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3.1 DESCRIPTION OF THE DEPOSITION TECHNIQUE. [SPRAY PYROLYSIS TECHNIQUE]

3.1.1 Introduction

Technological progress in many domains of modern society is ultimately dependent on the materials science and the engineering community's ability to conceive of novel materials with extraordinary combinations of physical and mechanical properties [1].

It is precisely the unusual combinations of physical attributes that are required of these materials that preclude their fabrication by conventional processing techniques. As a result, the successful development of such materials depends on the conception of radically different processing schemes. Research in the materials science and engineering driven in parts by this critical need, has progressively shifted towards the study and applications in the variety of devices [2].

There are various techniques by which one can deposit thin films. Thin films deposition techniques can be broadly classified in Table 3.1.

The choice of the particular method depends on several factors like

1. Material to be deposited as thin films
2. Nature of the substrate
3. Thickness of the film
4. Structure of the film
5. Application of the film

Among the methods, the chemical methods are relatively economical and easier than the physical methods. But there is no ideal method, to prepare the compounds and alloys in the form thin film, which will satisfy all the possible requirements. Among the chemical methods mentioned above, spray pyrolysis technique (SPT) is the most popular due its simplicity and low cost. A large number of conducting, semi conducting, noble metal oxides, spinel oxides, chalcogenide and super conducting materials can be prepared in the form of thin film by this technique.

Compounds in the thin film form on a variety of substrates like glass, ceramic or metallic, have been prepared by SPT. Many studies have been conducted over about three decades on SPT and the mechanism of thin film formation and influence of variables on the 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. 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 chalcogenide [17-22], ternary chalcogenide [23,24], superconducting oxides [25-28] etc.

Table 3.1 THIN FILM DEPOSITION TECHNIQUES

PHYSICAL		CHEMICAL	
Sputtering	Evaporation	Gas Phase	Liquid Phase
1) Glow discharge DC Sputtering	1) Vacuum Evaporation	1) Chemical vapour deposition	1) Electro-deposition
2) Triode Sputtering	2) Resistive heating Evaporation	2) Laser chemical vapour deposition	2) Chemical bath deposition (CBD)
3) Getter Sputtering	3) Flash Evaporation	3) Photo-chemical vapour deposition	3) Electro less deposition
4) Radio Frequency	4) Electron beam	4) Plasmaenhanced vapour deposition	4) Anodisation
5) Magnetron Sputtering	5) Laser Evaporation	5) Metal-Organic Chemical Vapour Deposition (MO-CVD)	5) Liquid phase Epitaxy
6) Face Target	6) Arc		6) Sol- gel
7) Ion Beam	7) R. F. Heating		7) Spin -Coating
8) A.C. Sputtering			8) Spray Pyrolysis Technique
			9) Ultrasonic (SPT)
			10) Successive-Ionic Layer Adsorption and Reaction (SILAR)

It is a simple and low cost technique and has capability to produce large area thin films. 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 vapour deposition method, spray pyrolysis does not require high quality targets and / or substrates nor 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 temperature (100-550°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 substrate, occur. Spray pyrolysis offers such an opportunity.

3.1.2 The Spray Pyrolysis Technique (SPT)

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. Other volatile by-products and solvents escape in the vapour phase. The substrates provided 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

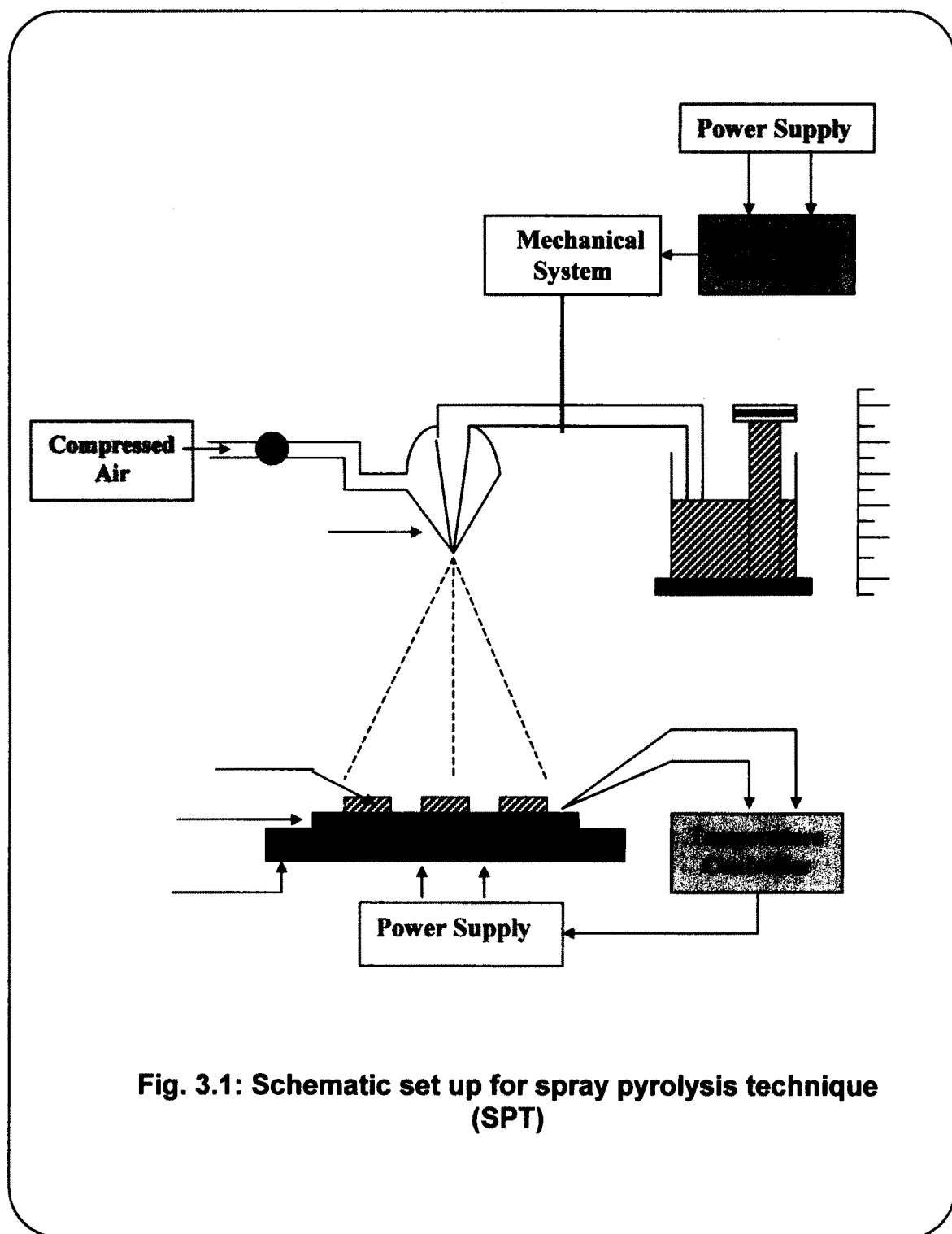


Fig. 3.1: Schematic set up for spray pyrolysis technique (SPT)

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 film thickness depends on the distance between the nozzle and substrate, solution concentration and quantity and substrate temperature. The film formation rely on the process of droplet landing, reaction and solvent evaporation, which are related to droplet size and its momentum. An ideal deposition condition is when the droplet approaches the substrate just as the solvent is completely removed. Lampkin [3] showed that, depending on droplet velocity and flow direction, a droplet would flatten, skip along the surface or hover motionless.

The schematic diagram of the spray pyrolysis technique is shown in figure 3.1. It consist 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 the change in height of the solution, forms liquid level monitor.

(d) Hot plate:

The iron disc, with diameter 16 cm and thickness 0.7cm, 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 centre 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 pressure of the gas. A corning glass tube of length 25 cm and a diameter of 1.5 cm 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 gasses evolved during spray deposition.

3.1.2 The Steps In Spray Pyrolysis Process

The chemical versatility of spray pyrolysis is multi component, non-oxide and composite powders synthesized as porous or nano particles. Based on the principles presented bellow the advanced fabrication is well-defined set of characteristics, including chemical purity and homogeneity. Therefore spray pyrolysis processes offer many opportunities to synthesize above components.

In spray pyrolysis the process parameters like precursor solution, evaporation period, thermolysis and atomization are very important in the study of structural properties, morphology and crystallinity of the thin films. These four process parameters are discussed in the following section.

- 1) **Precursors:** - Precursor solutions play a vital role in the formation of thin film of various compounds. The true solutions, colloidal dispersions, emulsions, and sols can be used as aerosol precursors. Aqueous solutions are commonly used due to ease of handling safety,

low cost, and availability of a wide range of water-soluble metal salts. The solute must have a high solubility increase in particle yield of the process. Increasingly, alcoholic and organic solutions have been studied due to the interest in the synthesis of inorganic materials from metal organic and undergo gelation or polymerization and for the synthesis of non-oxide ceramic solutions.

In general metal chlorides and oxy-chlorides are the highest water solubilities relative to other metal salts and are used for industrial production. The corrosive nature of the product gases at the adverse effect of residual chlorine on ceramic sintering decreases the general attractiveness of these salts for advanced ceramic solution synthesis, but the technology for handling such systems is available. Other water-soluble metal salts such as nitrates, acetates and sulfates can also introduce impurities, which may adversely affect subsequent processing, sintering or properties. The low solubility of metal acetates and high decomposition temperature of metal sulfates limit the use of these water-soluble salts. Therefore hybrid systems in which one of the components is added via a solution and remainder as particles have also been reported. A physical and chemical characteristics of soluble chemical precursors strongly influence a characteristics of particles formed by spray pyrolysis. Unlike most solution precipitation processes

here the metal ions precipitate as sparingly soluble salts like hydroxides, oxalates, etc., the dissolved precursor salts precipitate during the evaporation stage of spray pyrolysis.

- 2) **Atomization:** - A variety of atomization techniques have been used for solution aerosol formation, including pneumatic, ultrasonic, and electrostatic. These atomizers differ in droplet size, rate of atomization and droplet velocity. The velocity of the droplet when it leaves the atomizer is important because it can determine the heating rate and the residence time of the droplet during spray pyrolysis. The size of the droplets produced with pneumatic or pressure nozzles decreases when the pressure difference across the nozzle is increased. Two-fluid atomizers represent off-the-shelf technology capable of atomizing large quantities of liquid at droplet velocities from 0.5 to 20 m/s but with minimum droplet sizes of only 10 μm . Ultrasonic nozzles, conversely, apply a relatively smaller amount of energy, but efficiently couple that energy to achieve droplet formation. Ultrasonic atomizers can easily produce droplets down to 2 to 4 μm but the atomization rate is limited to less than 2 cm^3/min . The concept of spray pyrolysis is to produce one particle per droplet because small particles are required for most advanced ceramic applications, there is a serious need to develop the techniques that can atomize large quantities of small droplets at low exit velocities.

Indeed, it is from production reasons that companies have used pressure atomizer instead of ultrasonic atomizers. For a specific atomizer the droplet characteristics depend on the solution density, viscosity and surface tension. The viscosity of metal organic and organic acid precursor can range orders of magnitude depending on chemistry as shown in Table 3.2.

Table 3.2: Characteristics of atomizers commonly used for spray pyrolysis

Atomizer	Droplet size μm	Atomization rate cm^3/min	Droplet velocity m/s
Pressure	10- 100	3- no limit	5- 20
Nebulizer	0.1 - 2.0	0.5 - 5.0	0.2 - 0.4
Ultrasonic	1- 100	< 2	0.2 - 0.4
Electrostatic	0.1 – 10	-----	-----

- 3) **Evaporation period:** - During first stage of spray pyrolysis, evaporation of the solvent from the surface of the droplet, diffusion of the solvent vapour away from the droplet in the gas phase, shrinkage of the droplet, change in droplet temperature and diffusion of solute towards the centre of the droplet. It is useful to compare the characteristic time constants of these processes to identify the most important factors during spray pyrolysis. The characteristic time refers to the time required for a process to reaches steady state; the shorter the time, the sooner it reaches

the steady state. The characteristic time for the diffusion of the solvent vapour is much shorter than that for subsequent droplet shrinkage. Therefore it is concluded that the vapour diffusion proceeds much faster than droplet shrinkage and reaches steady state before there is a significant change in the droplet size. The temperature profile of the air and droplet can be assumed to be reaching steady state before droplet shrinkage. Solute diffusion at high humidities is the slowest process but at the low humidities the rate of droplet shrinkage may be comparable to the rate of solute diffusion. Therefore the factors control particle formation are according to 1) Evaporation of liquid droplets 2) evaporation from solution droplets 3) temperature of liquid droplets 4) temperature of solution droplets 5) Solute diffusion in a droplet 6) solute condensation etc. The various steps of spray pyrolysis process are shown in Figure 3.2.

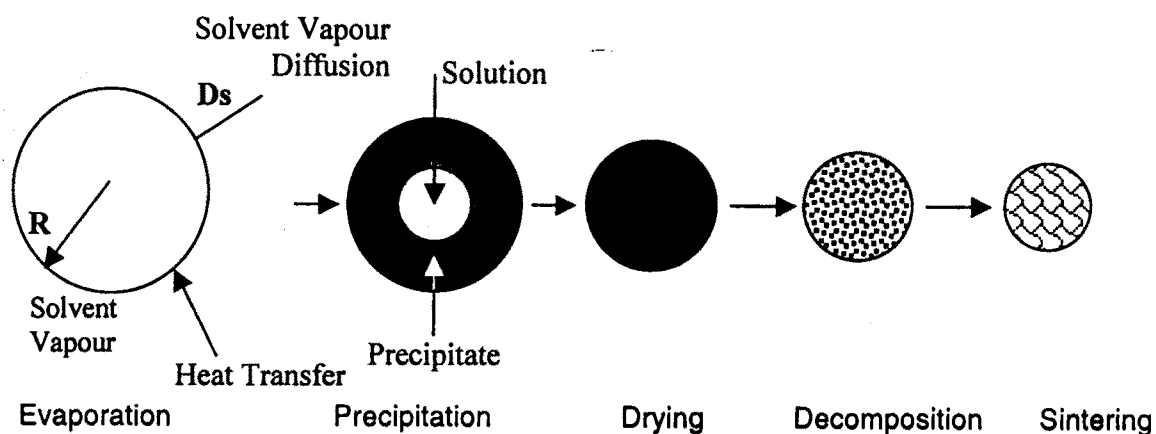


Fig. 3.2 The Steps of Spray Pyrolysis Process.

- 4) **Pyrolysis:** It is believed that the processes of evaporation pyrolysis and sintering should be conducted in separate reactors to obtain maximum control of individual process and because time temperature conditions are significantly different. In most of spray pyrolysis techniques pyrolysis and sintering stages are conducted after spray pyrolysis as a consequence of insufficient droplet residence time to complete the pyrolysis reaction and sintering. Since the particles are reactive after the pyrolysis it is important to take full advantage of the spray pyrolysis process. The particles densifying the solid state mechanism do not undergo interparticle sintering during spray pyrolysis because of inter particle collision times are too short for neck formation by surface diffusion and the striking coefficient of micrometer size particles are small. The melting temperature of most metal oxides is generally outside the furnace capabilities of most spray pyrolysis processes.

3.2 CHARACTERIZATION TECHNIQUES

3.2.1 Introduction:

In this section, the theoretical aspects of various characterization techniques like thermo gravimetric analysis (TGA), differential thermal analysis (DTA), scanning electron microscopy (SEM), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), electrical resistivity measurements, thermoelectric power (TEP) and optical absorption are

introduced. These techniques are used for thermal, structural, electrical and optical characterization of SnO₂ thin films. The electrochemical techniques like cyclic-voltammetry (CV) and chronoamperometry (CA) have also been discussed.

3.2.2 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 result 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 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.).

3.2.3 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 peak. 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.

3.2.4 Thickness Measurement

3.2.4.1 Weight Difference Method:

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.

$$t = m / A.\rho_b \quad \dots\dots\dots(3.1)$$

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.

3.2.4.2 Interference Method:

Optical interferometric method was used to measure the thickness of the as-deposited tin oxide thin films. The transmittance spectrum shows maxima and minima for the continuous scan of all the samples in the wavelength range 350-850 nm, due to optical interference between film layer and surface of the substrate. The thickness (t) of the films can be determined from any two maxima (or two minima) using the relation, (3.2),

$$t = \frac{M\lambda_1\lambda_2}{2 [n_f(\lambda_1)\lambda_2 - n_f(\lambda_2)\lambda_1]} \quad \text{----- (3.2)}$$

Where, M is the number of oscillations between two extrema occurring for λ_1 and λ_2 , $n_f(\lambda_1)$ and $n_f(\lambda_2)$ are the corresponding refractive indices.

3.2.4.3 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 using XRD 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, (3.3),

$$2d \sin\theta = n\lambda \quad \dots\dots\dots(3.3)$$

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 for known values of λ and n. The X-ray diffraction data thus obtained is printed in a tabular form on paper and is compared with JCPDS (Joint Committee of 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.

3.2.4.4 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 the specimen surface) if the low energy secondary electrons (< 50 eV) are collected.
- (ii) 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 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 images which underlines the value of high magnification SEM images of rough surfaces.

3.2.4.5 Fourier Transform Infrared Spectroscopy (FTIR) and

Raman Spectra:

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 (ν), 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 gives the 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.

Usual optical materials, glass or quartz cannot be used for sample handling because it strongly absorbs IR radiations. Usually sample is prepared transparent to IR radiations.

Raman Scattering is the powerful light scattering technique used to diagnose the internal structure of molecules and crystals. In a light scattering experiment, light of a known frequency and polarization is scattered from a sample. The scattered light is then analysed for frequency and polarization. Raman scattered light is frequency-shifted with respect to the excitation frequency, but the magnitude of the shift is independent of the excitation frequency. This "Raman Shift" is therefore an intrinsic property of the sample.

The rule of conservation of energy dictates that some energy is deposited in the sample. A definite Raman shift corresponds to excitation energy of the sample (such as the energy of a free vibration of a molecule). In general, only some excitations of a given sample are “Raman active”, that is, only some may take part in the Raman scattering process. Hence, the frequency spectrum of the Raman scattered light maps out part of the excitation spectrum. Other spectroscopic techniques, such as IR absorption, are used to map out the non-Raman active excitations.

Information related to the spatial form of the excitation, derives from the polarization dependence of the Raman scattered light. The shape of the excitation in a material, for example a vibration pattern of the atoms in a molecule, and the polarization dependence of the scattering, are determined by the equilibrium structure of the material through the rules of group theory. By this route one gains valuable and unambiguous structural information from the Raman polarization dependence.

The frequency is plotted relative to the laser frequency, so the frequency scale represents the Raman shift. The peaks in the intensity occur at the frequencies of the Raman active modes. The spectra differ because of different polarization conditions enforced on the incident and scattered light. Different polarization conditions select different sets of Raman active excitations.

3.3 TRANSPORT PROPERTIES

Surface transport phenomena are well known to have a strong influence on the electronic properties of bulk semiconductors. These phenomena play an important role in the transport properties of semi conducting film of about 1 μm thickness. This role results from the fact that when transport takes place through thin specimens, the carriers are being subjected to considerable scattering by the boundary surface in addition to normal bulk scattering. This additional scattering will reduce the effective carrier mobility below the bulk value and will thus give rise to conductivity size effects. Study of these size effects can yield information on the electronic structure of a surface and is therefore of considerable fundamental and practical importance. Surface transport phenomena in bulk semiconductors has received much attention in recent years. An excellent review of the subject is given by Pulliam et al. [30]. The important transport properties i.e. electrical resistivity and thermoelectric power are discussed in next sections.

3.3.1 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 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. Uniform sample resistivity is given by equation 3.4.

$$\rho = (A/I) (V/d) \quad \text{-----} \quad (3.4)$$

In the case of semi conducting thin films, the resistivity decreases with increase in temperature. The thermal activation energies E_a are calculated by using conductivity relation 3.5,[31].

$$\rho = \rho_0 \exp (-E_a/kT) \quad \text{-----} \quad (3.5)$$

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

3.3.2 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 junction 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 types of carriers in the semiconductors.

3.3.3 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.

The optical absorption spectra of semiconductors generally exhibits a sharp rise at a certain value of the incident photon energy which can be attributed to the excitation of electrons from valence to conduction band (may also involve acceptor or donor impurity levels, traps, excited etc.). The

conservation of energy and momentum must be satisfied in optical absorption process. Basically there are two types of optical transitions that can occur at the fundamental edge of the crystalline semiconductor, direct and indirect. Both involve the interaction of an electromagnetic wave with an electron in the valence band, which is rose across the fundamental gap in the conduction band. However, indirect transition also involves simultaneous interaction with lattice vibration. Thus the wave vector of the electron can change in the optical transition. The momentum change being taken or given up by phonon. 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 figures 3.3 a) Hence a wave vector k for electron remain unchanged in E-K space. The optical transition is denoted by a vertical upward narrow. For simple parabolic bands and for direct transition, absorption coefficient α is given by using the relation 3.6, [32].

$$\alpha = \alpha_0 (h\nu - E_g)^n / h\nu \quad \text{-----} \quad (3.6)$$

Where E_g is the separation between bottom of the conduction 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 α_0 is a constant depending upon the transition probability for direct transition. For

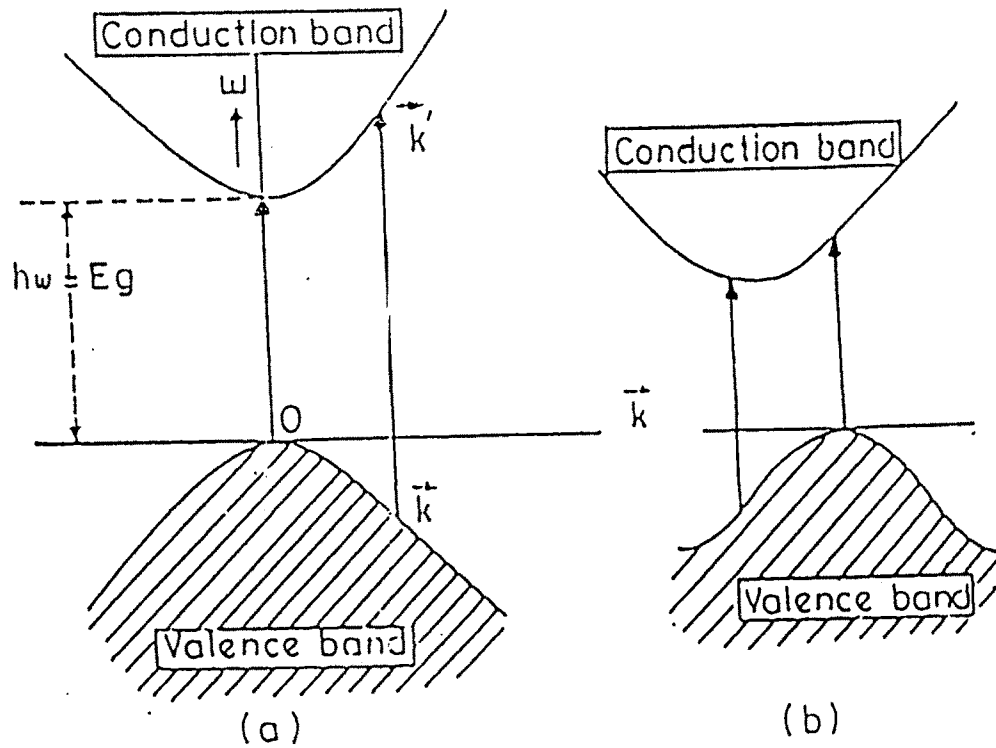


Figure 3.3 E-K diagram showing a) direct and b) indirect inter-band transition.

allowed direct transitions $n = 1/2$ and allowed indirect transition $n = 2$. Thus if the plot of $(h\nu)^2$ 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 $\alpha = 0$.

Let's visualize a situation in figure 3.3b) where interband transition takes places between different k -states. Since these must satisfy the momentum conservation laws. The only way such transition can take place is through the emission or absorption of a phonon with wave vector q as by equation 3.7.

$$K' \pm q = k + K \quad \dots\dots\dots(3.7)$$

The transition defined by equation (3.6) is termed indirect transition. For indirect transition equation (3.8) prevails.

$$\alpha = \alpha_0 (h\nu - E_g)^n / h\nu \quad \dots\dots\dots(3.8)$$

Where $E_g = E_g' \pm E_p$, E_g is indirect band gap energy and E_p is the phonon energy. For allowed transition $n = 2$ and for forbidden transition $n = 3$. The band gap energy is determined by extrapolating the linear portion of the plot $(h\nu)^n$ versus $h\nu$ to the energy axis at $\alpha = 0$

3.4. ELECTROCHEMICAL CHARACTERIZATION:

Electro analytical 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 electro analytical 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 as the working electrode. The second one, termed the reference electrode, is of constant potential

3.4.1 Cyclic Voltammetry (CV):

Cyclic voltammetry is the most widely used technique for acquiring qualitative information about electrochemical reactions. The power of cyclic voltammetry results from its ability to rapidly provide considerable information on the thermodynamics of redox processes and the kinetics of heterogeneous electron transfer reactions and adsorption processes. Cyclic voltammetry is often the first experiment performed in an electroanalytical study. In particular, it offers a rapid location of redox potentials of the electroactive species, and convenient evaluation of the effect of media upon the redox process.

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. It is assumed that only the oxidized form O is present initially. Thus, a negative going potential scan is chosen for the first half cycle, starting from a value where no reduction occurs. As the applied potential approaches the characteristic E° (Standard electrode potential) for the

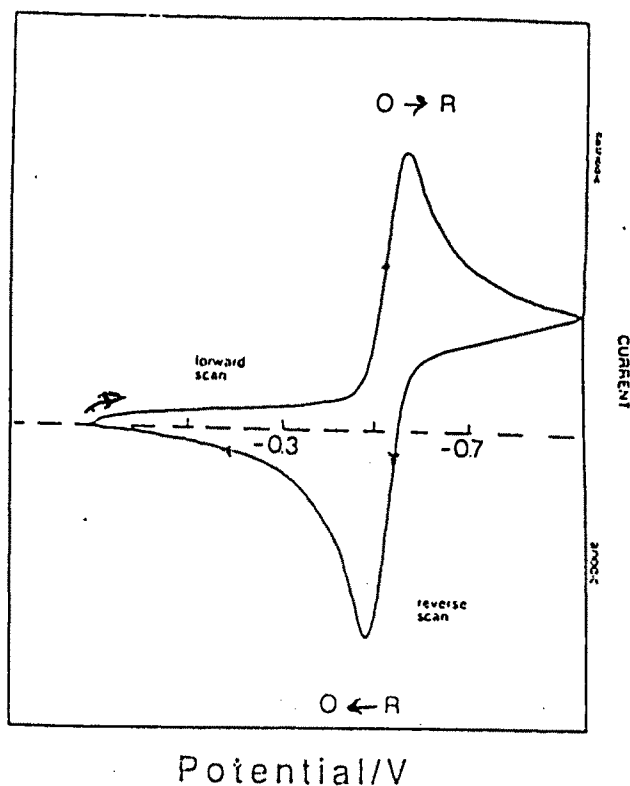


Figure 3.4 Typical cyclic voltammogram for a reversible $O + ne^- = R$ redox process.

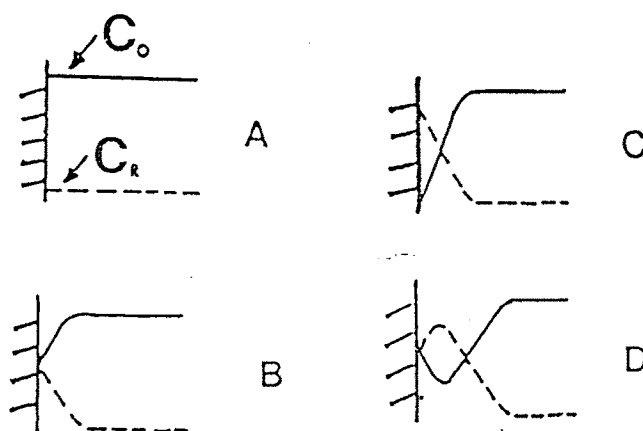


Figure 3.5 Concentration distribution of the oxidized and reduced forms of the redox couple at different times during a CV experiment corresponding to (A) the initial potential, (B) and (D) the formal potential of the couple during the forward and reverse scans, respectively, and (C) the achievement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

redox process, a cathodic current begins to increase, until a peak is reached. At least $90/n$ mV beyond the peak), the direction of the potential sweep is reversed. During the reverse scan, R molecules (generated in the forward half cycle and accumulated near the surface) are reoxidized back to O, and anodic peak results.

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 gradient 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 interaction and intercalation processes in the electrochromic materials.

3.4.2 Chronoamperometry (CA):

CA involves stepping the potential of the working electrode (WE) from a value at which no faradic reaction occurs to a potential at which the surface concentration of the electroactive species becomes effectively zero (figure 3.6). 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. This involves a gradual expansion of the diffusion layer associated with the 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, (3.9).

$$i(t) = nFACD^{1/2} / \pi^{1/2}t^{1/2} = kt^{-1/2} \quad \text{-----(3.9)}$$

Such a $i(t^{1/2})$ constancy is often termed a “Cottrell behaviour”.

CA is often used for measuring the diffusion coefficient of electroactive species or the surface area of the WE. The potential step experiment can also be used to record the charge versus time dependence. Such a charge measurement procedure, known as chronocoulometry, is useful for measuring the quantity of adsorbed reactants. It has been widely used to investigate the diffusion coefficient, the response times and amount of charge intercalated into the SnO₂ thin films. This technique is helpful in studying the intercalation/ deintercalation kinetics in electrochromic cell systems.

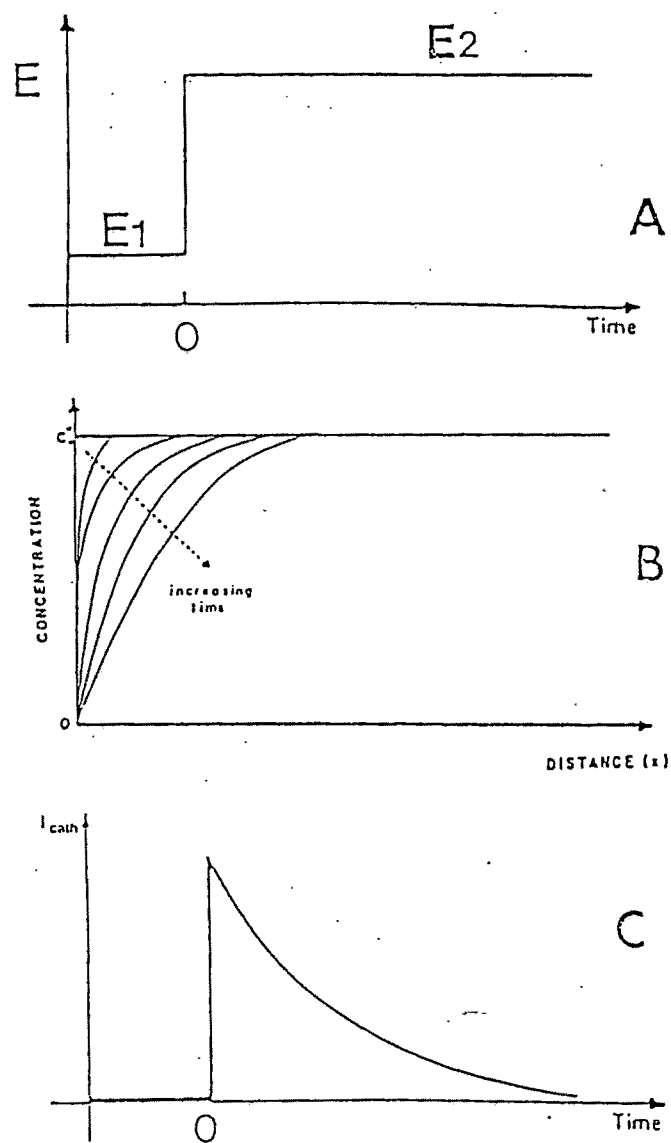


Figure 3.6 CA experiment: (A) potential-time waveform; (B) change of concentration profiles as time progresses; (C) the resulting current-time response.

3.5 EXPERIMENTAL

3.5.1 Substrate Cleaning:

Cleanliness of the substrates, for thin film deposition is most 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, and lint and oil particles. Cleanliness is the process of breaking the bonds between substrates and contaminants without damaging the substrates. There are various methods to supply energy for breaking such bonds, such as heating, bombarding by ions scrubbing etc. 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 vapour of the alcohol.

3.5.2 Preparation of F.T.O. coated glass substrates.

A 100 cc of 2M stannic chloride ($\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$) solution was prepared in doubly distilled water and 14.285 gm of ammonium fluoride (NH_4F) was dissolved in it, to obtain 40% doping concentration of fluorine. From the above mixture, 10 cc solution was taken and 20 cc of propane 2-ol (isopropanol) was added. The final solution was sprayed through the specially designed glass nozzle at the rate of 5 cc./min. The substrates were kept at 525°C . It was found that these conducting glasses have $10\text{-}50 \Omega / \text{cm}^2$ sheet resistance and about 90% transparency.

3.5.3 PREPARATION OF PRECURSOR SOLUTIONS

3.5.3.1 Preparation of stannic chloride solution

An appropriate weight of penta-hydrated stannic chloride ($\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$) Powder (A.R. grade, Merck Make, 98% purity) was taken using digital microbalance so as to get the required concentration of the solution. The weighed stannic chloride powder was dissolved in an appropriate quantity of doubly distilled water to obtain desired concentration of the solution. This solution was taken as a starting solution to be sprayed onto the hot substrates. The pyrolytic decomposition of the solution results in to the formation of tin oxide thin films.

3.5.3.2 Preparation of tributyltin acetate (TBTA) solution.

The appropriate quantity of precursor powder (TBTA) was taken using digital microbalance so as to get required concentration of solution and was dissolved in methanol at room temperature. The required concentrations of the TBTA solution was obtained by adding appropriate quantity of the methanol.

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