

# **CHARACTERIZATION AND STUDIES OF METAL SULPHIDE THIN FILMS IN SOL-GEL MATRIX PREPARED BY SPIN COATING TECHNIQUE**

A minor research project report  
Submitted to the  
**UNIVERSITY GRANTS COMMISSION**



By  
**Prof. Rosmin John**



**Assistant Professor**  
**Department of Physics**  
**St. Aloysius College , Edathua**

**MRP(S)-0795/13-14/KLMG019/UGC-SWRO**

## **ACKNOWLEDGMENT**

*I would like to thank God Almighty for his abundant blessings throughout my project work.*

*I acknowledge with thanks the support in the form of financial assistance from **University Grants Commission, New Delhi** for sanctioning the project.*

*It is with pleasure that I express my sincere gratitude to the Supervisor of this project **Dr. Jochen Joseph** for his valuable guidance and to the co-investigator **Prof. Lizymol Xavier** for her keen interest throughout the progress of the work .*

*I express my sincere gratitude to all faculties of Dept.of physics, **St.Aloysius College Edathua** for their constant encouragement and support.*

*I am thankful to **Mahatma Gandhi University, Kottayam, Cochin University of Science And Technology , Kochi and St.Berchmans Collge , Changanacherry** for providing some of the experimental facilities.*

Prof. Rosmin John

# **CONTENTS**

## **CHAPTER 1**

### **GENERAL INTRODUCTION**

- 1.1 THIN FILM
- 1.2 SOL-GEL MATRIX
- 1.3 ZINC SULPHIDE
- 1.4 CADMIUM SULPHIDE

## **CHAPTER 2**

### **FILM DEPOSITON**

- 2.1 THIN FILM DEPOSITION TECHNIQUES
  - 2.1.1 Chemical Deposition
  - 2.1.2 Physical Deposition
- 2.2 COATING PROCESS USED
  - 2.2.1 Dip coating method

## **CHAPTER 3**

### **PREPARATION&CHARACTERIZATION TECHNIQUES**

- 3.1 PREPARATION OF ZnS THIN FILM
- 3.2 PREPARATION OF CdS THIN FILM
- 3.3 CHARACTERIZATION TECHNIQUES USED
  - 3.3.1 UV-VISIBLE spectroscopy
  - 3.3.2 Determination of band gap energy
  - 3.3.3 X-Ray diffraction Analysis
  - 3.3.4 Photoluminescence spectroscopy
  - 3.3.4 Fourier Transform Infra-Red spectroscopy

### 3.3.5 Thin Film Thickness- Air wedge Method

## **CHAPTER 4**

### **RESULTS AND DISCUSSION**

#### 4.1 CHARACTERISATION OF ZnS THIN FILM

##### 4.1.1 XRD Analysis

##### 4.1.2 FTIR Studies

#### 4.2 CHARACTERISATION OF CdS THIN FILM

##### 4.2.1 UV-VISIBLE studies of thin films

##### 4.2.2 Optical Band gap study

##### 4.2.3 FTIR Characterization of thin films

##### 4.2.4 PL analysis of Thin Film

##### 4.2.5 Thin Film Thickness- Air Wedge Method

## **CHAPTER 5**

### **SUMMARY AND CONCLUSION**

### **REFERENCE**

# CHAPTER 1

## GENERAL INTRODUCTION

### 1.1 Thin Film

Thin films are thin material layers ranging from fractions of a nanometer to several micrometers in thickness. Electronic semiconductor devices and optical coatings are the main applications benefiting from thin film construction. So a thin film is defined as a low dimensional material created by condensing, one by one, atomic/molecular/ionic species of matter. The thickness is typically less than several microns. Thin - less than about one micron (10,000 Å, 1000 nm) Film - layer of material on surface. If no substrate it is foil.

Thin film materials are the key elements of continued technological advances made in the fields of optoelectronic, photonic, and magnetic devices. The processing of materials into thin films allows easy integration into various types of devices. The properties of material significantly differ when analyzed in the form of thin films. Most of the functional materials are rather applied in thin film form due to their specific electrical, magnetic, optical properties or wear resistance. Thin film technologies make use of the fact that the properties can particularly be controlled by the thickness parameter.

#### 1.1.1 Properties of Thin Film

The properties of a thin film may be different from those of the bulk particularly, if the thin film thickness is very small. These 'anomalous' properties are due to the peculiar structure of the film. More generally, thin films are prepared by depositing the film material atom by atom on a substrate.

#### Optical Properties

The optical properties of the thin films show profound sensitivity on the film microstructure. Since various deposition parameters affect the microstructure, the optical properties strongly depend on the deposition conditions. Also the optical properties change due to annealing of the films.

The optical constants of metal thin films show marked thickness dependence. Nearly dielectric behavior is exhibited by ultra-thin discontinuous metal films. A change to metallic behavior takes place when the film becomes physically continuous and electrically conducting with increasing thickness.

A typical absorption curve for bulk metal consists of absorption peaks corresponding to the inter band electronic transitions, superimposed on the absorption by the conduction electrons. The absorption in a film can be expressed as

$$\text{Absorption} = n_0(1-R-T)/T$$

$n_0$  = refractive index of substrate

R = reflectance of the film at normal incidence

T = transmission of the film at normal incidence

### Electrical Properties

The film thickness, the lattice dimensions, the purity, the surface roughness, and imperfect level on the layer are most significant parameters that define the type, mechanism and the stability of electrical transport. Electrical conductivity of a granular film is many orders of magnitude smaller than that of the bulk material and is generally characterized by the negative temperature coefficient of resistivity [TCR]. The conductivity is found to vary exponentially with the inverse of temperature, suggesting that the conduction mechanism is thermally activated. It is linear at low applied fields, but nonlinear at high fields.

A large separation [ $d > 100 \text{ \AA}$ ]. Calculation shows that thermionic and Schottky emission predominate only for particles with  $d = 20$  to  $50 \text{ \AA}$  and with typical metal work function 4 to 5 eV, tunneling is the dominant mechanism of electron transport unless the temperature is higher than  $300 \text{ K}$ . Thermionic emission depends exponentially on the height of the barrier, which may decrease significantly because of the overlap of the image-force potentials, thus giving rise to higher conductivity. Based on this theory the conductivity

$$S = (ArT/k) \exp\left(\frac{-\phi - Be^2/d}{kT}\right)$$

Ar = a constant characteristic of each film

T = Temperature

k = Boltzmann constant

e = electric charge

d = distance between particles

$\phi$  = the bulk work function of the metal

The term  $(Be^2/d)$  represents the contribution of the image forces. If 'd' is sufficiently small, the effective work function.

Thus, Schottky emission leads to an  $\exp(-1/T)$  dependence of the conductivity, an ohmic behaviour at low fields, and an  $\exp$  independence at high fields.

## **Mechanical Properties**

Thin films are solids, however, they are peculiar in several respects. The most important peculiarities are: - geometry (thin film), - structure, - stresses, - film edges, flaws and other defects. Usually, the film is formed by deposition of a certain material on top of a different one. The body coated by the film is called substrate. In particular we call a film thin if this restricted dimension has an effect on the properties of this film. Examples for such thickness effects are - a thickness dependent electrical conductivity due to scattering of charge carriers at film surface and film-substrate interface, optical interference effects, a dependence of the mechanical behaviour of the film on the mechanical properties of the substrate. This is usually the case for a film thickness  $< 1 \mu\text{m}$ , the thinnest films which are intentionally formed are as thin as about 1 nm. Considering this, thickness of a thin film is both  $\ll$  its lateral extension and  $\ll$  substrate thickness.

### **1.1.2 Applications of Thin film**

Electronic semi-conductor devices and optical coatings are the main applications benefiting from thin film construction. A familiar application of thin films is the household glass to form a reflective interface. Thin film science has now tremendous applications in military science and space science. The greatest stimulus has been from the micro-electronics industries. Thin films have also found extensive applications as discrete passive components, in fixed resistors, capacitors etc. Devices or components that are made from thin film have advantage over those made from bulk materials, because of,

- Low cost of production
- High reliability
- Superior performance
- Extreme compactness
- Reduction in size and weights
- Low power consumption etc.

We can list the applications of thin film as follows;

- Optical devices;
  - Antireflection coatings
  - High reflecting mirrors
  - Monochromators
  - Interference filters
  - Solar energy absorbers
- Superconducting devices
- Memory storing
- Bolometers
- Highly sensitive volt meters

- Magnetometers
- Semiconductor rectifiers etc.

## 1.2 Sol-Gel Matrix

The sol-gel technique is one of the most promising tools in material science. The versatility of this method allows designing desired materials at low temperatures, alternatively to conventional methods for manufacturing glass and other products. Sol-gel produced oxides are used in numerous applications, such as coatings and thin films in electronic or optical components and devices. Sol-gel monoliths and coatings have been investigated as matrices for catalysts, optical filters or as biosensors in diagnostic applications. In addition to sensors development many investigations have been conducted on the use of sol- gel matrices for entrapment of laser dyes, proteins, enzymes, microbial cells and porous membranes. Sol-gel processes offers advantages such as low processing temperature with high homogeneity and purity of the material enabling preparation of hybrid materials and incorporation of drug substances or even cells.

### 1.2.1 Sol –Gel Process.

Generally, it is a process concerning transition of a system of Metal alkoxides from liquid ‘sol’ (the colloidal suspension of particles) into solid ‘gel’ .There are three steps for sol-gel processing; the first method is gelation of colloidal particles, the second is the hydrolysis and poly condensation reactions of alkoxide precursor followed by hypercritical drying, while the third method is similar to the second one: the only difference is in the drying process, which takes place at ambient temperatures. Metal alkoxides are very famous precursors; as soon as they are exposed to water they are hydrolyzed. The partially hydrolyzed alkoxide molecules react with each other or with the un-hydrolyzed ones to undergo a condensation reaction and form a cross-linked matrix liberating water or alcohol.

In materials science, the **sol-gel** process is a method for producing solid materials from small molecules. The method is used for the fabrication of metal oxides, especially the oxides of silicon and titanium. The process involves conversion of monomers into a colloidal solution (sol) that acts as the precursor for an integrated network(or gel) of either discrete particles or network polymers. Typical precursors are metal alkoxides.In this chemical procedure, the ‘sol’ (or solution) gradually evolves towards the formation of a gel-like diphasic system containing both a liquid phase and solid phase whose morphologies range from discrete particles to continuous polymer networks. In the case of the colloid,the volume fraction of particles maybe so low that a significant amount of fluid may need to be removed initially for the gel-like properties to be recognized.

This can be accomplished in any number of ways. The simplest method is to allow time for sedimentation to occur, and then pour off the remaining liquid. Centrifugation can also be used to accelerate the process of phase separation.Removal of the remaining liquid (solvent) phase requires a drying process, which is typically accompanied by a significant amount of shrinkage and densification. The rate at which the solvent can be removed is ultimately determined by the distribution of porosity in the gel.The ultimate microstructure of the final component will clearly be strongly influenced by changes imposed upon the structural template during this phase of processing.

Afterwards, a thermal treatment, is often necessary in order to favor further poly condensation and enhance mechanical properties and structural stability via final sintering, densification and grain growth. The sol-gel process involves many stages to completion Initially a precursor solution is formed from all the components required for the film in the form of soluble precursor compounds Mixing can be considered to be at the molecular level at this stage. This precursor then undergoes hydrolysis, condensation and gelation between the homogenous or molecular phase and the heterogeneous or polymeric phase. Between these two, a transition state exists which can be described as a colloidal state. The molecular and colloidal states are defined as the 'sol' state. The polymerized multiphase state is defined as the 'gel' state The transition from sol to gel can be achieved in three different ways

- (1) Growth of polymeric molecules which crosslink randomly to form a three-dimensional network
- (2) Growth of individual particles, which grow together as they become larger
- (3) The stabilization of colloids by surface charges by a change of the zeta potential followed by an interparticular condensation, which leads to gelation

Due to the large number of parameters numerous reaction paths exist The main influencing parameters are:

- (1) Precursor choice
- (2) Reaction conditions= which include pH solvents catalysts and temperature considerations, and
- (3) Mechanical parameters

### **1.2.2 Sol Gel Matrix - Advantages**

1. Its reaction can be controlled easily by chemical methods.
2. It allows introducing a permanent organic group to form inorganic –organic hybrid materials
3. The process takes place at low temperature
4. The matrix is chemically inert and low poisoning
5. It has excellent optical low intrinsic fluorescence
6. The process provides good flexibility during polymerization steps
7. Ability to be functionalized before or after polymerization
8. The major advantages of sol gel matrix is in formation of thin films of extremely small layer heights in the nanometer range. These thin layers are produced by spin coating or dip coating methods.

### **1.2.3 Sol-Gel Matrix –Disadvantages**

1. Long processing time
2. Large shrinkage during process
3. At high pH value Si-O-Si bond is breaking

## **1.3 Zinc Sulphide**

Zinc sulfide is an inorganic compound with the chemical formula of ZnS. This is the main form of zinc found in nature, where it mainly occurs as the mineral sphalerite. Although this mineral is usually black because of various impurities, the pure material is white, and it is widely used as a pigment. In its dense synthetic form, zinc sulfide can be transparent, and it is used as a window

for visible optics and infrared optics. ZnS films are suitable for use as the buffer layer of the Cu(In, Ga)Se<sub>2</sub> solar cells.

### **Structure**

ZnS exists in two main crystalline forms, and this dualism is often a salient example of polymorphism. In each form, the coordination geometry at Zn and S is tetrahedral. The more stable cubic form is known also as zinc blend or sphalerite. The hexagonal form is known as the mineral wurtzite, although it also can be produced synthetically.

### **Applications of ZnS**

#### **a) Luminescent material**

Zinc sulfide, with addition of few ppm of suitable activator, is used as phosphor in many applications, from cathode ray tubes through X-ray screens to glow in the dark products. When silver is used as activator, the resulting color is bright blue, with maximum at 450 nanometers. Using manganese yields an orange-red color at around 590 nano meters. Copper gives long-time glow, and it has the familiar greenish glow-in-the-dark. Copper-doped zinc sulfide ("ZnS plus Cu") is used also in electroluminescent panels. It also exhibits phosphorescence due to impurities on illumination with blue or ultraviolet light.

#### **b) Optical materials**

Zinc sulfide is also used as an infrared optical material, transmitting from visible wavelengths to just over 12micrometers. It can be used planar as an optical window or shaped into a lens. It is made as microcrystalline sheets by the synthesis from hydrogen sulfide gas and zinc vapour, and this is sold as FLIR-grade (Forward Looking IR), where the zinc sulfide is in a milky-yellow, opaque form. This material when hot isostatically pressed can be converted to a water-clear form known as Cleartran (trademark). Early commercial forms were marketed as Irtran-2 but this designation is now obsolete

## **1.4 Cadmium Sulphide**

Cadmium sulphide is a semiconductor material used as optical window jointed with the active cadmium telluride(CdTe)semiconductor for thin film solar cell fabrication. The chemical bath deposition technique used to prepare CdS films, normally requires agitation to uniform the chemical bath since the formation of colloids and precipitates affects the film surface quality jointed with the composition and the temperature of the chemical bath. Cadmium Sulfide is also used in the production of solar cells where it is used as a buffer layer in the manufacture of CIGS (Copper -Indium-Gallium-Selenide) solar cells. With an increasing interest and uptake of solar cells, this application for cadmium sulfide could also increase.

Cadmium sulphide thinfilm is a direct semiconducting material with a fundamental band gap of 2.42 eV and has been used as a window material in heterojunction solar cells together with several narrow bandgap semiconductors like CuS<sub>2</sub>S, InP, CuInSe<sub>2</sub>, CdTe etc. CdS is one of the important material for application in electro-optical devices such as laser materials, Transducers, photoconducting cells ,photosensors , optical waveguides and nonlinear integrated optical devices.They are also used in the manufacture of light dependent resistors/photoresistors for light sensors.

## Structure and physical properties

Cadmium sulfide has, like zinc sulfide, two crystal forms. The more stable hexagonal wurtzite structure (found in the mineral Greenockite) and the cubic zinc blende structure (found in the mineral Hawleyite). In both of these forms the cadmium and sulfur atoms are four coordinate. There is also a high pressure form with the NaCl rock salt structure. Cadmium sulfide is a direct band gap semiconductor (gap 2.42 eV). The magnitude of its band gap means that it appears coloured. As well as this obvious property other properties result:

- the conductivity increases when irradiated, (leading to uses as a photoresistor)
- when combined with a p-type semiconductor it forms the core component of a photovoltaic (solar) cell and a CdS/Cu<sub>2</sub>S solar cell was one of the first efficient cells to be reported
- when doped with for example Cu<sup>+</sup> ("activator") and Al<sup>3+</sup> ("coactivator") CdS luminesces under electron beam excitation (cathodoluminescence) and is used as phosphor<sup>[23]</sup>
- both polymorphs are piezoelectric and the hexagonal is also pyroelectric<sup>[24]</sup>
- electroluminescence
- CdS crystal can act as a solid state laser
- In thin-film form, CdS can be combined with other layers for use in certain types of solar cells.
- Thin films of CdS can be piezoelectric and have been used as transducers which can operate at frequencies in the GHz region.
- Nanoribbons of CdS show a net cooling due annihilation of phonons, during anti-Stokes luminescence at ~510 nm. As a result, a maximum temperature drop of 40 and 15 K has been demonstrated when the nanoribbons are pumped with a 514 or 532 nm laser.

# CHAPTER 2

## THIN FILM DEPOSITION

This chapter explains various deposition techniques used for thin film production.

### 2.1 Thin Film Deposition Techniques

The act of applying a thin film to a surface is thin-film deposition – any technique for depositing a thin film of material onto a substrate or onto previously deposited layers. "Thin" is a relative term, but most deposition techniques control layer thickness within a few tens of nanometers.

Deposition techniques fall into two broad categories, depending on whether the process is primarily chemical or physical.

#### 2.1.1 Chemical Deposition

Here, a fluid precursor undergoes a chemical change at a solid surface, leaving a solid layer. An everyday example is the formation of soot on a cool object when it is placed inside a flame. Since the fluid surrounds the solid object, deposition happens on every surface, with little regard to direction; thin films from chemical deposition techniques tend to be conformal, rather than directional.

Chemical deposition is further categorized by the phase of the precursor:

- Plating relies on liquid precursors, often a solution of water with a salt of the metal to be deposited. Some plating processes are driven entirely by reagents in the solution, but by far the most commercially important process is electroplating
- Chemical solution deposition (CSD) or Chemical bath deposition (CBD) uses a liquid precursor, usually a solution of organometallic powders dissolved in an organic solvent. This is a relatively inexpensive, simple thin film process that is able to produce stoichiometrically accurate crystalline phases. This technique is also known as the sol-gel method because the 'sol' (or solution) gradually evolves towards the formation of a gel-like diphasic system.
- Spin coating or spin casting, uses a liquid precursor, or sol-gel precursor deposited onto a smooth, flat substrate which is subsequently spun at a high velocity to centrifugally spread the solution over the substrate.
- Chemical vapor deposition (CVD) generally uses a gas-phase precursor, often a halide or hydride of the element to be deposited. In the case of MOCVD, an organometallic gas is used. Commercial techniques often use very low pressures of precursor gas

- Plasma enhanced CVD (PECVD) uses an ionized vapor, or plasma, as a precursor. Unlike the soot example above, commercial PECVD relies on electromagnetic means (electric current, microwave excitation), rather than a chemical reaction, to produce a plasma.
- Atomic layer deposition (ALD) uses gaseous precursor to deposit conformal thin films one layer at a time. The process is split up into two half reactions, run in sequence and repeated for each layer, in order to ensure total layer saturation before beginning the next layer. Therefore, one reactant is deposited first, and then the second reactant is deposited, during which a chemical reaction occurs on the substrate, forming the desired composition. As a result of the stepwise, the process is slower than CVD; however it can be run at low temperatures, unlike CVD.

### 2.1.2 Physical Deposition

Physical deposition uses mechanical, electromechanical or thermodynamic means to produce a thin film of solid. An everyday example is the formation of frost. Since most engineering materials are held together by relatively high energies, and chemical reactions are not used to store these energies. Commercial physical deposition systems tend to require a low-pressure vapor environment to function properly; most can be classified as physical vapor deposition (PVD). The material to be deposited is placed in an energetic, entropic environment, so that particles of material escape its surface. Facing this source is a cooler surface which draws energy from these particles as they arrive, allowing them to form a solid layer. The whole system is kept in a vacuum deposition chamber, to allow the particles to travel as freely as possible.

Examples of physical deposition include:

- A thermal evaporator :Uses an electric resistance heater to melt the material and raise its vapor pressure to a useful range. This is done in a high vacuum, both to allow the vapor to reach the substrate without reacting with or scattering against other gas-phase atoms in the chamber, and reduce the incorporation of impurities from the residual gas in the vacuum chamber. Obviously, only materials with a much higher vapor pressure than the heating element can be deposited without contamination of the film.
- An electron beam evaporator: Fires a high-energy beam from an electron gun to boil a small spot of material; since the heating is not uniform, lower vapor pressure materials can be deposited. The beam is usually bent through an angle of  $270^\circ$  in order to ensure that the gun filament is not directly exposed to the evaporant flux. Typical deposition rates for electron beam evaporation range from 1 to 10 nanometers per second.
- In molecular beam epitaxy (MBE), slow streams of an element can be directed at the substrate, so that material deposits one atomic layer at a time. Compounds such as gallium arsenide are usually deposited by repeatedly applying a layer of one element (i.e., gallium), then a layer of the other (i.e., arsenic), so that the process is chemical, as well as physical.
- Sputter Deposition: Relies on a plasma (usually a noble gas, such as argon) to knock material from a "target" a few atoms at a time. The target can be kept at a relatively low temperature, since the process is not one of evaporation, making this one of the most flexible deposition techniques. It is especially useful for compounds or mixtures, where

different components would otherwise tend to evaporate at different rates. Pulsed laser deposition systems work by an ablation process. Pulses of focused laser light vaporize the surface of the target material and convert it to plasma; this plasma usually reverts to a gas before it reaches the substrate.

- Cathodic arc deposition (arc-PVD): Which is a kind of ion beam deposition where an electrical arc is created that literally blasts ions from the cathode. The arc has an extremely high power density resulting in a high level of ionization (30–100%), multiply charged ions, neutral particles, clusters and macro-particles (droplets). If a reactive gas is introduced during the evaporation process, dissociation, ionization and excitation can occur during interaction with the ion flux and a compound film will be deposited.
- Electro hydrodynamic deposition (electro spray deposition): Is a relatively new process of thin film deposition. The liquid to be deposited, is fed to a small capillary nozzle (usually metallic) which is connected to a high voltage. The substrate on which the film has to be deposited is connected to ground. Through the influence of electric field, the liquid coming out of the nozzle takes a conical shape (Taylor cone) and at the apex of the cone a thin jet emanates which disintegrates into very fine and small positively charged droplets under the influence of Rayleigh charge limit. The droplets keep getting smaller and smaller and ultimately get deposited on the substrate as a uniform thin layer.

## **2.2 Coating Process Used**

Out of different Thin film coating methods , I have used dip coating method for producing ZnS and CdS thin films in sol-gel matrix.

### **2.2.1 Dip Coating Method**

Dip Coaters are robust computer-controlled instruments for precise thin film deposition. They provide solutions for dip coating of small to large samples in either single or multiple vessels that are suitable for both simple and complex vessel sequencing. Parts to be coated should be cleaned to remove contaminants . This results in superior primer adhesion as well as improved corrosion resistance. If adhesion to the part is desired, application of a primer is required on all sections where polymer coating will be applied. The primed part is flash dried and baked to set the primer and ready the part for the hot dipping operation. The primed part, hot from the primer conversion bake, is immersed in the liquid material. All hot parts of the product immersed in the liquid polymer will coat upon withdrawal from the bath with a layer of semi-fused polymers. The amount deposited will depend on the length of time the part was immersed, the metal temperature that the part was immersed at, and the general formulation of the compound used. The higher the metal temperature and the longer the immersion time, the greater the polymer thickness. The part covered with the semi-fused polymer is baked to a temperature dependent upon the specific compound formula. This completes the fusion of the coating, and adhesion to the product. When the hot part coated with fused polymer comes out of the oven, it is very sensitive to surface marring. The part is cooled down before handling. The finished

coated product is then removed from the conveyors, inspected and readied for packing and shipment.

- **DIP COATING UNIT WITH HOT CHAMBER**



*Figure 2 DIP COATING UNIT  
WITH HOT CHAMBER*

### **Features and Benefits of Dip coating**

The Windows-based Dip Coating software enables easy programming of a dipping sequence into either single or multiple vessels. The dipping sequences can be stored in the computer for further use. Computer-controlled deposition features include setting the substrate resting positions, immersion speed, submersion period, withdrawal speed, drying period and number of dip cycles. Vibration free immersion and withdrawal. The dipping mechanism enables vibration-free immersion and withdrawal of samples into the liquid vessels for precise and uniform coatings.

- Dip coatings provide safe, durable and beautiful finishes. This process deposits a coat of your choice of material from natural latex, synthetic latex, or neoprene, or PVC/Plastisol adding a protective layer which enhances the handling, safety, and appearance of your product.
- Dip coating provides a protective shield that resists corrosion.
- Insulates against heat, cold, stress and electrical currents.
- Adaptable to high volume orders requiring fast delivery.
- Durable and UV resistant.
- Alternative colors and finishes (glossy and matt) can be created easily and economically.
- A wide range of thickness, textures, and durometers (hardness) are available.

- Dip Coating is sound damping and eliminates the need to debur base materials.

Hot dip coating is a great process for adding corrosion protection, increasing friction or grip, or simply adding aesthetics and protection to most any metal. Many types of polymers are available with many color choices, sheen, and texture. Dip coating of plastisol/PVC is a well-known method of applying a protective, decorative, or functional plastic vinyl coating to a variety of metal parts. It is much more cost effective to do a one step dip to coat a product. Applications for dip coating are extensive and include: Amusement Park Lap Bars, Bumpers, Seat Belt Tongues,

The following surface coatings can be created by dip coating method

- Sol-gel coatings
- Layer-by-layer assemblies
- Self-assembled minelayers



Here I used the dip coating unit in which, the substrate is dipped in the solution and then withdrawn in to a heating chamber. Temperature of the chamber can be controlled and fixed up to  $75^{\circ}\text{C}$  from ambient. The system has a user friendly front panel with key board and LCD display. Dip duration, dip speed, withdrawal speed etc. are programmable features. Servo motor is used as actuator for vibration free dipping and withdrawal. The device is designed and manufactured as table top device with entire electronics and servo motor housed in a compact unit. A number of substrate can be held to the holder at the same time. Height of the substrate holder can be adjusted with respect to the level of the solution during the experiment.

In present study I have used this dip coating method for the preparation of ZnS&CdS thin film for different normality in sol-gel matrix.

## CHAPTER 3

### PREPARATION&CHARACTERIZATION

#### TECHNIQUES

This chapter deals with the preparation method adopted for making ZnS and CdS thin films and the different characterization techniques used to identify and study its various properties.

#### **3.1 Synthesis of ZnS Thin Film**

The sol-gel dip coating method is a chemical deposition technique where a coating of the desired material is spread on to the substrate by dip coating technique. Prior to deposition the substrates were washed with soap solution, acetone and then kept in distilled water. Finally the substrates were ultrasonically cleaned for 30 minutes. After deposition, annealing of the samples was carried out for the removal of solvent and residual organics. The dip coating method was used to prepare ZnS thinfilms on the glass substrates using Zinc Acetate and sodium sulphide as precursor solutions. Annealing temperature is one of the parameters which influence the stiochiometry and structural properties of the films.

25ml of Zinc acetate and the 25ml of sodium sulphide solution is mixed and stirred for 1 hour at room temperature using a constant magnetic stirrer to get 50ml Zinc sulphide solution. 10ml ethanol and 20ml Tetra ethyl orthosilicate (TEOS) are mixed and stirred for half an hour at room temperature in a magnetic stirrer, to get 30ml sol gel matrix.

30ml solution of the sol gel matrix and 50ml of the Zinc sulphide solution is mixed together and stirred for 1 hour using the constant magnetic stirrer.

The solution is made to deposit on the cleaned glass plate using the Dip coating unit, with the hot chamber by fixing the program as follows:

Dip Speed :	1mm/s	Retrieval Speed :	1mm/s
Dip Duration :	3min	Dry Duration :	3min
No. of Dips :	10	Drying Temperature :	75°C

The samples prepared as mentioned above are annealed at 200<sup>0</sup> C, 300<sup>0</sup> C and 400<sup>0</sup> C for one hour. The thin films were analysed by X-Ray Diffraction , FTIR Spectroscopy ,interference method.

## 3.2 Synthesis Of CdS Thin Films for .1&.2m Normality

Materials used in the present synthesis were cadmium acetate as cadmium source, sodium sulphide ( $\text{Na}_2\text{S}$ ) as sulphur source, sol gel as capping and dispersing agent. Deposition of CdS thin films on glass plates were done by dip coating method. The steps involved in this methods are;

### 1) Preparation of Cadmium sulphide solution

0.1m and 0.2m Cadmium acetate and Sodium Sulphide solutions are prepared separately. 25ml of Cadmium acetate solution and 25ml of sodium sulphide solution are stirred separately for 30 minutes and then mixed together and stirred for 1 hour at room temperature using a constant magnetic stirrer. This step is done for both the molarities.

### 4) Preparation of sol gel matrix

10 ml ethanol and 20 ml TEOS solution is mixed and stirred for  $\frac{1}{2}$  an hour at room temperature ( $30^\circ\text{C}$ ) using a constant magnetic stirrer.

Above 30ml solution and 50 ml Cadmium sulphide solution are mixed together and stirred for 1 hour. Excess amount of solution is deposited on the glass plates using dip coater unit with hot chamber by fixing the programs as follows;

Dip speed - 1mm/s

Retrieval speed - 1 mm/s

Dip duration – 3 min

Dry duration - 4 min

No of dips – 10

Temperature -  $75^\circ\text{C}$

The samples are annealed at temperatures  $400^\circ\text{C}$  for 1 hour and then cooled slowly.

## 3.3 Characterization Techniques Used

Assessment of the structural, chemical and physical properties of the prepared thin film is an essential part of the study. This enables to decide on a suitable material for a specific application and device fabrication. Also, one can find ways to improve the required qualities of the material. This chapter presents a comprehensive description on the techniques that have been employed to characterize the prepared thinfilms in the present research work. The instrumentation used in each case is described briefly. Zinc sulphide & cadmium sulphide thin films were prepared using sol-gel method and characterized by photoluminescence spectroscopy, UV-visible spectroscopy and Fourier transform infrared spectroscopy (FT-IR). This group of techniques use a range of principles

to reveal the bandgap, composition variation, crystal structure and photo luminescent properties of materials.

### 3.3.1 UV-Visible Spectroscopy

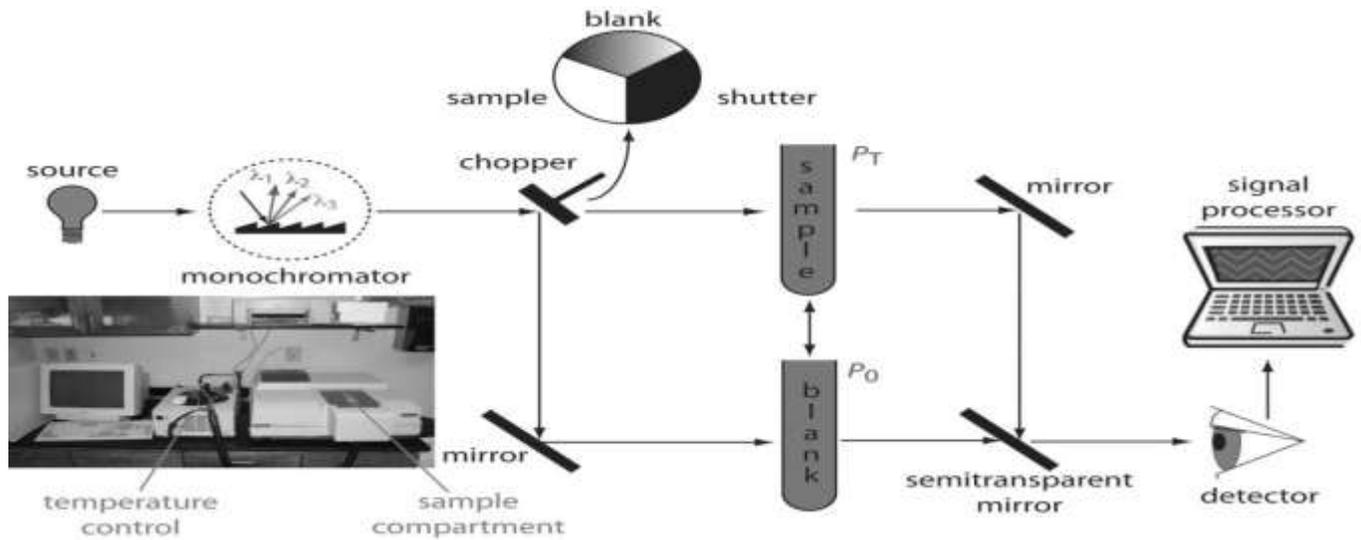
UV-Vis spectroscopy refers to absorption spectroscopy or reflectance spectroscopy in the ultraviolet - visible spectral region. UV-vis spectroscopy is based on the principle of electronic transition in atoms or molecules upon absorbing suitable energy from an incident light that allows electrons to excite from a lower energy state to higher excited energy state. While interaction with infrared light causes molecules to undergo vibrational transitions, the shorter wavelength with higher energy radiations in the UV (200-400 nm) and visible (400-700 nm) range of the electromagnetic spectrum causes many atoms/molecules to undergo electronic transitions.

The fraction of sunlight that can be absorbed is specific for each material and varies with its chemical structure. Band gap and molecular energy levels control are of crucial importance for device performance. The mismatch of the polymer absorption spectra and the solar irradiance spectrum is one of the reasons for low efficiencies of devices. Chemical modification of the semiconducting polymers structure is a common approach that leads to tuning of the band gaps. The alignment of the polymer on the film plays an important role in the solar cell device performance since it affects carrier mobility. The maximum absorption wavelength, of the polymer in the solid state is, in general, bathochromically shifted when compared to the solution spectra, due to major conformational order, resulting in different energy levels distribution. Another way to improve the absorption by reorganizing the intermolecular packing, therefore changing the properties of the material, is through the annealing process. The maximum absorption increases and broadens to a longer wavelength for corresponding transitions. This means that because the optical absorption corresponds to differences in energy states, it can be considered an indirect measure of the electronic structure. The optical band gap, expressed in electronvolts, depends on the incident photon wavelength by means of Planck's relation

$$E_{\text{opt}} = h\nu = hc/\lambda$$

Where  $h$  is the Planck constant,  $\nu$  is the wave frequency and  $c$  is the light speed in vacuum. Experimentally, the optical band gap of the polymer thin film is estimated by linear extrapolation from the absorption feature edge to and subsequent conversion of the wavelength (nm) into energy value versus vacuum (eV).

Since the absorption spectrum reveal information on electronic transition, the onset of absorption is considered as the band gap of semiconductor or conjugated polymers. Many also consider the peak of the absorption spectrum as the band gap. Generally, the color of a molecule in solution or film gives an indication of their band gap. The color of a film or solution that an observer perceives is usually the complementary wavelength of the electromagnetic spectrum that the molecule absorbs.



**Figure 3.1** the schematic diagram of a UV-Vis spectrometer

### 4.3.2 Determination of band gap energy

Optical absorption studies of the thin film are made by using UV-VIS-NIR (ultra violet-visible-near infrared) spectrometry. From the absorption spectra optical parameters like absorption co-efficient ( $\alpha$ ), optical band gap ( $E_g$ ) have been evaluated. The absorption co-efficient ( $\alpha$ ) was calculated from the equation

$$\alpha = 2.303(A/t)$$

where  $t$  is the thickness and it is measured by using air wedge arrangement.  $A$  is absorbance of the ZnS film. The direct optical band ( $E_g$ ) was determined by fitting absorption data to the equation

$\alpha h\nu = B (h\nu - E_g)^2$  for absorption coefficient  $\alpha = 10^4$  cm. The exponent  $n$  can take the values 2.3, 1/2, 3/2 for indirect allowed and direct forbidden transition respectively. Glass is an indirect band gap amorphous material, therefore the value of  $n=2$ . Then,

$$\alpha h\nu = B (h\nu - E_{opt})^2$$

$$(\alpha h\nu)^{1/2} = A(h\nu - E_{opt})$$

Where  $A$  is another constant,  $h\nu$  is the photon energy,  $B$  is the constant related to the material.  $E_g$  is found by extrapolating the straight line in the  $(\alpha h\nu)^{1/2}$  versus  $h\nu$  graph.

### 3.3.3 X - Ray Diffraction Analyses

X - ray diffraction is one of the important techniques for material characterization. The diffraction experiments using X - rays help to study the structural properties of materials on atomic scale. The technique is also used to measure crystallite size and to calculate lattice strain, chemical composition, state of ordering and to determine phase diagrams as well.

#### Principle

Crystals are regular arrays of atoms, and X-rays can be considered waves of electromagnetic radiation. Atoms scatter X-ray waves, primarily through the atoms' electrons. Just as an ocean wave striking a lighthouse produces secondary circular waves emanating from the lighthouse, so an X-ray striking an electron produces secondary spherical waves emanating from the electron. This phenomenon is known as elastic scattering, and the electron (or lighthouse) is known as the *scatterer*. A regular array of scatterers produces a regular array of spherical waves. Although these waves cancel one another out in most directions through destructive interference, they add constructively in a few specific directions, determined by Bragg's law:

$$n\lambda = 2d \sin\theta$$

Here  $d$  is the spacing between diffracting planes,  $\theta$  is the incident angle,  $n$  is any integer, and  $\lambda$  is the wavelength of the beam. These specific directions appear as spots on the diffraction pattern called *reflections*. Thus, X-ray diffraction results from an electromagnetic wave (the X-ray) impinging on a regular array of scatterers (the repeating arrangement of atoms within the crystal).

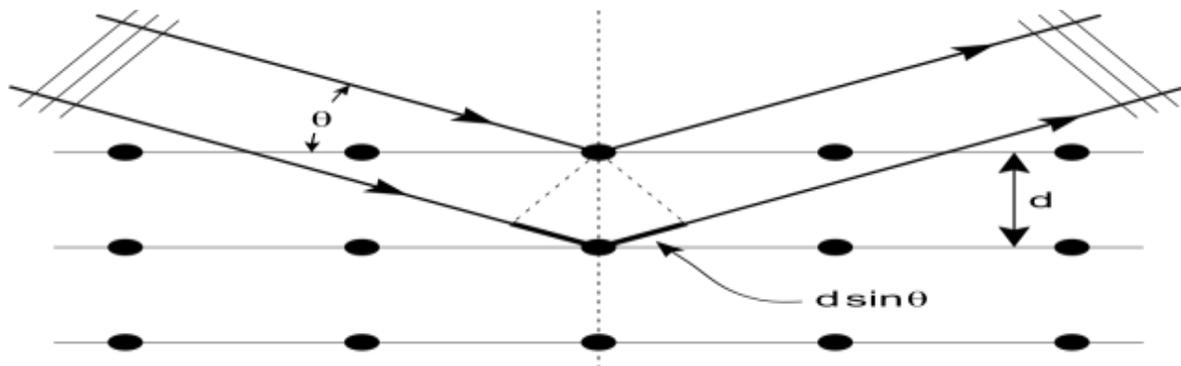


Fig 3.2 X-Ray Diffraction

The incoming beam (coming from upper left) causes each scatterer to re-radiate a small portion of its intensity as a spherical wave. If scatterers are arranged symmetrically with a separation  $d$ , these spherical waves will be in sync (add constructively) only in directions where their path-length difference  $2d \sin \theta$  equals an integer multiple of the wavelength  $\lambda$ . In that case, part of the incoming beam is deflected by an angle  $2\theta$ , producing a *reflection* spot in the diffraction pattern.

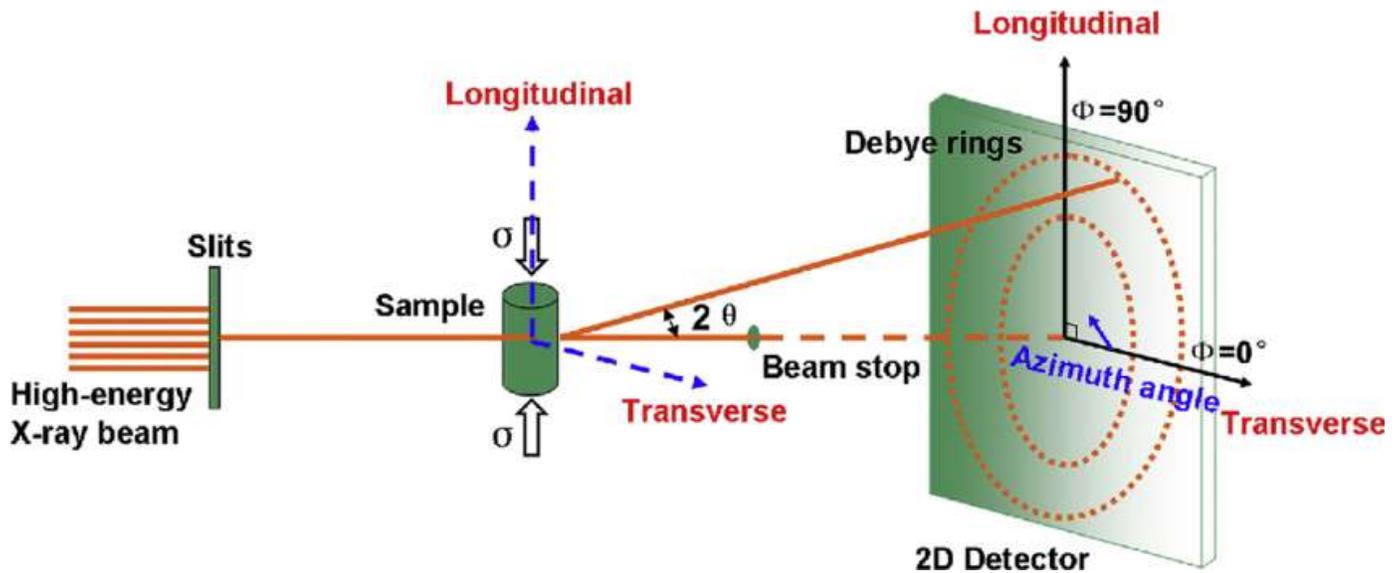


Fig.3.3 Schematic diagram of X-Ray Diffractometer

### 3.3.4 Photoluminescence Spectroscopy

Photoluminescence (PL) spectroscopy is a contactless, nondestructive method to probe the electronic structure of materials. Its capabilities include: various excitation wavelengths that allow for varying levels of volume excitation; a detection range extending from 0.4 to 2.7  $\mu\text{m}$ ; sample temperatures of 4 to 300 K; and mapping capabilities with 1- to 2- $\mu\text{m}$  spatial resolution on the Fourier-transform-based system. The intensity and spectral content of the emitted photoluminescence is a direct measure of various important material properties, including:

#### 1. Bandgap Determination:

The spectral distribution of PL from a semiconductor can be analyzed to nondestructively determine the electronic bandgap. This provides a means to quantify the elemental composition of compound semiconductor and is a vitally important material parameter influencing solar cell device efficiency.

#### 2. Impurity Levels and Defect Detection:

The PL spectrum at low sample temperatures often reveals spectral peaks associated with impurities contained within the host material. The high sensitivity of this technique provides the potential to identify extremely low concentrations of intentional and unintentional impurities that can strongly affect material quality and device performance.

#### 3. Recombination Mechanisms:

The quantity of PL emitted from a material is directly related to the relative amount of radiative and nonradiative recombination rates. Nonradiative rates are typically associated with impurities

and thus, this technique can qualitatively monitor changes in material quality as a function of growth and processing conditions.

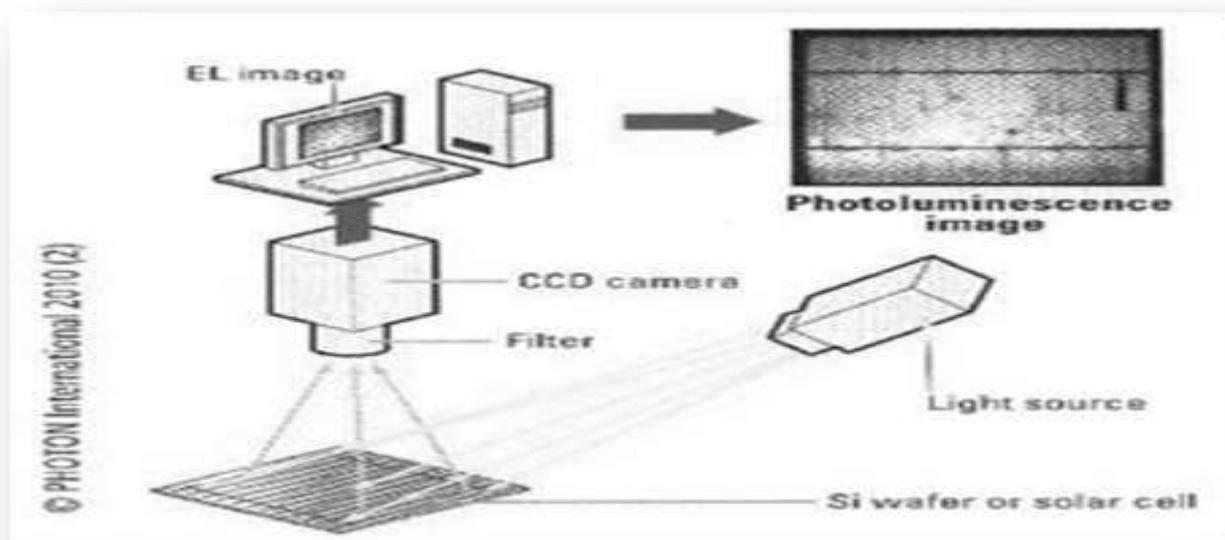


Fig: 3.4 schematics of photoluminescence

### 3.3.5 FT-IR Spectroscopy

Fourier Transform Infra-Red spectroscopy (FT-IR) has wide applicability in structure elucidation, which are either synthesized chemically or of natural origin. Now a day, Fourier Transform Infra-Red (FT-IR) Spectroscopy is extensively used for quantitative as well as for qualitative analysis in almost all fields of science. It has many advantages and applications as compared to dispersive infra-red technology.

FT-IR stands for Fourier Transform Infra-Red, the preferred method of infrared spectroscopy. In infrared spectroscopy, IR radiation is passed through a sample. Some of the infrared radiation is absorbed by the sample and some of it is passed through (transmitted). The resulting spectrum represents the molecular absorption and transmission, creating a molecular fingerprint of the sample.

- It can identify unknown materials
- It can determine the quality or consistency of a sample
- It can determine the amount of components in a mixture

An infrared spectrum represents fingerprint of a sample with absorption peaks which correspond to the frequencies of vibrations between the bonds of the atoms making up the

material. Because each different material is a unique combination of atoms, no two compounds produce the exact same infrared spectrum. Therefore, infrared spectroscopy can result in a positive identification of every different kind of material. In addition, the size of the peaks in the spectrum is a direct indication of the amount of material present. With modern software algorithms, infrared is an excellent tool for quantitative analysis

Experimental arrangement of FT-IR is shown in fig.3.5. The normal instrumental process is as follows:

**1. The Source:** Infrared energy is emitted from a glowing black-body source. This beam passes through an aperture which controls the amount of energy presented to the sample (and, ultimately, to the detector).

**2. The Interferometer:** The beam enters the interferometer where the “spectral encoding” takes place. The resulting interferogram signal then exits the interferometer.

**3. The Sample:** The beam enters the sample compartment where it is transmitted through or reflected off of the surface of the sample, depending on the type of analysis being accomplished. This is where specific frequencies of energy, which are uniquely characteristic of the sample, are absorbed.

**4. The Detector:** The beam finally passes to the detector for final measurement. The detectors used are specially designed to measure the special interferogram signal.

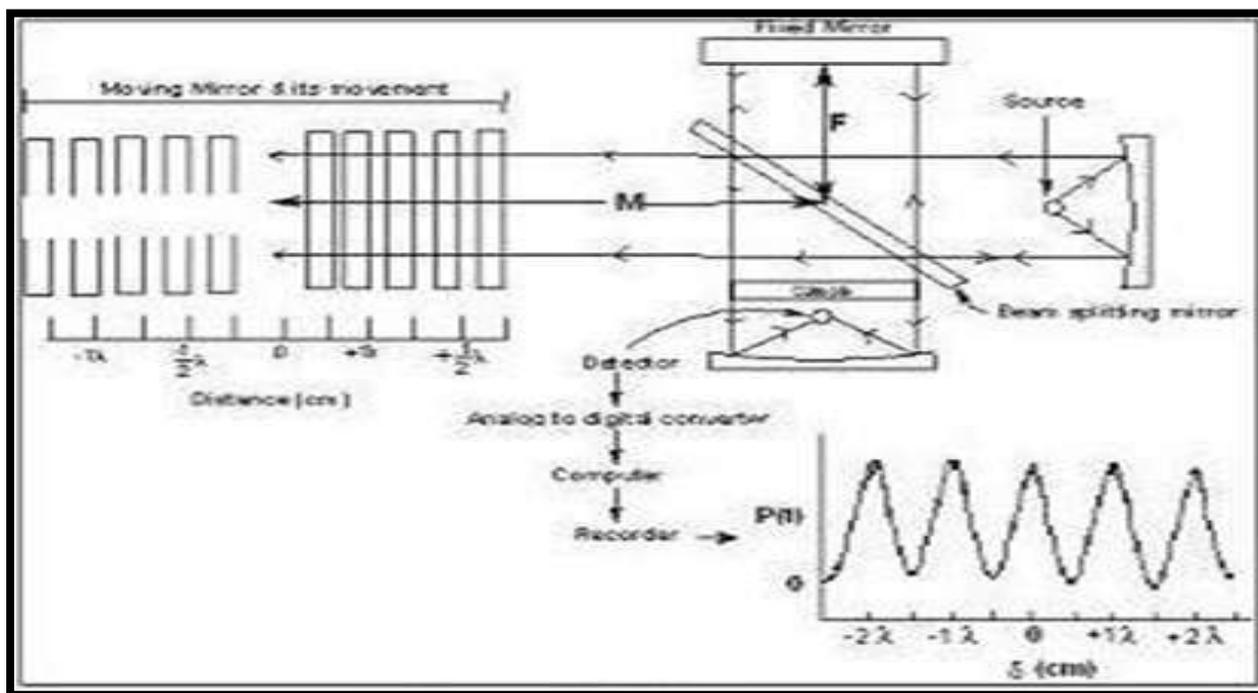


Fig. 3.5 FT-IR Instrumentation

**5. The Computer:** The measured signal is digitized and sent to the computer where the Fourier transformation takes place. The final infrared spectrum is then presented to the user for interpretation and any further manipulation.

FT-IR consists of a moving mirror, fixed mirror, beam splitter, IR radiation source and detector. Instead of using monochromator, Michelson interferometer is used for analysis of IR radiation after passing through sample. Radiation from IR source is collimated by mirror and the resultant beam is divided at beam splitter. Half of beam passes through mirror (fixed) and half refracted to moving mirror. After reflection by these two mirrors, two beams recombined at beam splitter and passes through cell and after that radiation is focused to detector. Movable mirror, moves back and forth at a distance of 21 cm. If round trip distance between beam splitter and fixed mirror is identical to that of beam splitter and movable mirror, then only the radiation from two mirrors arise in phase at beam splitter, cell and to detector. As the movable mirror changes its position, the distance between mirror and beam splitter no longer identical and radiation of fixed wavelength will arrive in phase only to cell and detector. So we have to add or subtracts whole number of multiple of wavelength of radiation in round trip distance between splitter and fixed mirror. If movable mirror moves by a factor  $\lambda/4$ , then round trip distance is altered by  $\lambda/2$  reflected radiation if out of phase with that from stationary mirror and interferes destructively while movable mirror moves by a factor  $\lambda/2$ , then round trip distance is altered by  $\lambda/2$  reflected radiation if in phase with that from stationary mirror and interferes constructively.

The radiation striking the detector, after passing through MI will be of lower frequency than source frequency. One cycle of the signal occurs when the mirror moves at a distance that corresponds to half of wavelength ( $\lambda/2$ ). If the mirror is moving at constant velocity and we define  $\tau$  as the time required for mirror to move distance of  $\lambda/2$ . As the distance changes, wavelength of radiation beams becomes in phase or out of phase depending on wavelength of incident radiation and rate at which movable mirror moves. So that by controlling the rate of mirror motion a series of simultaneous signals that oscillate frequency which is directly proportional to EMR frequency arrive at detector and oscillate slowly for detector to measure. The detector simultaneously measures all of frequencies that pass through the cell and routes the information to computer and this information are decoded by FT and decoded spectrum is directed to read out device. Time from insertion of sample to recording of plot is about 2 min.

### 3.3.6 Thin Film Thickness-Air Wedge Method

The interference fringes formed in an air wedge and those based on the theory of two beam interference such as the Pluta microscope and Michelson interferometer. The theory of the methods are presented and their applications to measurements of film thickness and refractive index are given. The accuracy of the measured film thickness is calculated. The three interference methods proved that they could be transformed into valuable technological tools. The study established that estimation of the thickness of thin film by the air wedge interference method is more simple and more accurate than the others. Films not more than 50 micrometer thickness are recommended in the Pluta interference microscope.

Thickness of thin film can be calculated using the formula;

$$T = (\Delta x / x) (\lambda / 2)$$

$\lambda$  = wavelength of light used

$\Delta x$  = step size       $X$  = fringe width

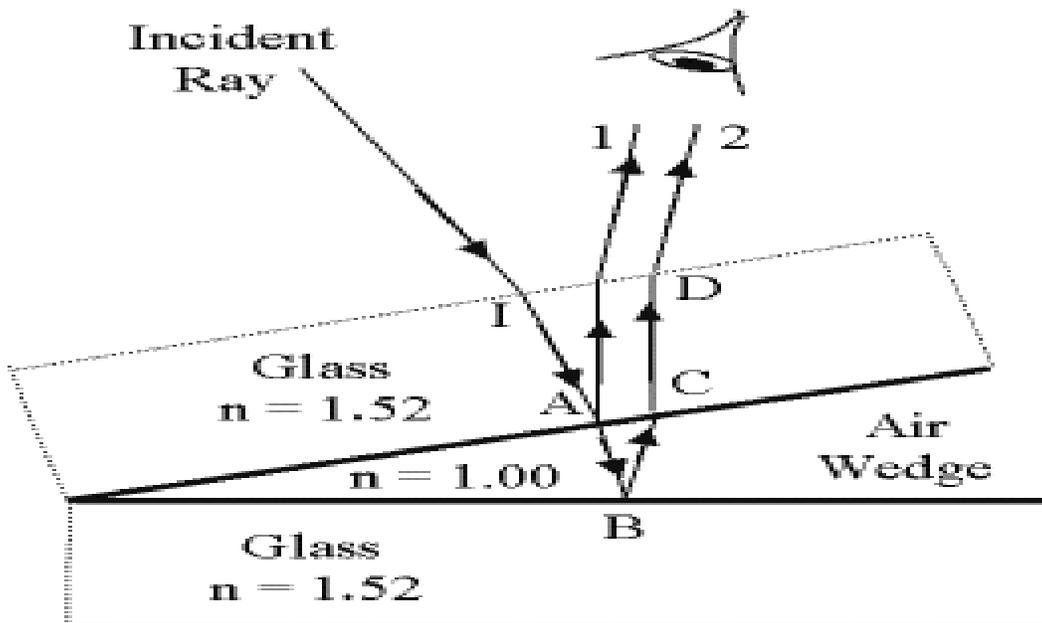


Fig.3.6 Thin film thickness-Air wedge method

# CHAPTER 4

## RESULTS AND DISCUSSION

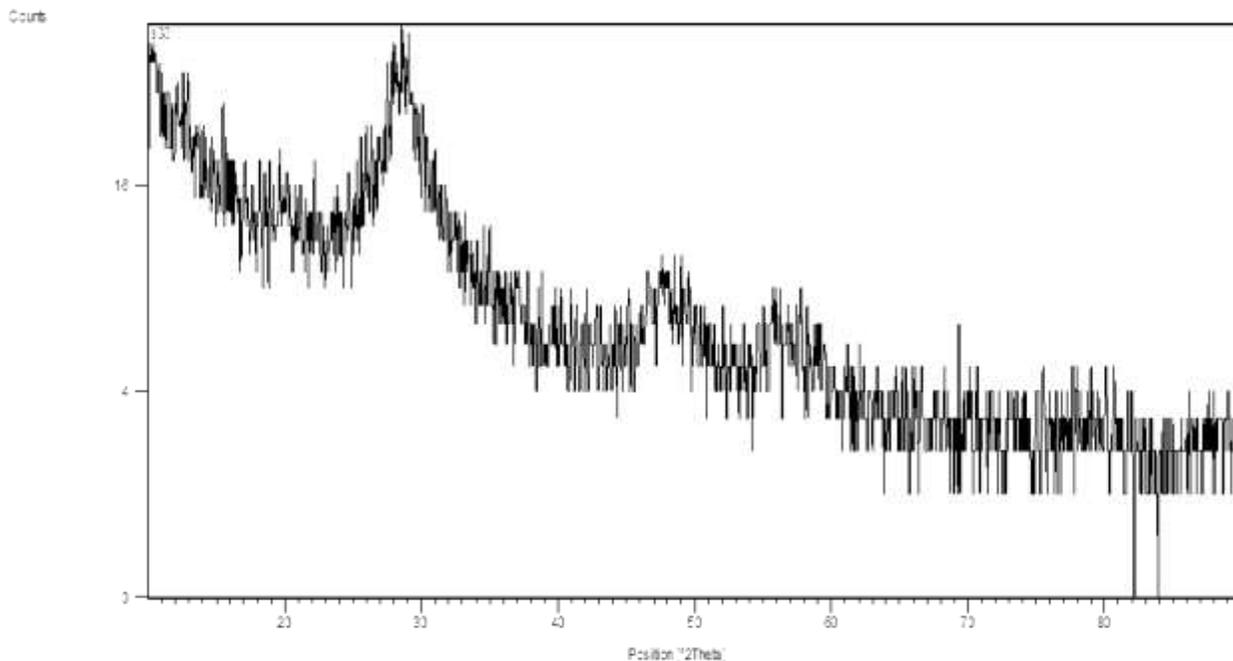
The thin films of Zinc Sulphide and Cadmium sulphide are prepared by the method of sol gel matrix, followed by dip coating method. The optical properties and structural properties of the prepared films are studied.

### 4.1 CHARACTERISATION OF ZnS THIN FILM

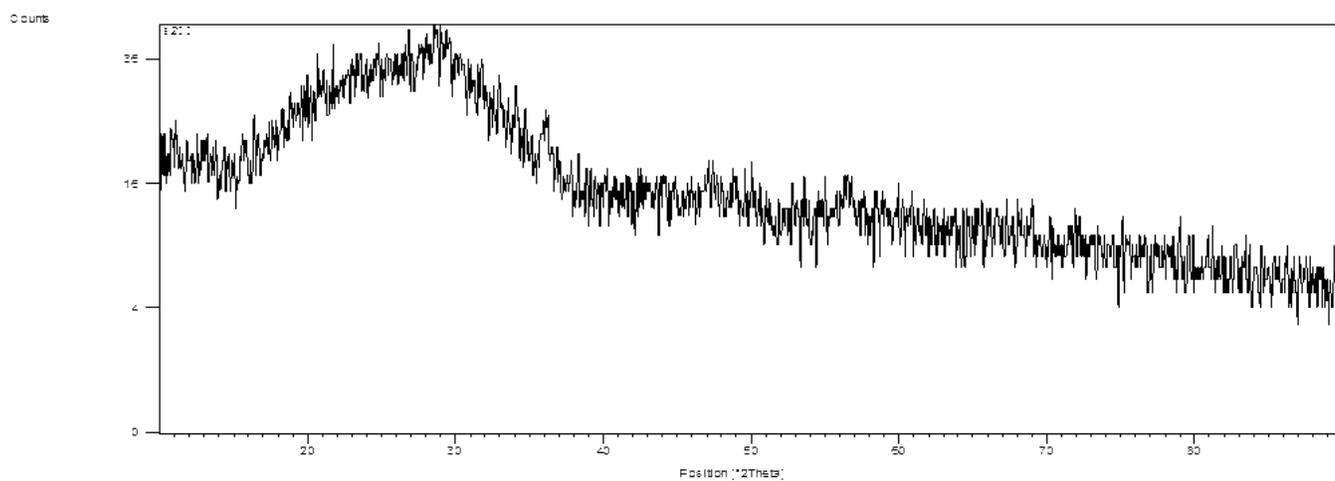
#### 4.1.1 XRD analysis

The comparative XRD patterns of ZnS thin films grown by dip coating method on glass substrates for different annealing temperatures such as 200<sup>0</sup>C, 300<sup>0</sup>C, 400<sup>0</sup>C and as deposite are shown in figures below.

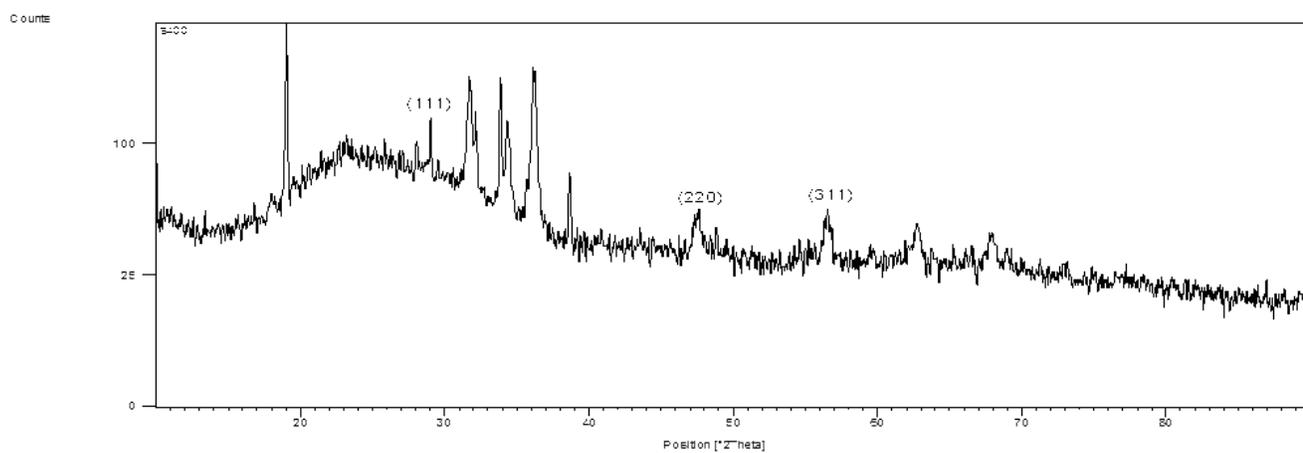
As deposite ZnS



# ZnS 200°C



# ZnS 300°C



# ZnS 400°C

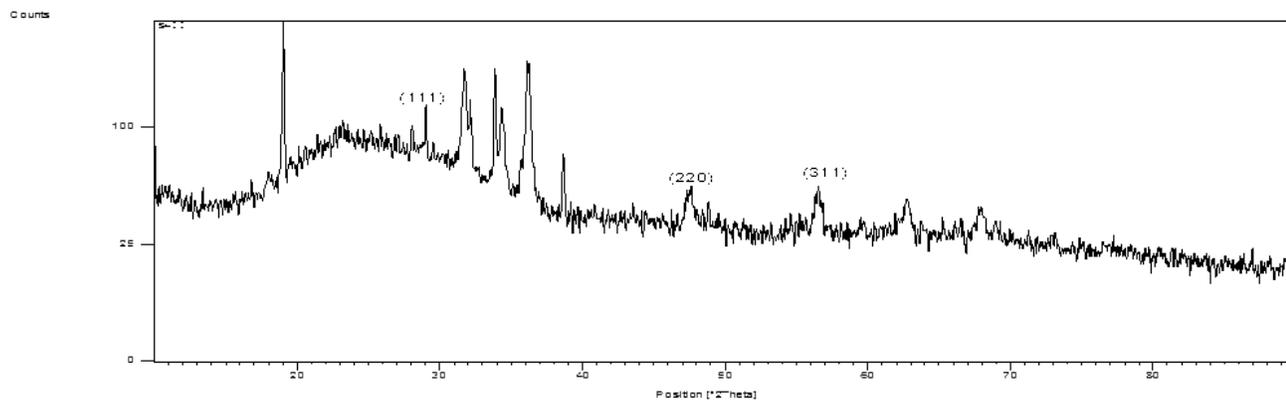


Fig.4.1 XRD patterns of ZnS thin films with different annealing temperatures

The comparative XRD patterns of ZnS thin films grown by dip coating method on glass substrates for different annealing temperatures such as 200<sup>0</sup>C, 300<sup>0</sup>C,400<sup>0</sup>C and as deposite are shown in figure. The crystallite sizes (D) of the films are estimated using the Debye-Scherrer formula:

$$D = 0.9 \lambda / \beta \cos \theta \quad (\text{nm})$$

Where D is the average crystallite size,  $\lambda$  is the X-ray wavelength,  $\beta$  is the fullwidth at half maximum(FWHM) of the dominant peak and  $\theta$  is the bragg angle.

The lattice strain ( $\epsilon$ ) of the ZnS thin films were evaluated according to the relation:

$$\epsilon = (\beta \cos \theta) / 4$$

The dislocation density ( $\delta$ ), which represents the amount of defects in the film, was determined from the formula,

$$\delta = 1/D^2 \quad \text{lines/m}^2$$

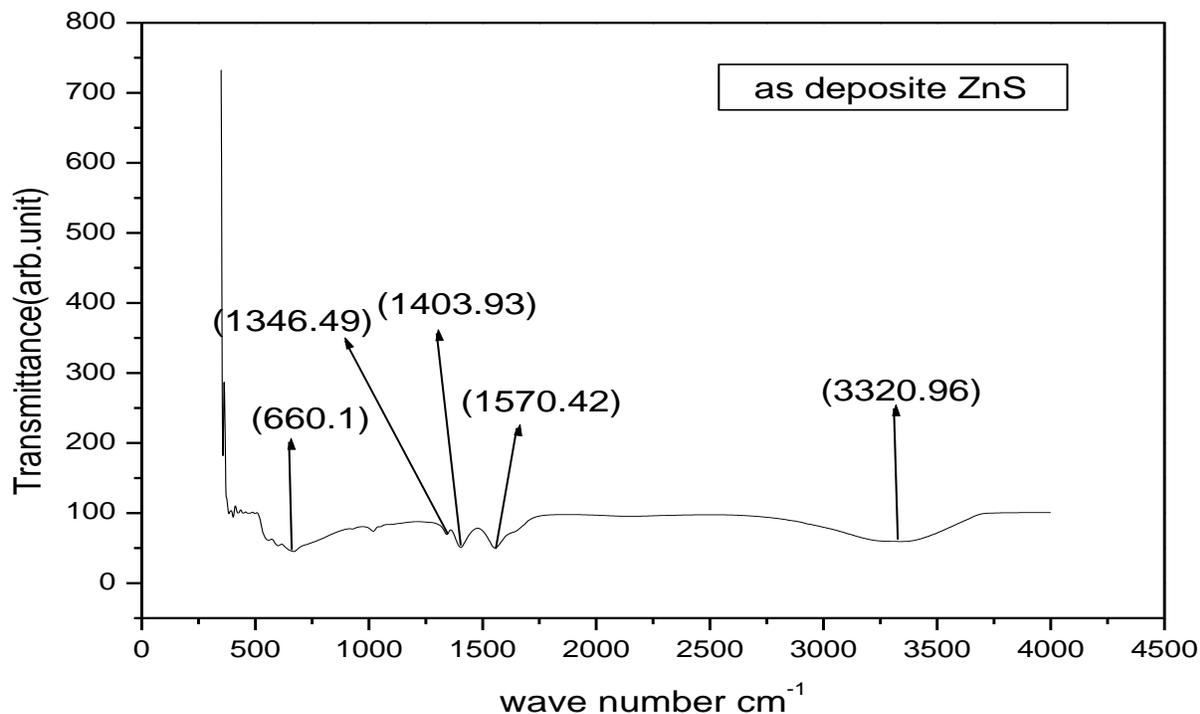
As the annealing temperature increases the dislocation density decreases which may lead to reduction in the concentration of lattice imperfections. The calculated crystallite size, dislocation density and lattice strain values have been summarized in Table 1. At a higher annealing temperature the crystallite size of the ZnS thin films was bigger whereas the dislocation density and strain values were found to be small.

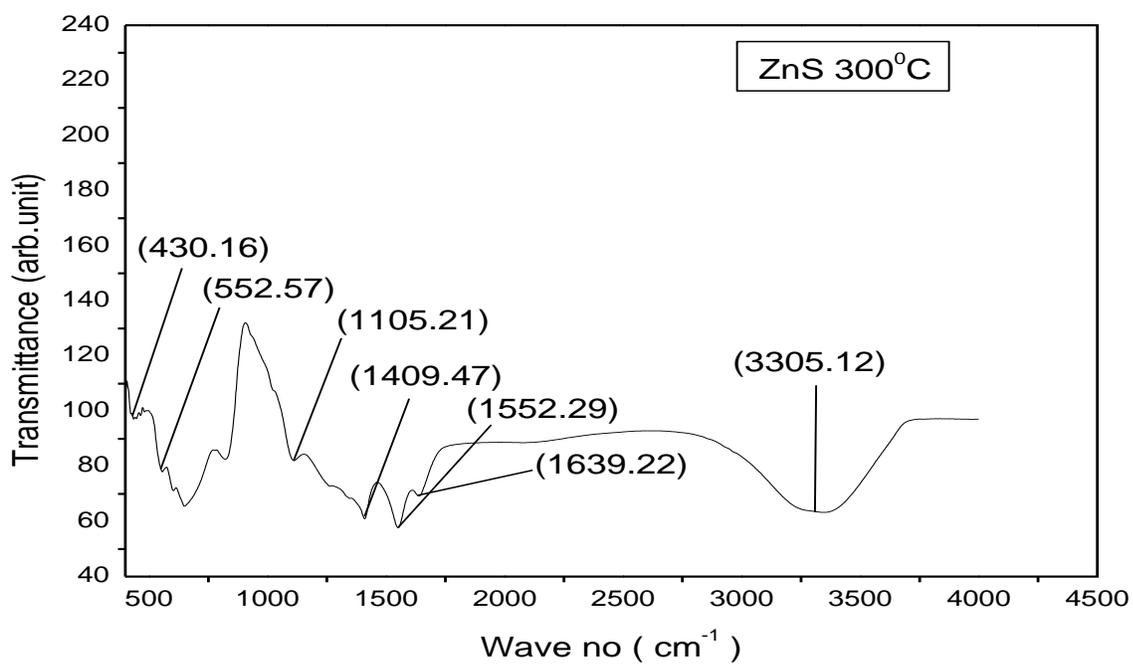
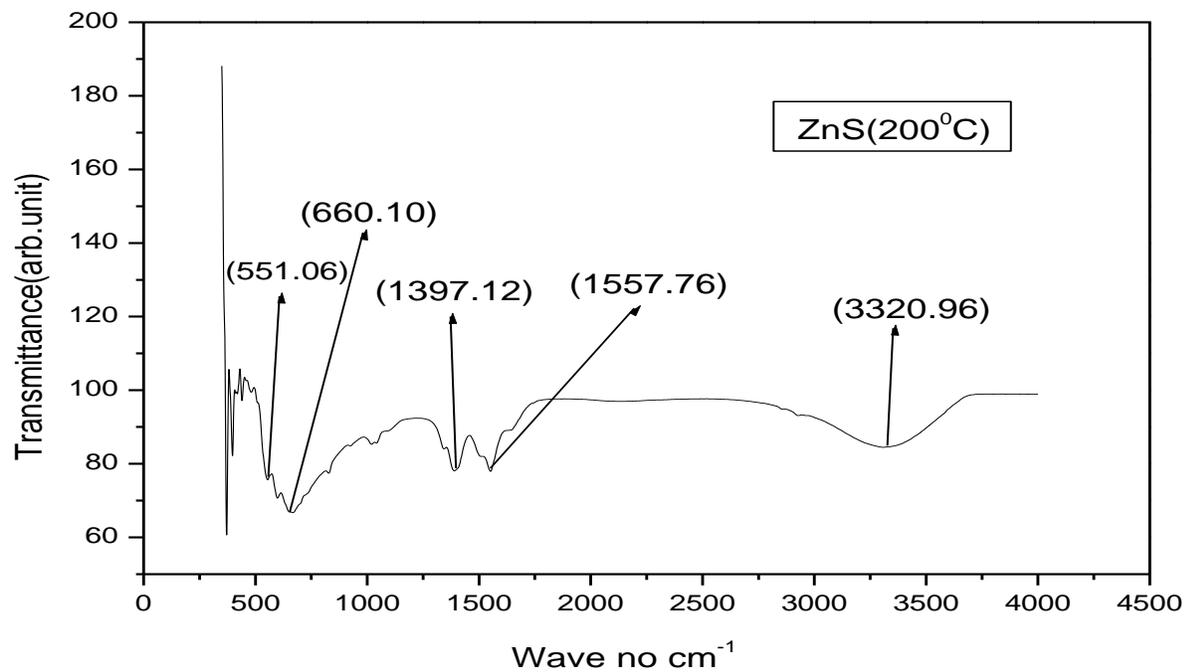
Annealing Temp.( <sup>0</sup> c)	Particle size from XRD(nm)	Lattice strain $\epsilon \times 10^{-3}(\text{line}^{-2} \text{ m}^{-4})$	Dislocation density $\delta \times 10^{14}(\text{line/m}^2)$
As prepared	3.19	45.55	982.31
200	3.25	31.63	946.96
300	13.38	12.92	55.85
400	20.41	5.43	24.01

Table 1. Variation of crystallite size(D),lattice strain ( $\epsilon$ ) and dislocation density ( $\delta$ ) for ZnS thin films annealed at different temperatures

## 4.2. FTIR studies of ZnS Thin Films

An infrared spectrum represents the fingerprint of a sample with absorption peaks which corresponds to the frequencies of vibrations between the bonds of the atoms making up the material. The FTIR Spectrum of ZnS thin films annealed at different temperatures are taken and plotted. The findings and assumptions are also given below.





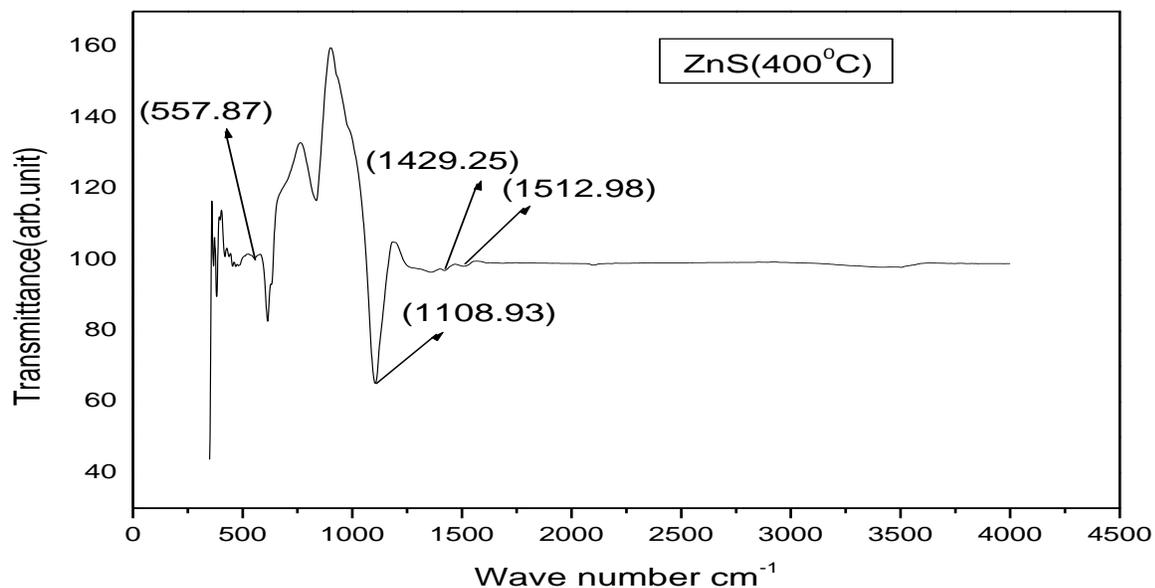


Fig.4.2 FTIR patterns of ZnS thin films with different annealing temperatures

FTIR spectra of “as deposited” shows strong peak around  $1570\text{ cm}^{-1}$  which represents the presence of C=O bond. The band  $1403\text{ cm}^{-1}$  and  $1346\text{ cm}^{-1}$  are related to C-H bond. The peak at  $660\text{ cm}^{-1}$  is represents the presence of stretching vibrational bond C-O-H.

From the FTIR spectra of ZnS thin film annealed at  $200^{\circ}\text{C}$ , it is clear that it shows peak at  $1397\text{ cm}^{-1}$ , which gives the presence of C-H bond. the band  $1559\text{ cm}^{-1}$  shows the presence of stretching vibrational bond of C=O. The band  $661\text{ cm}^{-1}$  and  $551\text{ cm}^{-1}$  are related to stretching vibrational bond of C-O-H.

FTIR spectra of  $300^{\circ}\text{C}$  shows strong peak around  $1639\text{ cm}^{-1}$  and  $1552\text{ cm}^{-1}$  which represents the presence of C=O bond. The band  $430\text{ cm}^{-1}$  and  $1409\text{ cm}^{-1}$  are related to C-H bond. The peak at  $552\text{ cm}^{-1}$  is represents the presence of stretching vibrational bond C-O-H. The band  $1105\text{ cm}^{-1}$  represents C-O-C bond.

Wavelength $\text{cm}^{-1}$	Assignment
1512	C-O
1429	C-H
1108	C-O-C
557	C-O-H

## 4.2 CHARACTERISATION OF CdS THIN FILM

The CdS thin films prepared at different molarities are analysed using various characterization techniques such as UV Visible spectroscopy, band gap study, FTIR spectroscopy and thickness study as given below.

### 4.2.1 UV Visible studies of CdS thin films

UV-visible spectrometer measures the intensity of light passing through a sample, and compares it to the intensity of light before it passes through the sample. The ratio between these two gives the transmittance and gives the inference about the absorbance.

**Optical properties** were studied by using a UV-Visible spectrometer. The optical properties of the film deposited on glass substrates were determined from the absorbance measurement in the range of 100-800nm.

#### 1.Absorption spectera

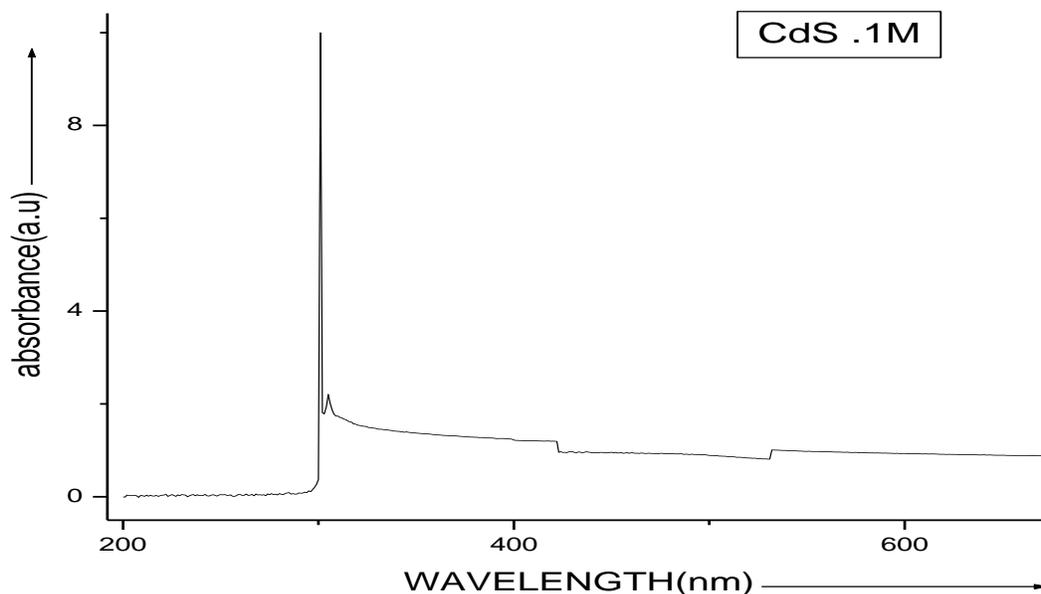


Fig 4.3 absorption spectra of 0.1M CdS

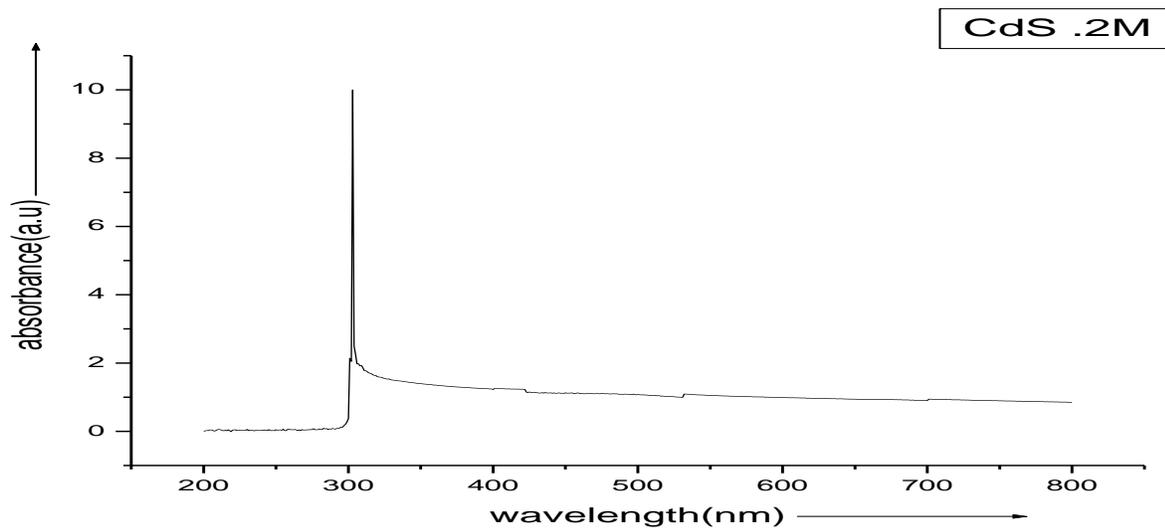


Fig 4.4 absorption spectra of 0.2M CdS

## 2. Transmittance Spectra

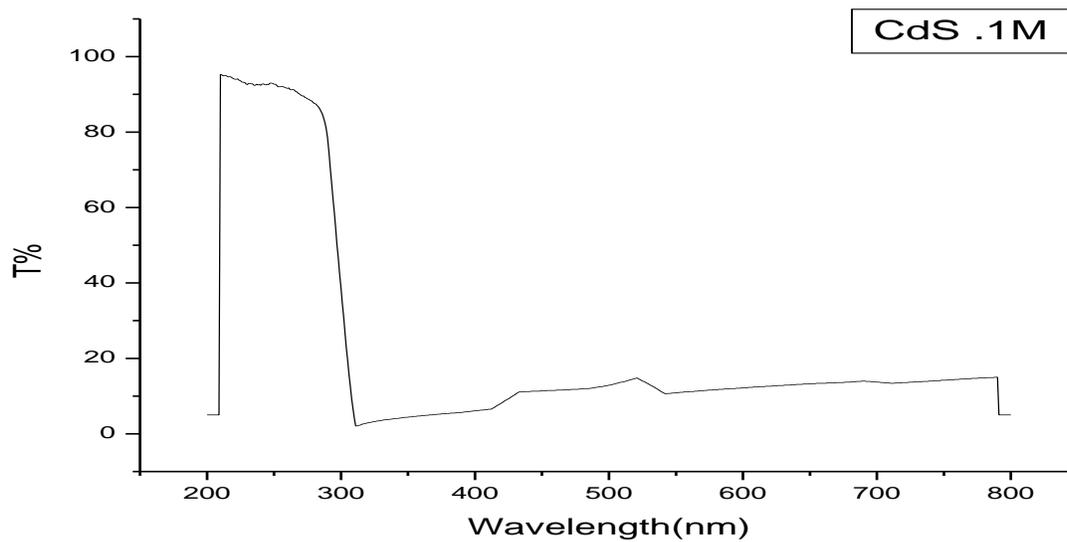


Fig 4.5 transmittance spectra of 0.1 M CdS

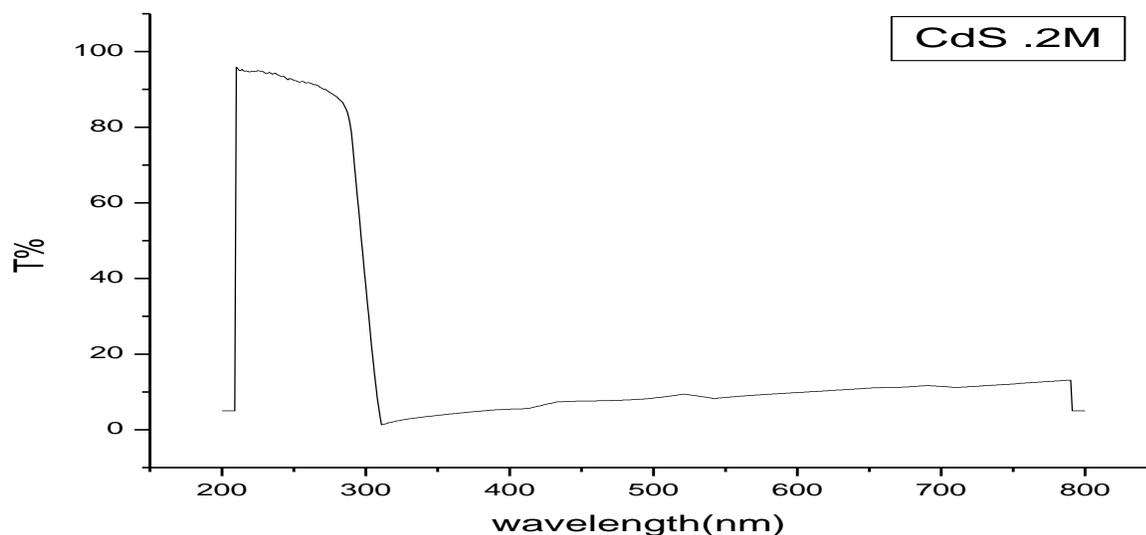


Fig 4.6 Transmittance spectra of 0.2 M CdS

From the both graphs it is clear that the CdS thin films shows absorbance & transmittance at around 300nm wavelength.

#### 4.2.2 Optical Band Gap Study

The band gap energy of the thin film can be observed from the optical absorption studies made by UV-VIS-NIR (ultra violet-visible-near infrared) spectrometry . The direct optical band gap energy (E) was determined by fitting absorption data to the equation

$$\alpha h\nu = B (h\nu - E_g)^2 \quad \text{for absorption coefficient } \alpha=10^4 \text{ cm}^{-1}$$

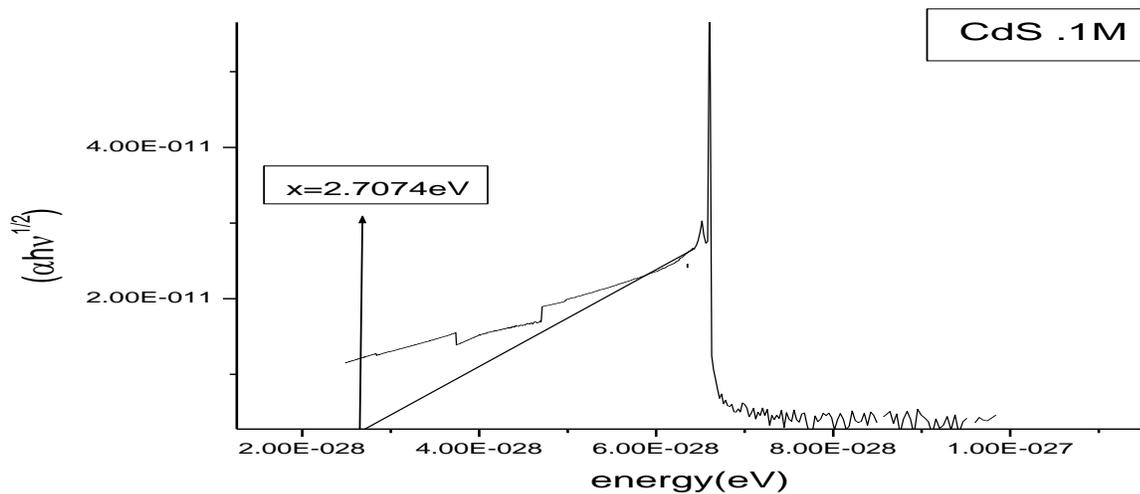


Fig 4.7 Bandgap of 0.1M CdS

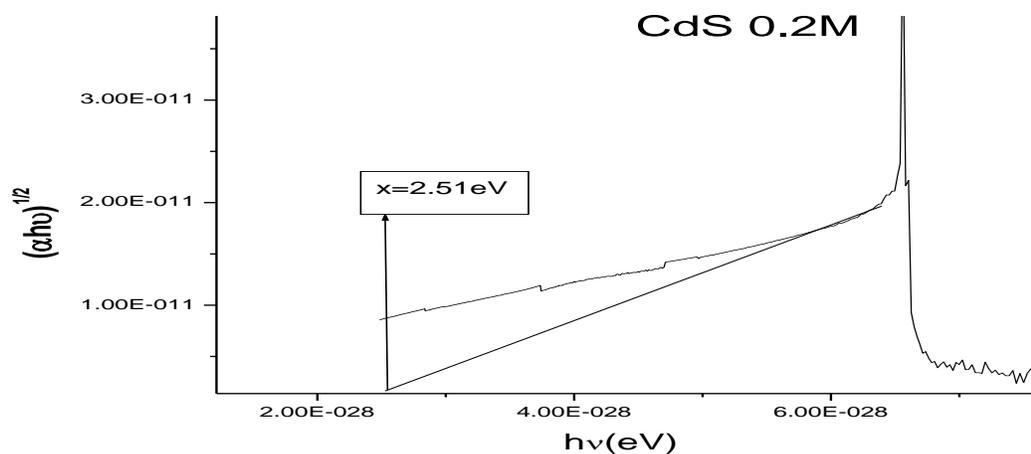


Fig 4.8 band gap of 0.2M CdS

Optical band gap has been calculated by plotting  $(\alpha hv)^2$  versus  $hv$ . By extrapolating the straight line portion of the curve to intercept the energy axis, the value of the band gap energy has been calculated. The calculated optical band gap values are found to be in the range 2.51-2.70 eV

### 4.2.3 FTIR characterization of CdS Thin film

An infrared spectrum represents the fingerprint of a sample with absorption peaks which corresponds to the frequencies of vibrations between the bonds of the atoms making up the material.

### a) FT-IR studies of 0.1m CdS

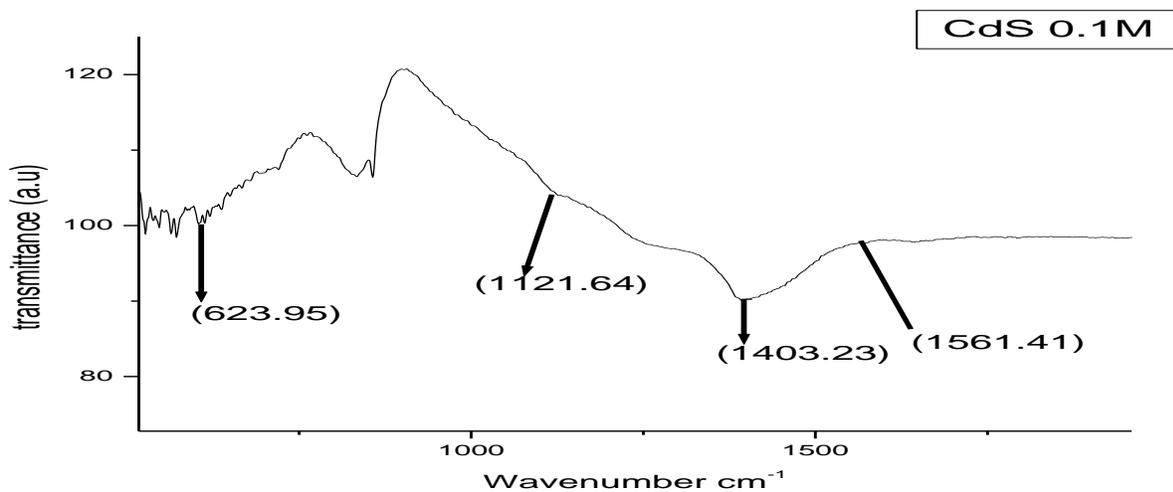


Fig 4.9 FT-IR spectra of 0.1M CdS

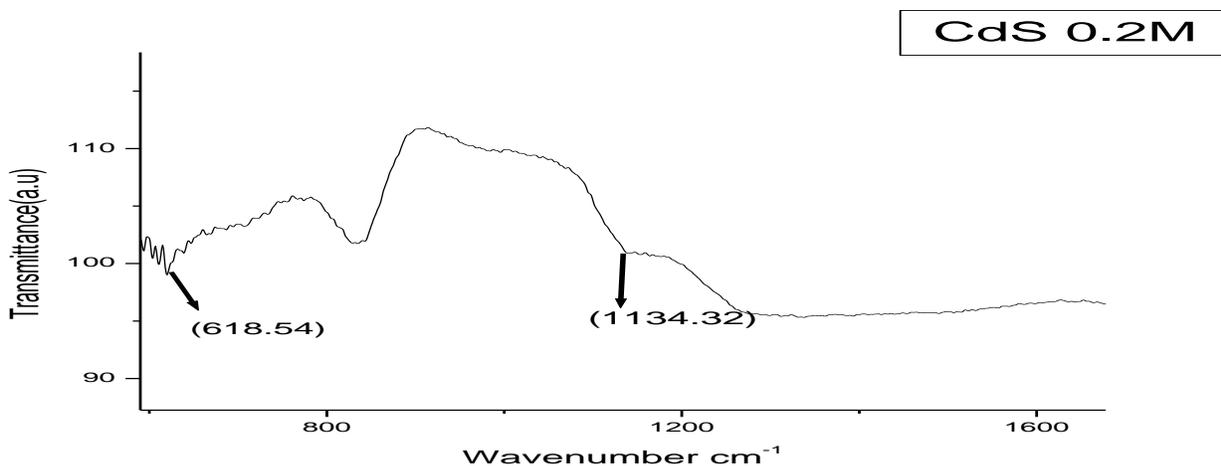


Fig 4.10 FT-IR spectra of 0.2M CdS

FTIR analysis was made from 400 cm<sup>-1</sup> to 2000 cm<sup>-1</sup>, From FT-IR spectra of CdS thin film .very weak bending vibration of water molecules are appeared at 1561.4cm<sup>-1</sup>.C-C stretching,medium strong band positions are appeared in the range of 1403 cm<sup>-1</sup> to 1560 cm<sup>-1</sup> and are possibly due to stretching vibrations of sulphategroup.The narrow absorption peak centred at around 1121 cm<sup>-1</sup> occurred in the above figure is ascribed to the C=O bonding. There are medium to strong absorbtion bands at 623cm<sup>-1</sup>,possibly due to Cd-S stretching.

**FTIR assignments are shown in table**

Wavelength( $\text{cm}^{-1}$ )	Assignment
1403	C-C
1561	C-C
1121	C=O
623	Cd-S

#### 4.2.4 Photoluminescence Analysis of CdS thin film

Photoluminescence (PL) spectroscopy is a contactless, nondestructive method to probe the electronic structure of materials. The intensity and spectral content of the emitted photoluminescence is a direct measure of various important material properties.

##### a) PL studies of 0.1m CdS Thin film

PL spectra of 0.1M ZnS thinfilm have been recorded at room temperature with an excitation wavelength 325nm.PL spectra of the ZnS film sample are shown in figure.

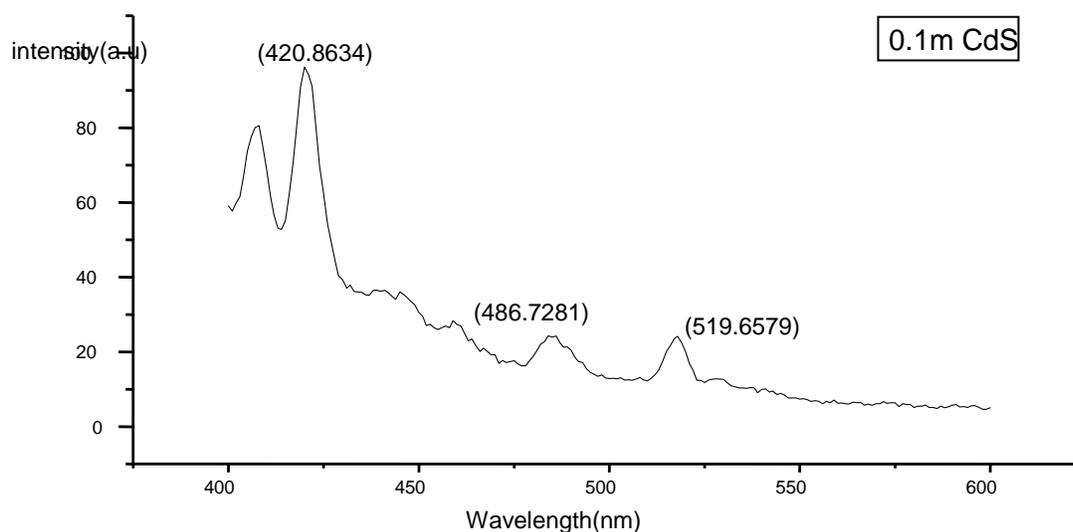


Fig.4.11 PL spectra of 0.1m CdS

The plot contains the peak centred at 420 nm. The PL peak at 420 nm has been known due to the recombination between the S-vacancy related donor and the valanceband. These plots contain three peaks centred at 420nm,486nm and 519nm. Appearance of these peaks in this region is due to

the presence of sulphur vacancies in the lattice (becker and bard, 1983; rabani, 1989; dhas et al, 1999). This emission results from the recombination of photo generated charge carriers in shallow traps. Peaks at 430-450 nm is due to the sulphur vacancy ie, the recombination of electrons at the sulphur vacancy with holes band also the peaks at 500-520 nm may be attributed to the stoichiometric defects which might be a vacancy or an interstitial states.

### b) PL studies of 0.2m CdS thin film

PL spectra of 0.2M CdS thin film have been recorded at room temperature with an excitation wavelength of 350 nm. PL spectra of the CdS film sample is shown in figure below

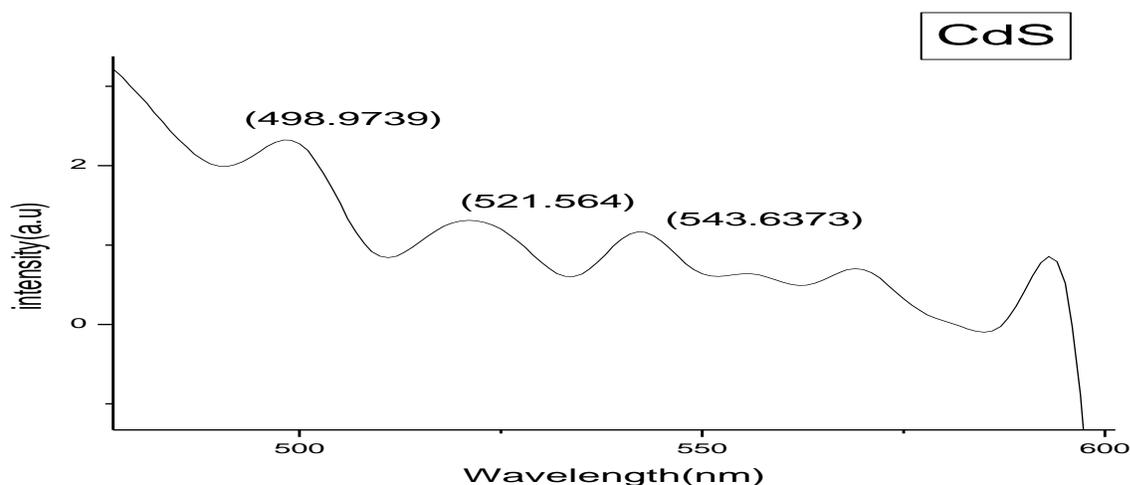


Fig 4.12 PL spectra of 0,2m CdS

The PL emission spectra of 0.2m CdS films exhibit emission peaks centred around 498 nm and 543 nm. The emission band present at 498 nm is known as green emission band in thin films. They may be due to i) recombination of free electrons from conduction band with holes captured on an acceptor level, ii) recombination of trapped electrons from a donor level with free holes and iii) recombination of electrons from a donor level with holes trapped on an acceptor level.

The emission band at 543 nm is known as yellow band and is ascribed to the donor level of the interstitial Cd atoms forming surface defects leading to trap emission in CdS.

### 4.2.5 CdS Thin Film Thickness– Air Wedge Method

The optical constants of metal thin films show marked thickness dependence. Nearly dielectric behavior is exhibited by ultra-thin discontinuous metal films. A change to metallic behavior takes place when the film becomes physically continuous and electrically conducting with increasing thickness.

**a) Thickness of 0.1 M CdS thinfilm**

Least count of microscope = .001 cm

Order	Microscope Reading	Width of 3 fringes	Mean (cm)
M	9.1073	0.5475 0.6278	0.5876
M+3	8.9663		
M+6	8.5598		
M+9	8.3385		

Fringe Width  $\beta = 0.19588 \times 10^{-2} \text{m}$

Wavelength of sodium light  $\lambda = 589.3 \times 10^{-9} \text{m}$

Distance of the film from the line of contact of the glass plate  $l = 2.4 \times 10^{-2} \text{m}$

Thickness of film  $= (\lambda/2\beta) = 3.61017 \mu\text{m}$

**b) Thickness of 0.2 M CdS**

Order	Microscope Reading	Width of 3 fringes	Mean (cm)
M	9.6471	0.399 0.2402	0.32006
M+3	9.4386		
M+6	9.2472		
M+9	9.1984		

Fringe Width  $\beta = 0.106683 \times 10^{-2} \text{m}$

Wavelength of sodium light  $\lambda = 589.3 \times 10^{-9} \text{m}$

Distance of the film from the line of contact of the glass plate  $l = 2.4 \times 10^{-2} \text{m}$

Thickness of film  $= (\lambda/2\beta) = 6.62859 \mu\text{m}$

# CHAPTER 5

## SUMMARY AND CONCLUSION

ZnS & CdS thin films have been successfully prepared in sol-gel matrix by dip coating method and the optical properties and structural properties of thin films are studied. The findings are listed below.

### 5.1 ZnS Thin Film

- ZnS Thin film in sol-gel matrix is coated on a glass substrate using dip coating technique and the samples are annealed at different temperatures.
- XRD Analysis confirms the formation of crystalline structure of the ZnS thin film at 300<sup>0</sup>C & 400<sup>0</sup>C.
- As deposit and ZnS at 200<sup>0</sup>C are shows amorphous state.
- Both XRD patterns(300<sup>0</sup>C & 400<sup>0</sup>C) have three major peaks at  $2\theta$  values of 28.877°, 48.038°, and 57.174° corresponding to a diffraction planes of (111), (221), and (311) planes, respectively .
- From the XRD analysis and by using the Scherer's formula calculated the particle size for crystalline samples.
- The particle size is found to be increasing with increase in annealing temperature.
- The average particle size is 10.078 nm
- FTIR Spectra gives the structural properties of the ZnS thin film.
- ZnS thin film annealed at 300<sup>0</sup>C gives comparatively large no of peaks corresponding to different bonds.
- From the FTIR analysis we obtained the broad spectrum which represents the presence of OH stretching bond of water for as deposit, 200<sup>0</sup>C, 300<sup>0</sup>C and disappears at 400<sup>0</sup>C.
- ZnS thin film annealed at high temperatures shows stretching and deformation peak at 1105 range.

## 5.2 CdS Thin Film

- CdS Thin film in sol-gel matrix of 0.1 and 0.2 molarity are coated on a glass substrate using dip coating technique and the samples are annealed at 400°C.
- The UV-Visible spectra of CdS reveals that both the absorption & transmittance at 300nm wavelength for the films.
- Optical band gap has been calculated by plotting  $(\alpha h\nu)^2$  versus  $h\nu$ . By extrapolating the straight line portion of the curve to intercept the energy axis, the value of the band gap energy has been calculated. The calculated optical band gap values are found to be in the range 2.51-2.70 eV. The observed values are found to be near to the theoretical values.
- FTIR spectra gives the structural properties of the ZnS&CdS thin films. In the spectra of CdS thin film very weak bending vibration of water molecules are appeared at 1561.4  $\text{cm}^{-1}$ . C-C stretching and band range of 1403  $\text{cm}^{-1}$  to 1560  $\text{cm}^{-1}$  are possibly due to stretching vibrations of sulphate group. The narrow absorption peak centred at around 1121  $\text{cm}^{-1}$  due to the C=O bonding.
- Photo Luminescence emission spectra of CdS films exhibit emission peaks centred around 498nm and 543nm, is due to the recombination of electron.
- The thickness of CdS thin films were studied using Air-wedge method and is found to be 3.61017  $\mu\text{m}$  for 0.1 m film and 6.62859  $\mu\text{m}$  for 0.2m film. The thickness of the film is found to be increasing with increase in molarity of the sol-gel matrix.

## REFERENCE

- M.Balachander, M.Saroja, M.Venkatalachalam. "preparation and characterization of zinc sulphide thin film deposited by dip coating method
- I.Rathinamala, j.Pandijarajan, N.jeyakumaran "synthesis and physical properties of nanocrystalline CdS thin films-influence of sol aging time & annealing temperature
- M.Thambidurai, N.Murugan, S.vasantha S.agilan "preparation and characterization of crystalline CdS thin films
- ThinFilm and InkTec awarded IDTechEx' Technical Development Manufacturing Award IDTechEx, April 15th 2009
- Major advance made in transparent electronics. December 28, 2004. Retrieved 2009-09-09.
- Functional Polymer Films Eds. R. Advincula and W. Knoll – Wiley, 2011, ISBN 978-3527321902.
- Hanaor, D; Triani G.; Sorrell C.C.; (2011). "Morphology and photocatalytic activity of highly oriented mixed phase titanium dioxide thin films". *Surface and Coatings Technology*: 205 (12): 3658–3664. doi:10.1016/j.surfcoat.2011.01.007.
- Frank, F. C.; van der Merwe, J. H. (1949). "One-Dimensional Dislocations. I. Static Theory". *Proceedings of the Royal Society of London. Series A, Mathematical and Physical Sciences* 198 (1053): 205–216. Bibcode:1949RSPSA.198..205F. doi:10.1098/rspa.1949.0095. JSTOR 98165.
- Frank, F. C.; van der Merwe, J. H. (1949). "One-Dimensional Dislocations. II. Misfitting Monolayers and Oriented Overgrowth". *Proceedings of the Royal Society of London. Series A, Mathematical and Physical Sciences* 198 (1053): 216–225. Bibcode:1949RSPSA.198..216F. doi:10.1098/rspa.1949.0096. JSTOR 98166.
- Frank, F. C.; van der Merwe, J. H. (1949). "One-Dimensional Dislocations. III. Influence of the Second Harmonic Term in the Potential Representation, on the Properties of the Model". *Proceedings of the Royal Society of London. Series A, Mathematical and Physical Sciences* 200 (1060): 125–134. Bibcode:1949RSPSA.200..125F. doi:10.1098/rspa.1949.0163. JSTOR 98394.
- Stranski, I. N.; Krastanov, L.(1938)."Zur Theorie der orientierten Ausscheidung von Ionenkristallenaufeinander". *Sitzungsber. Akad. Wiss.Wien. Math.-Naturwiss.* 146:797–810.
- I. Gorelikov and E. Kumacheva, *Chem. Mater.* 16 (2004) 4122.
- W. Caseri, *Macromol. Rapid Commun.* 21 (2000) 705.
- L.L. Beecroft and C.K. Ober, *Chem. Mater.* 9 (1997) 1302.
- A. Convertino, A. Capobianchi, A. Valentini and E.N.M. Cirillo, *Adv. Mater.* 15 (2003) 1103.
- A. Ershad-Langroudi, C. Mai, G. Vigier and R. Vassoile, *J. Appl. Polym. Sci.* 65, (1997) 2387.
- G. Cartenuto, Y.S. Her and E. Matijevic, *Ind. Eng. Chem. Res.* 35 (1996) 2929.
- B. Wang, G. L. Wilkes, J. C. Hedrick, S. C. Liptak and J. E. McGrath, *Macromolecules*, 24 (1991) 3449.

- H. Lu , H. Wang and S. Feng, *J. Photochem. Photobiol. A*, 210 (2010) 48.
- M. Yoshida and P. N. Prasad, *Chem. Mater.* 8 (1996) 235.
- S.F. Wang, Y.R. Wang, K.C. Cheng and S.H. Chen, *J. Mater. Sci. Mater. Electron.* 21 (2010)104.
- K. Iuchi , Y. Ohko, T. Tatsuma and A. Fujishima, *Chem. Mater.* 16 (2004)1165.
- M. Biancardo, R. Argazzi and C.A. Bignozzi, *Inorg. Chem.* 44 (2005) 9619.
- A.F. Wells, *Structural Inorganic Chemistry*. Clarendon Press, Oxford, (1975).
- T. Peng, D. Zhao, H. Song, C. Yan, *J Mol Catal A Chem*, 238 (2005) 119.
- Q.Z. Yan, X. T. Su, Z.Y. Huang and C.C. Gea, *J. Eur. Ceram. Soc.* 26 (2006) 915.
- J. Zhu, J. Yang, Z.F. Bian, J. Ren, Y.M. Liu, Y. Cao, H.X. Li, H.Y. He and K.N. Fan, ***Appl. Catal. B*, 76 (2007) 82.**
- M. Zheng, M. Gu, Y. Jin, H. Wang, P. Zu, P. Tao and J. He, ***Mater. Sci. Eng. B*, 87 (2001)197.**
- W. T. Carnall, P. R. Fields, K. Rajnak, *J. Chem. Phys.* 49 (1968) 4424-4442.
- S. P. Sinha, *Complexes of the rare earths*, first ed., Pergamon Press, Oxford, 1966.
- B.R. Judd, *Phys. Rev.* 127 (1962) 750-761.
- G.S. Ofelt, *J. Chem. Phys.* 37 (1962) 511-520.
- Matras-Postolek M, Bogdal D (2010) *Adv Polym Sci* 230:221
- Hietala S, Holmberg S, Karjalainen M, Paronen M, Serimaa R, Sundholm F, Vahvaselka S (1997) *J Mater Chem* 7:721
- He F, Fan J, Lau S (2008) *Polym Test* 27:964
- Mawson S, Johnston KP, Combes JR, DeSimone JM (1995) *Macromolecules* 28:3182
- Scheinbeim JI (1999) In: Mark JE (ed) *Poly(vinylidene fluoride)*. Oxford University Press Inc, New York
- Gregorio R Jr, Cestari M (1994) *J Polym Sci B* 32:859
- Tazaki M, Wada R, Okabe M, Homma T (1997) *J Appl Polym Sci* 65:1517
- Cheng LP (1999) *Macromolecules* 32:6668
- Salimi A, Yousefi AA (2004) *J Polym Sci B* 42:3487
- Hsu CC, Geil PH (1989) *J Mater Sci* 24:1219. doi:10.1007/ BF02397050
- Volmer, M.; Weber, A. (1926). "Keimbildung in übersättigten Gebilden". *Z. Phys. Chem* 119: 277–301.
- Flexible Cell Construction. Mpoweruk.com. Retrieved on 2012-01-15.
- Manfred L. Hallensleben "Polyvinyl Compounds, Others" in *Ullmann's Encyclopedia of Industrial Chemistry*, 2000, Wiley-VCH, Weinheim. doi:10.1002/14356007.a21\_743