Chapter II

Experimental

2.1 Introduction

The development of modern society is purely depending on the advancement of technology, which in turn is not possible with technological progress in the field of thin film science. Mechanical, electrical, as well as optical properties of the thin films are different than that of the bulk. It has been shown that many thin film properties are often far better than the bulk properties. Thin film synthesis has directly or indirectly advanced in many new areas of materials science and applications including research areas such as, solid-state physics and chemistry. Which are based on the phenomena characteristics of the physical properties of the films such as thickness, geometry, and crystal structure. Thin films are peculiar in several respects. Thin film technology has revolutionized the field of optics, electronics and magnetism, considering the new and improved optics, electronics, magnetic devices and photovoltaic etc. Efficiency of the materials increases as the particle size of the materials goes on decreasing due to increase in the surface area of the films. Further research in the nano structured materials is increasing in the recent years.

The advantages of nanostructured thin film device are low material consumption and possible use of flexible substrates. Spray pyrolysis technique is very suitable method for the preparation of the metal oxide thin films. Various metal oxide semiconductors (MOS) such as TiO_2, Zn_2SnO_4, WO_3, SnO_2, ZnO, V_2O_5, $SrTiO_3$ etc. have been prepared by spray pyrolysis technique. ZnO thin films have been prepared using various techniques such as vacuum evaporation, sputtering, sol-gel, spray pyrolysis, pulsed laser deposition (PLD), molecular beam epitaxy (MBE), and chemical vapor deposition (CVD), magnetron sputtering etc. These physical and few chemical methods require high quality of targets and also the costly equipments which is reduced in spray pyrolysis technique. Among these the chemical spray pyrolysis technique is simple, low-cost and can used for deposition of large area thin films.

This chapter explains working and film formation mechanism using spray pyrolysis technique (SPT). Factors affecting thin film formation and its growth are explained in detail. Processes to be carried out before actual experiments like substrate cleaning, precursor solution preparation for different dopants and undoped ZnO thin films have also been illustrated. Mechanism of the doped and undoped thin film formation is given step wise which gives idea about the structural variation in the films.

2.2 Apparatus and methods

Nowadays there is demand for thin film deposition and their wide range of potential applicability in the various fields of science and technological progress. A lot of efforts have been taken to deposit thin films of required properties with different physiography such as thickness, texture, uniformity, orientation etc. for particular application. Physicochemical properties of thin films such as structural, morphological, electrical, optical, stoichiometry etc. of a given material are strongly dependent on the method of deposition, the types of substrates, the deposition temperature, and time for deposition etc. [1].

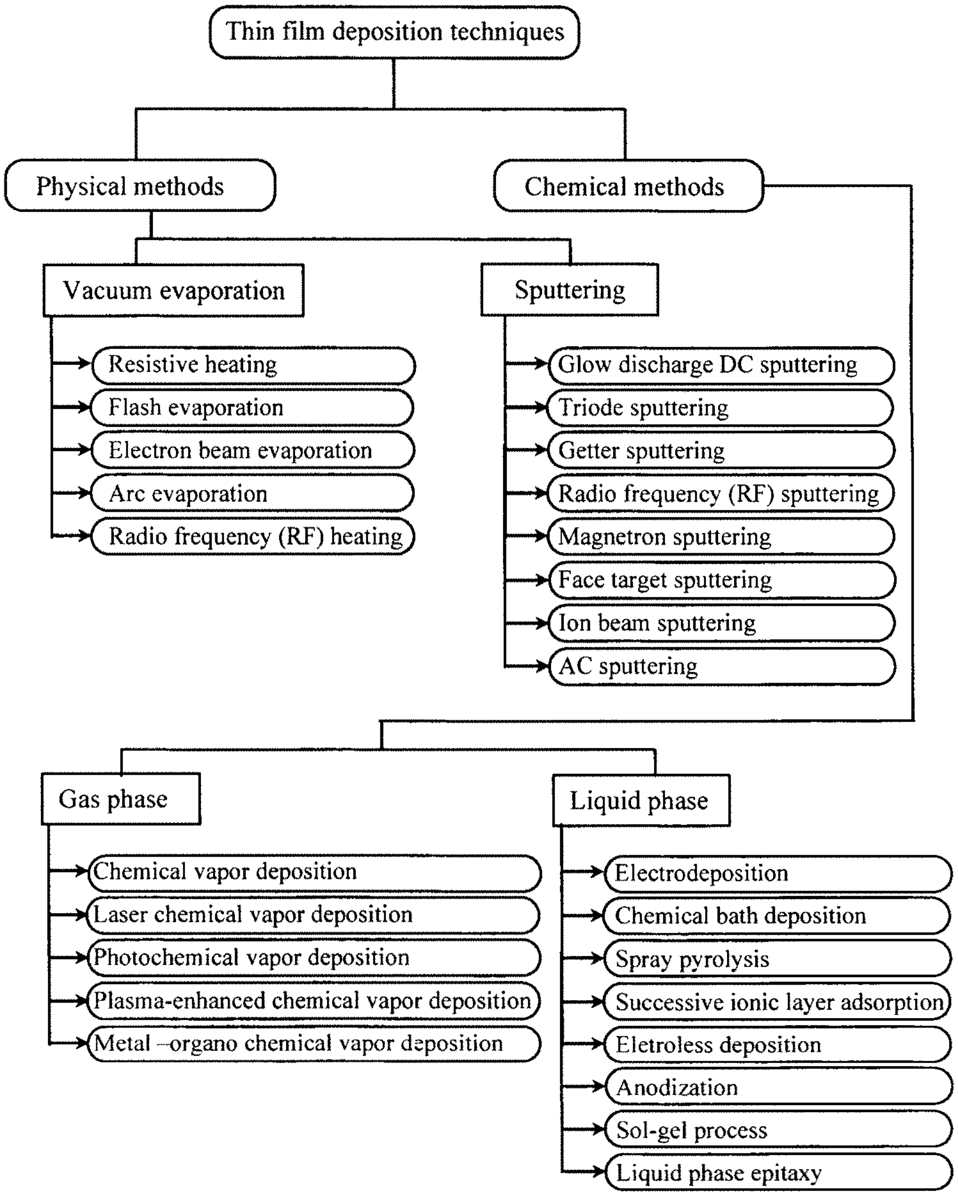

Fig.2.1. Classification of thin film deposition techniques.

Modern technology requires thin films for different applications due to the enhanced efficiency of the materials [2]. The application and properties of the material determines the most suitable technique for the deposition of thin films which gives enhanced results. Thin films can be deposited by number of physical and chemical techniques and can be classified as shown in figure 2.1.

Among the various available methods the chemical methods are cost-effective and easier as compared with the physical methods. There is no unique method to prepare thin films, which will fulfill all probable requirements. Method of selection depends on the purpose of application of the films and on the environment in which films are being used. Among the chemical methods, the spray pyrolysis technique (SPT) is the most popular and economic method because of large number of transparent conducting and semiconducting thin films can be prepared by this technique. In this technique, thin films can be deposited on different types of substrates like glass, metallic, alumina, ceramic, silicon etc. Overall studies have been carried out, about three decades on spray pyrolysis processing and preparation of thin films. The influence of various preparative parameters on the film formation process has been reviewed in the literature. Thomas et al [3] deposited SnO_2 thin films by spray pyrolysis technique for LPG sensor. Shinde and Rajpure [4] reported the application of the spray deposited ZnO thin films for high-performance UV detectors. Due to the reproducibility of this technique on a large scale and instrumentation simplicity, it offers most attractive alternative for preparation of various metal oxide thin films [5-7].

2.2.1 Spray pyrolysis technique

2.2.1.1 Basics and working of spray pyrolysis technique

The basic working principle in the spray pyrolysis technique is decomposition of salts of a desired compound to be deposited due to the temperature gradient. The precursors used for making preparation of solution are selected such that the byproducts of the reaction other than the material to be formed should be volatile at the deposition temperature. Spray pyrolysis technique involves spraying of a precursor solution prepared using soluble salts on to the preheated substrates, where the constituents react to form a chemical compound.

Along with the simplicity, spray pyrolysis technique has a number of advantages. Spray pyrolysis is easy simple and low-cost method for the semiconductor thin films preparation. Large area adherent films of high quality with uniform thickness could easily be produced using spray pyrolysis technique. Spray pyrolysis does not require high quality targets, it uses cheaper salts which usually, are water soluble. Also any type of substrates can be used for the deposition of thin films, which deals a great advantage to be scaled up for bulk industrial applications. The deposition rate and thickness can be easily controlled by controlling the preparative parameters over a wide range by changing the spray parameters. Besides this major advantage of spray pyrolysis technique is the moderate operating temperature ranging from 100–500°C, which could produce thin films on different materials. It offers a very easy way to dope films with almost any elements in any ratio, by simply, adding it in some form to the spray solution. 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.

When precursor solution is sprayed, it forms aerosols due to the pressure of the carrier gas. Aerosol droplets reaching the hot surface of substrate undergo thermal decomposition and forms cluster of crystallites as a product. Byproducts formed in the process escape in the vapor phase of the film formation prior to reaching substrate. The heating elements provide thermal energy which decomposes and causes subsequent recombination of the constituent elements, follows sintering and crystallization of the material forming coherent film. The required thermal energy for the decomposition is different for the different materials and solvents. Atomization of the precursor solution depends on the spray rate and pressure of a carrier gas.

Due to the simplicity of the apparatus and the good productivity of this technique on a large scale, it gives extremely fascinating way for the formation of thin films of metal oxides [8-14], metallic spinel by oxides [15-16], group I-VI, II-VI, III-VI, IV-VI, V-VI, VIII-VI, binary chalcogenides [17-20], group I-III-VI, II-II-VI, II-III-VI,II-VI-VI and V-II-VI ternary chalcogenides [21-22]. Recently chemical SPT has also been successfully employed for the formation of superconducting oxide films [23-25], etc. The chemical versatility of spray pyrolysis is multi component, and composite films synthesized as porous or nanoparticles. Therefore, spray pyrolysis process offers many opportunities to synthesize thin films with different components as motioned above. We have used locally fabricated spray pyrolysis system throughout our experiments.

2.2.1.2 Essentials of spray pyrolysis technique

Fig.2.2 shows the schematic of the spray pyrolysis technique. It mainly consists of rotor for spray nozzle, spray nozzle, liquid level monitor, gas regulator, gas valve, hot plate and airtight fiber chamber.

a) Spray nozzle

It is made up of glass and consists of the solution tube surrounded by the glass bulb. With the application of pressure to the carrier gas, the vacuum is created at the tip of the nozzle, and sucks solution in the solution tube and the spray starts.

b) Rotor for spray nozzle

Stepper motor-based microprocessor controller is used to control the linear simple harmonic motion of the spray nozzle over the required length of the hot plate. Hence, the to-n-fro motion and the speed of the spray nozzle is monitored in a controlled manner.

c) Liquid level monitor

The spray rate at a fixed air pressure depends upon the height of the solution measured with respect to the tip of the nozzle. The arrangement for the change in height of the solution forms the liquid level monitor.

d) Hot plate

The iron disc (with diameter 16 cm and thickness 0.7 cm to which 2000 W heating coil is fixed) served as a hot plate. Maximum temperature of 600 ± 5°C can be achieved. Substrate temperature is measured using chromel-alumel thermocouple. It is fixed at the center of the front side of the iron plate. The temperature of the hot plate is supervised with the help of temperature controller (SELEC TC 203).

e) Gas regulator valve

The gas regulator valve is used to control the pressure of the carrier gas flowing through the gas tube of the spray nozzle. Gas flow meter is used to measure air flow rate through the nozzle. Air pressure depends upon the size of the air flow meter, the air flow meter is usually calibrated from nozzle to nozzle.

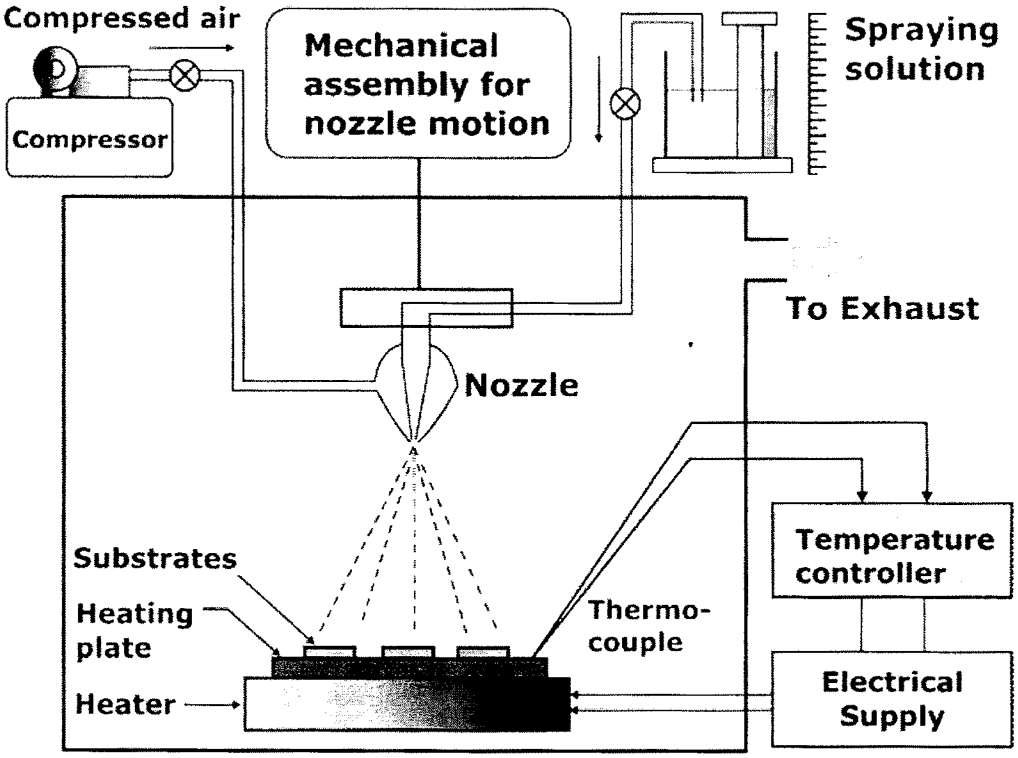

Fig 2.2 Schematic diagram of the spray pyrolysis method

f) Air tight fiber chamber

Since the number of toxic gases are evolved during the thermal decomposition of sprayed solution, spraying system is fixed inside airtight chamber. An airtight chamber of the size (35 cm x 65 cm x 100 cm) was used. The outlet of chamber is fitted to exhaust fan to remove the gases evolved during thermal decomposition.

2.2.1.3 Factors governing spray pyrolysis technique (SPT)

In spray pyrolysis, the process parameters like precursor solution, aerosol formation of solution, aerosol transport and decomposition are very important while studying the structural, optical, electrical properties, crystallinity and morphology of the thin films. These spray parameters are discussed as follows,

a) Precursor solution

Precursor solution plays a vital role in the formation of thin films. The true solutions, emulsions, colloidal solution, and sols can be used as precursors. Aqueous solutions are generally preferred due to easy handling, environmental friendliness, low cost, and abundance of a wide range of water-soluble metal salts. The solute must have high solubility, which increases the yield of the process. Increasingly, alcoholic and organic solutions have been studied due to the interest in the synthesis of organic materials from metal organic and undergo polymerization and for the synthesis of non-oxide ceramic solutions.

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

b) Atomization of precursor solution

The critical operation of the spray pyrolysis technique is to produce uniform and fine droplets by thermal decomposition. A variety of atomization techniques have been used for solution aerosol formation, including pneumatic, ultrasonic, and electrostatics. Some of spray atomization techniques include (a) improved spray pyrohydrolysis [26], (b) microprocessor based spray pyrolysis [27], (c) electrostatic spray pyrolysis [28,29], (d) corona spray pyrolysis [30,31],(e) ultrasonic nebulized atomization technique [16] etc. These atomizers differ in formation of different sized droplets, atomization rate and velocity of droplets. The velocity of the droplet when it leaves the atomizer is very important as it determines 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 nuclei is increased. For a specific atomizer the droplet characteristics depend on the density, viscosity and surface tension of the solution.

The quality of film also depends on the flow rate of the carrier gas it carries solution from the nozzle. When the air pressure is high, droplet size is small and vice versa. However, this causes decrease in substrate temperature due to rapid splashing of droplets. On the other hand, if the air pressure is too small, the larger droplets fall onto the substrates and cools down even faster. Hence, it is very important to optimize the air pressure.

c) Aerosol transport

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 on to the preheated substrates. The pyrolytic decomposition of the aerosols depends on the substrate temperature. The formation of thin films with desired properties is possible only at optimum substrate temperature.

In an aerosol, the droplet is transported and eventually evaporates. In case of dense films, it is important during transportation as many droplets as possible fly to the substrate without forming particles in the air before reaching the surface. Sears et al. investigated the mechanism of SnO_2 film growth [31]. The influence of forces, which determine both the trajectory of the droplets and evaporation, were examined and a film growth model was proposed. Gravitational, electric, thermophoretic and Stokes forces were considered for the same. Due to thermophoretic force droplets repelled away from a hot surface, as the gas molecules from the hotter side of the droplet rebounded with higher kinetic energy as compared with the cooler side. Thermophoretic forces keep most droplets away from the surface in non-electrostatic spray systems. In conclusion it is said that the film grows from the vapour of droplets passing very close to the hot substrate in a manner of chemical vapour deposition (Fig. 2.3). Droplets that strike the substrate form a powdery deposit. It is suggested that forcing droplets closer to the substrate while avoiding actual contact would improve the efficiency of film growth.

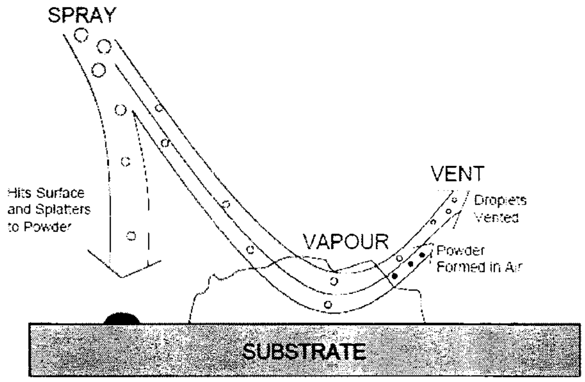

Fig.2.3 Schematic of aerosol transport

The aerosol droplets experience evaporation of the solvent during the transport to the substrate. This leads to reduction in the size of the droplets and also to the formation of a concentration gradient within the core of droplet. The precursor solution precipitates within the droplets, when the concentration exceeds the solubility limit of the compound. This is due to solvent evaporation at higher rate and slow solute diffusion. This forms porous crust and hollow particles, which increases the film roughness.

d) Decomposition of precursor

As droplets reach in the vicinity of the substrate and hits it, many processes occur simultaneously such as residual solvent evaporation, droplet spreading over the surface of substrate, and decomposition of the salt due to the high temperature. Many models have been put forth explaining the process of decomposition of a precursor and film formation. Well satisfying model suggested by many researchers is that only a kind of CVD process gives high quality films by spray pyrolysis.

Viguie and Spitz [32] classified chemical spray deposition processes according to the type of reaction that occurs during the film formation. Usually, the important variables are temperature of the surrounding, gas flow rate, distance between nozzle and substrate, viscosity of the solution, solution concentration, spraying rate, and motion of the nozzle. Further chemical composition of the carrier gas and/or environment, are also important.

Various steps during pyrolysis of aerosols are as explained below (Fig. 2.4).

- At first, aerosol formation of the droplets takes place at the tip of the nozzle and due to the temperature gradient solvent evaporation starts, (Process A).
- Secondly, solvent evaporation continues and it forms precipitate as the droplets are travelling towards high temperature, (Process B).
- Successively pyrolytic decomposition of the precipitate occurs due to the temperature gradient before the precipitate reaches the substrate, (Process C).
- Pyrolysed precipitate when reaches the substrate, nucleation and growth of film starts on the substrate, (Process D).
- Nuclei growth leads to the formation of continuous thin layer of metal oxide, (Process E).
- With deposition time, film thickness increases (Process F).

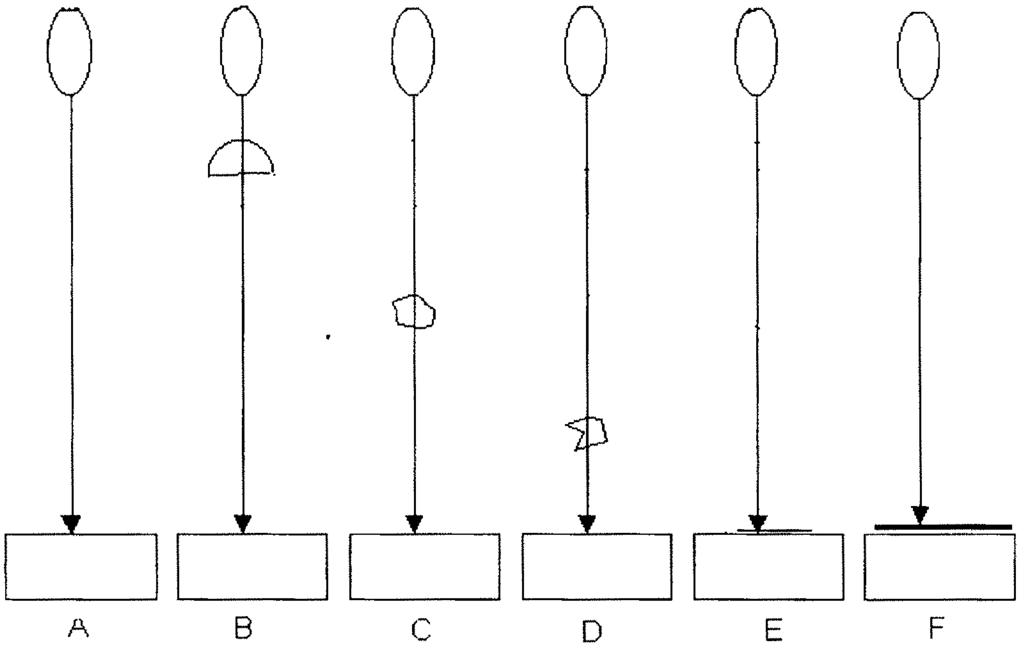

Fig. 2.4 Mechanism of thin film formation by spray pyrolysis method

2.3. Thin film deposition

2.3.1. Preparation of ZnO thin films

2.3.1.1 Substrate cleaning

Substrate cleaning is the process of breaking the bonds between substrates and contaminants without damaging the substrates. In thin film deposition process substrate cleaning is an important factor to get reproducible films as it affects the uniformity, smoothness, porosity and adherence of the films. The substrate cleaning process depends upon the nature of the substrate, degree of cleanliness required and nature of contaminates to be removed. The common contaminates are oil, water due to moisture, dust, grease particles etc. The micro slides of dimensions 0.135 cm x 2.5 cm x 7.5 cm supplied by Blue Star have been used for deposition. Following method is used to clean substrates.

1. Substrates were first washed with liquid detergent 'Labolene' and then with double distilled water.
2. Substrates were boiled in chromic acid for about five minutes to remove contaminants.
3. Substrates were cleaned with distilled water.
4. Then substrates were kept in Sodium Hydroxide solution to remove the

acidic contaminations.

5. The substrates were again washed with distilled water and cleaned ultrasonically.
6. Finally, the substrates were dried in alcohol (methanol) vapors.

2.3.1.2 Preparation of solution

Double distilled water is used to prepare the ZnO precursor solution. Initial ingredients were used as Zinc acetate ($Zn(CH_3CO_2)_2.2H_2O$); molecular weight=219.5 g mol^{-1} (AR grade, 98.8 % pure) supplied by HIMEDIA Pvt. Ltd. Mumbai. To make 100 ml of 0.1M solution of zinc acetate, the required quantity (i.e. 2.195 gm) of zinc acetate is dissolved in double distilled water. The clear solution is obtained and used for deposition of ZnO thin films

2.3.1.3 Formation of ZnO thin films

The following experimental steps were involved in the formation of ZnO thin films using a spray pyrolysis technique.

- Firstly, the glass nozzle was washed using diluted hydrochloride acid and then double distilled water.
- The cleaned substrates were placed in the uniform temperature region of hot plate. Hot plate is heated using temperature controller.
- Then ambient air is passed as a carrier gas through glass nozzle and again hot plate is heated till desired temperature is achieved.
- By mixing the precursors, spraying solution is prepared.
- Adjusting the constant spray rate, spraying was started onto the hot glass substrates maintained at desired substrate temperature.
- As spraying is completed, system is allowed to cool to room temperature and substrates were taken out of the deposition chamber at room temperature.

The zinc oxide thin films were deposited on soda lime glass substrate using the chemical spray pyrolysis technique. The spraying solution consisted of 0.1M zinc acetate ($Zn(CH_3CO_2)_2.2H_2O$) in a double distilled water. Compressed air was used as the carrier gas and substrate temperature was kept at optimized value of 450 °C. The total volume of sprayed solution was 100 ml and the spray rate was 5 ± 1 cc min^{-1}. When the droplets of the sprayed solution, reach the hot substrates, then the pyrolytic decomposition of the solutions take place; finally we get uniform, pinhole-free and well-adherent ZnO thin films of desired properties.

2.3.2 Preparation of Co doped ZnO thin films

2.3.2.1 Substrate cleaning

The substrates were cleaned using procedure discussed in section 2.3.1.1.

2.3.2.2 Preparation of solution

The double distilled water was used as solvent to prepare Co doped ZnO thin films. The precursor used for formation of Co doped ZnO thin films were Zinc acetate ($Zn(CH_3CO_2)_2.2H_2O$), molecular weight=219.5 g mol^{-1} (AR grade, 98.8 % pure) supplied by HIMEDIA Pvt. Ltd. Mumbai and Cobaltous Nitrate ($Co(NO_3)_2.6H_2O$), molecular weight=291.04 g mol^{-1} (AR grade, 98.8 % pure) supplied by QUALIGENS Fine chemicals Pvt. Ltd. Mumbai. The ratio of Co:Zn calculated on atomic percent used in the starting solution were 1%, 2%, 3% and 5%. It was seen that when the ratio was higher than 5% the degraded films resulted due to the chemical reaction between zinc and cobalt.

2.3.2.3 Formation of Co doped ZnO thin films

The resulting precursor solution was sprayed onto the preheated glass substrate held at optimized substrate temperature of 450 °C. The compressed air was used as a carrier gas at a constant spray rate (5 ml/min). The other preparative parameters such as concentration of solution (0.1M), quantity of the solution (100 ml) and nozzle to substrate distance were kept constant throughout the experiment.

2.3.3 Preparation of Ni doped ZnO thin films

2.3.3.1 Substrate cleaning

The substrate were cleaned using procedure discussed in section 2.3.1.1

2.3.3.2 Preparation of solution

The double distilled water was used as solvent to prepare Ni doped ZnO thin films. The precursor used for formation of Ni doped ZnO thin films were Zinc acetate ($Zn(CH_3CO_2)_2.2H_2O$), molecular weight=219.5 g mol^{-1} (AR grade, 98.8 % pure) supplied by HIMEDIA Pvt. Ltd. Mumbai and Nickel Nitrate ($Ni(NO_3)_2.6H_2O$), molecular weight=290.78 g mol^{-1} (AR grade, 98.8 % pure) supplied by QUALIGENS Fine chemicals Pvt. Ltd. Mumbai. The ratio of Ni:Zn calculated on atomic percent used in the starting solution were 0.5%, 1%,1.5 %, 2 %, and 2.5 at %. It was seen that when the ratio higher than 2.5 at % the degraded films resulted due to the chemical reaction between nickel and zinc.

2.3.3.3 Formation of Ni doped ZnO thin films

The resulting precursor solution was sprayed onto the preheated glass substrate held at optimized substrate temperature of 450 °C. The doping percentage of Ni was varied from 0.5 to 2.5 at % in the starting solution. The compressed air was used as a carrier gas at a constant spray rate (5 ml/min). The other preparative parameters such as concentration of solution (0.1M), quantity of the solution (100 ml) and nozzle to substrate distance were kept constant throughout the experiment.

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