applications [1,2]. There are various techniques by which one can deposit 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, solution spraying on hot substrate (spray pyrolysis) method is most popular today because large number of 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.

Apart from its simplicity, 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 it 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°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, dimension 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 usually aqueous containing soluble salts of the containing atoms of the desired compound on to preheated substrates. Every sprayed droplet reaching the surface of the hot substrate 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 also 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 figure 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.

(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

An electric car wiper (12V, 2A) is used to rotate the spray nozzle along with a speed controller.

(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

(d) Hot plate

The iron disc, with diameter 16 cm and thickness 0.7 cm, was supported on the electric heater (2000W). Maximum temperature up to 600°C 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 coming glass tube of length 25cm and a diameter of 1.5cm was converted into a gas flow meter.

(f) Air tight metallic chamber

Since numbers 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. The formation of thin films with desired properties are possible only at optimum substrate temperature. Various

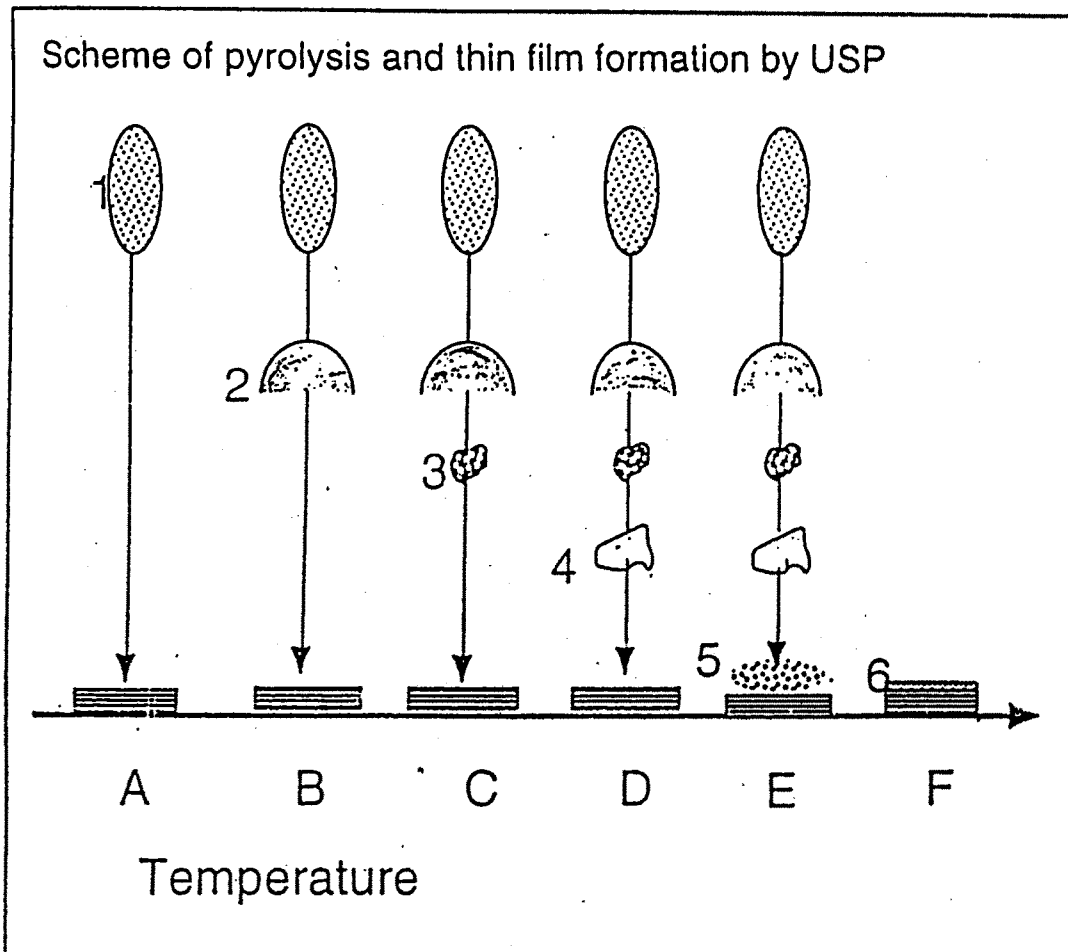
steps during pyrolysis of aerosols are depicted in figure 3.2 and summarized in this section.

- 1) In the first step, an aqueous precursor solution is converted into aerosols by spray nozzle.
- 2) Solvent evaporation takes place in the second step.
- 3) In this step, vaporization of the solvent leads to precipitate formation as the droplets / aerosol approaches 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 focuses on the theoretical aspects of various characterization techniques used for studying the properties of thin film materials. X-ray diffraction (XRD), scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR), electrical resistivity measurements, thermoelectric power (TEP) and optical absorption has been discussed. These techniques are used for structural, electrical and optical characterization of Nb₂O₅ thin films.



1. Aerosol of aqueous solution of Niobium
2. solvent evaporation
3. precipitate
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.

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 for measuring the film thickness, the weight difference method is simple and convenient and thickness 't' is measured using the relation,

$$t = m / A \cdot \rho_b \quad \text{----- (3.1)}$$

where 'm' 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 'm' 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 spacing of the planes (d-spacing) 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,

$$2d \sin \theta = n\lambda \text{ ---- (3.2)}$$

where 'd' is the lattice 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 Scanning electron microscopy (SEM)

The SEM technique is used primarily for the examination of thick (i.e., electron opaque) samples. Electrons, which are emitted or back scattered from the specimen, are collected to provide:

- (i) The topological information (i.e. detailed shape of specimen surface) if the low energy secondary electrons (< 50eV) are collected.
- (ii) An atomic number or orientation information if the higher energy backscattered electrons are used, or if the leakage current to earth is used.

Imaging of magnetic samples using secondary and or backscattered electrons reveals magnetic domain contrast. In addition two other signals can be collected, the electron beam induced current and light cathodoluminescence.

SEM operates generally in the range 2.5 to 50 eV, with probe size available at the specimen between 5nm and 2 μ m. The convergence angle of the probe at the specimen is controlled by the diameter of the final aperture and this angle determines the depth of field of SEM. Thus the large depth of field F which is commonly associated with SEM images is in fact due to the small convergence angle at the specimen, which is much smaller than the corresponding angle in optical microscopes. A very large value of depth of field for high-resolution image, which underlines the value of high magnification SEM images of rough surfaces.

Microstructural aspects of the film were studied with SEM microscopes. The film was coated with gold-palladium (Au-Pd) of thickness 150 Å using polaron SEM sputter coating with, E-2500. The SEM micrographs are obtained with Cambridge stereoscan 250-MK3 assembly.

3.2.5 Fourier transform Infrared Spectroscopy (FTIR)

Electromagnetic radiations in which wavelength lies in the range of 1 micron to 1 mm 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 (waves 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 composing 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 $300\text{-}700\text{ cm}^{-1}$ 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.

3.2.6 Transport properties

3.2.6.1 Electrical resistivity

The use of thin films as resistors, contacts and interconnections has led 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,

$$\rho = (A / I) (V / d) \text{ -----(3.3)}$$

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].

$$\rho = \rho_o \exp (-E_a / kT) \text{ ----- (3.4)}$$

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

3.2.6.2 Thermoelectric power (TEP)

It is well known that if a metal is connected at its two ends with a second metal and if 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 up to 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.

3.2.7 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) valance 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 valance band would be completely full of electrons, so that electron could not be excited to a higher energy state from the valance band. Absorption of quanta of sufficient energy tends to transfer the electrons from valance band to conduction band.

There are two types optical transitions that can occur at the fundamental edge of the crystalline semiconductor, direct and indirect. The direct interband 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 α is [31]

$$\alpha = \frac{\alpha_0 (h\nu - E_g)^n}{h\nu} \quad \text{----- (3.5)}$$

Where E_g is the separation between bottom of the conduction band and top of the valance 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 α_0 is a constant depending upon the transition probability for direct transition. For allowed direct transitions $n = 1/2$ and allowed indirect transition $n = 2$. Thus if the plot of $(\alpha h\nu)^2$ against $h\nu$ is linear then the transition is direct allowed. The band gap energy ' E_g ' is determined by extrapolating the linear portion of the curve to the energy axis at $\alpha = 0$. In indirect interband transitions the wave vector k for electron changes in the E-k space, situation is shown in figure 3.3(b).

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.

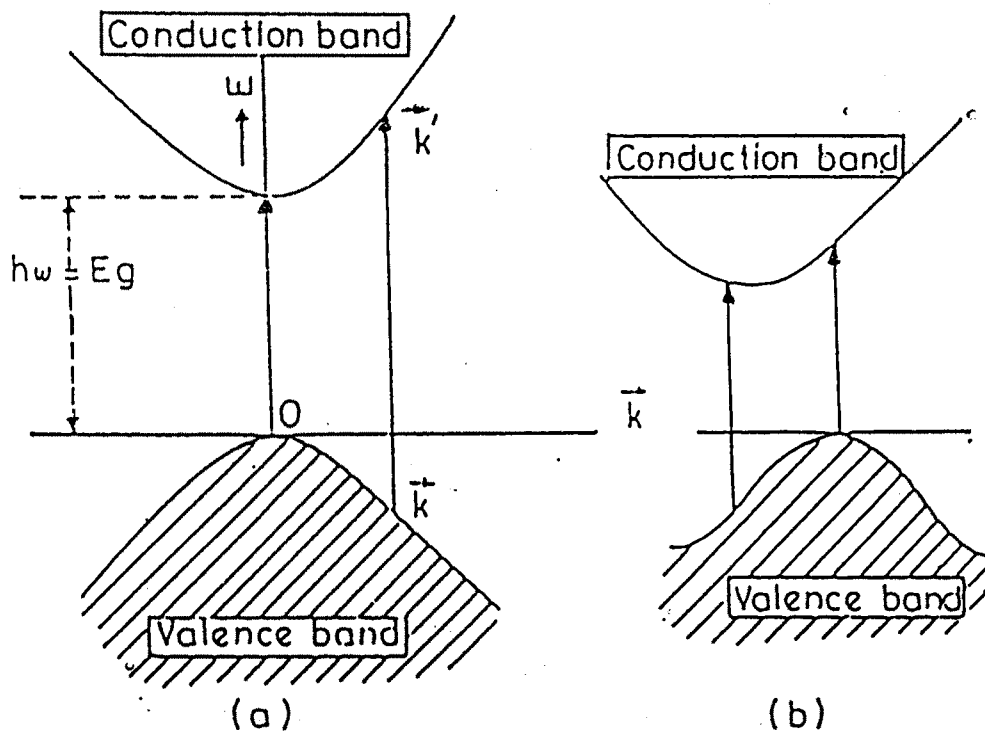


Fig. 3.3 E-K diagram showing a) direct and b) indirect inter- band transition.

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

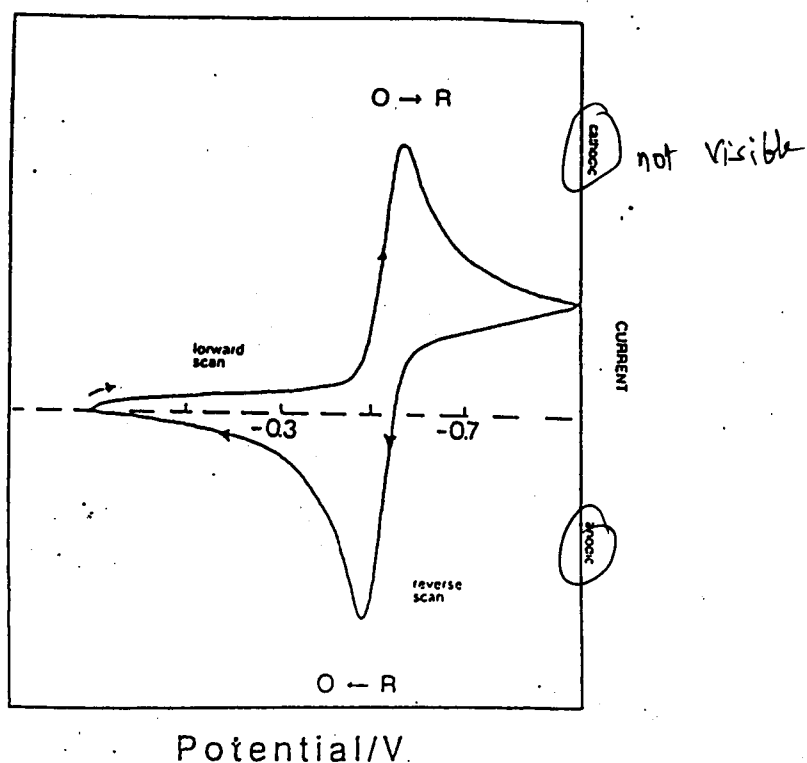


Fig. 3.4 Typical cyclic voltammogram for a reversible $O + ne^- = R$ (redox) process.

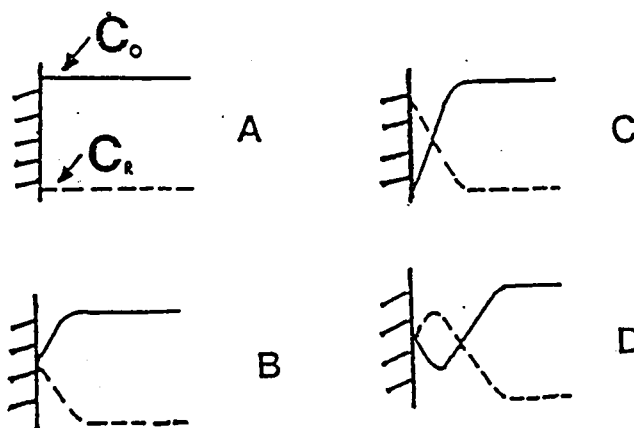


Fig. 3.5 Concentration distribution of the oxidized and reduced forms of the redox couple at different times during a CV experiment corresponding to (A) the initial potential, (B) and (D) the formal potential of the couple during the forward and reverse scans, respectively, and (C) the achievement of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

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.

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 becomes effectively zero (figure 3.6 A). 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 3.6 B). Accordingly, the current decays with the time (figure 3.6 C) as given by Cottrell equation;

$$i(t) = nFACD^{1/2} / \pi^{1/2}t^{1/2} = k t^{-1/2} \quad \text{---- (3.6)}$$

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

This technique has been widely used to investigate the diffusion coefficient, the response times and amount of charge intercalated into the Nb₂O₅ thin films. This technique is helpful in studying the intercalation / deintercalation kinetics in electrochromic cell systems.

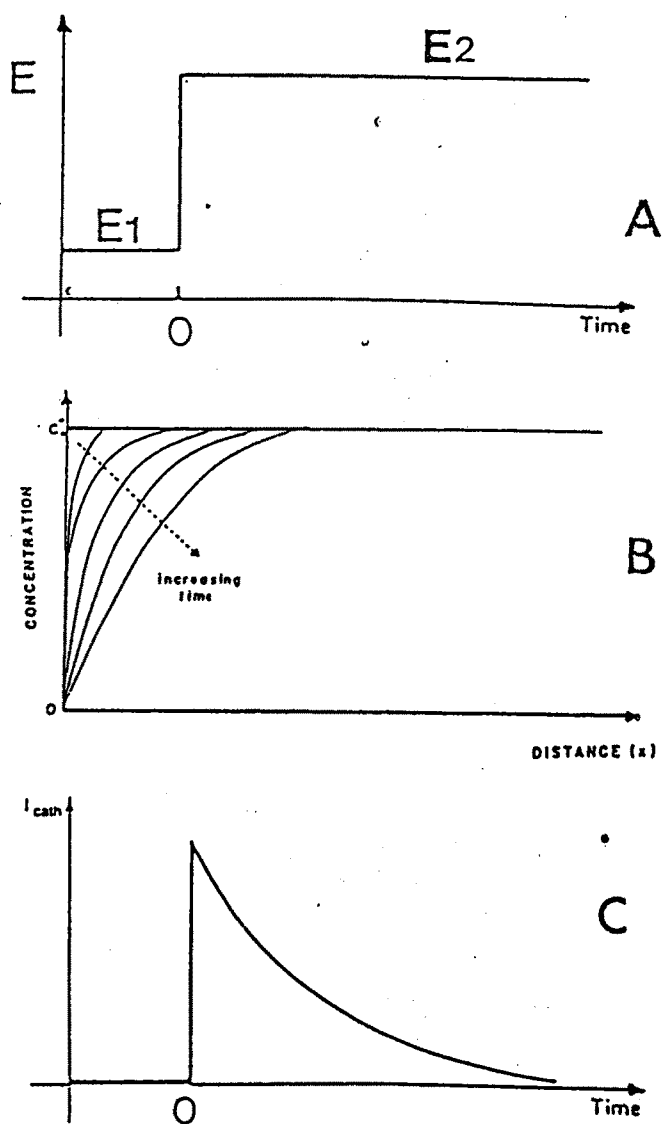


Fig. 3.6 CA experiment: (A) potential-time waveform; (B) change of Concentration profiles as time progresses; (C) the resulting current-time response.

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” 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

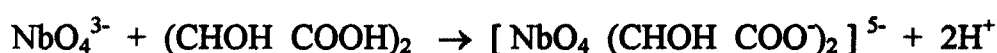
A 100 c.c. of 2 M stannic chloride solution was prepared in double distilled water and 14.285 gm of ammonium fluoride was dissolved in it, to obtain 40% doping concentration of fluorine. From the above mixture, 10 c.c. solution was taken and 20 c.c. of propane 2-ol (iso-propanol) was added. The final solution was

sprayed through the specially designed glass nozzle at the rate of 5 c.c. / min. The substrates were kept at 525 °C. It was found that these conducting glasses have 10-50 Ω/cm^2 sheet resistance and about 90% transparency.

3.3.3 Preparation of niobium solution

The 0.0715 gm of pure niobium pentoxide (Fluka AG, Buchs SG Niobium (V) oxide, Switzerland, 99.99 % pure) fused with 3 gm of potassium pyrosulphate in a silica crucible. The melt was dissolved in 1 M tartaric acid and diluted to 100 ml with the same solution. This forms the 0.05 % standard Nb solution. From this solution 0.005 % Nb solution is obtained by dilution with tartaric acid. This solution was taken as a starting solution to be sprayed on to the hot substrates.

The following reaction may take place.



3.3.4 Optimization of preparative parameters

In order to obtain Nb_2O_5 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, 350, 400 and 450°C.

Table 3.1: Optimized preparative parameters for Nb₂O₅ thin films.

Serial No.	Preparative parameter	Optimized Values
1	Solution concentration	0.005 M
2	Solution quantity	50 cc
3	Spray rate	8 cc/min.
4	Nozzle-substrate distance	25 cm
5	Air pressure	1 kg/cm ²

3.4 References

1. K. L. Chopra and I. J. Kaur, "Thin Film Device applications", Plenum Press, New York, 1983.
2. K. L. Chopra and S. R. Das, "Thin Film Solar Cells", Plenum Press, New York, 1983.
3. C. M. Lampkin, *Prog. Crystal Growth Charact.*, 1 (1979) 395.
4. P. S. Patil, *Materials Chemistry and Physics*, 59 (1999) 185.
5. R. R. Chamberline and J. S. Skarman, *J. Electrochem. Soc.*, 113 (1966) 86.
6. M. Fujimoto, T. Urano, S. Murai and Y. Nishi, *Jpn. J. Appl. Phys.*, 28 (1989) 2587.
7. I. Yagi, K. Kazikawa, K. Murakami and S. Kaneko, *J. Ceram. Soc. Jap.*, 102 (1994) 296.
8. C. H. Lee and L. Y. Lin, *Appl. Surface Sci.*, 92 (1996) 163.
9. A. Aoki and G. Nogami, *J. Electrochem. Soc.*, 143 (1996) L191.
10. P. S. Patil and P. R. Patil, *Tr. J. Phys.*, 18 (1994) 1330.
11. L. D. Kadam, C. H. Bhosale and P. S. Patil, *Tr. J. Phys.*, 21 (1997) 1037.
12. D. Craigen, A. Mackintosh, J. Hickmann and K. Colbow, *J. Electrochem. Soc.*, 133(1986) 1529.
13. C. H. Chen, A.A. Busyman, E.M. Kelder and J. Schoonman, *Solid State Ionics*, 80 (1995) 1.

14. R. N. Singh, J. F. Koenig, G. Pollierat and P. Chartier, *J. Electroanal. Chem.*, 314 (1991) 241.
15. B. Lefez, P. Nkeng and J. Lopitiaux, *Mat. Res. Bull.*, 31(1996) 1263.
16. C. S. Huang, C. S. Tao and C. H. Lee, *J. Electrochem. Soc.*, 144(1997) 3556.
17. A. G. Valyomana, S. Mathew, K. P. Vijaykumar and C. Purushottam, *Bull. Mater. Sci.*, 16(1993) 55.
18. J. P. Mangalhara, R. Thangraj and O. P. Agnihotri, *Bull. Mater. Sci.*, 10(1998) 333.
19. J. De Merchant and M. Cocivera, *J. Electrochem. Soc.*, 143(1996) 4054.
20. K.Y. Rajpure, A. M. Patil, C.D. Lokhande and C.H. Bhosale, *Thin Solid Films*, 331(1997) 114.
21. V. V. Killedar, C.D. Lokhande and C.H. Bhosale, *Thin Solid Films*, 289(1996) 14.
22. S. Lopez, S. Granados and A. Ortiz, *Semiconductor Sci. Technol.*, 11(1996) 433.
23. W.A.S.A. Ghafor, A.A. Awad and N. S. Othman, *Ind. J. Pure and Applied Phys.*, 31(1993) 123.
24. Y. D. Tembhurkas and J. P. Hirde, *Bull. Mater. Sci.*, 17(1994) 465.
25. S.P.S. Arya and H.E. Hinterman, *Thin Solid Films*, 193(1990) 841.
26. S. Kumari, A.K. Singh and O.N. Srivastava, *Supercond. Sci. and Technol.*, 9(1996) 405.

27. S.H. Pawar and P.N. Pawaskar, *Mater. Res. Bull.*, 30(1995) 277.
28. Y. Moriwaki, T. Sugano, C. Gasser, A. Fukuoka, K. Nakanishi, S. Adachi and K. Tanabe, *Appl. Phys. Lett.*, 69(1996) 3423.
29. H.P. Klug and H.A. Alexander, *X-ray Diffraction procedure*, 2 nd Edition, New York, Wiley VCH, 1974.
30. J. George and M.K. Radhakrishnan, *Solid State Commun.*, 33(1980) 987.
31. F. Micheltti and P. Mark, *J. Appl. Phys. Lett.*, 10(1967) 136.