SYNTHESIS AND CHARACTERIZATION OF ZnO THIN FILMS BY SPIN COATING METHOD

DISSERTATION II

SUBMITTED BY

JYOTI

TO

DEPARTMENT OF PHYSICS

IN THE PARTIAL FULFILMENT OF THE RECQUIREMENT FOR THE

AWARD OF DEGREE IN MASTER IN PHYSICS

UNDER THE GUIDANCE OF

DR. RAJESH KUMAR

MAY, 2015

CERTIFICATE

This is certify that **Ms.JYOTI** has completed the M.Sc. project titled **"SYNTHESIS AND CHARACTERIZATION OF ZnO THIN FILMS BY SPIN COATING METHOD"** under my guidance and supervision. To the best of my knowledge, present work is the result of this investigation and study. No part of the project been submitted for any degree or diploma.

The project is fit for the submission for the partial fulfillment of the condition for the award of M.Sc. in physics**.**

-

(**DR. RAJESH KUMAR)**

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Declaration

I hereby state and declare that the project entitled, **"SYNTHESIS AND CHARACTERIZATION OF ZnO THIN FILMS BY SPIN COATING METHOD"** submitted for the M.Sc. degree. This is entirely my original work and all ideas and references have been duly acknowledged. This project has not submitted to any other university, fellowship or institute the basis for the award of any degree or diploma**.**

Date: Ms. JYOTI SHEORAN

REGD.NO. 11309974

Acknowledgement

I have taken effort in this project entitled "**SYNTHESIS AND CHARACTERIZATION OF ZnO THIN FILMS BY SPIN COATING METHOD".** It would have been very difficult for me to complete this project without the kind support. No amount of words can adequately express the debt I owe to my Guide, Dr. Rajesh Kumar, Dept. of Physics, and LPU for their continuous encouragement and thoughtful discussion during the course of present work. I am very grateful to them.I am highly indebted to my guide for giving me the opportunity to do this project. I would like to give my heartfelt thanks to Dr. Kailash Chandra Juglan, Head of the department for giving the advice of complete the project at the given time.

I would like to express my heartfelt thanks to my beloved parents for their blessing, all the lab members of Physics Department, Lovely professional University as well as my friends for their help and wishes for the successful completion of this project.

DATE:Ms. JYOTI SHEORAN

CONTENTS

ABBREVATIONS

AFM	ATOMIC FORCE MICROSCOPY
UV	ULTRA VIOLET
XRD	X-RAY DIFFRACTION
PVD	PHYSICAL VAPOR DEPOSITION
CVD	CHEMICAL VAPOR DEPOSITION

CHAPTER---1

1.1 Introduction

A layer of material deposited on a substrate having range of thickness from few nanometers to micrometers is known as thin film. These layers are not only of a solid material but also of a gaseous or liquid phase. Thickness of the thin films is divided in following categories:-

(1) Ultra-thin : 50- 100 Å
(2) Thin films : 100-1000 Å
(3) Thicker films : > 1000 Å

Thin films properties (optical, electrical and physical) are determined by many factorslike deposition rate; temperature used substrate and also depend upon environmental condition in many deposition process. We can prepare thin films by number of materials such as metals semiconductors and insulators and dielectrics. The general uses of thin films are that the optical components are coated with the different material for changing either the physical or optical property. The main purpose of depositing thin film is providing the optical coating on a surface for improving optical performance. The performance of optical coatings depends upon number of layers, thickness of layer and refractive index difference at layer interfaces. The most common type of coating is anti-reflective coating. Optical coating is made up of combination of thin film layers which result in the interference of waves. This effect is used to increase transmission or reflection properties in a optical system. Optical coatings are made by depositing a dielectric and metallic material such as Al_2O_3 in between thin layers. For making mirror like surface optical coating is used in which thin films of aluminum are deposited on glass substrate. This process of depositing thin layers of silver metal on substrate is known as silvering.

Material Science is an interdisciplinary field which deals with the discovery of new materials for technological applications. This relatively new scientific field involves studying materials through synthesis, determination of the structure, properties and performance of the thin films. In recent years, most of the research workers work in the field of material science and used ZnO material which have a large band gap. Thin film properties are sensitive to not only to their structure but also to many other parameters like thickness in the film regions. Thickness is very important parameter which decides the range of the film [1].

1.2 SYNTHESIS OF THIN FILMS

We can form thin films by depositing the thin layers of material by using number of depositing techniques. There are mainly two type of deposition method by which we can apply a thin layer of material on a substrate.

(1) Chemical deposition method
(2) Physical deposition method

CHEMICAL DEPOSITION METHOD:-

Chemical deposition method is a method of formation of thin films by depositing a thin layer of material on a substrate using chemical reaction. There are number of techniques which follow chemical deposition method. Some of them are following

1. CVD (Chemical Vapor deposition)
2. ALD (Atomic Layer Deposition)
3. Spin coating method
4. Electroplating
5. Thermal oxidation
6. Epitaxy

PHYSICAL DEPOSITION METHOD:-

Physical deposition method is a method of formation of thin films by depositing a thin layer of material on a substrate in which chemical reaction are not used. There are number of techniques which follow physical deposition method. Some of them are following

1. Evaporation
2. Casting
3. Sputtering

SPIN COATING:- Spin coating is a process which is used for depositing thin films on the metal substrate. In this method, very few amount of the material which is to be coated is applied on centre of substrate and then rotate the substrate at high speed at 300 rpm. This material is spread by centrifugal process and the thin films are formed at the surface of the substrate. The factor which determine the thickness of the films are nature of fluid, and the quality by which films become sticky and thick , drying rate. one of the most important factor in the spin coating is repeatability.

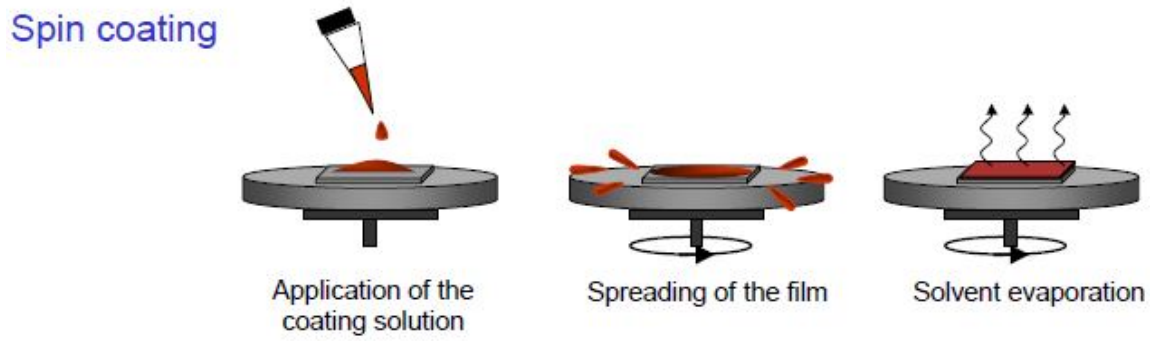


Fig. 1 The above diagram shows the spin coating techniques for thin film deposition

SPIN COATING PROCESS

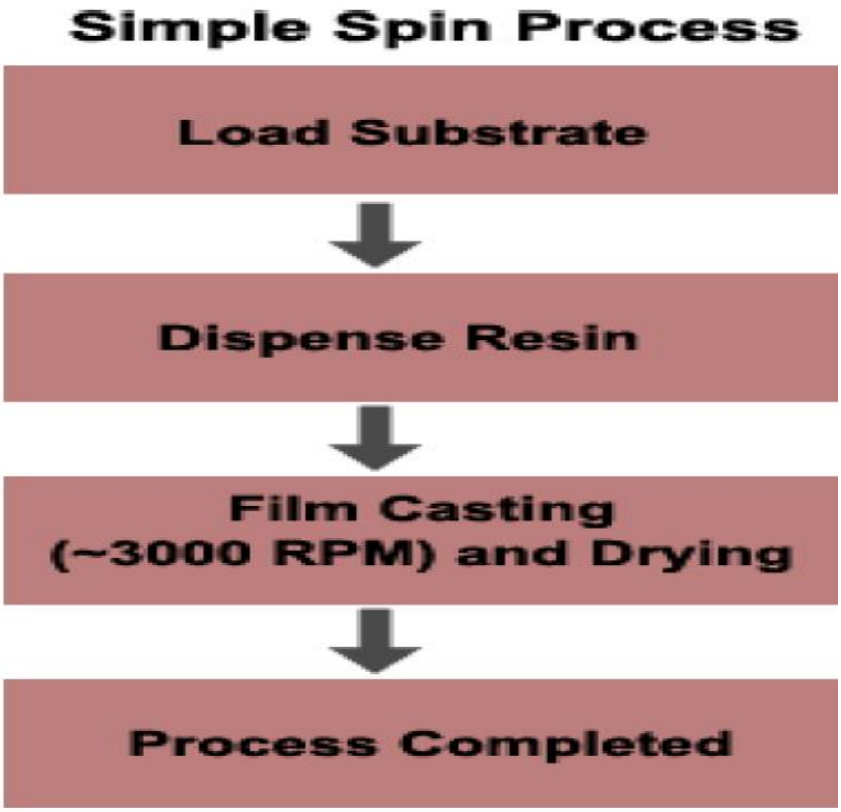


Fig. 2 The above diagram shows the spin coating process involved in thin film fabrication

SPIN COATING PROCESS HAS FOLLOWING STAGES:-

- Deposition of coating material on the substrate.
- It is rotated with constant speed and the thickness of the films is measured by viscous force.
- Substrate is accelerated so that coating material is spread uniformly on the substrate.
- Solvent is evaporated and a thin layer of fluid is formed at the substrate [2].

ATOMIC LAYER DEPOSITION (ALD):-Atomic layer deposition is vapor phase technique used at low temperature for depositing films. ALD has emerged as a powerful tool for many industrial and research applications.ALD has demonstrated potential advantages over alternative deposition methods, such as CVD and various PVD techniques, due to its con formality and control over materials thickness and composition. In this method film is formed on a substrate by exposing its surface to gaseous species (precursor). This precursor reacts with surface in a self-limiting way.. By rotating the number of cycles it is possible to grow materials uniformly. Atomic layer deposition is used in microelectronics and biomedical applications. It is used in fabrication of microelectronic because of its ability to produce accurate thickness and uniform surfaces. By this method a good quality of film is produced using different material [3].

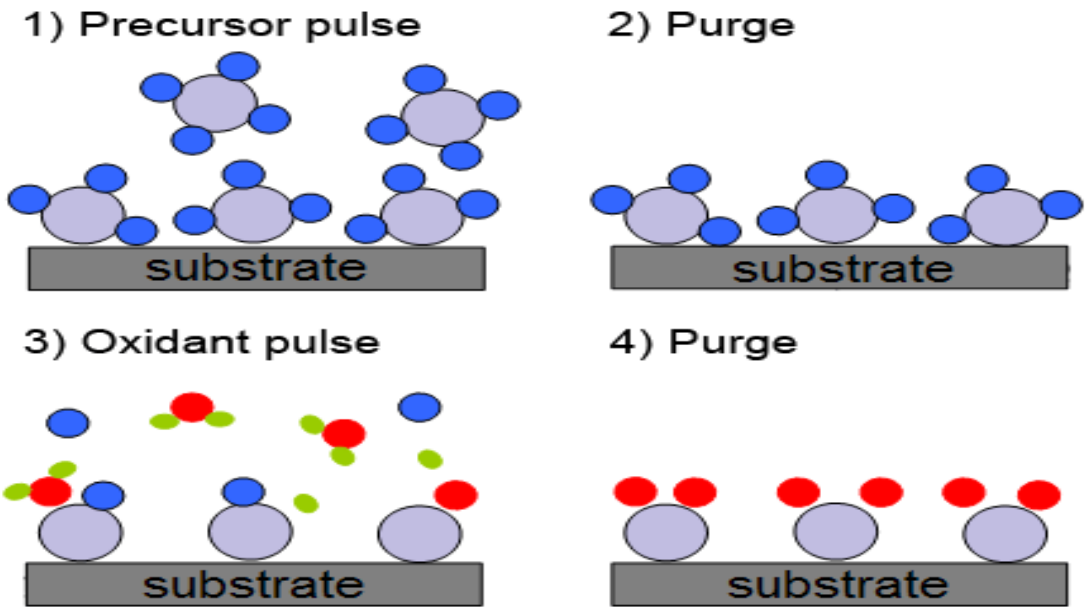


Fig.3 The above diagram shows atomic layer deposition process

CHEMICAL VAPOR DEPOSITION (CVD) : It is a technique in which thin films are deposited by carried some chemical reaction. In this process take a reactor; put the substrate and passes number of gases. The occurring of the reaction between the gases is the principle of chemical vapor deposition. After reacting the gases product is formed in the form of solid material. The solid material is obtained in the form of powder, or as single crystals and the by varying the experimental conditions like the temperature of substrate, applied pressure and

quantity of the reacting mixture it can be changed. This method is used very less because it has a major disadvantage that process is occur in presence of high temperature.

CVD is classified by operating pressure:

- Atmospheric pressure CVD (APCVD)

This process occurs at atmospheric pressure.

- Low- pressure CVD (LPCVD)

In this process CVD occur at sub- atmospheric pressure. By using low pressure film uniformity can be increased on wafer by reducing unwanted gas-phase reaction

- Ultra-High Vacuum CVD (UHCVD)

CVD at very low pressure say below 10^{-6}Pa. Most common CVD used are LPCVD and UHCVD [4].

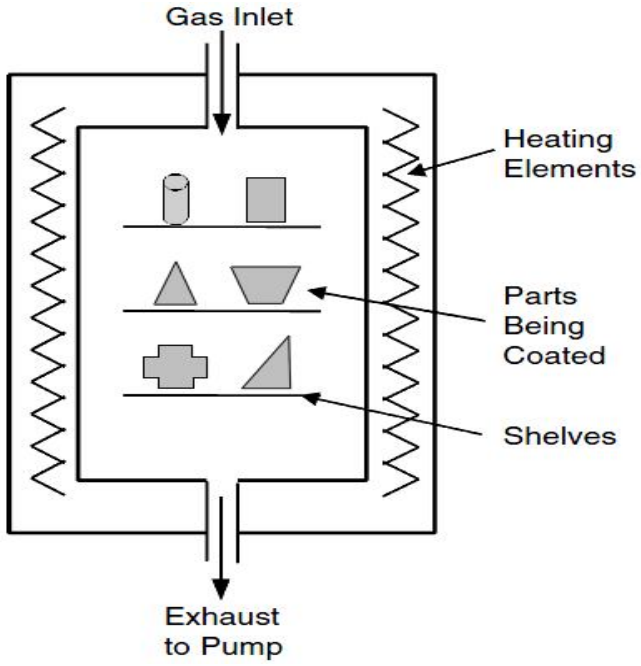


Fig.6 The above diagramshowsCVD reactor used to coat multiple parts

ELECTRODEPOSITION:-Electro deposition is process that is known as “electroplating”. Two types for plating are electroplating and electro less plating. A chemical solution is used in the electro less plating. In this process, deposition takes place at the surface of electrode which forms high electro potential with solution. This method is popular because during this process it don’t

require an extra potential. The contact of the substrate is not necessary in the electro-less plating. The disadvantage of this method is that it is impossible to control the thickness of thin films.

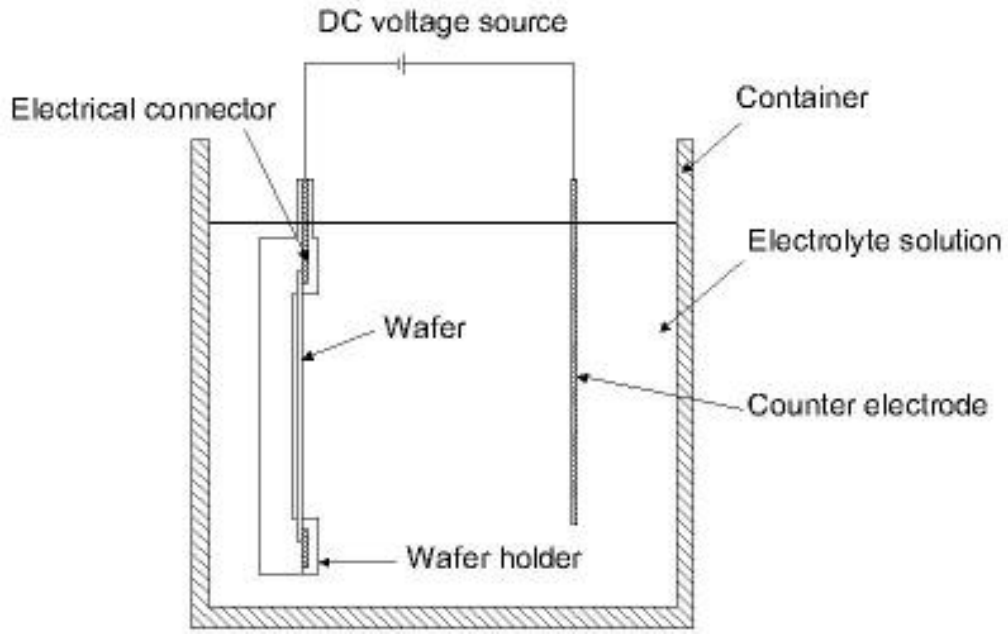


Fig.4 Setup for electro-deposition

The electro deposition method is desirable method for making thin films of metal like nickel, zinc, cadmium, manganese etc. The thickness of the films lies in the range of ~ 1- 100 µm. When an external electrical potential is used deposition is best controlled. In this process the contact of the substrate is required. In any process it is required before deposition an electrical coating is deposited on the surface.

THERMAL OXIDATION: - Thermal oxidation is basic deposition technique. In this process the temperature is raised to 800 to 1100 ^{0}C in furnaces. This method has an advantage that a single furnace can occupy many materials at same time. It is a process of producing the thin layer of oxide on wafer (wafer is substrate/ thin slice of semiconductor material). The film growth can be decreased by increase the availability of oxygen into the substrate so that growth of films is normally downward in to the substrate. With increasing the extent of films of oxidized layer, diffusion of oxygen in to the substrate became more laborious. This method is applied only to that material which can be oxidized. Thermal oxidation is applied on many materials but it is the classical method used to form SiO_2 on a silicon substrate.

Fig.5 The above diagram shows thermal oxidation process

EPITAXY: This method of deposition of thin layers of material on a substrate to form films is similar to chemical vapor deposition technique. If an crystalline substrate is used then produced film will be crystalline and if the substrate used is amorphous / polycrystalline then film will be amorphous or polycrystalline.

During the processing, numbers of gases are passed through the reactor rector where the substrate is heated. The temperature used for producing thin films using epitaxy method is half of the melting point of the substrate which is used for deposition.

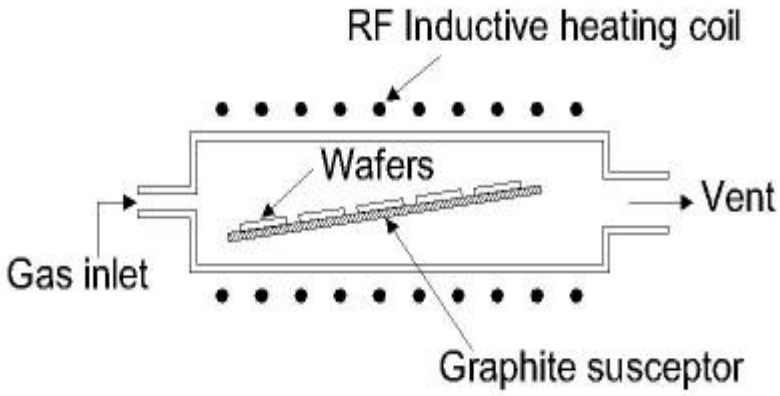


Fig.7 The above diagram shows vapor phase Epitaxial reactor process.

EVAPORATION:- Evaporation is the method in which the substrate is put in a vacuum chamber in which source of material is also deposited. Heat is supplied to the chamber till the material start boil and get evaporated. Heating is required for allowing the molecules to evaporate freely in reactor and molecules condense on all surfaces. Thermal evaporation is the type of this method which is most popular evaporation technologies. In this method, heating is produced at the material for evaporation by passing the electron beam. Resistive evaporation is

used in vacuum deposition in which electrical energy is used for heating the material for evaporation.

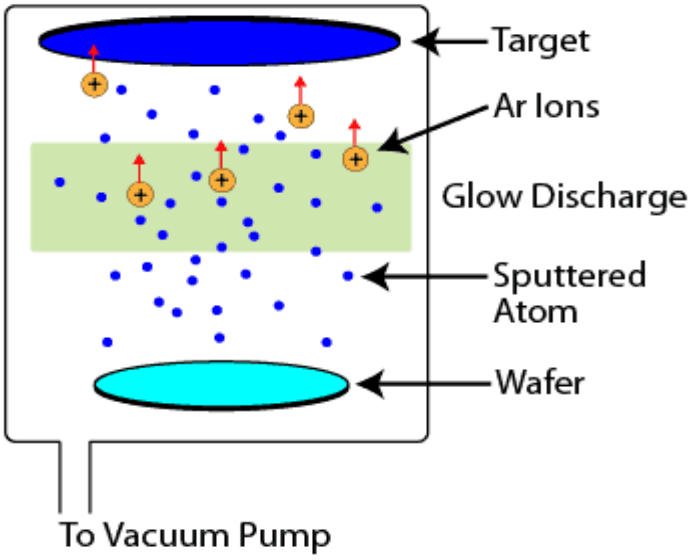


Fig.8 The above diagram shows Thermal evaporation technique

SPUTTERING:-It is a technique in which the layers are formed at surface at low temperature. The temperature used in sputtering is low than the temperature using in evaporation. In this process the substrate is put in vacuum chamber and plenty of gases are supplied at low pressure.Sputtering is a process of ejection of electron from the substrate by the supplying of energetic particle. This process is occurs when thermal energy is much less than kinetic energy. The sputter atom (atom rejected from the target) will depend upon the angle by which ion are incident at target and mass of ions. Sputtering has many advantages over the method of evaporation. One of them is that no container contamination will occur.

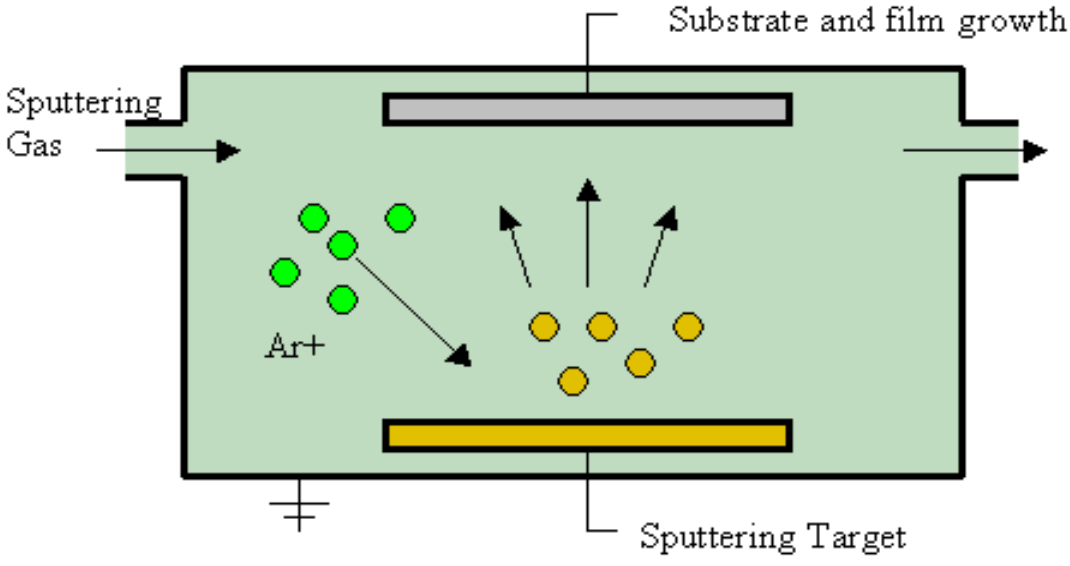


Fig.9The above diagram showsthe thin film formed by sputtering method

1.3. ZnO Material

A compound which contains lacking of carbon atom means not an organic compound with formula ZnO is known as zinc oxide. In periodic table zinc belong to second group of table and oxygen belongs to sixth group of table. In case of solubility, it is not soluble in water and

alcohol. But it is soluble in acids like hydrochloric acid. Zinc oxide is found in powder form and it is non-toxic material. It is environmental co-friendly.

Zinc oxide is obtained by oxidation of zinc metal in the range of low temperature 500-600 ^{o}C. The structure of prepared zinc oxide by oxidation of zinc metal was analyzed in range of high temperature 700- 1000 ^{o}C. Oxidation is a low-cost effective method used for the synthesis of ZnO nanostructure. The synthesized ZnO has needle like, wire like morphology. The color of the zinc oxide is white. Due to addition of impurities, the mineral form of zinc oxide is of yellow or red color.

Zinc oxide is a semiconductor compound having different properties such as electrical properties, optical properties and chemical properties. It became a very useful compound because of having all these different properties. Zinc oxide is used on large commercial scale during last 100 years.

Due to its large band gap and exciting binding energy, zinc oxide became a promising candidate for the optoelectronics device which can be operated in blue and ultra-violet region. The band gap of zinc oxide material is 3.37eV and it has 60meV energy at room temperature. Reducing electric noise and raising breakdown voltage are the advantages of having large band gap.

It has wide sensing application (gas sensor, electrical –mechanical sensor and biological sensor). It can be used in formation of sunscreen cream because it absorbs harmful ultra-violet light. One of the largest applications of zinc oxide is in rubber industry and the photocopying paper is prepared by using zinc oxide. Zinc oxide is widely used in biomedical application.

Zinc oxide is considered as a soft material. There are three form of crystal of zinc oxide. Hexagonal wurtzite, cubic zinc blende and cubic rock salt are form of structure of zinc oxide. The stability of hexagonal wurtzite is high and therefore it can be widely used. The inversion symmetry is not followed by zinc blende structure and it is responsible for piezoelectric and pyro electricity property [5].

1.4. Method of preparation of Zinc oxide:-

There are three main process by which zinc oxide can be produced. These are given as following:

1. **Direct process:-**

In this process the zinc oxide can be prepared by the ore of zinc or calcite. Zinc is expelled as vapor when carbon monoxide is generated. Again, the zinc is re oxidized and when low temperature is used particulate of zinc oxide is formed.

The product formed has different physical characteristics because combustion of zinc is occurring with monoxide at different temperature. There is requirement of further processing in crude zinc to form zinc oxide.

2. **In-direct process:-**

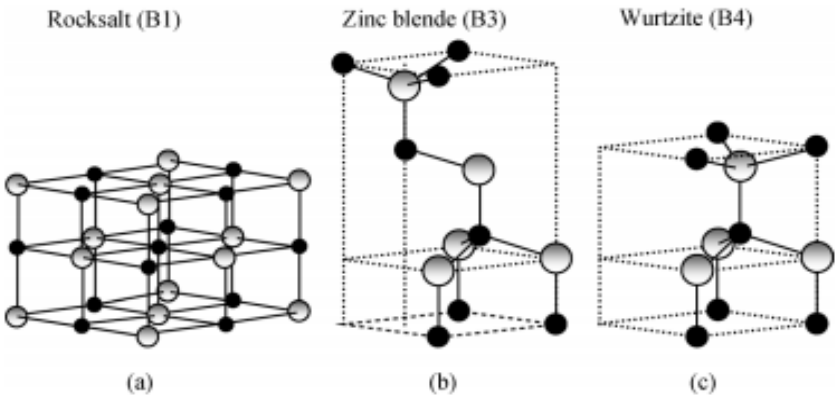
In this process take a graphite crucible in which zinc metal is melted at temperature of 1273K. Zinc metal start vaporized and the vapors of zinc react with the oxygen in air to give Zinc Oxide (ZnO). By this method we can produce zinc oxide particle of size 0.1 to a few micrometer. These particles can be transported in cooling duct and collected in a bag house.

3. **Chemical process:-**

By this process a small amount of zinc oxide can be produced. The precipitated zinc carbonate and zinc hydroxide can be produced by the aqueous solution of zinc salts. Then the precipitate is then filtered, washed and dried at temperature.

1.5. PHYSICAL PROPERTIES

STRUCTURE OF ZINC OXIDE:-

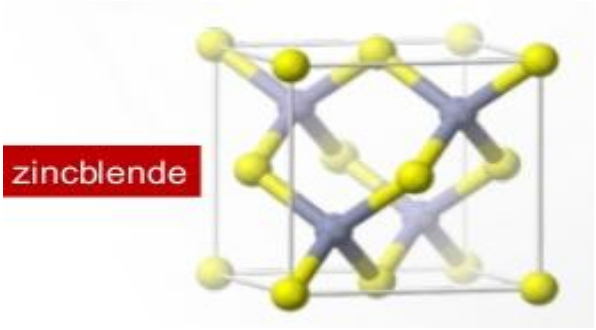


Zinc oxide has two types of structure known as

1. Zinc blende structure
2. Wurtzite Structure

Zinc blende Structure:-

In the zinc blende structure, a hollow circle shows the presence of the zinc ion and the solid sphere represented the oxide ion. The main features of the structure are followings



- Yellow sphere – oxygen
- White sphere - Zinc
- The oxide ions are arranged at the corner of the cube and the center of the each phase. This arrangement is known as ccp arrangement.
- Half of the tetrahedral sites are occupied by zinc ion. There are two tetrahedral sites per oxide ion O^{2-} because in the closed packed lattice only two tetrahedral sites per atom.

- The ratio of the cation to anion is 1:1 because each oxide ion (O^{2-}) has one Zn^{2+}. The coordination number of Zn^{2+} and O^{2-} ions in zinc blende structure is 4:4 because each zinc ion is surrounded by 4 oxygen ions.

- 1.60 is the radius ratio of zinc blende and lattice constant is 3.25Å. The compound such as Zno, Zns, CuCl, CuBr, CuI has zinc blend structure.

Wurtzite Structure:-

In the wurtzite structure, a hollow circle shows the presence of the zinc ion and the solid sphere represented the oxide ion. The main features of the structure are followings:

Yellow:- Zn^{2+}

White:-O^{2-}

- The arrangement of oxide ion is hexagonal closed packed (hcp) and half of tetrahedral sites are occupied by zinc ion.

- The anion to cation ratio is 1:1 because for each O^{2-} ion, there are two tetrahedral sites in the lattice and only half of them are occupied by Zn^{2+} ions.

- Each Zn^{2+} ions are surrounded by four O^{2-}, therefore the coordination number is 4.

- The crystal has tetrahedral structure having coordination number of 4 and radius ratio is 1.60. The compound such as AgI, ZnS has wurtzite structure [12].

TABLE 1

Table for the physical property of ZnO:-

PROPERTY	**VALUE**
Formula	ZnO (zinc oxide)
Type of compound	Inorganic compound
Molar mass	81.4083g/mole
Melting point	1702K
Boiling point	2087K
Color	White in color
Solubility	Insoluble in water
Form	Powder form
Energy Band gap	3.6Ev
Exciton Energy	60 MeV
Refractive index	2.004
Odors	Odorless

1.6. CHEMICAL PROPERTIES

- Zinc oxide is mixture of zinc containing 80.34% of zinc and 19.6% of oxygen

- The atomic number of zinc is 12 and its electronic configuration is $1s^2\ 2s^2\ 2p^6\ 3d^{10}\ 4s^2$.

- The atomic number of oxygen is 16 and its electronic configuration is $1s^2\ 2s^2\ 2p^4$.

- ZnO is amphoteric compound; it reacts with both acid and base. It is insoluble in water. The level of solubility is 0.005 g/lit.

$ZnO + 2\ HCl \rightarrow ZnCl_2 + H_2O$

- When zinc oxide are reacted with phosphoric compound it form cement like compound which can be used in dentistry.
- For producing carboxylate zinc oxide can be reacted with the fatty acids .
- Zinc carbonate can be prepared by the zinc oxide when it is exposed in air.
- Zinc oxide can be used in vacuolization of rubber.
- Zinc oxide can be used in removing the harmful gases like hydrogen sulphide from the cigarettes.

$ZnO + H_2S \rightarrow ZnS + H_2O$

- When zinc oxide is dissolves in dilute acids forming salts [6].

$Zn(OH)_2 + 2\ NaOH \rightarrow Na_2[Zn(OH)_4]$

ELECTRICAL PROPERTIES:-

Zinc oxide is in powder form of white color having band gap of 3.3eV at room temperature. Due to having large band gap the electric noise is low and breakdown voltage is high. The excitation binding energy of zinc oxide is 60 meV. Therefore, zinc oxide can be used in chemical sensor as well as in solar cell. Due to presence of interstitial defect and impurities zinc oxide is referred as n-type semiconductor. N-type doping is easily achieved by dopant (group III elements) such as Al, GA, In by substituting Zn and by dopant (group IV elements) such as chlorine and iodine.

Laser diode (LDs) and light emitting diode (LEDs) are fabricated from n-type ZnO. Complementary logic circuit can be formed by field effect transistor (FETs) which are fabricated by n-type zinc oxide. With the variation of temperature, electron mobility of zinc oxide can be varied. ZnO has maximum electron mobility of ~ 2000 cm^2 / (V.s) at nearly 353 ^oC. For transparent electrode, Al- doped ZnO layer is used. Zinc oxide can be used in the fabrication of the Thin Film Transistor (TFTs). ZnO can be used in solar cell and gas sensor.

Zinc oxide Nano rod sensor

Due to absorption of gas molecule, the variation in electric current passing through the zinc oxide nanowires are detect by a device that is known as zinc oxide Nano rod sensor. The sensitivity of the sensor can be increased by adding Pd across the hydrogen atom. At room temperature the sensor detect hydrogen concentration down to 10 ppm.

OPTICAL PROPERTIES:-

For the designing of photonic devices the optical properties of zinc oxide is used. A Photoluminescence spectrum of zinc oxide nanostructure rod was studied and excitation emission was observed. If we decrease the diameter of nanowires, the green emission intensities increase. Zinc oxide has application in acoustic, optical fiber and solar cell. Optical band gap of films decreases with the increasing the concentration of doping material [7].

1.7. APPLICATIONS

In the field of material science ZnO is very powerful candidate because of having unique properties of UV-analysis, electrical properties and optical properties. Due to the large band gap it can be used in the formation of number of devices such as laser diode (LDs).
It has following application:-

ANTI CORROSIVE COATING:

Zinc oxide is non-toxic compound means it has no harmful effect.Zinc oxide is very powerful compound which prevents from the fungi. When we apply a layer of zinc oxide it prevents from the corrosion. Zinc oxide is very useful in paint and this paint is used for the coating of metal like galvanized zinc. Zinc oxide is an inorganic compound which is not affected by the presence of sulphur in atmosphere. For the steel structure, the coating of zinc oxide is very helpful. It gives a anti corrosive coating to the surface of under water tank.

RUBBER MANUFACTURING:

Zinc oxide is used on the large scale in the rubber industries. It helps in the vacuolization of rubber. It is used in car tyres for increasing the thermal conductivity and the span life gets increased. When zinc oxide is used with stearic acid, rubber curing became more faster. Zinc oxide is very is very essential part for the formation of tiles.

MEDICAL USES:

Zinc oxide is much less antiseptic but it is useful in sunscreen creams because it has very large capability of absorbance of UV-rays. It protects our screen without causing a harmful effect. Calamine is lotion is prepared by the zinc oxide in which a very few ferric oxide is added. It is also used by dentists in the manufacturing of toothpaste. Zinc oxide proves very powerful compound for removing the presence of sulphur from variety of gases. It can be used for removing the harmful substance like H_2S and HCN in cigarettes (used in formation of cigarette filter). The fine particles of zinc oxide are anti-microbial in nature and therefore it can be used in the packing purpose. Zinc is very needful nutrient; therefore it can be added to food products [8].

APPLICATION OF THIN FILMS COATINGS:-

Ant reflecting coating:-

It means reflection is low and transmission is high.Ant reflecting coating is the coating of material for increasing the optical performance of a device. Ant reflecting coating is also called anti- glare coating because it improves the vision through lenses and appearance of eyeglass both. In thin films, the anti- reflecting coating reduces the light loss.

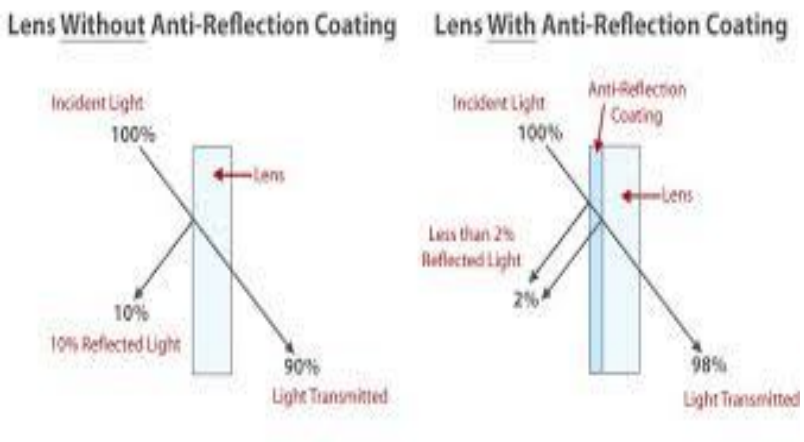


Fig.10. The above diagram showsantireflective coating

- Ceramic thin films are in widely used in industry and for research purposes. These films are used for the prevention of substrate material which are corroded, oxidation and wear and tear because of the hardness and inertness of ceramic materials.

1.8. METHODS OF MEASURING THICKNESS OF FILMS

For the properties of thin films thickness play a very important role**.** The success of fabricated film is deposited over the material is depend upon the thickness of layers. It is not necessary to give a specific thickness but a good control over the thickness must be necessary. Thickness lies in the range between of few nm to micrometer.

Films thickness measurements depend upon the different principles such as mass difference, high absorbance, interference effect.Some of the method for measuring the techniques is given as following:-

MICROBALANCE TECHNOQUE:-

This method is depending upon the increase of the weight of the films, density, and area of deposited material. Thickness can be calculated by the given formula

$$T = W / (\rho A)$$

REFLECTION ABSOPTION SPECTROSCOPY:-

This is very useful method for measuring the thickness of deposited film on a metal substrate as well as non- metallic substrates such as glass and silicon etc. it is an external reflection method in which angle of incidence is greater than 70^{o}.For measuring the thickness (inμm) high sensitivity reflection method is used [1].

UV METHOD

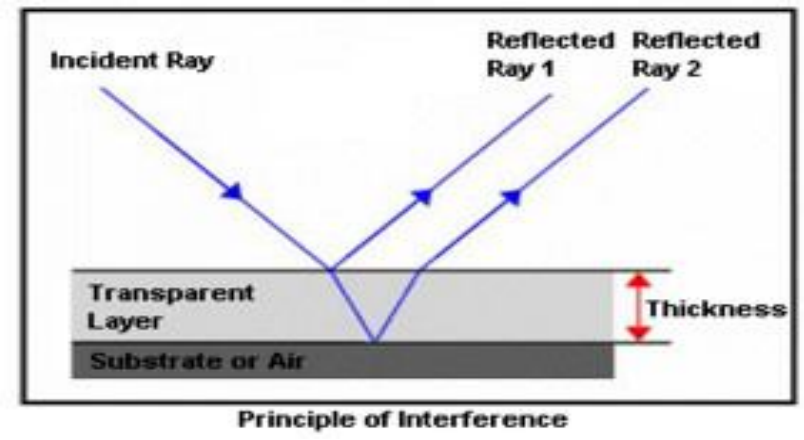


Fig.11 The above diagram showsthe measurement of thickness by UV method

1.9. OBJECTIVE OF STUDY

The objective of our study is to prepare thin films by using sol-gel spin coating method. The characterization of thin films will be done by UV and XRD spectrographs. From these characterization studies, the attenuation properties, grain size and crystallinity of the thin films will be determined.

SCOPE OF STUDY

These thin films appear to have application in the fabrication of

- Antireflective coating
- Gas sensors
- Thin film transistors
- Solar cells

CHAPTER --- 2

REVIEW OF LITERATURE

3.1V.Musat et al. (2003)

Al-doped ZnO films were prepared by sol- gel method on one of the variety of glass using zinc acetate and aluminum chloride , 2-methoxyethanol as solvent and mono ethanolamine as sol stabilizing agent. There are many of the methods of deposition by which we can deposit the thin layers on a glass substrate. The deposition of films was operated by the dip coating method using process of removing of 1.5cm min^{-1}.

Thin films are prepared by the dip coating and the results are varying with the variation of concentration of aluminum. With increasing the concentration of the Al from 1 – 2 wt%, electrical conductivity improves but obtained data is not certainly conclusive. During the first post-heat treatment conductivity of the films is affecting by the atmosphere (oxidizing, inert, and reducing) [9].

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3.2 M.Khaleeq-ur-Rahman et al. (2008)

Layers of material of Zinc oxide were prepared by the Pulse Laser Deposition on calcium carbonate substrate. Zinc oxide material is used because of their various application in different types of LED and laser diodes due to having a large band gap of 3.3 eV. Zinc oxide has been proved a successful candidate for single crystal, bulk and thin film gas sensor. PLD process was carried out using Nd : YAG laser having wavelength of 1064 nm. Polishing was done on the surface of both target and substrate for using pulse laser deposition technique. 4n purity sample of zinc was used for the process of forming layers of material on the calcite substrate. This process is carried out at ~10^{-3} torr in presence of oxygen in controlled spherical chamber. The material is sputtered due to interaction of laser and matter. A good quality of crystalline thin film is deposited on the substrate and the improvement in film is increased by annealing of this film. Using SEM the surface morphology of thin film is studied. X- Ray diffraction technique showing the polycrystalline nature of thin films. Resistivity of thin films were found >200MΩ [10]**.**

3.3. S.Ilican et al. (2008)

A layer of zinc oxide was formed by applying many of the method like spin coating method, pulse laser deposition technique, dip coating and sputtering etc. In this paper a discussion on sol-gel spin coating method were held.

In this method a transparence & homogenous mixture of solvent and solute were formed by dissolving the zinc acetate dehydrates as precursor, mono ethanolamine as stabilizing agent and isopropanol as solvent. This mixture is heated at 60 ^{o}C for 2 hrs. A homogenous and clear solution is obtained and this solution can be used for preparing thin film. Thin films are prepared by pour a few drop of this solution on the glass substrate and then put this substrate in to a spin coater (equipment). Using ~ 2000 to 3000 rpm a film is deposited on the glass substrate and annealing it 550 ^{o}C for 1 hr. and zinc oxide thin film are prepared [11].

The transmission and absorbance percentage can be studied by UV – analysis, transmission is found up to 92%. The crystal structure and orientation of zinc oxide thin film are analyzed by X-ray diffraction.

3.4. J.Pattaret. al.(2009)

Thermal evaporation method is used for preparation of thin film on a glass substrate keeping the vacuum 10^{-5} torr. In this method pure zinc telluride was used as source material. The material was placed at the center such that it acts as a point source in a boat of molybdenum. By passing the current through the electrode the boat can be heated. Glass slides were used as substrate after cleaning with soap, water acetone isopropanol.

For obtaining a uniform coating rotary device is used. A small current is used after achieving a high vacuum. The deposition rate should be ~ 1.4Å/sec and for stop the deposition rate source shutter is used. In this method room temperature is used for preparing thin film and then annealed the zinc telluride thin films at 400K for 3 hours. For doping of indium these films were heated in a vacuum at 400K for 3 hours.

The conductivity of these films is less than the conductivity of films which are doped with indium by ion exchange method. In X-ray diffraction the broad peak shows that films are amorphous in nature. These films have good surface morphology because of heated

Treatment applied before and after the doping material. From the optical absorption spectra the optical band gap can be find out and it was found decrease with the doping concentration. In electronic device field, zinc telluride is most applicant material due to having large band gap. The photorefractive response can be improved by doping zinc telluride to with vanadium [12].

3.5. Y.H.Hwang et al.(2010)

In this paper highly transparent ZnO transparent film transistor's fabricated by a sol-gel process.0.3M concentration of precursor solution is taken in this process and annealing is done at 600 C. thus, obtained films exhibit orientation of (002) plane, which increase conductivity and surface density. The results show that microstructure of deposited layers are connected to the electrical property. At high annealing temperature good quality of layers crystalline were obtained. It is investigated that by applying an additional post annealing process in N_2, the conductivity of the film can be improved. Zinc oxide thin films are used in transistors [13].

3.6. Z.R.Khan et al. (2011)

Sol-gel method is used for the fabrication of highly transparent zinc oxide thin films. Zinc oxide became an attractive candidate for the researcher due to its wide band gap and optical property. For the characterization of these films UV-V IS analysis is used for the optical property (transmission) and XRD is used for the phase structure nature of crystal. The optical band gap energy is found ~ 3.4 eV. By the x-ray analysis the structure of thin film was found tohexagonal-wurtzite structure [14].

3.7. A.Ghadri.et.al.(2011)

Thermal evaporation method is used for the preparation of layers of material of different thickness of deposition at room temperature. The vapor pressure used in this technique is 5.54×10^{-5} mbar. It is necessary to keep the target substrate distance constant. The microstructural characteristics and the variation in thickness can be obtained by XRD.
In this method, zinc granules are placed in the vacuum chamber in which substrate is placed. The system was pumped up to a pressure of 5.54×10^{-5} mbar and deposition was carried out by the

variation in time. X-ray diffraction was used for the crystallinity of structure of thin films. The thin films structure is mono-crystal in nature. The surface topography is studied by the atomic force microscopy and it was found that roughness of surface is low.
Four probe method is used for studied the electrical property of zinc oxide thin films [15].

3.8. M.Sathya et al (2012)

Thin films solar cells are produced by depositing two or more thin layers on a substrate such as glass. ZnO thin films are formed by electro deposition of Zinc Nitrate. This is inexpensive method for the synthesis of materials from solutes. This technique is based on controlled potential electrochemical deposition on an electrode from a solution containing the appropriate compounds. For glass substrates an additional procedure of dip coating was done before electro deposition as it was found to be non- wetting during electro deposition. Their structural and optical properties were characterized by UV-VIS absorption and emission. The transmission curve was analyzed and found that 28% absorption against the 72% transmission achieved for electro deposited sample. The FTIR of thin films was also investigated. Their photoconductivity was verified which makes them promising candidate for solar cells [16].

3.9. I.Nkrumah et al (2013)

ZnO thin films are deposited on silica glass substrate by chemical bath deposition method. This method has advantage that it is very simple method and it does not require sophisticated equipment. It uses low temperature and low cost deposition. The elemental composition and morphology of the film have been studied using energy dispersive X-Ray diffractions. It was observed that image shows Nano rods of ZnO thin films. The band gaps for as-deposited, annealed at 200C to 300 C are 2.27, 2.66 and 2.60 eV respectively. E_g was observed as the annealing temperature increased. This is happened due to improvement in crystallinity of ZnO thin films [17].

3.10. S.Agarwal et al (2013)

ZnO is very promising compound for the formation of thin films. In this paper, a discussion is held on the Magnetron sputtering technique of depositing film on a glass substrate using oxygen gas. By using this technique approximate 600nm thick film of ZnO deposited. After deposition sample, it is heated at 300C for 2h in vacuum environment.
The transparency, and after annealing at 300C for 2h in reduced environment shows the 1.6 $\times 10^{-3}$ resistivity. The resistivity of zinc oxide thin films is decreased by doping of aluminum. Doping should be less than 0.02 of atomic weight to maintaining the same transparency [18].

3.11. A. Rahal et al (2014)

Thin films are prepared by many of the technique. Ultrasonic Spray is one of them technique using for depositing the transparent conductive of un-doped films on glass substrate. This technique can be used at different substrate temperature between 300 to 400 ^{o}C.

In Ultrasonic spray technique sol-gel solution is prepared. Concentrated HCL is used as stabilized agent, few drop of HCL is added to the solution of methanol and zinc acetate dehydrates**.** For obtaining the transparence solution this mixture is heated at 30 ^{o}C for 4 hrs. The solution was sprayed on heated glass substrate by Sonic (device which transform the liquid to a stream formed with uniform drops. This process of spraying is till up to 2 min. at different temperature 300, 350 and 400 ^{o}C. Increase in temperature show the improvement in optical transmission property. By using X-ray diffraction technique phase structure of thin films were determined [19].

3.12. K.Rathiet. al (2013)

Sputtering technique is used for the deposition of thin film. The electrical property, optical and structural properties are depending upon the deposition rate. A silicon substrate is used on which a layer of amorphous tantalum oxide is deposited by using the above giving technique (sputtering technique). For obtaining the films of different densities, oxygen flow rate should be varied. By this oxygen flow rate the deposition rate and refractive index of tantalum oxide can be studied.

In this method silicon wafer is cleaned chemically by etched in dilute HF solution. All films are deposited on crystalline substrate. The deposition is doing in a chamber at 100 torr pressure and power was 100watt. The films can be analyzed by the various techniques such XRD techniques. X- ray diffraction pattern show that the oxygen rate must be amorphous in nature [20].

3.13. M.Fakhar-E-Alam et.al. (2014)" Characterization of zinc oxide thin films coated by thermal evaporation technique"

Thermal deposition is the deposition technique for depositing the zinc oxide thin film of zinc metal. Researcher found that Zinc oxide as a future material because of their wide band gap and wide properties. It is non- toxic material. There are many method of formation of zinc oxide such as sol-gel spin coating method, sputtering and thermal evaporation.

Thermal evaporation is the best method for depositing multiple layer of material on a substrate. Silica and glass can be used as substrate on which film is grown but glass substrate is very low in cost and easily available. Therefore, it can be more used. Thermal evaporation is friendly to environment and the deposition rate can be easily controlled in this method.

In this paper, microstructure layers were created by the thermal evaporation method. These films were annealed at different temperature for obtaining good result for optical transmission. The transmission can be increased by the process of annealing. In this method, first of all the substrate is cleaned with distilled water then clean it with acetone and isopropanol in ultrasonic equipment. This glass substrate was placed in a vacuum chamber in which zinc powder is placed in the boat made up of tungsten in the vacuum chamber under the pressure of 10^{-3} torr. For evaporating the material power supply was used and the evaporated material can be used for the deposition on the substrate. The films were prepare by following above method and annealed at temperature at 300-350 ^{o}C for 2 hours. X-ray diffraction method used for the studied of structure and crystallinity of thin films. With increasing the temperature intensity of peak can be increased and SEM structure shows grain size. Thus, variation in temperature has an effect on the surface morphology of the film [21].

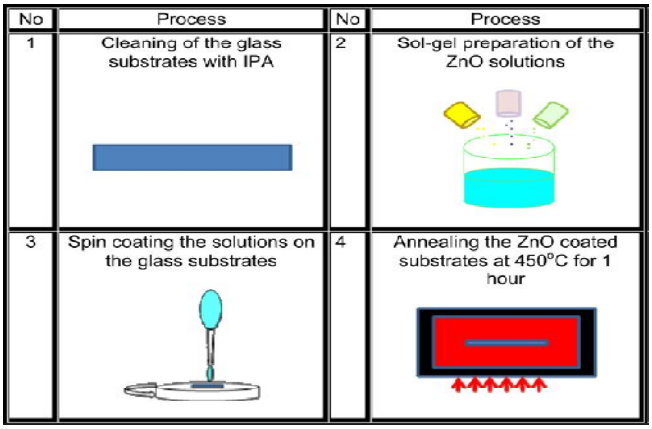
CHAPTER --- 3

3.1. RESEARCH METHDOLOGY

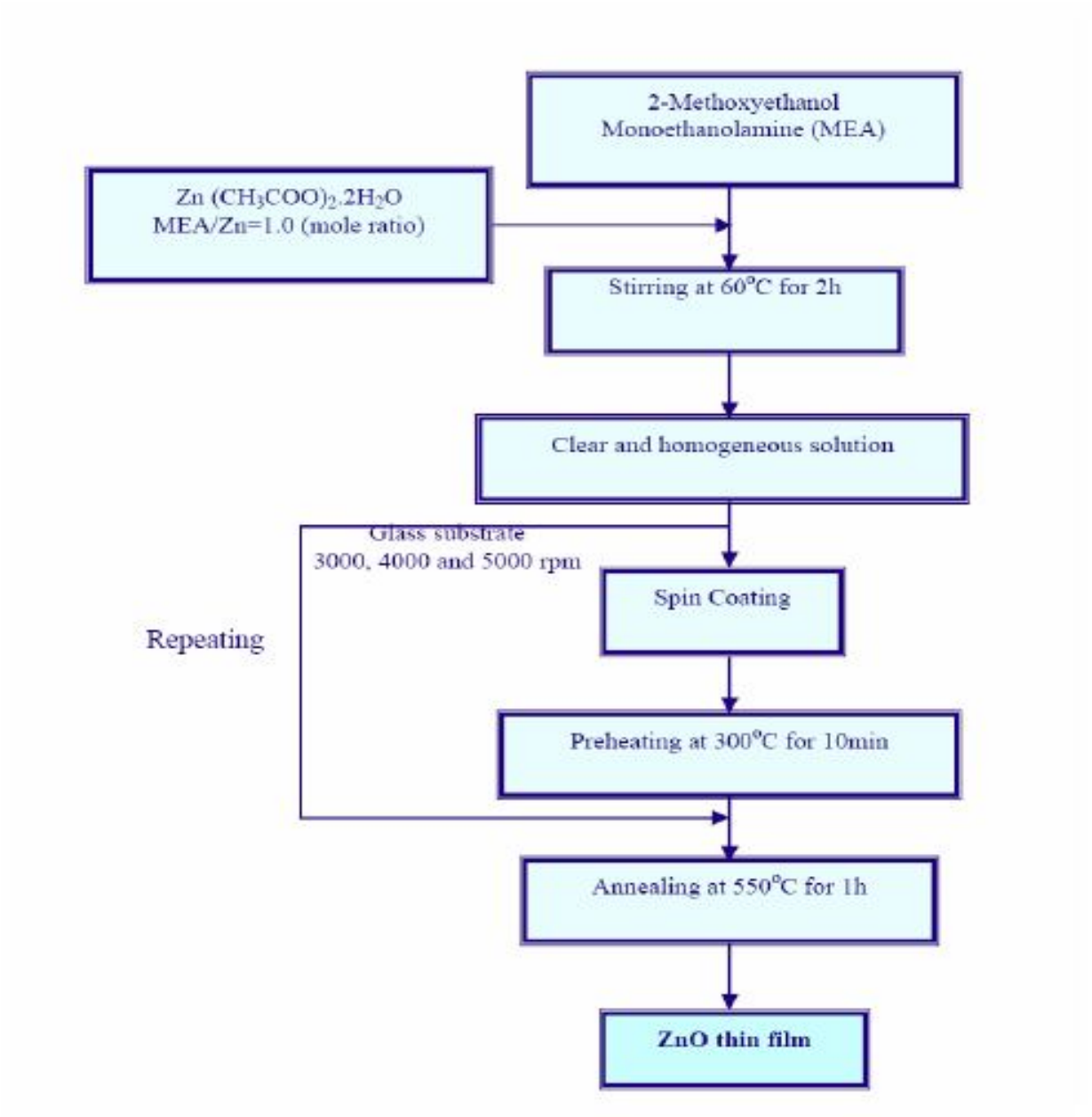
Procedure:-

First of all prepare the sol-gel (colloidal solution of particle in which dispersed phase is solid and dispersion phase is liquid). It is a viscous liquid. The solution for ZnO will be made using Zinc acetate dehydrate [Zn $(CH_3COO)_2$. $2H_2O$] as a precursor, [C_3H_7OH] as solvent and mono ethanolamine [C_2H_7NO] as a stabilizing agent.The resultant solutions will be stirred at an appropriate temperature and for suitable period of time in accordance with time in which viscous liquid is formed.Take few drops of this viscous liquid and put these drop on the glass slide. Before putting these drops the glass slides are cleaned. For cleaning the slides, Tiepolo solution is used as solvent. Take 3-4 drops of solution on the slides and wash with normal water. Now deep these slides into beaker in which water is filled up to 20ml and stir for 5 mint. Put these slides into deionized water for the process of sonication for 5-15 minutes. Now use acetone for cleaning these slides and apply the sonication process again for 30-35 minutes. Again the process of sonication is used for cleaning. The slides are placed in isopropyl alcohol. Finally the slides are cleaned and we can use theses slides for depositing layers of materials.Now put a drop of the prepared solution and place these slides into spin coater and giving the speed (2000-3000 rpm) to the coater for 1 minute and the layers get deposited. The complete process for fabrication of thin films is depicted in the following diagram:

Process of fabrication of thin films



The stepwise flowchart for the preparation of thin films is shown in the diagram:



Experimental set-up used in the research investigations:-

The following diagrams show the magnetic stirrer, ultrasonic cleaner and spin coater used in experimental work.

- **Magnetic stirrer**

1. **Ultrasonic cleaner**

Spin coater

CHAPTER --- 4

RESULT AND DISCUSSION

X-RAY DIFFRACTION (XRD) STUDIES

XRD investigates the crystal structure of an unknown material. It is identify the crystalline phase and find the average spacing between layers or rows of atoms. XRD is also used to find out the orientation of a single crystal or grain. It measures the size, shape and internal stress of small crystalline regions and find the crystallinity of the thin films,

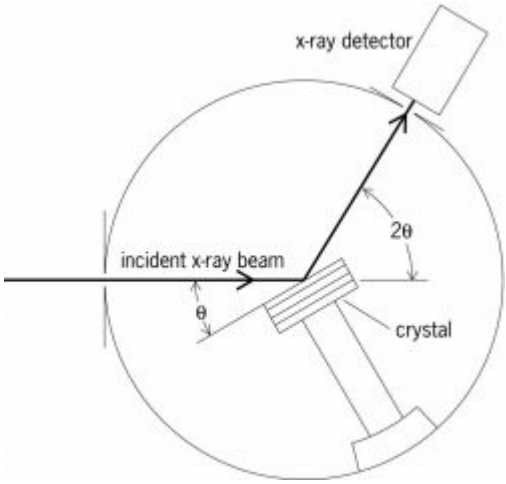


Fig.13.The above diagram shows XRD Spectroscope

The grain size of the thin films can be found by using the Debye- Scherer formula

$$D = 0.9 \lambda / (FWMH \cos\theta)$$

Where Θ is angle of scanning, D is grain size, λ is wavelength used for X-ray diffraction

andFWMH is full width at half maximum

For 0.4M

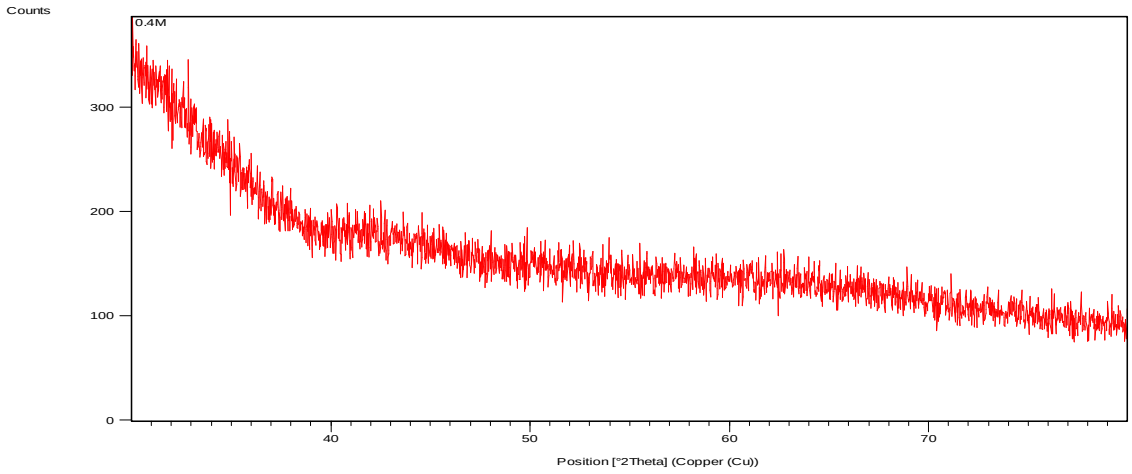


Fig.14. the above diagram shows the XRD spectrograph of 0.4M concentration of precursor solution (Zinc Acetate Dehydrate)

For 0.6M

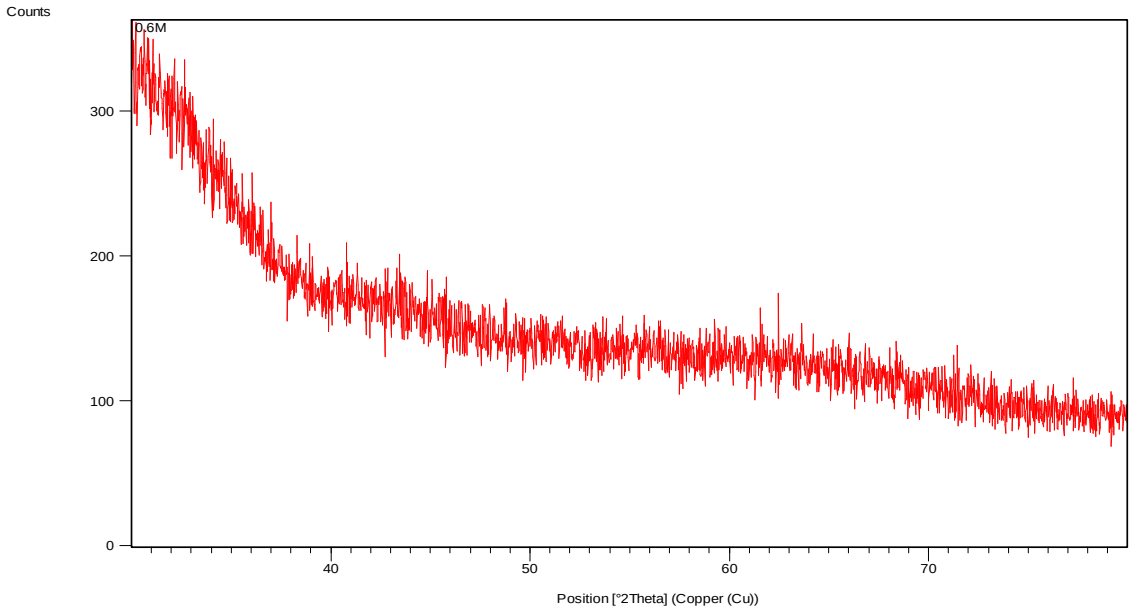


Fig.15. the above diagram shows the XRD spectrograph of 0.6M concentration of precursor solution (Zinc Acetate Dehydrate)

The following table 2 gives XRD data obtained from the X- Ray diffractometer.

TABLE 2

Pos. [°2Th.]	FWHM [°2Th.]	d-spacing [Å]	Rel. Int. [%]	Area [cts*°2Th.]
30.5680	0.1673	2.92461	99.42	338.50
31.9599	0.1673	2.80034	100.00	340.49
43.8009	0.1171	2.06688	22.08	52.61
44.8184	0.1338	2.02230	36.25	98.75
55.2893	0.2007	1.66155	7.17	29.30
62.4503	0.0836	1.48714	8.68	14.77

63.6999	0.4684	1.46095	2.34	22.29
64.5317	0.1171	1.44411	6.68	15.92
72.3453	0.1004	1.30619	3.09	6.32
73.1252	0.2676	1.29417	3.10	16.90
79.4171	0.2040	1.20570	4.73	26.57

Used X-ray wavelength is 1.54060Å

Now, as we know that

$$D = 0.9\,\lambda / (FWMH \cos\theta) \qquad (1)$$

The average grain size was calculated using Debby- Scherer equation (1). It was found out to be 62nm. The obtained spectrographs confirm the polycrystalline nature of the thin films.

UV-ANALYSIS

Ultraviolet-visible absorption spectroscopy is used to study the attenuation of the light beam after it passes through the material or after the reflection from the surface of material. UV-visible includes transmittance, absorption and reflection measurements. From the UV-graphs, the band gap was calculated by drawing a tangent tp the curve which cut X-axis. The point on the X axis at which the tangent intersect gives the band gap. The band gap was found out to be 3.2eV which is in close agreement with the actual value that is 3.3eV.

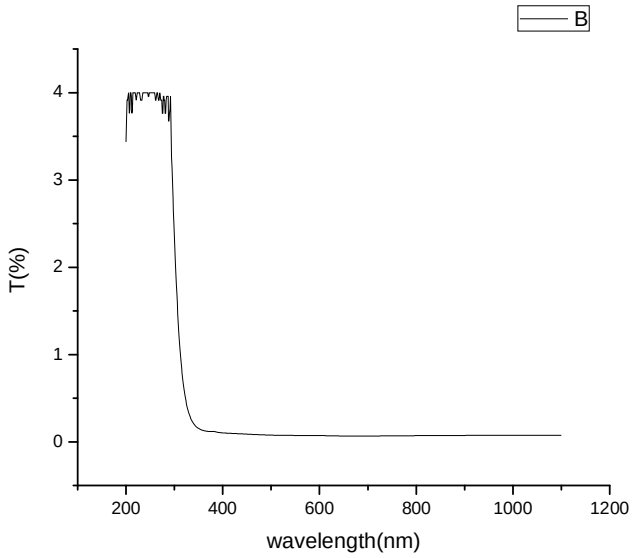


Fig.14 the above diagram shows the UV-spectrograph of 0.6 M concentration of Zinc Acetate Dihydrate.

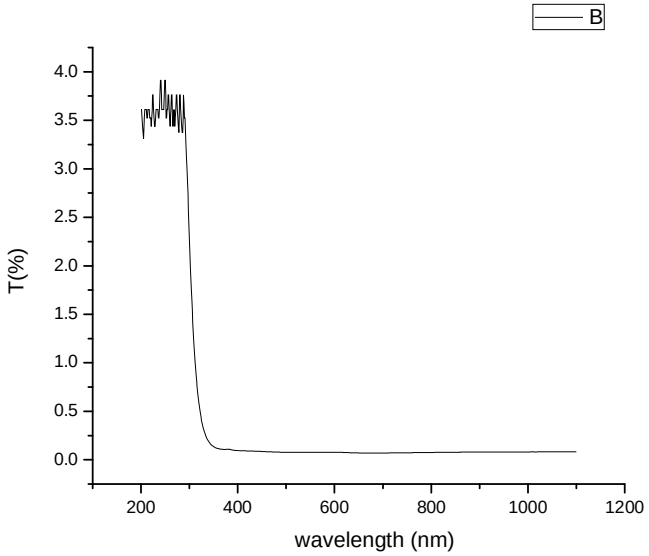


Fig.15. The above diagram shows the UV-spectrograph of 0.4 M concentration of Zinc Acetate Dihydrate.

Transmission spectra of ZnO sample

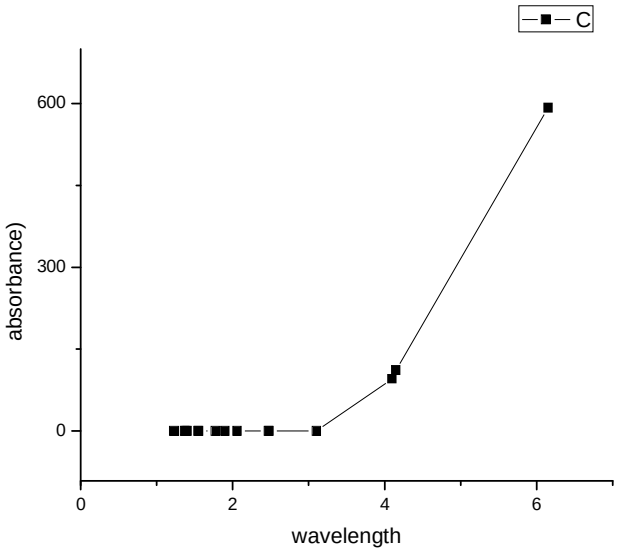


Fig.16 the above diagram shows the UV-spectrograph of 0.4M concentration of Zinc Acetate Dihydrate.

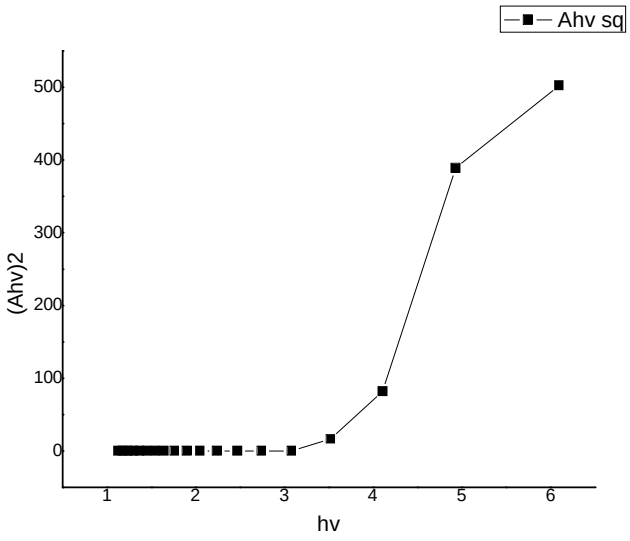


Fig.17 the above diagram shows the UV-spectrograph of 0.6 M concentration of Zinc Acetate Dihydrate.

CONCLUSION

ZnO is used for the deposition material which has a great applicability in rubber industry and has wide band gap of 3.3eV. ZnO is taken for the preparation of sol-gel by which thin film can be prepared. Spin coating method is used for the resulting thin film. Uniformity of layer plays an important role in the formation of thin film which can be achieved by using spin coating method. In the introductory part of the thesis, introduction of thin film, ZnO material, its chemical properties as well as physical properties, method of preparation of films, application of material and thin films, methods of measuring the thickness of these films has been discussed. The second gives the information about the literature survey related to the problem under consideration given by the various authors. In the next chapter, how the thin films are prepared and in last chapter experimental work was discussed.

References:-

[1] Thin films Fundamentals by A. Goswami (2005)

[2] www.brewerscience.com/uploads/equipment/datasheets/**spin**theory.pdf

[3] K. Seshan, Handbook of Thin Film Deposition Processes and Techniques, Norwich, N.Y. : Noyes Publications / William Andrew, Pub.(2002)

[4] www.asminternational.org

[5] Zhong Lin Wang, Zinc oxide nanostructures: growth, properties and applications, Journal of Physics: Condensed Matter. Vol. 16 (2004) p.829- 858

[6] Principle of Inorganic Chemistry by Puri,Sharma andKalia, p. 259-260.

[7] T. K. Subramanyam, B. Srinivasulu Naidu, S. Uthanna, Structure and Optical Properties of DC Reactive Magnetron Sputtered Zinc Oxide Films. Cryst. Res. Technol. Vol. 34 (1999)p. 981–988

[8] Espitia, P.J.P.; Soares, N.F.F.; Coimbra, J.S.R.; de Andrade, N.J.; Cruz, R.S.; Medeiros, E.A.A. Zinc oxide nanoparticles: Synthesis, antimicrobial activity and food packaging applications. Food Bioprocess Technol. Vol. 5(2012)p.1447–1464.

[9] V.Musat, B. Teixeira , E. Fortunato ,R.C.C. Monterio , P.Vilarinho "Al-doped ZnO thin films by sol-gel method"Surface and Coatings Technology, Vol. 180 –181 (2004)p.659–662

[10] M.Khaleeq-ur- Rahman et al."Deposition of zinc oxide thin film on calcite($CaCO_3$),Journal of Optoelectronics and Biomedical Materials, Vol. 6, Issue 2, (2014), p. 35 - 40

[11] S. ILICAN*, Y. CAGLAR, M. CAGLAR,Preparation and characterization of ZnO thin films deposited by sol-gel spin coating method, JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS Vol. 10, No. 10, (2008)p. 2578 - 2583

[12] J. Pattar et.al. 1 Structural Optical and Electrical Properties of VacuumEvaporated Indium Doped Zinc Telluride Thin Films JayadevInt. J. Electrochem. Sci., 4 (2009) 369 - 376.

[13] Young Hwan Hwang, Seok-Jun Seo,andByeong-SooBae "Fabrication and characterization of sol-gel-derived zinc oxide thin film transistor" ,Vol.25, no.4(2010)p.695

[14] ZiaulRazaKhan,MohdShoeb Khan, Mohammad Zulfequar, MohdShahid Khan, Optical and Structural Properties of ZnO Thin Films Fabricated by Sol-Gel MethodMaterials Sciences and Applications, Vol. 2(2011)p.340-345

.

[15] A .Gadhari et al. “Thickness dependence of the structural and electrical properties of ZnO thermal-evaporated thin films” PRAMANA-Journal of Physics, Vol. 77, No. 6 (2011)p. 1171–1178

[16] M. Sathya, A. Claude, P. Govindasamy and K. Sudha “Growth of pure and doped ZnO thin films for solar cell applications”Advances in Applied Science Research, Vol.3(5)(2012)p.2591-2598

[17] I.Nkrumah et al. “SYNTHESIS AND CHARACTERIZATION OF ZNO THIN FILMS DEPOSITED BY CHEMICAL BATH TECHNIQUE”.Vol2 (2013) p.809

[18] S.Agarwal, R.Rane, and S.Mukherjee “ZnO Thin film Deposition for TCO Application in Solar Cell” Volume 2013 (2013), p.1-4

[19] AchourRahal, Said Benramache and BoubakerBenhaoua “Substrate Temperature Effect on Optical property ofZnO Thin Films” Vol.18(2013) p.81.

[20] KantaRathee,B P Malik, “Synthesis and Characterisation of Ta_2O_5Thin Films For Microelectronics Application” Vol.3,Issue 6(2013) p.486

[21] M. Khaleeq-ur-Rahman, A. Sattar, M. S. Rafique and A. Usman“CHARACTERIZATION OF ZINC OXIDE (ZnO) THIN FILM COATED BY THERMAL EVAPORATION TECHNIQUE” Pak. J. Engg. & Appl. Sci. Vol. 2 (2008) p.88.

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