Preparation and Characterization of Nebulised Spray Pyrolysis Transparent Conducting (TCO) Thin Film Material

[Coated at 0.1M, 0.2M and 0.3M]

By

KARTHIKA. S

(16PPH004)

A dissertation submitted to the

AVINASHILINGAM INSTITUTE FOR HOME SCIENCE

AND HIGHER EDUCATION FOR WOMEN

COIMBATORE- 641 043

In partial fulfilment of the requirements for the degree of

MASTER OF SCIENCE IN PHYSICS

APRIL 2018

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CERTIFID AS A BONAFIDE RESEARCH WORK

10/4/18 10/4/18

Signature of the Head of the Department **Signature of the Supervisor**

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CONTENTS

IV	**RESULTS AND DISCUSSIONS**	

LIST OF FIGURES

LIST OF TABLES

INTRODUCTION

REVIEW OF LITERATURE

MATERIALS AND METHODS

RESULTS AND DISCUSSION

SUMMARY AND CONCLUSION

REFERENCES

CHAPTER-I

INTRODUCTION

1.1 INTRODUCTION

The beginning of “Thin film science” can be possibly be traced to the observations of Grove who noted that metal films were formed by sputtering of cathodes with high energy positive ions. Since then it has come a long way and today it is no long a subject of some casual academic interest but has become a full-fledges discipline. The phenomenal rise in thin film researches is, no doubt, due to their extensive applications in the diverse fields of electronics, optics, space science, aircrafts, defence and other industries. These investigations have led to numerous inventions in the forms of active devices and passive components, rectification and amplification, sensor elements, piezo-electric devices, micro-miniaturisation of power supply, storage of solar energy and its conversion to other forms, magnetic memories, superconducting films, inter- ference filters, reflecting and antireflection coatings and many others. The present developmental trend in towards newer types of device, monolithic and hybrid circuits, field effect transistors (FET), metal oxide semiconductor transistor(MOST),sensor for different applications, switching device, cryogenic applications, high density memory systems for computers, etc.

Intensive investigations are going on not only in the field of basic thin film physics, but also in material science, thin film circuit designs, production engineering concerning thin films, etc., to hope up the demand of industries. Film properties are also sensitive not only to their structures but also to many other parameters including their thickness especially in thin film regions. Hence a stringent control of the later is imperative for reproducible, electronic, dielectric, optical and other properties. All basic researchers on thin film are generally confined to a limited range of thickness, between a few Å to about 5000Å depending on the properties to performance is the most important criterion, the thickness at the lower range is generally higher than 1000Å and can be as high as 5-10µm or even more. Within the connotation of thin film, often a further subdivision of thickness is made under three categories ultra-thin, thin (or very thin) and comparatively thicker ones, the last one generally being greater than1000Å. Some of the factor which determine the physical, electrical, optical, and other properties of a film are the following viz. Rate of deposition, substrate temperature, environmental conditions, residual gas pressure in the system, purity of the material to be deposited, inclusion of foreign matter in the deposit, inhomogeneity of the film, structural and composional variations of the film in localised or wider areas etc. A transition from the bulk to the thin film state may even cause a drastic change in its properties. [1]

An important application of thin film technology is the conversion of solar radiation into useful electrical energy without which we cannot manage our future life in this sophisticated modern society. The efficiency of flat plate collectors gets reduced considerably due to the infra-red radiation which escapes in the form of thermal energy. This has forced the photovoltaic industry to a revolution for the search of transparent conducting oxide (TCO) coating which allows the visible light to penetrate through it but reflects the IR radiation back to the atmosphere. [2]

Thin films are used in optical windows for the solar spectrum to convert the solar energy for low temperature applications, we require the solar collectors. The performance of solar collectors is enhanced by coating its surface properly. The coating helps in reducing reflective losses, increasing energy absorption and in reducing the energy losses, increasing energy absorption from the collector by radiation emittance through radiation. So thin film coating is very much needed in solar energy conversion.

A great advantage with a thin film device is the small amount of material used and the compact volume of the device. In an energy efficient window in a warm climate for example a coating i.e transparent to visible light but reflecting in the near IR region may be used, thereby preventing overheating inside the building. Thin film science & technology plays a crucial role in microelectronics communications, optoelectronics, integrated optics, photovoltaic devices and wave guides. Thin film devices for windows, mirrors, rechargeable Li ion batteries and space applications have become an essential part of modern technology. A thin material created by an atom/ molecule/ ion/ cluster of species condensation process is defined as “Thin film” [3]. Although the study of thin film phenomena dates back well over a century, it is really only over the last four decades that they have been used to a significant extent in practical situations. The requirement of microminiaturisation made the use of thin and thick films virtually imperative. The development of computer technology led to a requirement for very high density storage technique and it is this which stimulated most of the research on the magnetic thin films. Many thin film devices have been developed which have found themselves looking for an application or, perhaps more importantly market. [4]

The fundamental research has led to a dramatic improvement in understanding of thin films and surfaces. This in turn has resulted in a greater ability to fabricate devices with predictable, controllable and reproducible properties [5] .The cleanliness and nature of the substrate, the deposition condition; post deposition heat treatment and passivation are vital process variables in thin film fabrication. Therefore, prior to this improvement in understanding of thin films, it had not really been possible to apply them to real devices. The finance for early thin films researches originated from space and defence programmes to which the device cost is less important than its lightweight and other advantages, the major applications of thin film technology are not now exclusively in these areas but rather often lie in the domestic in which low cost essential. [6]

Thin film materials have already been used in the semiconductor devices, wireless communications, telecommunications, integrated circuits, rectifiers, transistors, solar cells, light- emitting diodes, photoconductors, light crystal displays, magneto-optic memories, multilayer capacitors, flat-panel displays, smart windows, computer chips, magneto-optic discs, lithography, microelectrochanical systems (MEMS), and multifunctional emerging coatings, as well as other emerging cutting technology. [7]

1.2 THIN FILM APPLICATIONS

- Electronic Components The fabrication of electronic components, especially solid-state devices and microelectronic integrated circuits, have undoubtedly found the widest and most demanding applications for thin film depositions. These films typically consist of semiconductor materials, dielectric and insulating materials, and metal or refractory metal silicide conductors.
- Electronic Displays Electronic displays are used for interfacing electronic equipment with human operators. Different components and device structures are required, such as:
    i. Liquid-crystal displays
    ii. Light-emitting diodes (LEDs)
    iii. Electroluminescent displays
    iv. Plasma and fluorescent displays
    v. Electrochromic displays

The fabrication of these displays requires conductive films, transparent and conductive films, luminescent or fluorescent films as well as dielectric and insulating layers. [8]

- Optical Coatings Optical coatings are applied for antireflection purposes, as interference filters on solar panels, as plate glass infrared solar reflectors, and for laser optics. In the fabrication of filter optics, thin films with refractive index gradients are deposited on preforms from which the optical fibers are drawn. These coatings require dielectric materials with precisely defined indices of refraction and absorption coefficients. Laser optics requires metal reflective coatings which can withstand high radiation intensities without degradation. Infrared reflecting coatings are applied to filament lamps to increase the luminous flux intensity.
- Magnetic Films for Data Storage Thin films of magnetic materials have found wide commercial applications for data storage in computers and control systems. The substrates can be metal, glass or plastic polymeric materials. Thin film deposition processes for magnetic materials and for materials with a high degree of hardness are required.
- Optical Data Storage Device Thin films are finding increasing commercial use for optical data storage devices in compact disks and computer memory applications. Processes for the deposition of organic polymer materials as storage media and as protective overcoats are required for this technology.
- Antistatic Coatings Thin films of conductive or semi conductive materials are deposited to provide protection from electrostatic discharges.
- Hard Surface Coatings Thin film coatings of carbides, silicide, nitrides, and borides are finding increased uses to improve the wear characteristics of metal surfaces for tools, bearings, and machine parts. Of particularly great current interest are films of diamond-like carbon because of this material's heat dissipation properties, electrical insulation, hardness, and resistance to high-temperature and high energy radiation. [9]

1.3 CLASSIFICATION OF THIN FILMS

Thin film can be classified into two types. These films have their own distinct properties.

i. Crystalline
ii. Amorphous

Crystalline

Crystalline thin film require smaller array of crystal for same output in the case of solar energy conversion device. Even though these films contain higher cost of technology, its installation cost is economic. These thin films are more suitable to temperature climates.

Amorphous

In contrast to crystalline films, these films require lower power to area ratio and it needs larger array of films for same output comparing to those of crystalline films. Since its array is larger, it requires high installation cost. It can be performed well in extreme heat and also able to operate in greater light range [1].

1.4 DEPOSITION TECHNIQUE

Thin-film deposition is any technique for depositing a thin film (about 1 µm) of material onto a substrate or onto previously deposited layers. Thin is a relative term, but most deposition techniques allow layer thickness to be controlled within a few nanometre's, and some (molecular beam epitaxy) allow one layer of atom to be deposited at a time. A variety of sophisticated thin film deposition techniques have been developed. Thin film can be fabricated by different method. These deposition techniques are generally classified as,

i. Physical deposition
ii. Chemical deposition

1.4.1 Physical Deposition

Physical vapour deposition (PVD) is a group of vacuum coating techniques used to deposit thin film of various materials onto the surfaces. In this mode of deposition, the transfer of ion s from the source to material to the substrate takes place. Typically the following steps involved in making thin film.

- Emission of particles from source
- Transport of particles to substrate
- Condensation of particle on substrate

Two technology are often used in physical deposition

1. Evaporation
2. Sputtering

In evaporation technique as indicated by material evaporation due to thermal energy. Here the materials get vapourized at sufficiently high temperatures. If these vapours are condensed on to a clean substrate a thin film is obtained. There are several methods of thermal evaporation techniques. Some of them a

- Resistive heating technique
- Flash evaporation technique
- Electron beam evaporation technique
- Laser evaporation technique
- Exploding wire technique
- Arc evaporation technique

The sputtering is a very old technique which has been known since 1852 and is utilized for thin film fabrication. It is based on the momentum transfer of atoms or ions from the surface of a material by the material by the bombardment with energetic particles. When this phenomenon is exploited for the film fabrication, the sputtered or ejection atoms can be condensed on a substrate [10]. Under this technique, three methods are employed as follows

- RF sputtering
- DC sputtering
- Magnetron sputtering

In sputtering, deposition rates are about 2 orders of magnitude lower and chamber pressure 4 orders of magnitude higher than for evaporation technique [10].

1.4.2 Chemical Deposition

These processes exploit the creation of solid materials directly from chemical reactions in gas and/or liquid compositions or with the substrate materials. The solid material is usually not the only product formed by the reaction. By products can include gases, liquids and even other solids. Here the fluid surrounds the solid object (substrate), deposition happen in every surface, with little regard to direction. So, the thin film from chemical deposition techniques tends to be conformal rather than directional.

Deposition that happen because of a chemical reaction;

- Chemical Vapour Deposition (CVD)
    i. Atmospheric Pressure CVD (APCVD)
    ii. Low Pressure CVD (LPCVD)
    iii. Plasma Enhanced CVD (PECVD)
    iv. Laser Enhanced CVD (LECVD)
    v. Metal Organic CVD (MOCVD)
    vi. Spray Pyrolysis
- Electro Deposition
    i. Electro Plating
    ii. Electroless Plating
- Epitaxy
    i. Vapour Phase Epitaxy (VPE)
    ii. Molecular Beam Epitaxy (MBE)
- Thermal Oxidation

Chemical Vapour Deposition (CVD) is a process of chemically reacting a volatile compound of a material to be deposited, with other gases, to produce a non-volatile solid that deposits atomistically on a suitable placed substrate. CVD does not require vacuum or unusual level of electric power like PVD. Moreover, CVD is practiced prior to PVD to deposit a protective tungsten coating. The ability to controllably create thin film of widely varying stoichiometry makes the CVD technique unique among other deposition methods. An impressive number of different CVD materials (metals, semiconductors, oxide etc.) are of scientific and technical interest for variety of (electrically, optically, mechanically and environmentally) functional purposes. [10]

In the electroplating process the substrate is placed in a liquid solution (electrolyte). When an electrical potential is applied between a conducting area on the substrate and a counter electrode (usually platinum) in the liquid, a chemical redox process takes place resulting in the formation of a layer of material on the substrate and usually some gas generation at the counter electrode. In the electroless plating process a more complex chemical solution is used, in which deposition happens spontaneously on any surface which forms a sufficiently high electrochemical potential with the solution.

Anodic or thermal oxidation of the substrate surface in an oxygen rich atmosphere. The temperature is raised to 800 °C - 1100 °C to speed up the process. The growth of the film is spurned by diffusion of oxygen into the substrate, which means the film growth is actually downwards into the substrate. This process is naturally limited to materials that can be oxidised, and it can only form films that are oxides of that material. In epitaxy process (molecular/vapour) beams of atoms or molecules are directed onto a substrate where layer by layer growth (epitaxy) of a crystalline film occurs.

Table 1.1 Comparison between chemical vapour deposition (CVD) and physical vapour deposition (PVD)

CVD	PVD
CVD is a method to deposit solid and form a thin film from gaseous phase material.	PVD is a solid form. It is mainly a vapourization coating technique.
Deposit at a high temperature in the range of 450℃ to 1050℃.	Deposit at a relatively low temperature in the range of 250℃ to 450℃.
Works under low vacuum.	Works under high vacuum.
Material is introduced in gaseous form onto the substrate.	Material is introduced in solid form onto the substrate.
Gaseous molecules react with substrate in CVD.	Atom are moving and depositing on the substrate.

From the above comparison of PVD and CVD process, the main similarities between two processes are vacuum system and temperature of the deposition. However, the level of vacuum and degree of temperature of each system are rather different. In contrast, the most remarkable difference is the form of introducing material. For instance, the form of introducing material on to the substrate in PVD and CVD in solid and gaseous form, respectively. It would seem that PVD and CVD are slightly similar. [11]

CVD has many advantages. Firstly, the pressure used in CVD allow in coating of three dimensional structures with large area aspect ratios. Secondly, high precursor flow rates in CVD give deposition rates several times higher than PVD. Also, the CVD reactor is relatively simple and can be scaled to fit several substrates. Ultra-high vacuum is not needed for CVD and changes or additions of precursors are an easy task. While for CVD stoichiometry is more easily controlled by monitoring flow rates of precursors. Growth of high purity films and the ability to fabricate abrupt junction. By considering the simplicity and economics, chemical methods commonly preferred for obtaining large area thin films. Chemical methods are divided into two subgroups, namely electroplating and chemical vapour deposition. Electrolytic deposition, electroless plating and anodization come under the former whereas pyrolysis is classified in the latter category. Among the different thin film preparation technique, spray pyrolysis is widely used method for the deposition of electrochromic material films due to the economic consideration and easy adaptability of this technique for commercial purpose.

Chemical spray deposition or reactive pulverization or more popularly known as spray pyrolysis is a simple technique to prepare thin films by condensation process of an atom by atom or molecule by molecule or an atom by atom. This technique lies in the region between that of a thick film and thin film technique depending upon the atom cluster size. Among these methods, spray pyrolysis is useful for large area applications. These methods are cheaper, simpler and permits to obtain films with the required properties of optoelectronic application. Thickness dependent on the structural, electrical and optical properties of the film have been carried out. [12]

1.5 TRANSPARENT CONDUCTING OXIDES

Transparent conducting oxides (TCOs) are electrical conductive materials with a comparably low absorption of light. Glass fibers are nearly lossless conductors of light, but electrical insulators; silicon and compound semiconductors are wavelength dependent optical resistors (generating mobile electrons), but dopant dependent electrical conductors. Transparent conducting oxides are highly flexible intermediate states. Low-emission windows that allow visible light through while reflecting the infrared; this keeps the heat out in summer, or the heat in, in winter. Novel functions may be integrated into the materials since oxides have a variety of elements and crystal structures, providing great potential for realizing a diverse range of active functions. TCO’s are wide band gap materials that have relatively high concentration of carriers in the conduction band. These arise either from defects in the material or from extrinsic dopants, the impurity level of which lie near the conduction band edge. The high carrier concentration would cause absorption of electromagnetic radiation. Thus a TCO represents a compromise between electrical conductivity and optical transmission. Reduction of resistivity involves either increase in the carrier concentration or in their mobility. These films are widely used today most of the solar cells, opto-electrical interfaces, gas sensors, heat reflecting filters, antireflection coatings, high sensitivity photo detectors, protective coatings to glass containers, antistatic surface layers on temperature control coatings in orbiting satellites and circuitries. Due to these facts increasing demands have stimulated in recent years, the production of transparent conductors in thin film form. [3]

1.5.1 Solar Cell Application Using TCO

The direct conversion of solar energy in to electricity by photovoltaic (PV) solar cells was studied for the past 30 years. We are still far from making these sources cost effective. Photovoltaic solar energy conversion offers one of the few ways of producing electricity in urban areas which is free of various emissions and noise. The development of photovoltaic system technology started with applications of solar cells in space. Thin film photovoltaic technologies are being considered as a means of substantially reducing the cost of photovoltaic systems. Solar selective surfaces in addition to be having high absorbance and low thermal emittance must be stable at high operating temperatures and resistant to atmospheric corrosion [13].

Solar selective surfaces are broadly classified into two: (1) opaque thermal absorbers and (2) transparent coatings. Of these two, the transparent conducting coatings are preferred due to their applications in a wide variety of fields of interest in solar energy conversion. For transparent conducting coatings, one can either use a metal film with high infrared reflectivity and very low visible absorption or a semiconductor with a bandgap sufficiently wide to be transparent in the visible range and a high enough carrier concentration to have high infrared reflectivity. Since metallic films are costlier, less stable and are corrosive in nature, much attention has been paid to the development of transparent wide bandgap semiconductor films to be used as transparent conductors. They are widely used in the fabrication of solar cells and as optically transparent and conducting electrodes in electrochemical science and technology and in other optoelectronic devices.

The only way to obtain good transparent conductors is to create electron degeneracy in wide band gap (> 3eV) oxides by controllably introducing appropriate dopant. These conditions can be obtained in oxides of indium, tin, zinc, cadmium and their alloys and they constitute the most widely investigated TCOs The required doping for achieving greater conductivity is often accomplished by the addition of a foreign element. Particularly good conductivity has been obtained with SnO_2:F, SnO_2:Sb, In_2O_3:Sn, ZnO:Al. Good examples of the other possibility of achieving higher conductivity through moderate oxygen deficiency without doping are; SnO_2 and In_2O_3. As mentioned earlier the transparent conductors most widely investigated are doped and undoped sub-stoichiometric oxides of tin, indium, zinc and their alloys with semiconducting properties. In this regard, recently magnesium (Mg) also used in the form of MgO to make alloy with these oxides, like $MgSnO_3$ and $MgSnO_4$ whose properties are varied between these oxides and magnesium tin oxide. [14]

1.6 NEBULIZER SPRAY PYROLYSIS

A Nebulizer is a small machine that is powered by an air compressor, which has ability to change the precursor solution into very tiny droplets like mist. Though it is portable, it requires electric power to operate air compressor. Tubing connects the compressor to a cub of the Nebulizer that holds the liquid. By applying the compressed air to the Nebulizer, it can convert the liquid into mist form.

Nebulizers are two types; they are Nebulizer Spray Pyrolysis (NSP) and Ultrasonic Nebulizer. Nebulizers are based on the Venturi principle, whereas Ultrasonic Nebulizers use the converse piezoelectric effect to convert alternating current to high frequency acoustic energy. Important variables for both types are treatment time required, particle size produced and aerosol liquid output. Two main parameters are generally used to evaluate the performance of nebulizer, the droplet size distribution of the aerosol and the liquid output rate and are basically determined by the design and user conditions of the nebulizer. The droplet size and rate of flow of solution in nebulizer is mainly depends on the geometry of nebulizer and carrier gas pressure. An attempt made to use the medical nebulizer as a spray gun for thin film preparation on any kinds of substrate by applying very high carrier gas pressure as inlet for producing chemical solution’s mist. A specially designed solution flow tube is used as an outlet with 25 cm horizontal length and 15 cm vertical length. The bottom of the vertical tube is designed carefully as a spray nozzle to spray the chemical liquid mist on the substrate smoothly. Nebulized spray pyrolysis is simple and low cost process by which we can deposit thin films. The solution is sprayed using nebulizer on to heated substrates and then the particles or films depending on the temperature. [15].

1.6.1 Advantages Of Nebulizer Spray Pyrolysis

1. Relatively low temperature is enough to get good oxide films.
2. For device fabrications, less heating effect required.
3. Additional accessories like burette etc. are not required.
4. Less quantity of precursor solution is enough.
5. The setup is Very small, compact and convenient to carryout spray pyrolysis

1.7 PROPERTIES OF USED MATERIALS

1.7. Magnesium Oxide (MgO)

Magnesium oxide or magnesia is an alkaline earth metal oxide. It is eighth most abundant element and equals about two per cent of the earth's crust and typically 0.12%of seawater. MgO has good refractoriness, high thermal conductivity, low electrical conductivity, good corrosions resistance and transparency to infrared. MgO is known to be extremely ionic, with the Mg atom giving up two of its electrons almost entirely to the 'O' atom and go to the food approximation, the O^{2+} and Mg^{2+} ions have both closed n=2 shells of electrons. MgO is also important component of glass, it is used as an electrical and thermal insulator and it is used as an ingredient in the production of fertilizer among other things. MgO is an important component of the earth's lower mantle. The typical applications are refractory applications, absorbent, catalyst, animal feed stuffs, fertilizers and a variety of magnesium chemicals. Dielectric MgO thin layers are electrical insulators. They are used primarily in capacitors and in electrical insulations. They should possess high dielectric strength to withstand high voltages without undergoing degradation and becoming electrically conducting. [16]

Among the many oxides, magnesium oxide is an excellent insulating material with exceptional properties such as chemical inertness, high electrical resistivity, optical transparency throughout the range 0.25 - 6.8 μm, low thermal conductivity and very high efficiency for secondary electron emission, especially at elevated temperatures, which make MgO a suitable material for numerous applications..[17]

Table 1.2 Properties of magnesium oxide

Property	Value
Molecular weight	40.31
Crystal system	Cubic
Density (X-ray),g/cm^3	3.581
Colour	Colourless, transparent
Melting point	2852℃
Boiling point	3600℃
Electrical resistivity at 27℃, Ω cm	1.3×10^{15}
Specific heat at 27℃ kg/(kg.k)[a]	0.92885
Heat of formation heat ΔH^o_{298}, kg/mol[a]	-601.70

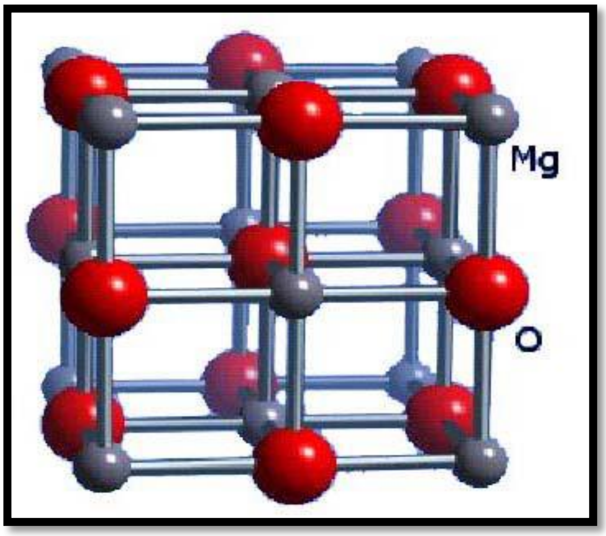

Fig 1.1 Structure of Magnesium Oxide

1.7.2 Tin Oxide (SnO_2)

Tin oxide also known as stannic oxide is an inorganic compound with molecular formula SnO_2. It is colourless, white to off white coloured powder. Its mineral form is a main ore of tin.it is diamagnetic and amphoteric in nature. It is a crystalline solid having rutile structure.

SnO_2 is an important n-type semiconductor of wide energy band gap (Eg=3.62 eV at 300 k) and presents special properties, such as transparency, chemical and thermal stabilities which are used in photoelectrons, catalysts for oxidation and hydrogenation, solar cells, semiconducting gas sensors, liquid crystal displays and protective coatings. A wide band gap SnO_2 (3.6-3.8 eV) has attracted considerable attention whenever doped with transition metal (TM) ions (Fe, Cu etc.) because of their remarkable electronic, optical and magnetic properties resulting from large sp-d exchange interactions between the magnetic ions and the band electrons.

Tin (IV) oxide adopts tetragonal rutile structure (cassiterite in its mineral form) with the (110) surface being the most stable one. SnO_2 is a semiconductor with a direct but forbidden wide bandgap of ca. 3.6 eV. Tin oxide is widely applied (in association with other metals to improve gas selectivity) as a sensor component, which is a consequence of the high sensitivity of its conductivity to the surrounding atmosphere. [18]

Table 1.3 Properties of tin oxide

Parameter Properties	**Value**
Lattice constant	a=, b=, c=, α= 90º, β=90º, γ=90º
Crystal structure	Tetragonal
Molecular mass	150.71 g/mol
Density	6.95 g/cm^3
Melting Point (°C)	1630°C
Boiling point	1800-1900°C
Dielectric constant (E_S)	9.0
Refractive index	2.006
Direct energy band gap	3.6 eV

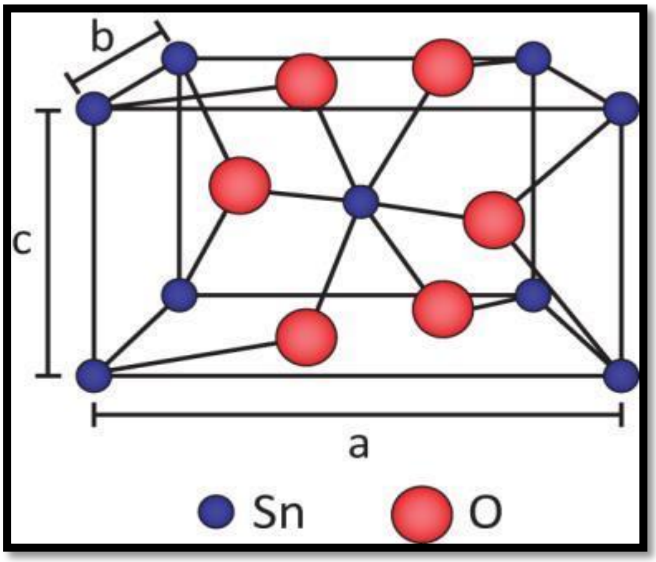

Figure 1.2 Structure of Tin Oxide

1.7.3 Magnesium Tin Oxide Thin Film

The alkali-earth stannates having the general chemical formula $MgSnO_3$ have recently been studied as potential electronic ceramics such as thermally stable capacitors with low resistivity electrodes for LCD, energy, conserving architectural windows, defogging aircraft, gas sensors, antistatic wind coatings and wear resistant layers on glass.

The recent and most useful applications are in energy conservation in which they serve as transparent protective coatings as well as terminals to make connectors. A number of techniques for material synthesis such as the conventional solid state reaction, self-heat sustained reaction, oregano metallic citrate complexation and sol gel were employed in the above mentioned MgO and SnO_2 systems. Systematic investigations with emphasis on material synthesis, phase relationship, micro, structural features and the electrical characteristics of the sintered bodies have also been carried out. Interestingly, the behaviour of magnesium metastannate ($MgSnO_3$) is totally different from the corresponding Ce, Ba and Sr counterparts. $MgSnO_3$ is unstable and disproportionates into orthostannate and SnO_2 open heating above ~700 °C. [19]

Table 1.4 Properties of magnesium tin oxide

Parameter Properties	Value
System	Hexagonal
Lattice	Rhombohedral
Lattice parameter (A)	a=b=5.234 c=13.86
Molecular weight	190.99
Volume	329.06
Density	5.783 gm/cm^3

CHAPTER-II

REVIEW OF LITERATURE

2.1 INTRODUCTION

Review of literature helps one to analyse the published information on a specific subject area and to do the detailed survey of any desired material which may contribute for improved in research. Magnesium tin oxide is an important material with numerous applications. It is most commonly used in solar cell, optical instrumentation, science and technology. Limited Literature are available on the work of $MgSnO_3$ thin film. Brief review is discussed in this section.

2.2 OVERVIEW OF LITERATURE

1. Abdul Rahman Aziz Sakhta et al.,(2017) reported the morphological and optical Properties of Pure and Mg Doped Tin Oxide Thin Film Prepared by Spray Pyrolysis. Pure Tin Oxide (SnO_2) and Magnesium (Mg) doped SnO_2 thin films have been deposited onto glass substrates by spray pyrolysis technique at the substrate temperature of 450°C. The doping concentration of Mg was varied from 1 to 9 wt% while all other deposition parameters such as substrate temperature, spray rate, carrier gas pressure and distance between spray nozzle to substrate were kept constant. The surface morphology and optical properties of the deposited thin films have been studied by Scanning Electron Microscopy (SEM) and UV visible spectroscopy. Average optical transmittance in the 400–900 nm range varies from 18.21% to 58.99% with varying Mg concentration in the film. Maximum band gap value of 3.90 eV is obtained for undoped SnO_2. [26]

2. M. Rouchdi et al., (2017) have synthesized and magnetic properties of Mg doped SnO_2 thin films. Mg-doped tin oxide (SnO_2) thin films were deposited using spray pyrolysis technique with an aqueous solution of $SnCl_2$ and magnesium sulfate ($Mg\ (SO_4){\cdot}_7H_2O$) on a heated glass substrate. In this work, the effect of Mg doping on the structural, optical and electrical properties of SnO_2 was investigated in some detail by X-ray diffraction, UV–Vis spectroscopy and Hall Effect measurements. The XRD diffractograms demonstrate that SnO_2 crystallized in tetragonal rutile structure with preferential orientation along (110) plane. The average transmittance in the visible range was increased from 65 to 78% and the values of energy band gap were found in the range of 3.62–3.87 eV. The lowest resistivity [1.021 × 101 (Ω.cm)] was obtained for the film doped with 5 at% Mg. The electronic structure and optical properties of the rutile structure $Sn_{1-x}Mg_xO_2$ were obtained by ab initio calculations using the Korringa-Kohn-Rostoker method (KKR) combined with the Coherent Potential Approximation (CPA), as well as CPA confirms our results. [41]

3. S. Palanichamy et al.,(2016) have reported the Structural and Optical Properties SnO_2 Thin Film by Nebulizer Spray Pyrolysis Technique. Nano crystalline tin oxide (SnO_2) thin film was prepared at optimized substrate temperature 300 °C with 0.05M concentration using a simple and easy nebulizer spray pyrolysis technique. The film was characterized by X-ray diffraction analysis (XRD), optical transmittance study (UV-Vis-NIR double beam Spectrophotometer), scanning electron microscopy (SEM) and photoluminescence analysis (PL). The film was shiny, uniform and good adherent with polycrystalline nature. The X-ray diffraction pattern shows the tetragonal structured SnO_2 film with (110) preferred orientation. The average crystalline size was found to be 53.17 nm. SEM image exhibits that the film has no voids and cracks. The higher transmittance (91%) of photon energy was observed by transmittance spectra. The band gap energy of the as prepared SnO_2 thin film was obtained to be 3.78 eV. [20]

4. Shia Lin Yung et al., (2016) have reported the structural and physical properties of tin oxide thin films for optoelectronic applications. Tin oxide films were deposited on glass substrates by RF magnetron sputtering. At a lower sputtering pressure, the Structural and physical properties of tin oxide thin films for optoelectronic applications tin oxide film comprised nano crystalline orthorhombic SnO with a (110) orientation, greater p-type conductivity and better hydrophobicity. Increasing substrate temperature resulted in the coexistence of nano crystalline orthorhombic SnO and tetragonal SnO_2 in the deposited film, favouring hydrophilicity, changing the p-type conductivity to n-type conductivity, and reducing resistivity. As the sputtering pressure or substrate temperature increased, the tin oxide film exhibited a lower surface roughness, a larger optical energy gap, and higher optical transmission. [32]

5. Abdul Rahman Sakhta et al., (2016) deposited the Structural Properties of Tin Oxide Thin Film of Mg Doping by the Spray Pyrolysis Technique. Mg doped tin oxide transparent conducting thin films were deposited at a substrate temperature of 450°C by spray pyrolysis method. Structural properties of the films were investigated as a function of various Mg-doping levels from 0 to 9wt% while all other deposition parameters such as substrate temperature, spray rate, carrier gas pressure and distance between spray nozzle to substrate were kept constant. The results of x-ray diffraction have shown that the deposited films are polycrystalline structure in tetragonal phase with preferential orientations along the (101), (301), and (211) planes. The relative intensities, distance between crystalline planes (d), crystallite size (D), dislocation density (δ) and lattice parameters (a), (c) were determined. The variations of the surface morphology have been studied by Scanning Electron Microscope (SEM). [40]

6. K.Ravindranadh et al., (2016) developed the spectroscopic and luminescent properties of Co^{2+} doped tin oxide thin films by spray pyrolysis. The wide variety of electronic and chemical properties of metal oxides makes them exciting materials for basic research and for technological applications alike. Oxides span a wide range of electrical properties from wide band-gap insulators to metallic and superconducting. Tin oxide belongs to a class of materials called Transparent Conducting Oxides (TCO) which constitutes an important component for optoelectronic applications. Co^{2+} doped tin oxide thin films were prepared by chemical spray pyrolysis synthesis and characterized by powder X-ray diffraction, SEM, TEM, FTIR, optical, EPR and PL techniques to collect the information about the crystal structure, coordination/local site symmetry of doped Co^{2+} ions in the host lattice and the luminescent properties of the prepared sample. Powder XRD data revealed that the crystal structure belongs to tetragonal rutile phase and its lattice cell parameters are evaluated. The average crystallite size was estimated to be 26 nm. The morphology of prepared sample was analysed by using SEM and TEM studies. Functional groups of the prepared sample were observed in the FT-IR spectrum. Optical absorption and EPR studies have shown that on doping, Co^{2+} ions enter in the host lattice as octahedral site symmetry. PL studies of Co^{2+} doped SnO_2 thin films exhibit blue and yellow emission bands. CIE chromaticity coordinates were also calculated from emission spectrum of Co^{2+} doped SnO_2 thin films. [52]

7. Ahmad Z. Al-Janaby et al.,(2016) developed the structural, optical and sensitive properties of Ag-doped tin oxide thin films. The present paper a SnO_2 (Pure) and Ag doped thin films at different concentration of Ag, were prepared by chemical spray pyrolysis. The films deposited onto glass slides were first cleaned with detergent water and then dipped in acetone and discuss the structural, optical and sensitive properties of Ag-doped tin oxide thin film prepared on glass substrate by the spray pyrolysis technique at a temperature of 400℃. X-ray diffraction study shows that the film was tetragonal rutile structure of SnO_2.

Morphology analysis studied by atomic force microscopy (AFM) and reveals that the grain size of the prepared thin film is approximately (73.41-111.62) nm, with a surface roughness of (2.18 – 2.79) nm as well as root mean square of (2.69 -3.39) nm for SnO_2(pure)and Ag-doping, Optical characteristics were studied by UV/VIS Spectrophotometer at (300- 1100 nm) and observed that the transmission value was more than 75 % at the visible wavelength range. The direct energy gap (Eg) ranged between (2.73-3.22) eV, is measured by UV/VIS., and studied the sensor properties t0 NO_2 gas with 3% ratio at a constant voltage of 6V, to found the optimum operation temperature at 150°C for all films, also the sensor work in room temperature. The sensitivity increases with temperature to arrive (81.6%) for SnO_2: Ag films at 250°C. The response time was (5.4sec) and the recovery time was (27sec) for SnO_2: Ag gas sensor. The results obtained that SnO_2 film prepared by chemical spray pyrolysis pure and doped by Ag were a good sensitive for NO_2 gas. [56]

8. Mitali Biswas et al.,(2016) characterized the structural and optical characterization of magnesium doped zinc oxide thin films deposited by spray pyrolysis. Pure and magnesium (Mg) doped zinc oxide (ZnO) thin films were prepared onto clean glass substrate by spray pyrolysis (SP) technique at the substrate temperature of 300°C. Various optical parameters such as absorption co-efficient, band gap energy, refractive index, extinction coefficient of the thin films were studied using UV-VIS-NIR spectrophotometer in the photon wavelength range of 300-2500 nm. Optical band gap increased from 3.24 to 3.46 eV with the increase of Mg concentration from 0 to 40%. Transmittance and refractive index of the Mg doped ZnO thin films decreased due to the increase of Mg concentration. The EDX spectra confirmed the increase of Mg and consequent reduction in Zn content in the Mg doped ZnO thin films. Pure and Mg- doped ZnO films were annealed at 425°C for 1 hour. X-ray diffraction (XRD) study of the annealed films showed hexagonal type of polycrystalline structure with the preferred orientation along (101) plane with some other peaks (100), (002), (102), (110), (103) and (112). From the XRD patterns it was found that grain size decreased from 63.45 to 36.56 nm, lattice constant and c remained almost constant with Mg doping concentration. [59]

9. Supriyono et al.,(2015) characterized the preparation and characterization of transparent conductive SnO_2-F thin film deposited by spray pyrolysis. Relationship between loading level and some physical properties of the SnO_2-F film has been investigated. SnO_2-F thin films were prepared by spray pyrolysis technique using modified respiratory therapist nebulizer at substrate temperature in the range of 400-520°C. A stannous chloride solution was used as precursor and ammonium fluoride (NH_4F) as dopant with 20% [F]/[Sn] ratio. The sheet resistance was found to decrease with the increasing loading level, and sheet resistance became steady after the loading level was greater than0.45 mg/cm^2. The transmittance was found to decrease with the increase of loading level but the decrease was not significant. The transparent conductive oxide of SnO_2-F thin films were obtained, with transmittance was greater than 82.5% and sheet resistance of 21.4 Ω/sq. This results are comparable with the reported values (81.9% and 21.8 Ω/sq) and this film can be used for efficient support of dye-sensitized solar cells electrode. [22]

10. Riti Sethi et al., (2015) have reported the structural, optical and electrical properties of tin oxide thin films for application as a wide band gap semiconductor. Tin oxide (SnO) thin films were synthesized using thermal evaporation technique. Ultrapure metallic tin was deposited on glass substrates using thermal evaporator under high vacuum. The thickness of the tin deposited films was kept at 100nm. Subsequently, the as-deposited tin films were annealed under oxygen environment for a period of 3hrs to obtain tin oxide films. To analyse the suitability of the synthesized tin oxide films as a wide band gap semiconductor, various properties were studied. Structural parameters were studied using XRD and SEM-EDX. The optical properties were studied using UV-Vis Spectrophotometry and the electrical parameters were calculated using the Hall-setup. XRD and SEM confirmed the formation of SnO phase. Uniform texture of the film can be seen through the SEM images. Presence of traces of unoxidised Sn has also been confirmed through the XRD spectra. The band gap calculated was around 3.6eV and the optical transparency around 50%. The higher value of band gap and lower value of optical transparency can be attributed to the presence of unoxidised Sn. The values of resistivity and mobility as measured by the Hall setup were 78Ωcm and 2.92cm2/Vs respectively. The reasonable optical and electrical parameters make SnO a suitable candidate for optoelectronic and electronic device applications. [31]

11. Meriem Reghima et al., (2015) characterized and preparation the MgS thin film using sprays pyrolysis technique. MgS thin films have been successfully prepared using low cost spray pyrolysis technique. The aim of this study is to establish the optimized experimental conditions needed to grown MgS thin films. X ray diffraction and atomic force microscopy (AFM) techniques are used to examine the effect of the concentration of the agent complex ant EDTA used to grow MgS thin films. The structural analysis shows the formation of MgS thin film with preferential orientation (200) for sprayed solution containing EDTA. It was revealed also the diffraction peaks belonging to the $MgSO_4$ thin films crystallizing in orthorhombic structure. All samples were well adhered to the substrate as revealed from

AFM images. The optical properties of MgS thin films were investigated using spectrophotometric measurements in the wavelength range 250–2500 nm. These films, because of their low reflectance and high transmittance in the infrared regions, are suitable for coatings on different types of solar collectors. [34]

12. S. Sujatha Lekshmy et al., (2015) characterized the structural and optical properties of tin dioxide thin films by sol-gel dip coating technique. Tin oxide (SnO_2) thin films were deposited on quartz substrates using sol-gel dip coating technique. X-ray diffraction (XRD) pattern indicated that the film annealed in air at 350°C was amorphous in nature, whereas, the films annealed in oxygen atmosphere at 350°C showed crystalline phase. The films were further annealed in oxygen atmosphere at 450°C and 550°C. All the diffraction peaks can be indexed to the tetragonal phase of SnO_2 .The surface morphology (SEM) showed that surface of all films were continuous and without micro cracks. The Energy dispersive X-ray spectroscopy (EDXS) spectra indicated an increase in the concentration of oxygen content with increase in annealing temperature. The energy band gap value for the film annealed in air was 3.88 eV. The optical band gap increased to 4.05 eV when annealed in O_2 atmosphere. The photoluminescence (PL) spectra showed the presence of emission peaks in UV region and visible region of the electromagnetic spectra. Transparent oxide semiconductor SnO_2 film finds potential application as an active channel layer for transparent thin film transistor. [37]

13. Y. S. Sakhare et al., (2015) developed the substrate temperature dependent structural, optical, and electrical properties of spray pyrolysis deposited MgSe thin film. MgSe thin films were prepared by spray pyrolysis method by varying substrate temperature. The effects of the varying substrate temperature on structural, electrical, morphological and optical properties of MgSe thin films were discussed. X-ray diffraction studies confirm the formation of cubic structure with (111) & (200) as the preferred orientation. The optical studies revealed that the deposited MgSe has direct band gap and it varies from 2.60 to 2.45 eV depending on substrate temperature. The electrical resistivity of MgSe decreases with temperature indicating its semiconducting nature. The electrical resistivity, activation energy and optical band gap energy is found to depend upon substrate temperature. Thermo-emf measurement showed that the electrical conductivity in spray deposited MgSe is of p-type. [42]

14. Muhammad Luqman Mohd Napi et al.,(2015) developed the surface morphology and electrical properties of FTO (Fluorine Doped Tin Oxide) with different precursor solution for transparent conducting oxide. Fluorine doped tin oxide (FTO) thin film was prepared by using two different precursor solutions which are tin (ii) chloride dihydrate and tin (iv) chloride pentahydrate. These two precursors are used in spray pyrolysis process to prepare the fluorine doped tin oxide thin film. Surface Morphology of the thin film was characterized using field emission scanning electron microscope (FE-SEM). FESEM image shows the particle distribution and the morphology of fluorine doped tin oxide thin film. Two point probe I-V measurement and UV-Vis spectroscopy were used to study the electrical and optical properties of both films. Both precursors produced different particles distribution, electrical properties and also optical properties. The results show that the sheet resistance of fluorine doped SnO_2 is about $49.24\times10^6\Omega$ for tin. [57]

15. O.V. Diachenko et al.,(2015) developed the surface morphology, structural and optical properties of MgO films obtained by spray pyrolysis technique. X-ray diffraction, atomic force microscopy, field emission scanning electron microscopy, UV–visible photometry, and photoluminescence measurements were used to investigate the surface morphology and structural and optical properties of MgO films. Magnesium oxide films deposited by the spray pyrolysis technique were studied. The substrate temperature was varied from Ts = 643 K to 693 K. Magnesium chloride hexahydrate ($MgCl_2$ $6H_2O$), dissolved in deionized water, was used as the precursor solution. It was established that the single phase films crystallize into a cubic structure with very fine crystallite size (about 2 nm). The optical band gaps of the samples were varied from 3.64 eV to 3.70 eV. Also, the films have a high level of transmittance of 90%. Photoluminescence spectra show the emission peaks at approximately 412 nm (3.00 eV) and 524 nm (2.38 eV). The peak with the energy of 3.00 eV is ascribed to holes trapped in magnesium ion vacancies acting as acceptors (F^+ center). The broad emission peak at 524 nm is related to the presence of defects (F^- centers) associated with oxygen ion. [60]

16. M.A Farag et al., (2014) investigated dielectric and optical properties of MgO thin films. The performance of silicon carbide (SiC) devices was limited to the breakdown of the widely used insulator (SiO2) between the layers of these devices. Therefore, magnesium oxide (MgO) with its relatively higher permittivity was suggested to replace SiO_2. MgO was prepared in thin films using spray pyrolysis technique and then its structure was investigated by x-ray diffraction (XRD). The dielectric properties were investigated in the frequency range (42 - 106 Hz) for films deposited at different substrate temperatures. It was found that as the deposition temperature increases, the permittivity gradually increases from about 5 to about 17, indicating enhancements in their dielectric properties. The transmission, reflection, extinction coefficient and refractive index of MgO thin films deposited at different substrate temperatures were also investigated in the wavelength range (290 – 2500 nm). Both transmission and reflection of these films showed an increase with the increase of substrate temperature. The permittivity and dielectric loss calculated from these optical parameters led to improvements of their properties for films deposited at high substrate temperature. [35]

17. A. V. Dyachenko et al.,(2014) developed the structural properties of magnesium oxide thin films deposited by spray pyrolysis technique. Structural properties of magnesium oxide films have studied by X-ray diffraction methods. MgO obtained by spray pyrolysis technique at the different substrate temperatures on the glass substrates. The 0.2 M magnesium chloride hexahydrate aqueous solution was selected as a precursor in the solution. The influence of substrate temperature on the phase composition, texture quality, coherent scattering domain size and lattice constant of the material was investigated. The research results can be used in the development of functional layers of solar cells thin film. [36]

18. S. Deepa et al., (2014) have reported the gas sensing properties of magnesium doped SnO_2 thin film. Conducting magnesium doped (0 to 1.5 wt %) tin oxide thin films prepared by Spray Pyrolysis technique achieved detection of 1000 ppm of LPG. The films deposited at 304 °C exhibit an enhanced response at an operating temperature of 350°C. The microstructural properties are studied by means of X-ray diffraction. AC conductivity measurements are carried out using precision LCR meter to analyse the parameters that affect the variation in sensing. The results are correlated with compositional parameters and the subsequent modification in the charge transport mechanism facilitating an enhanced LPG sensing action. [39]

19. Saeed Moghadam et al., (2014) have reported the gold and silver contacts on tin oxide thin films produced by spray pyrolysis on SiO_2 Substrates. Thin layers of tin oxide have numerous applications in various branches of microelectronics as transparent conductors and active elements in chemical sensors. While forming different metallic contacts to these layers are required for different applications, noble metals are of particular use in gas sensor fabrication as these devices operate at elevated temperatures and harsh environments. The background literature on the quality and electronic features of gold and silver contacts on SnO_2 layers is limited. Moreover, it has been shown that both gold and silver electrodes exhibit different electronic features on TiO_2 at different thermal and atmospheric conditions.

Here, we report the I-V characteristics of Au/SnO_2 and Ag/SnO_2 contacts formed on SnO_2 layers deposited on SiO_2 substrates by ultrasonic spray pyrolysis. The obtained I-V plots proved the Au/SnO_2 and Ag/SnO_2 contacts to be independent from the temperature, in the range of 300-700 K, and the composition of the surrounding atmosphere. [43]

20 Sushant Gupta et al., (2014) have reported the structural/microstructural, optical and electrical investigations of $Sb\text{-}SnO_2$ thin films deposited by spray pyrolysis. The structural, optical and electrical properties of spray deposited antimony (Sb) doped tin oxide (SnO_2) thin films, prepared from $SnCl_4$ precursor, have been studied as a function of antimony doping concentration. The doping concentration was varied from 0 to 1.5 wt.% of Sb. The analysis of x-ray diffraction patterns revealed that the as deposited doped and undoped tin oxide thin films are pure crystalline tetragonal rutile phase of tin oxide which belongs to the space group. The surface morphological examination with field emission scanning electron microscopy (FESEM) revealed the fact that the grains are closely packed and pores/voids between the grains are very few. The transmittance spectra for as-deposited films were recorded in the wavelength range of 200 to 1000 nm. The sheet resistance of tin oxide films was found to decrease from 48 Ω/sq for undoped films to 8 Ω/sq for antimony doped films. [45]

21. S. Sakthivel et al., (2014) have reported structural and optical properties of indium tin oxide thin films by spray pyrolysis method. Transparent, conducting thin films of indium tin oxide (ITO) have prepared by spray deposition. Films grown from 2 M stannic chloride solution of 100 cc was prepared in doubled distilled water and 14.285 g/m of Indium chloride dissolved in it, to obtain the 20% doping concentration of Indium. ITO film has resistivity of 2.4×10- 4 Ω cm and transparency greater than 95% over the visible spectrum. The resistivity of these ITO films was 2.4×10-4 Ω/cm which is comparable to high quality films reported in the literature. X-ray diffraction and Hall measurements can used to further characterize these films and refine deposition parameters. The structure confirmed by XRD, SEM. The optical analysis reveals the bandgap, Refractive Index (n), Absorption coefficient more than 104 cm^{-1}, Optical conductivity, and electrical conductivity of the film have potential application in photovoltaic devices.[46]

22. Gresh, Robert William., (2014) characterized the Vapor Deposited Thin Films of Magnesium and Magnesium Alloys. Magnesium and magnesium-aluminum alloy thin films were created by physical vapor deposition using a dual gun electron beam physical vapor deposition (EBPVD) system for the purpose of evaluating their corrosion properties. A surface profilometer was used to measure the thickness of the films, which was then used to calculate the deposition rate. Energy dispersive x-ray spectroscopy (EDS) was used to determine the composition of thin films. The cross sections of thin films were analyzed usinga field-emission scanning electron microscope (FESEM) to provide information about the structure and morphology of the films. X-ray diffraction (XRD) was used to measure the x-ray spectra of thin films and determine the phases and crystal structures present in the thin films. Electrochemical testing was conducted to determine the corrosion characteristics of the samples. The open circuit potential (OCP) was measured along with corrosion rates calculated from polarization resistance (PR) and electrochemical impedance spectroscopy (EIS) data. Magnesium films were deposited with deposition rates ranging from 9.27 to 126.60 Å/s and angles from 0° to 38°. Magnesium films with low deposition rates (less than 20 Å/s) showed a denser morphology with columns of 500-700nm diameter and a preferred orientation to the (0002) plane of the hcp magnesium structure. Higher deposition rates (40 to 126 Å/s) for magnesium films resulted in a less dense morphology with thin columns of 200-300nm diameter and a preferred orientation of the (103) plane for hcp magnesium crystal structure. The magnesium-aluminum films were produced using the two gun system with deposition rates ranging from 14.42 to 34.58 Å/s and with compositions ranging from 2.97 to 58.71 wt. % Al. The best Mg-Al film had an open circuit potential of -1.856 V and a corrosion rate of 5.85 mpy. These characteristics make this film an ideal candidate for a protective coating. [58]

23. Syed Mansoor Ali et al., (2013) reported the effect of doping on the structural and optical properties of SnO_2 thin films fabricated by aerosol assisted chemical vapour deposition. In order to achieve high conductivity and transmittance of transparent conducting oxide (TCO), we attempted to fabricate Mg doped SnO_2 (MgxSn1-xO_2) thin films and characterized them for their structural and optical properties. The MgxSn1-xO_2 thin films had been deposited on glass substrate by using aero-sole assisted chemical vapour deposition (AACVD). The molar concentration of Mg concentration was changed from 0 to 8%. The confirmation of tetragonal structure and particle size (32 to 87nm) has been calculated of thin films by XRD. The surface roughness was decreased with the increase of the dopant concentration, which had been investigated by atomic force microscopy (AFM). The optical transmission has increased from 54 to 78% and the band gape of pure SnO_2 has been found to be in the range of 3.76eV and it was shifted to 3.69eV for 6Wt % Mg doping and then increase on further increasing the Mg doping. [28]

24. Jeon IY et al., (2013) fabricated the electrical properties of magnesium incorporated zinc tin oxide thin film transistor by solution process. Zinc tin oxide (ZTO) films were fabricated on SiO_2/Si substrate as a function of Mg concentration (the ratio of 3 to 10 atomic%) using a spin-coating process. For the characterization of thin film transistors (TFTs), Zn0.3Sn0.70 channel TFT exhibited a higher on/off ratio compared to Zn0.5 Sn.0.5O channel TFT because the higher Sn concentration can induce more charge carriers. 3 atomic% Mg incorporated Zn0.3Sn0.7O channel TFTs showed stable electrical performances such as I(on/off) - 1 x 10(7), micro(sat) = 1.40 cm^2 and S = 0.39 V/decade. However, 10 atomic% Mg incorporated Zn0.3Sn0.7O channel TFTs deteriorated their electrical performances due to Mg segregation. [38]

25. Benjamin Victor Odari et al.,(2013) have reported the optoelectronic properties of F-co-doped PTO thin films deposited by spray pyrolysis. F-co-doped Palladium Tin Oxide (PTO) thin films were pyrolytically deposited on glass substrate at 4500C using an alcoholic precursor solution consisting of Tin (IV) Chloride ($SnCl_2.5H_2O$), Palladium Chloride ($PdCl_2$) and Ammonium Fluoride (NH_4F). A resistivity of 0.3-6.9×10 $^{-2}$ Ωcm obtained in F-co-doped PTO films prepared with a Pd content of 3.68% and F content of 0 – 23.96% under optimized conditions. [51]

26. S. Praveen Banu et al.,(2013) synthesized the effect of temperature on the structural and optical properties of spray pyrolysis SnO_2 Thin Films. SnO_2 thin films were synthesized at 300-500ºC temperature by spray pyrolysis method using tin chloride pentahydrate, acetic acid, ammonia solution. The films were characterized by XRD, SEM and UV-Vis-NIR. XRD analysis of nanocrystal prepared with three different temperatures which shows the crystalline nature, structure as well as particle size of the prepared SnO_2 particles. From the peaks position of XRD shows that the deposited films possess tetragonal structure with most prominent reflection along (200) plane. The Parameters such as crystalline size, strain and dislocation density has been analysed. Surface morphology and film composition have been analyzed using scanning electron microscopy, the images of SnO_2 nanoparticles showed their morphology, particle size and crystalline respectively. From the structural and SEM analysis it has been confirmed that phase change can be achieved by varying the temperature. The band gap of the prepared nanoparticles is found to be in the range 2.7 to 2.95eV, it is clear that by increases the temperature, energy gap was decreased. [62]

27. R. Udayakumar et al., (2013) synthesized and structured thin films characterized the SnO_2 Prepared by spray pyrolysis technique. Thin films of Tin dioxide (SnO_2) thin films are a special class of metal oxides that combine high electrical conductivity with optical transparency. Such Transparent Conducing Oxide (TCO) provides an important component for optoelectronic applications. Spray pyrolysis deposition for thin film preparation is a simple and relatively cost effective technique. This work consists of the synthesis of thin films of tin dioxide using automated spray pyrolysis technique and its structural characterization. Tin oxide films were prepared from different concentrations of the precursor solution. These films were found to be transparent at low concentration of the precursor solution. Characterization of these prepared films using X-ray diffraction technique is presented and discussed. Spray deposited thin films of tin dioxide have a number of applications, mainly as electrode materials in solar cell. [63]

28. G. E. Patil et al(2012) reported the nanostructured SnO_2 thin films spray pyrolysis deposition by the chemical spray pyrolysis (CSP) method. Homemade spray pyrolysis techniques are employed to prepare thin films. SnO_2 are wide bandgap semiconductor material whose film are deposited on glass substrate using aqueous solution of $SnCl_4 \cdot 5H_2O$ as a precursor. XRD (X-ray diffraction), UV (ultraviolet visible spectroscopy), FESEM (field emission scanning electron microscopy), and EDS (energy dispersive spectroscopy) analysis are done for structural, optical, surface morphological, and compositional analysis. XRD analysis shows polycrystalline nature of samples with pure phase formation. Crystallite size calculated from diffraction peaks are 29.92 nm showing nanostructured thin films. FESEM analysis shows that SnO_2 thin film contains voids with nanoparticles. EDS analysis confirms the composition of deposited thin film on glass substrate. UV-visible absorption spectra show that the bandgap of SnO_2 thin film are 3.54 eV. Bandgap of SnO_2 thin film can be tuned that it can be used in optical devices. [27]

29. R. Mariappan et al., (2012) prepared the pure and tin doped zinc oxide thin film effect of doping concentration on the structural and optical properties by nebulizer spray pyrolysis (NSP) technique. Pure and tin doped zinc oxide (Sn:ZnO) thin films were prepared for the first time by NSP technique using aqueous solutions of zinc acetate dehydrate, tin (IV) chloride fendahydrate and methanol. X-ray diffraction patterns confirm that the films were polycrystalline in nature exhibiting hexagonal type, with (0 0 2) as preferred orientation. The structural parameters such as lattice constant (‘a’ and ‘c’), crystallite size, dislocation density, micro strain, stress and texture coefficient were calculated from X-ray diffraction studies. Surface morphology was found to be modified with increasing Sn doping concentration. The ZnO films have high transmittance 85% in the visible region, and the transmittance was found to be decreased with the increase of Sn doping concentration. The corresponding optical band gap decreases from 3.25 to 3.08 eV. Room temperature photoluminescence reveals the sharp emission of strong UV peak at 400 nm (3.10 eV) and a strong sharp green luminescence at 528 nm (2.34 eV) in the Sn doped ZnO films. The electrical resistivity is found to be 106 X-cm at higher temperature and 105 X-cm at lower temperature. [21]

30. K. Fleischer et al., (2012) reported the transparent conducting oxide with tunable optical and electrical properties of aluminium doped $Zn_{1-X}Mg_xO$. A ternary mixed oxide Zn1−xMgxO has been doped with aluminium to create a range of transparent conducting oxides (TCOs) with tunable refractive index as well as work function. Conductive material was synthesised up to a magnesium concentration of x=0.45, although the conductivity is reduced compared to standard ZnO:Al. The changes in band gap, work function and conductivity have been attributed to a modified band structure and energetic position of the aluminium induced donor state. [30]

31. Mario Albert Sanchez-Garcia et al., (2012) developed the characteristics of SnO_2:F thin films deposited by ultrasonic spray pyrolysis. Fluorine doped tin oxide, SnO_2:F, thin films were deposited by ultrasonic chemical spray starting from tin chloride and hydrofluoric acid. The physical characteristics of the films as a function of both water content in the starting solution and substrate temperature were studied. The film structure was polycrystalline in all cases, showing that the intensity of (200) peak increased with the water content in the starting solution. The electrical resistivity decreased with the water content, reaching a minimum value, in the order of 8 × 10–4 Ω/cm, for films deposited at 450°C from a starting solution with a water content of 10 ml per 100 ml of solution; further increase in water content increased the corresponding resistivity. Optical transmittances of SnO_2:F films were high, in the order of 75%, and the band gap values oscillated around 3.9 eV. SEM analysis showed uniform surface morphologies with different geometries depending on the deposition conditions. Composition analysis showed a stoichiometric compound with a [Sn/O] ratio around 1:2 in all samples. The presence of F into the SnO_2 lattice was detected, within 2 at % respect to Sn. [47]

32. Sumanta Kumar Tripathy et al.,(2012) synthesized the tin oxide thin film and effect of number of coating on transmittance and film thickness. This paper studies the synthesis of semiconducting tin oxide thin film on a glass substrate by dip coating method using Tin (II) chloride as precursor and methanol as solvent. The optical properties were studied by UV/VIS Spectrophotometer. The thickness of the film has been calculated from the interference pattern of the transmission spectrum for each coat. It was concluded that thickness of the thin film increases nearly linearly with the number of coating. The effect of multiple applications on transmittance is also studied. [61]

33. P. Saikia et al., (2011) reported the structural optical and electrical properties of tin oxide thin film deposited by APCVD method. Tin oxide (SnO_2) thin films have been grown on glass substrates using atmospheric pressure chemical vapour deposition (APCVD) method. During the deposition, the substrate temperature was kept at 400°C–500°C. The structural properties, surface morphology and chemical composition of the deposited film were studied by X-ray diffraction (XRD), scanning electron microscope (SEM) and Rutherford back scattering (RBS) spectrum. XRD pattern showed that the preferred orientation was (110) having tetragonal structure. The optical properties of the films were studied by measuring the transmittance, absorbance and reflectance spectra between $\lambda = 254$ nm to 1400 nm and the optical constants were calculated. Typical SnO_2 film transmits ∼ 94% of visible light. The electrical properties of the films were studied using four-probe method and Hall-voltage measurement experiment. The films showed room temperature conductivity in the range 1.08×102 to $1.69 \times 102\ \mathbf{\Omega}^{-1}\text{cm}^{-1}$. [29]

34. K.Punitha et al., (2011) have reported structural and surface morphological studies of magnesium tin oxide thin films of transparent conducting oxides (TCOs) have been well known in the form of undoped single cation oxides such as SnO_2 and In_2O_3. These were degenerate semiconductors which were simultaneously transparent and highly conductive, useful in many optical and electrical device developments. Starting from 1990s, however, multication TCOs began to develop. Since then new TCOs are being reported with increasing frequency as their technological interest and importance increased in various fields of technological development. In this paper, we have attempted to use magnesium tin oxide as new TCO which possess more than 80% of transmittance for a 320 nm film. The precursor of magnesium tin alloy was prepared through a new way called “protective flux route” method. Magnesium tin oxide thin films were prepared by electron beam evaporation technique. The coated film was then annealed to get oxide layer and hence magnesium tin oxide thin films.

Their structural analysis optical studies, electrical properties and surface morphology were studied using XRD, UV-Vis-NIR, linear four probe resistivity and SEM, respectively. [33]

35. Demet Tatar et al.,(2011) have reported the effect of substrate temperature on the crystal growth orientation and some physical properties of SnO_2:F thin films deposited by spray pyrolysis technique. SnO_2:F thin films were prepared by the spray pyrolysis (SP) technique at substrate temperature in the range 360-520°C using dehydrate stannous chloride ($SnCl_2.2H_2O$) and ammonium fluoride (NH_4F) as precursors, and mixture of water and methanol as solvent. Optical micro slide glass plates were used as substrates. The X-ray diffraction studies confirmed the tetragonal structure with polycrystalline nature. The preferred directions of crystal growth appeared in the diffractogram of SnO_2: F (FTO) films prepared with different substrate temperature were correspond to the reflections from the (110), (200) and (211) planes, respectively. The film thickness and the grain size vary from 305 to 204 nm, from 20.94 to 33.09 nm, respectively. AFM study reveals the surface of FTO to be made of nano crystalline particles. The electrical study reveals that the films have degenerate and exhibit n-type electrical conductivity. The sprayed FTO films have minimum sheet resistance of 9.03 Ω/cm_2, highest figure of merit of 558.1x10-3 Ω-1 at 800 nm. The average visible transmittance (800 nm) of the deposited films is 80.664 %. In the visible region of the spectrum, the transmission is very high. For films prepared at 520°C, relatively higher transmittance of about 92.78% at 800 nm has been observed. The transmission attained in this study is greater than the values reported for tin oxide films prepared at substrate temperature 520°C, from aqueous solution of $SnCl_2.2H_2O$ precursor. Resistivity is smaller than the values reported. The obtained results revealed that the structures and properties of the films were greatly affected by substrate temperature. [49]

36. V. Arivazhagan et al.,(2011) have reported the influence of In/Sn on nano crystalline indium tin oxide thin films by spray pyrolysis method. Nano crystalline Indium Tin Oxide thin films were prepared by spin cum spray pyrolysis technique with varying wt % of indium and tin. The polycrystalline nature of the films observed from XRD pattern with cubic structure. The various structural parameters were calculated and reported in this paper. Increasing the indium wt % helps to improve the structural optical and electrical properties of the films. The absorption edge towards blue wavelength indicates the presence of nano particles. The films prepared with high indium wt % have the good optical band gap of 3.7 eV. The electrical conductivity of the films increases with increasing the indium wt % on the formation of ITO thin films. [53]

37. L.S. Chuah et al.,(2011) synthesized the Porous Ni-Doped SnO_2 thin film by using spray pyrolysis. Doping SnO_2 with metal cations has been tested for photo-catalytic applications by shifting the threshold for photonic excitation of the tin oxide (SnO_2) towards the visible. Nevertheless, as far as we know, there is no report on how Ni-doping of SnO2thin films by the spray pyrolysis method has been carried out. In this work, we report a new kind of experimental realization of a porous Ni-doped SnO_2 thin film on glass, which was based on a spray pyrolysis process at room temperature. To prepare porous structures, the Ni-doped SnO_2 thin film samples were annealed at 400° C for 1 h in air. As a result, this porous Ni-doped SnO_2 thin film possesses a high specific surface area and unbroken porosity, which is especially desirable for gas sensor design. The surface morphology of the porous Ni-doped SnO_2 films was examined using scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDX), and atomic force microscopy (AFM). The root-mean-square (rms) surface roughness value determined from AFM image is 11.85 nm on a $5 \times 5\ \mu m^2$ scan area. [54]

38. A.Moses Ezhil Raj et al.,(2007) characterized the spray pyrolysis deposition of highly (100) oriented magnesium oxide thin films. Transparent dielectric thin films of Mgo has been deposited on the quartz substrate at different temperatures between 400 and 600°C by a pneumatic spray pyrolysis technique using $Mg\ (CH_3COO)_2.4H_2O$ as a single molecular precursor. The thermal behaviour of the precursor magnesium acetate was described in the results of thermogravimetry analysis (TGA) and differential thermal analysis (DTA). The prepared films are reproducible, adherent to the substrate, pinhole free and uniform. Amongst the different spray process parameters, the substrate temperature effect has been optimized for obtaining single crystalline and transparent MgO thin films. The films crystallize in a cubic structure and X-ray diffraction measurements have shown that the polycrystalline MgO films prepared at 500°C with (100) and (110) orientations were changed to (100) preferred orientation at 600°C. The MgO phase formation was also confirmed with the recorded Fourier Transform Infrared (FTIR) results. The films deposited at 600°C exhibited highest optical transmittivity (>80%) and the direct band gap energy was found to vary from 4.50 to 5.25 eV with a rise in substrate temperature from 500 to 600°C. The measured sheet resistance and the resistivity of the film prepared at 600°C were respectively 1013Ω/m and 2.06x107Ω cm. The surface morphology of the prepared MgO thin films was examined by atomic force microscopy. [25]

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40. D.Jadsadapattarakul et al., (2007) investigated the tin oxide thin film by ultrasonic spray pyrolysis. This study investigated microstructure of SnO_2 thin films deposited by ultrasonic spray pyrolysis technique using 0.2 M of $SnCl_4·5H_2O$ in absolute ethanol as a precursor. The deposition temperature (350–450 °C) and time (20–90 min) were varied. The influence of film-deposition conditions on grain size and orientation were discussed. The deposited SnO_2 films were textured polycrystalline films. The preferred orientation of SnO_2 films were quantitatively evaluated by texture coefficient (TC). The mean grain size and film thickness determined by SEM could be controlled over a range of 50–325 nm and 80–2690 nm, respectively. [44]

41. E. Cetinorgu et al.,(2007) developed "Optical and structural characteristics of tin oxide thin films deposited by filtered vacuum arc and spray pyrolysis". Tin oxide (SnO_2) thin films were deposited on commercial microscope glass and UV fused silica substrates (UVFS) using spray pyrolysis and filtered vacuum arc deposition (FVAD) system. During deposition, the substrates temperature was kept at 400 °C. The structure and composition were determined using X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS), respectively.

The XRD patterns of SnO_2 thin films deposited with the two systems on hot substrates were found to be polycrystalline. The average transmission of the films in the VIS was 80% to 85%. The film optical constants were determined by normal incidence transmission measurements. The refractive indices of FVA deposited films were in the range 2.11 to 2.0, and those of spray deposited ones were 1.97 to 1.93. The extinction coefficients of the deposited films were in the range 0.29 and 0.11 to approximately 0 for FVAD and spray pyrolysis, respectively, depending on wavelengths. The optical band gap, E_g, was determined from the dependence of the absorption coefficient on the photon energy at short wavelengths, and were 3.80 eV and 3.90 eV for spray pyrolysis and FVA deposited SnO_2 thin films, respectively. [50]

42. E. Elangovan et al.,(2004) deposited SnO_2 thin films developed by physical properties of spray pyrolysis. Thin films of tin oxide (SnO_2) were deposited on various substrates by spray pyrolysis technique using $SnCl_2$ as precursor. The as-prepared films were characterized for their electrical, optical and structural properties. Films deposited on optical glass showed the better electrical properties as compared to those deposited on other substrates. Further, fluorine- and antimony- doped SnO_2 films were deposited on these substrates. The fluorine-doping resulted in enhancing both the electrical and optical properties of these films. On the other hand antimony- doping enhanced the electrical properties of the films but decreased the optical properties. The preferred orientation (211) of undoped films was found shifted to (200) for both the dopants. The change in orientation was reflected in SEM studies as they have different grain shapes. The minimum sheet resistance of 1.8 and 2.2 W/ cm obtained for the films SnO_2:F and SnO_2:Sb deposited on glass are the lowest among the reported values for these materials prepared from $SnCl_2$ precursor. The 42 % transmittance of undoped films found increased to 85 % on fluorine- doping (15 wt. %) but decreased to 20 % on antimony doping (2 wt. %). [55]

43. M.G.M Choudhury et al., (2003) have reported the properties of cadmium-doped tin oxide prepared by spray pyrolysis method. Cadmium doped Tin Oxide Thin Films have been prepared by Spray Pyrolysis Method on glass substrates at 350°C. Structural, electrical and optical properties have been measured. From XRD it is found that films deposited are crystalline in nature with tetragonal structure having lattice constant a=b=3.86 A° and c=5.62A°. Hall Effect measurements show that films prepared are of n-type and the carrier concentration (≈1018 cm-3) and room temperature conductivity decreases with the increases in cadmium concentration in the films. Activation energy has been calculated from conductivity measurements and it was found that conduction within the temperature range we have measured is due to hoping of carriers through the spectrum of localized states. Band gap of the un-doped films calculated from transmission spectrum is about 3.1 eV and the value decrease slightly with the addition of cadmium. The refractive index, extinction coefficient, real and imaginary parts of the dielectric constant has been calculated from the optical spectra. The refractive index decreases with photon energy and also decreases slightly with cadmium concentration while extinction coefficient increases with photon energy. [48]

44. Abdul-Majeed Azad et al.,(2001) reported novel synthesis of high Phase- Purity Mg_2SnO_4 from metallic precursors via Powder Metallurgy Route. Magnesium orthostannate Mg_2SnO_4, a potential candidate for applications in high temperature-high frequency domain as a ceramic capacitor element was synthesized from metallic tin and magnesium powders. The alloy prepared at 775℃ from metallic tin and magnesium characterized by XRD patterns. Comparison with the standard cards shows all the major diffraction peaks belonging to the compound Mg_2Sn (JCPDS 7-0724) alone with the metallic tin (JCPDS 4-0673) present in traces only. Very sharp and narrow diffraction peaks also signify the formation of the precursor in highly crystalline state with small crystalline size [23].

45. Alexandra Navrotsky and Robert B.Kasper(1976) reported the spinel disproportionation at high pressure: calorimetric determination of enthalpy of formation of Mg_2SnO_4 and Co_2SnO_4 and some implications for silicate. The enthalpies of formation from the oxides of $MgSnO_4$ and Co_2SnO_4 were found by oxide melt solution calorimetry to be +1.13, ±0.28 kcal/mol, respectively [24].

CHAPTER-III

MATERIALS AND METHODS

3.1 INTRODUCTION

Thin films are the important application of material science. It can be prepared in variety of methods from different materials depending on our interest. Also, thin film can be produced in different phases such as solids, liquids. Even in gaseous phase also thin film can be fabricated using suitable technique. The quality of thus produced thin films mainly depends on the choice of deposition method. Even though there are some free standing thin film also possible, a substrate forms a frim basis to all thin films. There are many solid substrates like glass, ceramics, metals, quartz, mica, semiconductors, insulators and organic materials like plastics, polymers, rubbers etc., available for thin film deposition. In this case, glass is taken as a substrate. Magnesium tin oxide is an important material which exhibits numerous applications in solar cells using spray pyrolysis technique.

Chemical spray deposition (CSD) or reactive pulverization or more popularly known as spray pyrolysis is a simple technique to prepare thin films by condensation process of an atom by atom or molecule by molecule or an ion by ion. This technique lies in the region between thick film and thin film depending upon the atom cluster size. Generally spray pyrolysis is extensively used to deposit transparent conducting oxide thin film. Spray pyrolysis involves a thermally stimulated reaction between clusters of liquids/vapour atoms of different chemical species [6].

3.2 MATERIAL DETAILS

3.2.1. Magnesium Acetate

Magnesium acetate have its chemical formula $Mg(CH_3COO)_2.4H_2O$. The compound magnesium has an oxidation state of 2^+. Magnesium acetate is the magnesium salt of acetic acid. It is deliquescent and upon heating, it decomposes to form magnesium oxide. Magnesium acetate appears as white hygroscopic crystals. It smells like acetic acid and is soluble in water. When it is in an aqueous solution its pH will be on the alkaline side of neutral.

3.2.2. Stannic Chloride

Tin (II) chloride, also known as stannous chloride, is a white crystalline solid with the formula $SnCl_2$. It forms a stable dehydrate, but aqueous solutions tend to undergo hydrolysis, particularly if hot. $SnCl_2$ is widely used as a reducing agent (in acid solution), and in electrolytic baths for tin-plating. $SnCl_2$ has a lone pair of electrons, such that the molecule in the gas phase is bent. In the solid state, crystalline $SnCl_2$ forms chains linked chloride bridges. [64]

3.3 CHOICE OF SUBSTRATE

The material or coating should be on a clean surface, called substrate. If there is no substrate, then thin film is called a foil. Substrate provides a strong base for any thin film deposition. It contributes in the nucleation and growth process. Structurally, the substrate should be flat, uniform and should not contain any form of crystalline defects. The chosen substrate should not undergo any chemical reaction with the material used during film fabrication. It should be stable for all types of environments, solvents and reagents. Also, it should not show any variation for different temperature. Substrate must be mechanically strong leading to repeated use which is desirable to reduce the cost of film. Hence the substrate plays an important role in determining the physical, chemical, mechanical, electrical and optical properties of the film. Depending on the application a large number of different types of coating layers will be deposited onto the substrate. Different applications require different types of substrate to fulfil the specific purpose. It is a desired property of the substrate to provide only mechanical stability, without interacting with the chemicals used. But, it should provide good adhesion to the film. Glass substrates are getting more and more attention, because it almost fulfils all these varied requirements best and it can be successfully used in spray pyrolysis. So, glass substrate is preferred for thin film fabrication.

The physical and chemical condition of the substrate play very important role in determining the structure of the film. Ideally a substrate should have the following.

i. A flat and automatically smooth surface.
ii. High dielectric strength.
iii. High mechanical strength.
iv. High thermal conductivity.
v. High thermal shock resistance.

vi. Low electrical conductivity.
vii. Readily available at low price.
viii. Zero porosity.

3.4 CLEANING OF SUBSTRATE

Substrate is a based on which the material is to be deposited. Substrate cleaning is done in order to remove all foreign objects in the substrate surface such as dirt and dust etc. The purity of the substrate provides great contribution to the characteristics of thin film. It is a very basic requirement that the substrate must be cleaned thoroughly to get the desired result in thin film preparation. It is very important to note that the coated films should not peel off from the substrate under any condition like stress and strain, temperature variations, and environmental difference. Also, the substrate should provide strong adherence to the coating material. We can choose any suitable method to clean the substrate out of many techniques.

Substrate can be cleaned chemically or mechanically. Mechanical method is a short duration method but large amount of stress is imparted on the substrate. So the substrate must be strong enough to tolerate these much of stress. The other method is chemically cleaning the substrate. The only consideration in this method is that only there should be a reaction between the chemical impurities and the chemical used in order to remove those impurities. The material chosen must not change its property due to the interaction between the chemicals and the substrate. Since chemical method is most economic, it is preferred commonly and the procedure is described below.

Chromic acid is satisfactory for cleaning glass. The chromic acid solution should be used only if it has its brown colour. If the colour is changed, the solution is decomposed.

The following steps to be followed to clean the substrate.

i. The substrate or glass plate is cleaned by soap solution.
ii. Dip the substrate in a heated chromic acid solution for about 45-60 minutes.
iii. Again the substrate is cleaned by soap solution.
iv. Wipe the substrate using cotton.
v. The substrate is then cleaned by acetone
vi. Wipe the glass plate thoroughly using fresh cotton.

3.5 THIN FILM DEPOSITION TECHNIQUE

Thin-film deposition is a vital technique of depositing a thin film (about 1µm) of material onto a substrate or onto previously deposited layers. “Thin” is a relative term, but most deposition techniques allow layer thickness to be controlled within a few tens of nanometres, and some (molecular beam epitaxy) allow one layer of atoms to be deposited at a time.[64]

Deposition of thin films involves consideration of both the source of atoms for thin film deposition and the substrates. Substrates are the base material of the film. The deposition geometry includes the characteristics of source and the orientation and placement of substrates. This influences the uniformity of the films. For obtaining high purity films, there should be control over the level and nature of impurities that initially present in the source and residual gases present in the case of vacuum systems. [1]

There are two broad categories of thin film deposition methods.

i. Physical Vapour Deposition (PVD)
ii. Chemical Vapour Deposition (CVD)

3.6 PHYSICAL VAPOUR DEPOSITION

PVD processes proceed along the following sequence of steps:

- The solid material to be deposited is physically converted to vapour phase;
- The vapour phase is transported across a region of reduced pressure from the source to the substrate;
- The Vapour condenses on the substrate to form the thin film [10].

The conversion from solid to vapour phase is done through physical dislodgement of surface atoms by addition of heat in evaporation deposition or by moment transfer in sputter deposition. The third category of PVD technique is a group of so called augmented energy techniques including ion, plasma or laser assisted deposition [65].

3.6.1 Thermal Deposition In Vacuum

The most commonly used technique adopted for the deposition of metals, alloys, and also many compounds. This involves the evaporation or sublimation of the material in vacuum by thermal energy and following the vapour stream of the charge to condense on a substrate so as to form a continuous and adherent deposit of desired thickness. The quality and the characteristics of the deposit will depend on the rate of deposition, substrate temperature, ambient temperature, etc. and the uniformity of the film on several factors the geometry of the evaporate source and its distance from the substrate.

Thermal evaporation is one of the most well-known physical vapour deposition techniques. It is very simple technique. It is a simple technique and one can evaporate a large variety of materials (metals, semiconductors and dielectric) onto different type of substrates (glass, quartz, polymer sheet). In thermal evaporation, the material is formed in a vapour form by means of resistive or RF heating. The atoms are transported through vacuum to get deposition on the substrate.

On heating a material in vacuum, it evaporates at a rate given by well-known Langmuir-Dustman equation. The vapour atoms thus formed are transported through to get scattered by collision with gas atoms. At pressures about 10^{-5} torr the mean free bath between collisions become large enough so that the vapour beam arises at the substrate unscattered. A low vacuum can result in contamination of the films. [66]

3.6.2 Evaporation

Evaporation or sublimation techniques are widely used for the preparation of thin layers. A very large number of materials can be evaporated and if the evaporation is undertaken in vacuum system, the evaporation temperature will be very considerably reduced; the amount of impurities in the growing layer will be minimized. In order to evaporate materials in a vacuum, a vapour source is required that will support the evaporation and supply the heat of vaporisation while allowing the charge of evaporant to reach a temperature sufficiently high to produce the desire vapour pressure, and hence rate of evaporation, without reacting chemically with the evaporant. To avoid contamination of the evaporant and hence of growing film, the support material itself must have a negligible vapour pressure and dissociation temperature of the operating temperature [65].

3.6.3 Sputtering

If a surface of target material is bombarded with energetic particles, it is possible to cause ejection of the surface atom: this is the process known as sputtering. The ejected atoms can be condensed on to a substrate to form a thin film. This method has various advantages over normal evaporation techniques in which no container contamination will occur.it is also possible to deposit alloy films which retain the composition of the parent target material. DC sputtering, radio frequency sputtering and magnetron sputtering methods are the oldest types of sputtering used. High pressure oxygen sputtering and facing target sputtering are the two new methods introduced for deposition of thin films for applications in superconducting and magnetic film [11].

3.6.4 Ion Plating

In this atomistic, essentially sputter- deposition process the substrate is subjected to a flux of high energy ions, sufficient to cause appreciable sputtering before and during film deposition. The advantages of physical methods are laid in dry processing, high purity and cleanliness, compatibility with semiconductor integrated circuit processing and epitaxial film growth. However, there are certain advantages such as slow deposition rates, difficult stoichiometry control, high temperature post deposition annealing often required for crystallization and high capital expenditure [67].

3.7 CHEMICAL METHOD

The different chemical methods available for film preparation are chemical vapour deposition, electrolyte deposition, electro less deposition, anodization. Through these methods appears simple and economical in practice. These are more complicated; the film properties are not easily reproducible and so the chemical methods are of limited use.

3.7.1 Chemical Vapour Deposition

The chemical vapour deposition is the condensation of compound or compounds from the gas phase on to a substrate where reaction occurs to produce a solid deposit. The gaseous compound, deposit materials, is formed by volatilization from either a liquid or a solid feed and is caused to flow either by a pressure differential or by the action of a carrier gas to the substrate. The chemical reaction is initiated at or near the substrate surface, which produces the desired material in the form of a deposit on the substrate. In some process, the chemical reaction may be activated through an external agency, such as, application of that, RF field, light or X-ray, an electric arc or glow discharge, electron bombardment. The morphology microstructure and adhesion of the deposit is strongly influenced by the nature of the chemical reaction and the activation process. [68]

3.7.2 Electro Deposition

Films can be grown on either metallic or non-metallic substrate by dipping them in appropriate solutions containing metal salts without the application of any electric field. Deposition occurs by homogeneous chemical reactions, usually reduction of a metal ion by a reducing agent. Compound films such as sulphides and selenides of Pb, Hg, Zn, and Cd can be deposited by this technique. The rate of the growth and degree of crystallinity depend upon the temperature of the solution. [69]

3.7.3 Anodic Oxidation

Anodic oxidation can be used as a method of depositing oxide films and the action depends upon the migration of oxygen ions to the anode surface through a medium that usually contains water growth rate of an anodic film depends on the current density and the temperature of the electrolyte.

When the current is constant, the growth increases linearly with time. For a constant voltage, the growth increases rapidly in several minutes to approach an asymptotic value. The maximum value of thickness developed on the applied voltage depends on the electrolyte and its temperature. The common materials that can be anodized successfully are aluminium, tantalum, zirconium, titanium, silicon etc.,

The anodic are generally amorphous. But the crystalline films may be obtained under certain anodization conditions. Aluminium oxide films of different thickness and hence different colours can be obtained by the wet anodization process. [68]

3.7.4 Spray Pyrolysis

The spray pyrolysis technique involves spraying of a solution (usually aqueous, containing soluble salts of the constituent atoms of the desired compound) onto a substrate maintained at elevated temperatures. The sprayed droplet reacts with the hot substrate surface and undergoes a pyrolytic (endothermic) decomposition and forms single crystallite or cluster of crystallites of the compounds. Thin-film deposition using spray pyrolysis can be divided into three main steps: (i) atomization of the precursor solution, (ii) transportation of the resultant aerosol, and (iii) decomposition of the precursor on the substrate. In spray pyrolysis, the important factor is to understand the basic atomization process of the atomization device used. Depending on the application of the films, one can choose the atomizers like air blast, ultrasonic, and electrostatic atomizers, etc.

The most important parameter is the substrate temperature and if the substrate temperature is higher, then the films possess more roughness as well as porous. When the temperature is too low, cracks would be observed in the films. The substrate temperature also influences the crystallinity, texture, and other physical properties of the deposited films. Another important spray parameter is the viscosity of the precursor solution that affects the morphology and properties of the deposited films. The film morphology and properties can also be changed by using various additives in the precursor solution with such advantages of this spray pyrolysis technique [69].

3.8 TECHNIQUE ADAPODED FOR THE PREPATION OF MATERIAL

Spray pyrolysis is one of the CVD methods. Spray pyrolysis involves spraying onto hot substrates with a solution containing salt of the corresponding metal elements dissolved in water or alcohol .The sprayed droplet undergo an endothermic reaction on the surface of the substrates initiates chemical reaction by providing the necessary thermal energy for decomposition of reacting materials into its constituents and recombination of these constituents to from desired films. The other volatile products formed during the process escape to the ambient temperature.

This is the thermally stimulated reaction between the clusters of liquid vapour atoms of different spraying solutions of the desired compound on to substrates maintained at elevated temperature. The sprayed droplets on reaching the hot substrates undergo pyrolytic decomposition and form a single crystal or cluster of the crystallites of the product. The thermal energy for decomposition, subsequent recombination of the species, sintering and recrystallization of the crystallites is providing by hot substrate. The nature of the fine spray droplets, with the help of a carrier gas depends upon spray nozzle. The growth of a film by a spray pyrolysis is determined by a nature of the substrate, solution as well as spray parameters. The films are general strong and adherent, mechanically hard, pinhole free and stable with temperature and time .The morphology of the film is general rough and that will depend upon the spray conditions. The surface of the substrates gets affected in the spray process and the choice is limited the glass, quartz, ceramics or oxides, nitride or carbide coated substrates [8].

Various deposition techniques have been widely used to produce TCO thin films. The most reliable and economical deposition technique is the main goal. The most intensively study techniques include, RF magnetron sputtering, chemical vapour deposition (CVD), sol-gel method, thermal evaporation and spray pyrolysis. Different types of spray pyrolysis are available for study.

Nebulizers are based on the Venturi principle. It consists of air compressor, which has ability to change the precursor solution into very tiny droplets like mist. The ability to produce good films depends on the proper choice of various process involved in the technique these include the substrate nature, spray-nozzle diameter, nozzle substract distance(SND),Substrate temperature (TS) during film deposition and solution concentration(C).The substrate morphology and nature affect the early growth phenomena including the nucleation and the growth process. Two main parameters are generally used to evaluate the performance of nebulizer, the droplet size distribution of the aerosol and the liquid output rate and are basically determined by the design and user conditions of the nebulizer.

Since nebulized spray pyrolysis enables one to build functional structures at atmospheric conditions using very simple and cost effective production used for large area depositions and film properties can be tailored by controlling spraying conditions. Therefore, many researches have been focused on the thin film deposition via nebulized spray pyrolysis especially in solar cell area.

By considering the simplicity and economics, chemical methods are commonly preferred for obtaining large area thin films. Chemical methods are divided into two subgroups, namely electroplating and chemical vapour deposition. Electrolytic deposition, electroless plating and anodization come under the former whereas pyrolysis is classified in the large category. Among the different thin film preparation technique, nebulized spray pyrolysis is widely used method for the deposition of electrochromic material films due to the economic consideration and easy adaptability for this technique for commercial purpose. Nebulized spray pyrolysis is a simple and cost effective technique to deposit thin films. So nebulized spray pyrolysis were chosen for this study. [15]

3.9. EXPERIMENTAL DETAILS

3.9.1. Chemicals And Glasswares Used

Magnesium acetate tetrahydrate pure $(CH_2COO)_2Mg.4H_2O$, Tin (II) chloride dehydrate $(SnCl_2.2H_2O)$, 2-propanol $(CH_3CHOCHO_3)$ purity(GC) ≥ 99.0 were used for preparation of precursor solution. Chromic acid H_2CrO_4, Acetone and distilled water were used for cleaning the substrate. Glasswares used for film coating are blue star glass slides of 1mm thickness and beakers.

3.9.2 Preparation Of Solution

The magnesium tin oxide thin films were deposited onto highly clean glass substrates. The spraying solution containing magnesium acetate + tin (II) chloride + 2-propanol. The suitable solvent for magnesium acetate and tin (II) chloride is 2-propanol.The solution were prepared in glass beaker by dissolving the known quantities of magnesium acetate tetrahydrate and tin (II) chloride dehydrate in 50ml 2-propanol. The solution was continuously stirred for about 30 min for dissolving the solvent.

Table 3. 1 Quantity of chemicals used for coating

Molarity (M)	Magnesium acetate (g)	Tin (II) chloride (g)	2-propanol (ml)
0.1:0.1	1.3694	1.4408	50
0.1:0.2	1.3694	2.8816	50
0.1:0.3	1.3694	4.3224	50

From the above (table 3.1) magnesium acetate $(CH_3COO)_2.4H_2O$ and stannic chloride $SnCl_4.2H_2O$ was prepared at three different molarity ratios (0.1M, 0.2M, 0.3, 0.4, 0.5). These three different solutions are sprayed at constant temperature and constant pressure (360°C at $2kg/cm^2$). The deposited $MgSnO_3$ thin film was annealed at 400°C to get oxides.

Figure 3.1 Schematic diagram of preparing solution for coating

3.9.3 Procedure For Magnesium Tin Oxide

$MgSnO_3$ thin film was prepared by nebulized spray pyrolysis technique. Nebulizer spray pyrolysis technique consists of a nebulizer unit, temperature controller, a “well” shaped furnace and a compressor unit. Nebulizer is a sprayer mainly used for curing asthma patients by spraying medicine into the mouth. This technique used the same nebulizer unit to spray mist like particles of solution. High purity magnesium acetate, stannic chlorides were dissolved in a solution containing 2-propanol. $MgSnO_3$ thin film was deposited on amorphous glass substrate by spraying an aqueous solution containing 0.1M, 0.2M, 0.3M, 0.4M and 0.5M with nebulizer spray pyrolysis technique. Well cleaned glass substrate of dimension 75mm x 25mm x 1mm was kept on the preheated hot plate. The substrate temperature was maintained at 360℃. The compressed air was used to carry the oxygen gas maintained at 2 Kg/cm^2 corresponding to average pressure solution rate of 50 ml per 30 minutes. The distance between nozzle and substrate was kept at 5cm. The sample was kept on the substrate until it reached the room temperature after the deposition was over. The deposited samples are annealed at the temperature of 400℃ .It does not require high quality target and vacuum. The thickness of the film and rate of deposition can be easily controlled.

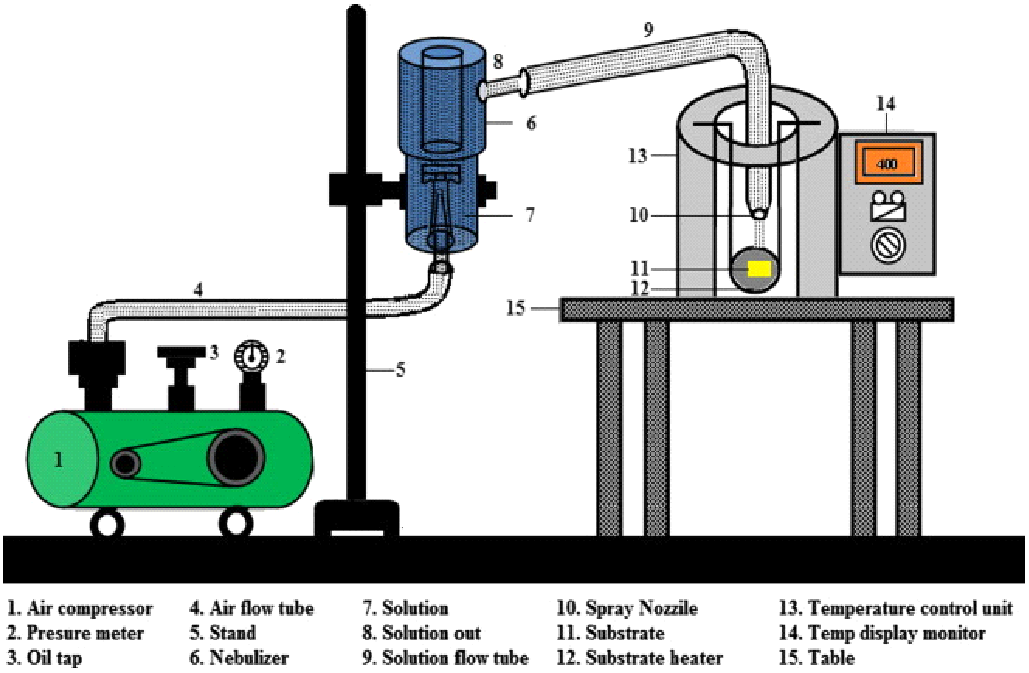


Figure 3.2 Experimental setup of nebulized spray pyrolysis

3.10 FILM THICKNESS

Thickness film is first quoted attribute of its nature. The reason is that thin film properties usually depend on thickness and it plays an important role in the film properties unlike a bulk material. Reproducible properties are achieved only when the film thickness and the deposition parameters are kept constant. Historically the use of films in optical applications spurred the development of technique capable of measuring film thickness with high accuracy.

Thickness is the most significant parameter of a thin film. All the physical properties of the film material are based on thickness. As already mentioned, thin films are often called as two dimensional forms of the solids. So the control of the thickness during the fabrication of the film is very important for tailoring the different physical properties of the film. Thickness monitoring during the fabrication of the films is called in-situ monitoring. After completion of the coating the film can be taken out and the thickness measured [1]. Otherwise, the thickness can be measured after the deposition process.

The varied type of films and their uses have generated a multitude of way to measure film thickness. In all thickness measurements it is generally assumed that these films are homogeneous and more or less uniformity deposited on the substrate. Thickness measurements methods are basically divided into optical, electrical, magnetic and mechanical are usually non-destructive but sometimes destructive in nature.

The physical properties based on the thickness have made thin films more important in technology. In thin film, the quantity of the material associated is smaller than for bulk material. This makes the material lighter and less costly. If a material is needed the device becomes heavier. Hence the microelectronics and optoelectronic industries utilize different materials in their thin film form [9].

Electrical methods of film thickness measurement involve film resistance method, capacitance monitor and ionization method. Film thickness can also be measured mechanically by mans of the following technique such as, Profilometry, Quartz crystal microbalance, Microbalance gravimetric and Ultrasonic multi-layer film metrology etc [64]. Microbalance gravimetric technique was used for thickness measurement.

3.10.1 Microbalance Gravimetric Technique

Instruments suitable for the gravimetric determination of small quantities of mass are summarily referred to as microbalance. This is one of the oldest methods for film thickness determination by weighting the substrate before and after deposition of the film.

Many sensing devices may be used for all types of materials. They are operated by determining the weight of the deposit. Since the measured quantity is accumulated mass of the deposit, conversion into film thickness requires knowledge of the density of the material. This method depends on the increase of weight of a film due its mass increase and from the knowledge of its density and deposited area, film thickness (t) can be calculated from the following relation,

$$\mathbf{t=W/\rho A}$$

Weight of the thin film on the deposition glass substrate (W) = weight after deposition – weight before

ρ= density of the material

A= deposited area

Here the microbalance SHIMADZU with 4-digit accuracy was used for measuring the weight of the deposited film. The basic requirement of Gravimetric technique is the weight measurement should be done on the same substrate before and after deposition of the film. Another requirement is that the substrate should not be prone to chipping or other type of materials loss and the deposition process should not result in the accumulation of material other than the desired film. The weighing should be very accurate since relatively small differences in large numbers are being sought. In actual laboratory the Gravimetric technique is more useful for determining film thickness [1].

3.11 X-RAY DIFFRACTION

X-rays are electromagnetic radiation similar to light, but with a much shorter wavelength. It provides information on structures, phases, preferred crystal orientations (textures) and other structural parameters, such as average grain size, crystallinity, strain and crystal defects. X-ray diffraction peaks are produced by constructive interference of a monochromatic beam of X-ray scattered at specific angles from each set of lattice in a sample. The peak intensities are determined by the atomic arrangements within the lattice planes. X-Ray diffraction techniques had played vital role in coordinate chemistry and determination of bond lengths, bond angle, residual stress, preferential orientation, grain size, particle size, temperature factor etc.

In thin films, only a small amount of scattering material is available for conventional structure analysis by X-ray.

Direction and planes in a crystal, a co-ordinate system is introduced whose unit vectors a, b, c are edges or axes of the unit cell. The orthogonal system is possible only for cubic, tetragonal and orthorhombic crystal. A plane in a crystal is given by its Miller indices. These are the (h k l) values, ie, the reciprocal intercepts of the plane with the, b, c axes reduced to the smallest integers having the same ratio.

A direction in a crystal is given as the triplets (h k l) of the smallest integer components of a vector in this direction, referred to a, b, c coordinate system. An important parameter is the inter planer spacing d_{hkl} between neighbouring planes.[72]

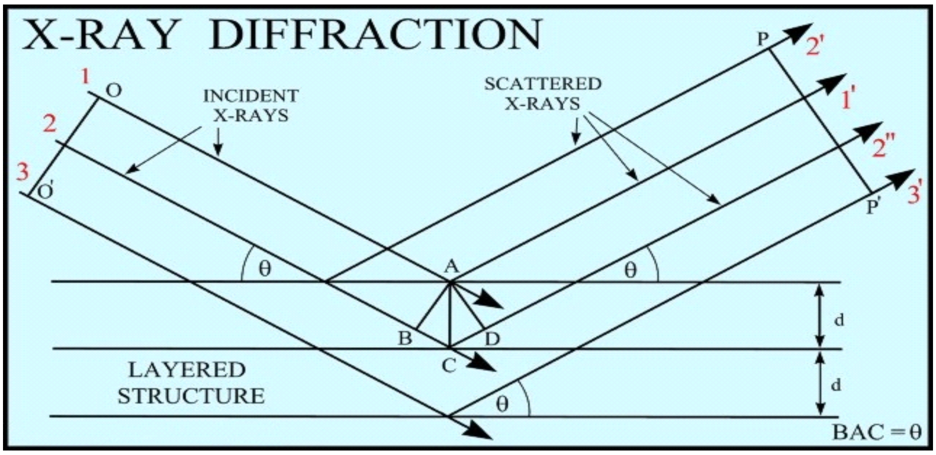


Figure 3.3 Bragg's x-ray diffractometer

Figure 3.4 X-ray diffractometer

Experimental Technique

The X-ray diffractometer is used as a powerful tool in diffraction analysis. This instrument is known as diffractometer when it is used with X-ray of known wavelength to determine the unknown spacing of crystal planes. X-ray diffraction is interior to microscopic examination in the accurate measurement of grain size. The advantage is that dynamic measurements can be made with the diffractometer. XRD is a versatile, non-destructive analytical technique for identification and qualitative determination of the crystalline compounds known as phases present in the polycrystalline films. X-ray techniques based on monochromatic radiation are generally important because it enables to determine 'd' spacing from observed angles. An important feature of X-ray diffraction is their ability to focus into a sharp diffraction line, which is Bragg reflected from a sharp extended area. This considerably improves the signal to noise ratio. One of the main applications of XRD techniques in thin film is in fact to make use of their good resolution of‘d’ spacing to investigate strains in the film. X-ray diffraction has many field applications not only in the structural analysis of crystalline and amorphous material. X-ray diffraction methods have advantages of relative ease and convenience, large diffraction angles making accurate measurement of spot pattern possible and simultaneous display of diffraction pattern from thin film thin film material and the substrate.

The X-ray diffractometer consists of three parts, a basic diffraction unit, a counter, goniometer and an electronic circuit panel with an automatic recorder. The diffraction angles and intensity of lines can be measured with great accuracy. The diffraction angle (2θ) and intensity of the lines are measured. The diffracted rays are received by a counter. The counter tube is moved along the goniometric circle. The equipment consists of a X-ray generator, diffractometer, proportional counter and single channel pulse height analyser.

The specimen is mounted in the center of the diffractometer and rotated by an angle around an axis in the film plane. The counter is attached to an arm rotating around the same axis by an angle (2θ).it can be observed that the diameter of the focusing circle continuously shrinks with increasing diffraction angle. Only (h k l) planes parallel to the film contributes to the diffracted intensity.

Structual Parameters

Inter planer spacing : (h k l)

From the XRD profiles by inter planer spacing d_{hkl} has been calculated using the Bragg’s relation.

$$d_{hkl}= n\lambda/2\sin\theta$$

Crystallite Size(D)

The crystallite size (D) was calculated using the Scherrer’s formula from the full width at half maximum (FWHM).

$$D=k\lambda/\beta\cos\theta$$

Where the constant ‘k’ is the shape factor=0.94

λ is the wavelength of X-ray, θ is the Bragg’s angle in degree and β is the FWHM in radian.

The basis of XRD is the Bragg’s law which describes the conditions for constructive interference of X-rays scattered from atomic planes of a crystal. The condition for the constructive interference is

$$\mathbf{2d \sin \theta = n\lambda}$$

Where λ the wavelength of X-rays, d is the lattice spacing, n is the order of diffraction and θ is the glancing angle of X- rays.

The factor ‘d’ is related to the (h k l) indices of the planes and the dimension of the unit cells. It is therefore seen that the diffraction direction is solely determined by the structure and size of the unit cell. [70]

3.12 UV-VISIBLE SPECTROSCOPY

The principle of UV/visible spectroscopy is the extension of electrons to higher energetic molecular orbitals because of absorption of UV/ visible radiation. UV Visible spectroscopy measures of a sample to ultraviolet and visible range of electromagnetic radiation. Ultraviolet and visible radiation interacts with matter which causes electronic transition (promotion of electrons from the ground state to a high energy state).

Absorption of visible and ultraviolet (UV) radiation is associated with excitation of electrons, in both atoms and molecules, in both atoms and molecules, from lower to higher energy levels. Since the energy levels of matter are quantized, only light with the precise amount of energy can cause transitions from one level to another level.

Of all these absorption processes the first three directly give to photoconductivity. The optical absorption and transmittance studies are useful for the identification of bandgap, impurity states and extinction coefficient etc. The optical absorption spectra of semiconductors generally exhibit a sharp rise at a certain value of the incident photon energy which can be attributed to the excitation of electrons from the valence band to the conduction band. In the optoelectronic application of thin films, the optical absorption studies play an important role giving the nature of transitions either direct or indirect. The absorption coefficient α can be calculated using the equation [71]

$$\text{Absorption coefficient } \boldsymbol{\alpha .=4\Pi k/\lambda}$$

K is calculated by the following formula

$$\mathbf{k=2.303*\lambda log(1/t)4\Pi d}$$

3.13 HALL EFFECT

Hall Effect plays an important role in the study of conduction process in solids. In fact this effect which determines the nature number and the mobility of charge carriers in materials.

Hall Effect was discovered by E. H. Hall in 1879, during an investigation of the nature of the force acting on a conductor carrying a current in a magnetic field. Hall found that when a magnetic field is applied at right angles to the direction of the current flow, an electric field is set up in a direction perpendicular to both the direction of the current and the magnetic field. The Hall Effect produces an electric field whose direction depends upon the sign of the charge carriers in the conductor.

Hall Effect makes possible to determine the charge carrier mobility in semiconductors. The measurement of electrical conductivity alone cannot reveal the type of charge carriers responsible for conductivity. However it is possible to obtain this information from a combination of Hall Effect and electrical conductivity measurements. [72]

Measurement Of Hall Parameters

Hall Effect was measured using Van der Pauw method. Thin copper wires are used as leads for the probe. The ohmic contact between the copper wire and the leads is obtained by employing a small amount of quick drying silver paint between the film and the lead. The whole substrate with the film and lead is mounted on a wooden scale for easy handling. Current is passed through two leads and two more connections are taken from the different points, which are perpendicular to the previous set, and are used digital millimeter for “Hall voltage” measurement.

The contacts to measure Hall voltage must be exactly opposite to each other. Unless this condition is fulfilled, the two contacts will be on different equipotential planes when the current flows through the specimen in the absence of magnetic field, an error voltage appear between the Hall contacts.

The magnitude of this error voltage may be as large as, or even larger than the Hall voltage measured with the magnetic field. Unless it can be eliminated by proper contact placement, it must be carefully measured in the absence of the magnetic field and corrected for all subsequent measurements. The effect of this error voltage can be eliminated by determining the de Hall voltage with the magnetic field in both the direction successively and averaging the two results.

When a current-carrying conductors is placed in a transverse magnetic field, the Lorentz force on the moving charges pushes them toward one side of the conductor producing a charge separation and, as a result, a voltage in the direction perpendicular to both the field and the current. This is known as the Hall Effect. The Hall voltage is the voltage transverse to both magnetic field and current.

Measurements of the Hall voltage are used to determine the density and sign of charge carriers in a conductor. When this is known, the effect is used as a probe for magnetic field measurements. In this experiment, samples of chromium and silver in the film of thin films of various thicknesses are available. [73]

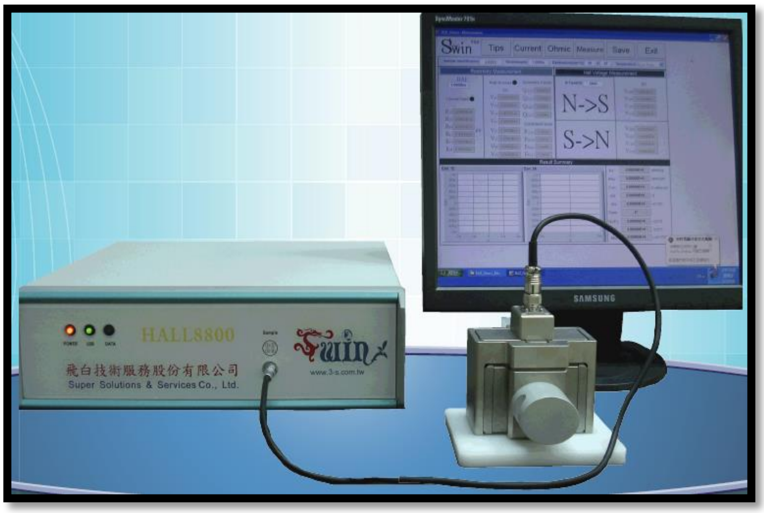


Figure 3.5 Hall Effect Measurement System

CHAPTER-IV

RESULT AND DISCUSSIONS

4.1 INTRODUCTION

In every scientific discipline, it is important to identify and differentiate their properties by suitable scientific equipment and measurement. A large variety of scientific tools are available for characterization of thin film in the present of technological revolution. The thin films can be utilized for commercial applications and research purpose by studying / analysing the different properties like structural, optical, thickness etc. In this chapter an attempt was made to discuss the observation taken for $MgSnO_3$ thin film prepared by nebulized spray pyrolysis technique were discussed. The structural, optical results were obtained from XRD, UV-Vis-NIR spectrometer; Hall Effect and the interpretations are discussed in this chapter.

4.2 OBSERVATIONS

4.2.1 Thickness Measurement

Microbalance gravimetric technique is one of the simplest techniques for thickness measurement, which was employed in this study for thickness measurement of $MgSnO_3$ thin film deposited by nebulized spray pyrolysis method. The films of different thickness were deposited on 1 mm glass substrate at different molar ratios at 360°C. The thickness was carried out for several samples, but the best fit sample parameters shown in Table-4.1. Weight of the deposited film was calculated from the measurement of substrate weight before and after deposition.

For all the deposition film, thickness falls in µm range. We observe that the value of the thickness of the samples agree well for same concentration. Thickness increases as concentration increases, which indicate the validity of the deposition technique adopted for the film. [1]

Table 4.1 Thickness of the $MgSnO_3$ thin films

Molarity Ratio (M)	**Temperature (°C)**	**Thickness (µm)**
0.1:0.1	360	0.23
0.1:0.2	360	0.27
0.1:0.3	360	0.32

From the above Table 4.1 concluded that when molarity ratio of the film is increased then the thickness of the film is also increased

4.2.2 X-ray diffraction

XRD spectra reveals the structural details and the crystalline nature of the thin film. The Figure 4.2 shows the XRD spectrum of $MgSnO_3$ thin film prepared by nebulized spray pyrolysis on glass substrate temperature at 360°C with the molar ratio (0.1:0.1M). All the diffraction peaks are indexed with JCPDS data card no. (21-1250 of SnO_2, 74-2152 of Mg_2SnO_4, 30-0798 of $MgSnO_3$, 77-2296 of SnO_2) and the corresponding 2θ, d-values and (hkl) Miller plane values are evaluated and the details are tabulated in Table 4.5. The 2θ peaks at (26.6^o, 34.09^o, 38.2^o, 51.9^o and 62.1^o) and its d-value are corresponding to SnO_2, Mg_2SnO_4, and $MgSnO_3$ respectively. The first and fourth peak corresponding to $2\theta=26.6^o$, 51.9^o is assigned for SnO_2 due to its reactive nature, it crystallizes in tetragonal phase and preferentially oriented in the (110,222) plane. The second peak corresponding to $2\theta=34.09^o$ when annealing time is increased formation of Mg_2SnO_4 phase occurs. The third and fifth peak corresponding to $2\theta=38.2^o$, 62.1^o corresponds to the rhombohedral structure of magnesium meta stannate phase. The relative intensity of the (303) plane is less and broader which shows that the crystallinity is poor and that must be improved by adjusting various parameters like molarity and temperature to obtain the desired

Table 4.2 Inter planar spacing $MgSnO_3$ thin film (0.1:0.1M)

d (Å)	h	k	l	JCPDS no.
3.341	1	1	0	(21-1250) SnO_2
2.628	3	1	1	(74-2152) Mg_2SnO_4
2.352	0	1	5	(30-0798) $MgSnO_3$
1.666	2	2	2	(77-2296) SnO_2
1.497	3	0	3	(30-0798) $MgSnO_3$

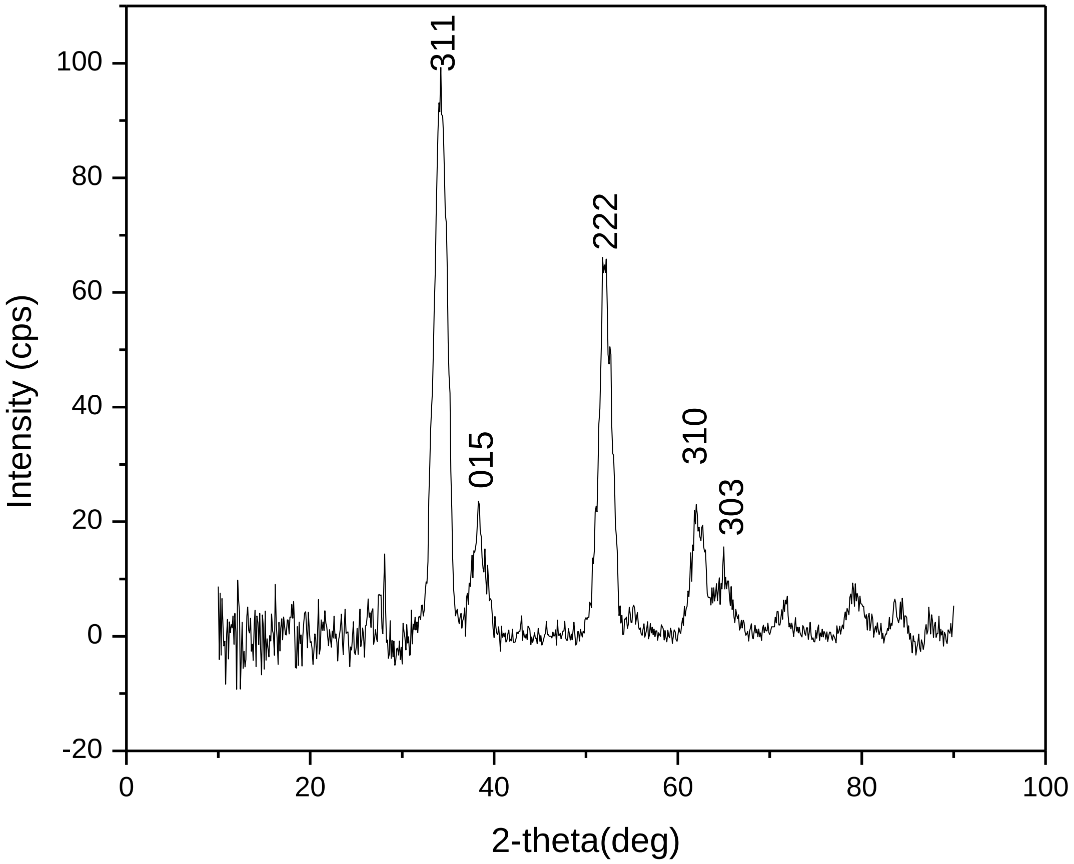


Figure 4.1 X-ray diffraction spectrum of $MgSnO_3$ film at (0.1:0.1M)

$MgSnO_3$ films prepared with molar ratio (0.1:0.2M) at substrate temperature 360°C on glass substrate are shown in Figure 4.3. The observed peak and ‘d’ value are compared with JCPDS card no. In this molar concentration ratio, XRD reveals that the peak corresponding to magnesium ortho stannate at 2θ=34.25^o and the d values are compared with JCPDS card no. (74-2152 of Mg_2SnO_4). The third and fourth peak corresponding to 2θ=52.15^o, 61.9^o is SnO2 tetragonal structure with JCPDS card no. (21-1250^o, 77-2296^o). Although the concentration of the stannic chloride is low, due its highly reactive, it crystallizes in tetragonal phase and preferentially oriented in the (310) plane. The second and fifth peak at 2θ=38.2^o, 64.9^o are comparable with $MgSnO_3$ with JCPDS card no. (30-0798) are rhombohedral structure.

Table 4.3 Inter planar spacing for $MgSnO_3$ film (0.1:0.2M)

d (Å)	**H**	**k**	**l**	**Phase**	**JCPDS no.**
2.616	3	1	1	Mg_2SnO_4	(74-2152)
2.350	0	1	5	$MgSnO_3$	(30-0798)
1.752	2	2	2	SnO_2	(77-2296)
1.497	3	1	0	SnO_2	(21-1250)
1.436	3	0	3	$MgSnO_3$	(30-0798)

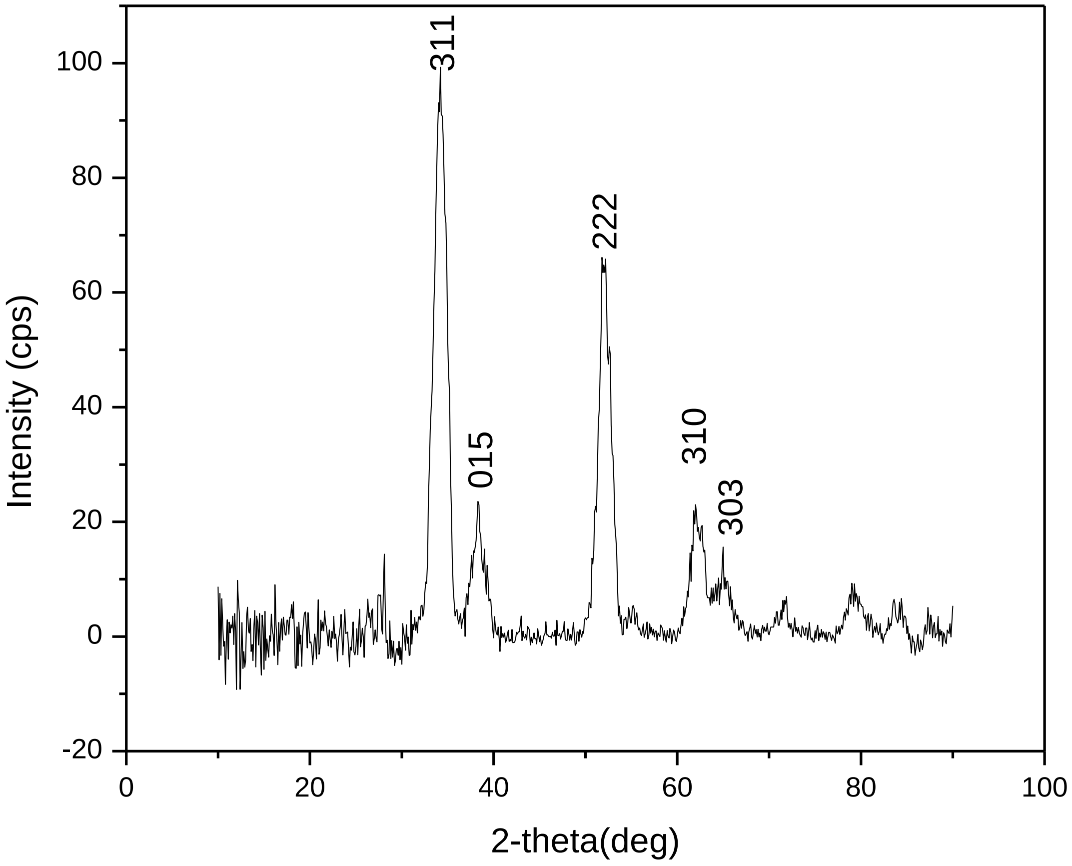


Figure 4.2 X-ray diffraction spectrum of $MgSnO_3$ film at (0.1:0.2M)

XRD pattern of $MgSnO_3$ film prepared with molar ratio (0.1:0.3M) at substrate temperature 360°C on glass substrate is shown in Figure 4.4. The observed peak and 'd' value are compared with JCPDS Card no. The first peak at $2\theta=27.2^o$ small amount of MgO is present in the precursor and it shows hexagonal phase with JCPDS card no. (27-0759). The second peak $2\theta=34.4^o$ corresponding to magnesium ortho stannate with JCPDS card no. (74-2152). The third peak $2\theta=38.2^o$ correspond to magnesium meta stannate with JCPDS card no. (30-0798). The other two peak $2\theta=52.0^o$, 54.8^o are comparable with SnO_2 phase and it is obvious to say that the precursor concentration of stannic chloride is higher than magnesium acetate. [70]

Table 4.4 Inter planar spacing for $MgSnO_3$ film (0.1:0.3M)

d (Å)	h	k	l	Phase	JCPDS no.
3.430	1	1	3	MgO	(27-0759)
2.624	3	1	1	Mg_2SnO_4	(74-2152)
2.349	0	1	5	$MgSnO_3$	(30-0798)
1.755	2	2	2	SnO_2	(77-2296)
1.673	2	2	0	SnO_2	(77-2296)

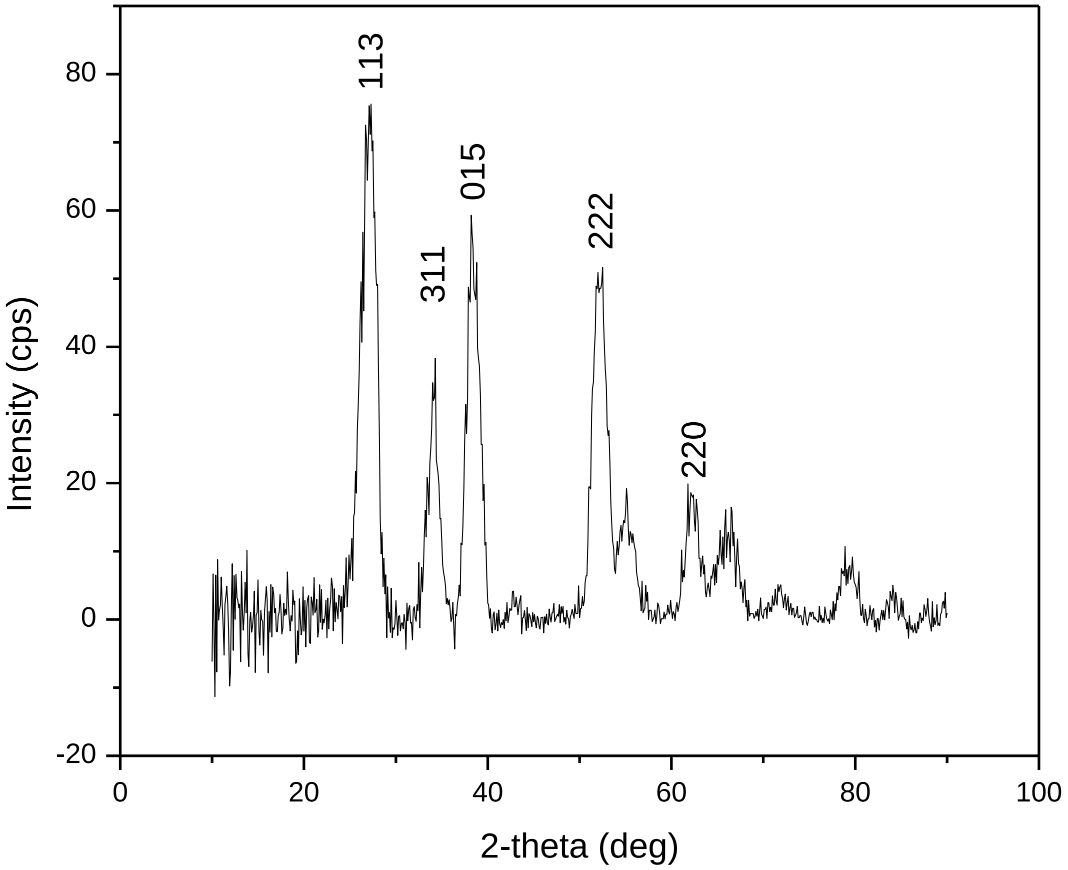


Figure 4.3 X-Ray diffraction spectrum of $MgSnO_3$ film at (0.1:0.3)

The crystalline size was calculated using the equation Debye Scherrer Formula. Generally, in the XRD pattern crystallite size depends on the full width half maximum and angle of the peak. Comparing the molar ratio of 0.1:0.1M, 0.1:0.2M and 0.1:0.3M is

5.29594E-09, 5.172E-09 and 4.44981E-09 the highest peak observed in the molar ratio 0.1:0.1M. The crystallite size for the $MgSnO_3$ was found to be 5.29594E-09 nm. The sharp and high intense peaks observed in the prepared $MgSnO_3$ are 0.1:0.1M due to the more periodicity i.e., long range order of atoms in the sample which may increase the crystallinity of the sample.

.Table 4.5 Measurement of crystallite size of $MgSnO_3$

Molarity ratio (M)	**2θ (deg)**	**FWHM (β)**	**Crystalline size (nm)**
0.1:0.1	34.095	0.028609	5.29594E-09
0.1:0.2	34.25	0.029307	5.172E-09
0.1:0.3	27.22	0.033493	4.44981E-09

Structural identification of the magnesium tin oxide film was carried out using X-Ray diffraction in the range 2θ between 10^o and 100^o as shown in the Figures 4.2, 4.3 and 4.4 values are Tabulated was found that the films are in crystalline nature consisting of $MgSnO_3$ phase, no other metal phase is detected.

4.2.3 UV-visble spectroscopy

The optical properties of the films were studied using an UV-Vis spectroscopy. The absorption and transmission measurement were made in the range of 200 nm to800 nm for three different molar ratio. From the figure we can observe that the annealed $MgSnO_3$ possess higher transmittance in the visible and IR region. Hence it is clear that the films obtained were highly transparent. Because of higher transmittance (above 80%) the indium tin oxide can be replaced by $MgSnO_{3.}$ The value of the energy bandgap is found to increase with increasing annealing time.

The transmittance spectra of the $MgSnO_3$ film with different molar ratios deposited at 360°C are shown in figure 4.5. The transmission measurements were made within the range of 200-800 nm. From the transmission spectrum of $MgSnO_3$ films, it is observed that the $MgSnO_3$ films with molar ratios are 0.1:0.1M, 0.1:0.2M and 0.1: 0.3M is 56.397, 53.959 and 76.536^o respectively in the visible region.

The absorption spectra of the $MgSnO_3$ films with different molar ratios deposited at 360°C are shown in the figure 4.6. The absorption edge occurs in the UV range. From the absorbance spectrum of $MgSnO_3$ films, it is observed that $MgSnO_3$ films with molar ratios are 0.1:0.1, 0.1:0.2, 0.1:0.3 is 0.3919, 0.6697 and 0.1589 in the UV range. This is important for application such as transparent conducting device and solar cell window. The bandgap of the deposited $MgSnO_3$ films is shown in the Table 4.8.

Table 4.6 Cut off wavelength of the deposited $MgSnO_3$ thin film

Molar ratio (M)	**Cut Off Wavelength (nm)**	
	Transmittance	**Absorbance**
0.1:0.1	615	336
0.1:0.2	554	360
0.1:0.3	470	371

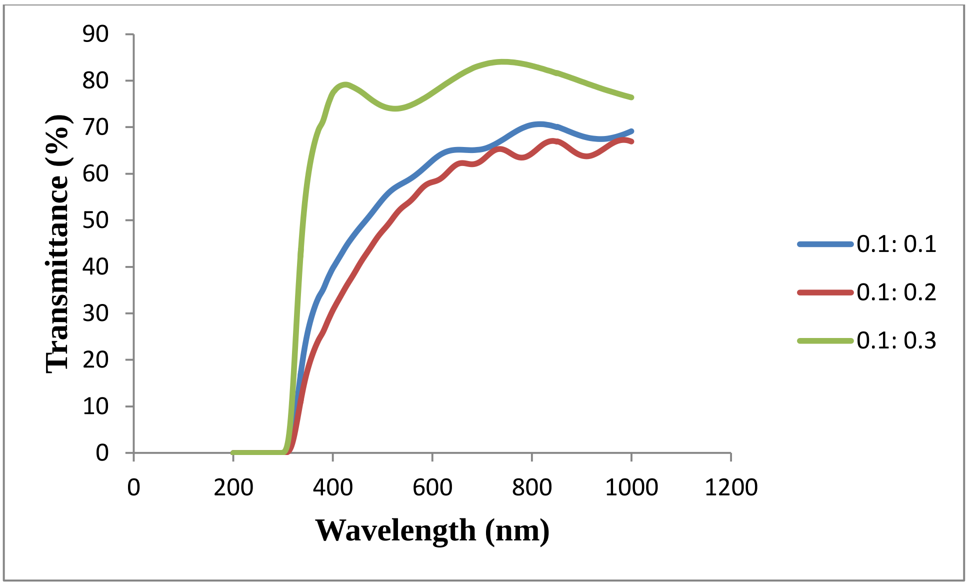


Fig 4.4 Transmittance spectrum of $MgSnO_3$ film

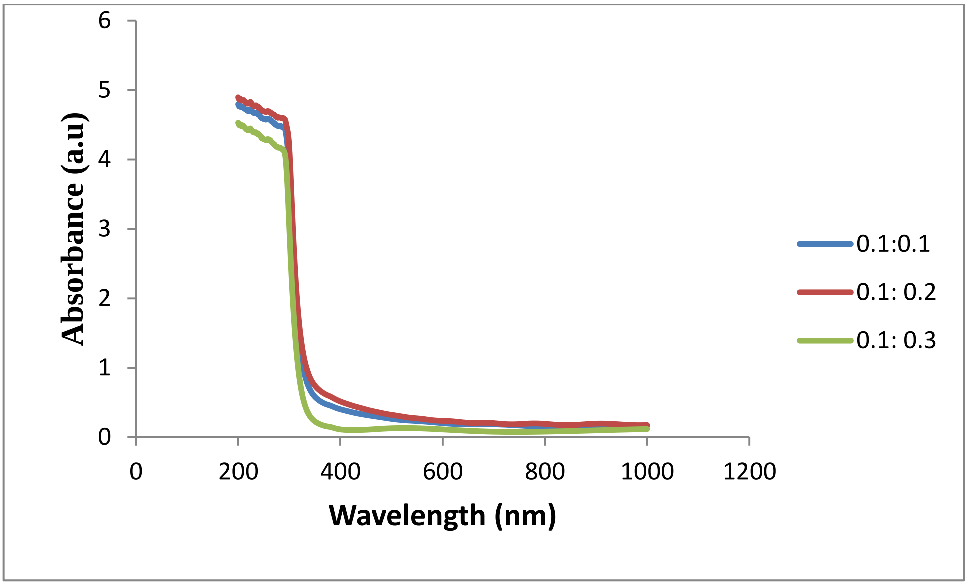


Fig 4.5 Absorbance Spectrum of $MgSnO_3$

The direct energy bandgap of the films were calculated using Tauc relation and the values are found to be 3.85 eV, 3.80 eV and 3.91 eV for the as-deposited and annealed films at 360 °C. The value of the energy bandgap is found to increase for 0.1:0.3M.

Table 4.7 Optical bandgap of the deposited $MgSnO_3$ thin film

Molar ratio (M)	Band gap (eV)
0.1:0.1	3.85
0.1:0.2	3.80
0.1:0.3	3.91

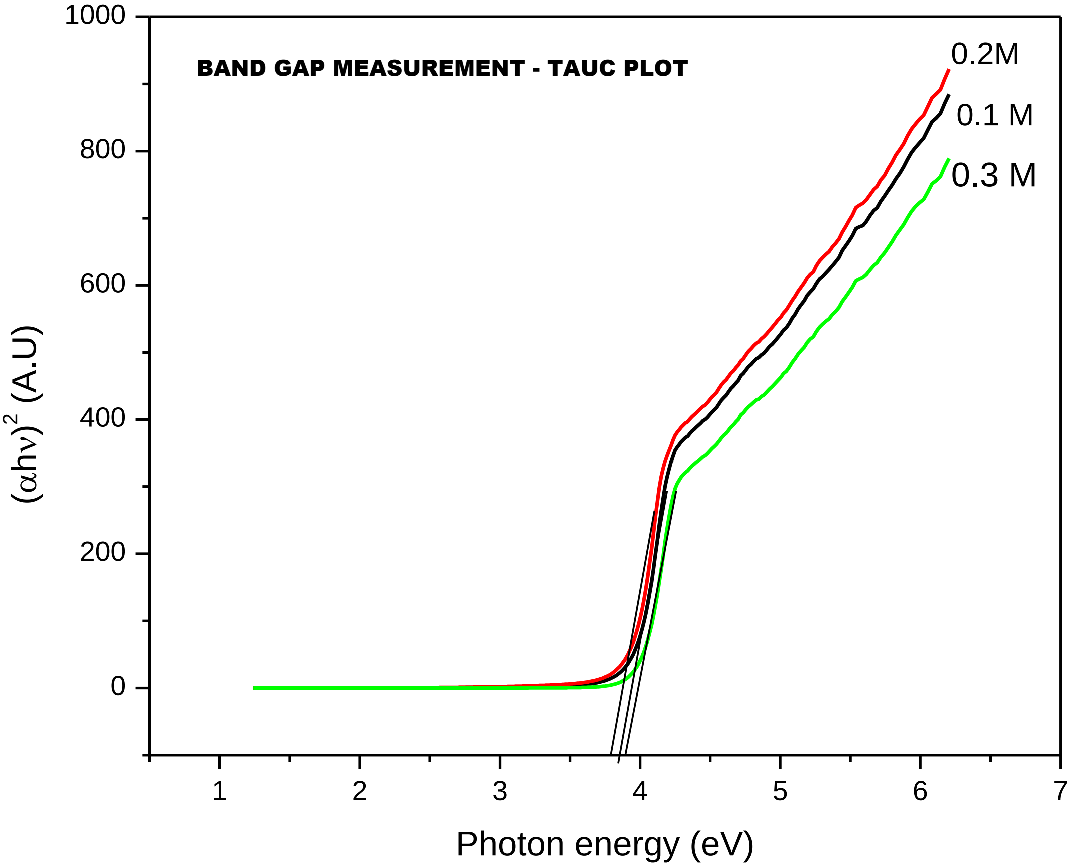


Figure 4.6 Optical bandgap for $MgSnO_3$ Film

From the graph 4.5 it is confirms that the percentage of transmission is nearly 80% it proves $MgSnO_3$ is the best TCO and it can be used as a substrate in solar cell fabrication like ITO substrate.

4.2.3 Hall Effect Measurement

The Hall Effect studies were conducted for thin films of different molar ratios (0.1:0.1M, 0.1:0.2M and 0.1:0.3M) at substrate temperature 360℃.

Table 4.8 Measurement of Hall Parameters

Molarity ratio(M)	**Bulk Concentration Nb (cm^2)**	**Mobility μ(cm^2/Vs)**	**Sheet Concentration Ns (cm^2)**
0.1:0.1	-3.9450×10^{19}	6.09007	-2.3670×10^{15}
0.1:0.2	-9.5087×10^{19}	28.85113	-5.7052×10^{15}
0.1:0.3	-7.0261×10^{19}	12.73647	-4.2156×10^{15}

From the above table it is clear that the majority charge carriers are electrons because of the negative values of bulk concentration. For the molarity ratio 0.1:0.2 the mobility is found to be is maximum (28.85113) with less sheet concentration (-5.7052×10^{15})

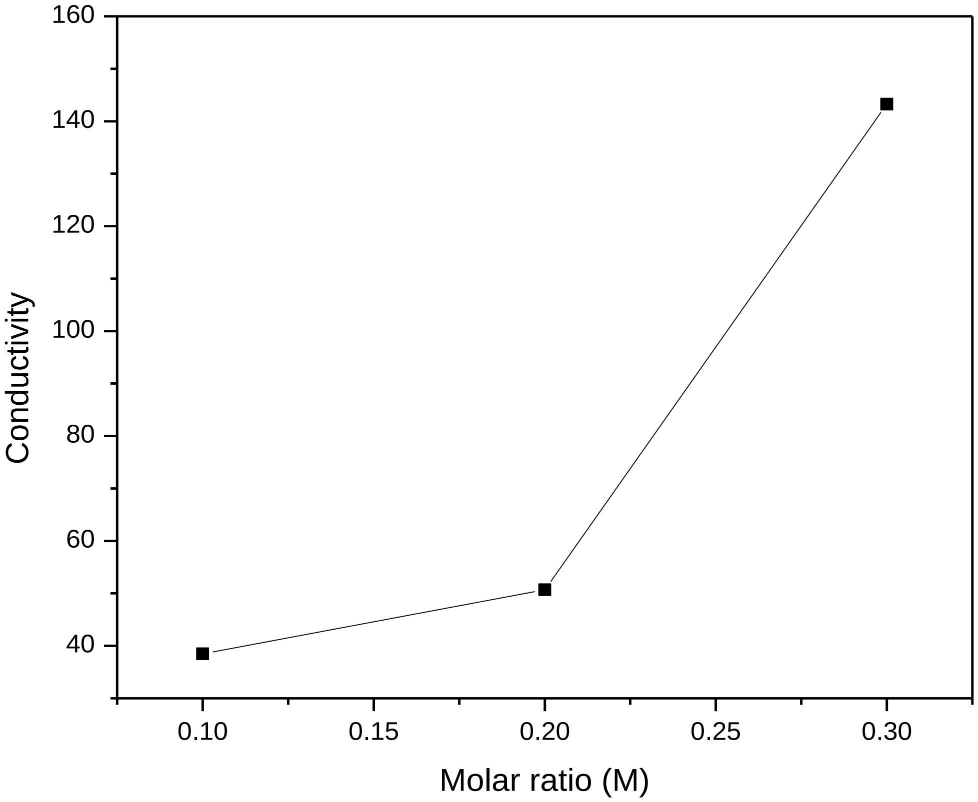
Table 4.9 Measurement of hall coefficient, conductivity and resistivity

Molarity ratio (M)	**Hall Coefficient R_H (m^2/C)**	**Conductivity σ (1/Ωcm)**	**Resistivity ρ (Ω cm)**
0.1:0.1	-0.15823	38.48188	2.5986×10^{-2}
0.1:0.2	-6.5647×10^{-2}	50.69533	1.9726×10^{-2}
0.1:0.3	-8.8844×10^{-2}	143.2584	6.9804×10^{-3}

From the Table 4.3 the hall coefficient of the film is found to be negative which ensures n-type conductivity of the material. Here the conductivity of the solid solution strongly depends on composition and is increased with increasing the molarity ratio of $MgSnO_3$ that used for preparation of thin films [2].

There is a tendency for crystals with small energy gap at direct band edges to have high values of the electron mobility. But here the $MgSnO_3$ films having the band gap 3.53 eV, so the electron mobility is somewhat decreasing. The hole mobility is smaller than the electron mobility, because of the occurrence of band degeneracy at the valence band edge, at the zone center, thereby making possible interband scattering processes that reduce the mobility considerably. The carrier concentration will be increased by increasing the temperature.

Hence it is clear that the negative hall voltage has been observed for films deposited at 360°C for 5 hours. The observed negative Hall voltages clearly suggest that the film deposited at 360°C are of n-type nature with electrons as majority charge carriers.[72]



. **Figure 4.7 Variation of conductivity with molarity ratio of $MgSnO_3$**

CHAPTER-V

SUMMARY AND CONCLUSION

Transparent and conductive $MgSnO_3$ films are deposited by nebulized spray pyrolysis method by varying molar ratio at 360℃ and the deposited films are annealed at 400℃ at 5 hours to obtain better film thickness.

From the XRD result, it is clear that sprayed films are rhombohedral in structure. Because of high annealing time, the prominent peak is matched with Mg_2SnO_4 phase. This is because $MgSnO_3$ is highly unstable at higher temperature and it will disproportionate to Mg_2SnO_4 phase.

From the UV, the band gap of material is about 3.9 eV. Because of high transmittance and absorbance the $MgSnO_3$ film can be developed as a TCO useful for solar cells and gas sensors.

Using the Hall voltage measurement it is observed that $MgSnO_3$ is n-type conductivity due to high concentration of negative carriers and conductivity of the thin film was increased with increased molarity value of $MgSnO_3$.

In our future work planned to construct solar cell by using $MgSnO_3$ as TCO substrate which has low resistivity and high transmittance.

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