

CHARACTERIZATION AND STUDIES OF METALSULPHIDE THIN FILMS IN PVA MATRIX PREPARED BY SPIN COATING TECHNIQUE

A minor research project report
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CHAPTER 1

INTRODUCTION

1. THINFILM

A thin film is a layer of material ranging from fractions of a nanometer (monolayers) to several micrometers in thickness. Electronic semiconductor devices and optical coatings are the main applications benefitting from thin film construction.

A familiar application of thin films is the household mirror, which typically has a thin metal coating on the back of a sheet of glass to form a reflective interface. The process of silvering was once commonly used to produce mirrors. A very thin film coating (less than about 50 nanometers thick) is used to produce two-way mirrors. Thin films are generally confined to a limited range of thickness of a few angstroms to about 5000 depending on the properties to be observed. Whereas for technological applications the thickness limit at lower range is generally higher than 1000Angstrom. In order to cover this wide range of film thickness both for researches and applications, a 'Thin film' may be arbitrarily defined as a solid layer having a thickness varying from a few Angstrom to about 10micrometer or so. Since the thickness limit is rather arbitrary, even somewhat thicker films may also come within the scope of the above definition. Within the connotation of thin film, often a further subdivision of thickness is under the following categories.

- 1 . Ultrathin [ranging from a few to about 50-100A°].
- 2 .Thin [about 100A°-1000A°]
- 3 . Comparatively thicker ones [greater than 1000A°]

Whatever be the thickness limit, an ideal film can mathematically be defined as a homogenous solid material contained between two parallel plates and whatever be the film thickness limit, an ideal film can extended infinitely in two directions [say x and y] but restricted along the third direction [z], which is perpendicular to x-y plane. The dimension along z-direction is known as the film thickness [d or t]. Its magnitude may vary from a limit

ed tens to 0 to any arbitrary value, but always remaining much less than those along the other two directions that is x and y. Areal film, however, deviates considerably from the ideal case since its two surfaces are never exactly parallel even when formed in the best experimental deposition conditions and also the material contained between the two surfaces rarely homogenous neither uniformly distributed nor of the same species. The film may also contain many imperfections, dislocations, grain boundaries and various other defects which may cause the film to be discontinuous. Further the top surfaces of a film often develops some discontinuities which is the characteristics of the growth conditions which may be visible even to the naked eye.

1.1 MAIN PROPERTIES OF THINFILMS

The properties of a thin film may be different from those of the bulk particularly, if the film thickness is very small. This 'anomalous' properties 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

➤ ELECTRICAL PROPERTIES

1.1.1 OPTICAL PROPERTIES

The phenomenal growth of thin film research contributed a lot in the application of optical film mirrors and interferometer. The theoretical and experimental investigations on the optical behavior of thin films deal primarily with optical constants of films. As results of these studies complex multilayer optical device system with remarkable reflection, antireflection, interference and polarization properties were developed. The absorption studies of thin films have led to a variety of interesting thin film optical phenomena to study the electronic structure of solids.

The optical properties of the thin films show profound sensitivity on the film microstructure. Since various deposition parameters affect the microstructure, the optical proportion strongly depends on the deposition conditions. Also the optical properties change due to annealing of the films. In this condition recrystallization as well as surface and volume oxidation may take place in the film. With increasing film thickness, the effect of the initial granular structure on the optical properties is decreased but not eliminated completely. Therefore thickness dependence is still observed, although the general behavior of the optical parameters follow that of the bulk.

The optical constants of metal thin film show a 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 consist of absorption peaks corresponding to the inter band electronic transitions, superimposed on the absorption by the conduction electrons for thin discontinuous poorly conducting metal films must be small. However, a marked abnormal absorption maximum appears at a position, which varies with the thickness of the film or with crystallite size. The absorption in a film can be expressed as

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

Where

n_0 = refractive index of substrate

R = reflectance of the film at normal incidence

T = transmission of the film at normal incidence

1.1.2 ELECTRICAL PROPERTIES

There are three types of electron materials; metals, semiconductors and dielectrics. Obviously the electrical transport nature is different in all types of materials, therefore it has influence on the electrical properties of materials by the same way. The film thickness, the lattice dimensions, the purity, the surface roughness and imperfect level on the layer are must significant parameters defined the type, mechanism and the stability of the electrical transport.

Electrical conductivity of a granular film in 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 be 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 when particles have $d = 20$ to 50 \AA and with typical metal work function of 4 to 5 eV. Tunneling is the dominant mechanism of electron transport unless the temperature is higher than 3000 K. Thermionic emission which depends exponentially on the height of the barrier may decrease significantly because of the overlap of the image-force potentials, thus giving rise to higher conductivity. Based on this theory the conductivity

$$S = (Ae^2/kT) \exp(-(\Phi - Be^2/d)/kT)$$

Where ,

A = a constant characteristic of each film

T = Temperature

k = Boltzmann constant

e = electric charge

d = distance between particles

Φ = 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.

1.2 APPLICATIONS OF THINFILM

A thin film is a layer of material ranging from fractions of a nanometer to several micrometers in thickness. Electronic semiconductor devices and optical coatings are the main applications benefitting 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 a electronic industries. Thin films have also found extensive applications as discrete passive component, 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.

Work is being done with ferromagnetic and ferroelectric thin films for use as a computer memory .it is also being applied to pharmaceuticals, via thin film drug delivery. Thin films are used to produce thin- film batteries and cells. Ceramic thin film films are of wide use. The relatively high hardness and inertness of ceramic materials make this type of thin coating of interest for protection of substrate materials against corrosion, oxidation and wear. In particular , the use of such coatings on cutting tools can extend the life of these items by several orders of magnitude . Research is beingdone on anew class of thin film inorganic oxide materials, called amorphous heavy metal cation multi components oxides, which could be used to make transparent transistors that are inexpensive, stable.

- Thin-film photovoltaic cells

Thin film technology are also being developed as a means of substantially reducing the cost of solar cells. The rationale for this is thin film solar cells are cheaper to manufacture owing to their reduced material costs, energy costs, handling costs and capital costs. This is especially represented in the use of printed electronics (roll to roll) processes. Other thin film

technologies, that are still in an early stage of ongoing research or with limited commercial availability , are often classified as emerging or third generation photovoltaic cells and include, organic, dye-sensitized, and polymer solar cells, as well as quantum dot, copper zinc tin sulfide, nanocrystal and perovskite solar cells.

- Thin – film batteries

Thin film printing technology is being used to apply solid-state lithium polymers to a variety of substrates to create unique batteries for specialized applications. Thin film batteries can be deposited directly on to the chips or chip packages in any shape or size . Flexible batteries can be made by printing on to plastic, thin metal foil or paper. One of the newest applications of thin film technologies is in circuit based films made from superconductors. For example Josephson junctions. Ferromagnetic thin films play a major role in magnetic recording and storage technology. CdS and PbS films have photoconductive property. They are used as solar cells.

We can conclude the applications as follows;

- Optical devices
 - Antireflection coatings
 - High reflecting mirrors
 - Monochromators
 - Interference filters
 - Solar energy absorbers
- Superconducting devices
- Memory storing
- Bolometers
- Highly sensitive voltmeters
- Magnetometers
- Semiconductor rectifiers etc.

CHAPTER 2

FILM DEPOSITION TECHNIQUES

2.1 THE FILM DEPOSITION

The act of applying a thin film to a surface is thin-film deposition – Any technique for depositing a thin film of material to a substrate or onto a previously deposited layers. “Thin” is a relative term, but most deposition techniques control layer thickness within a few tens of nanometers. Molecular beam epitaxy allows a single layer of atoms to be deposited at a time. It is useful in the manufacture of optics (for reflective, anti- reflective coating s or self-cleaning glass for instance), electronics (layer of insulators, semiconductors, and conductors from integrated circuits), and packaging (i.e, Aluminium a coated PET film).Similar processes are sometimes used where thickness is not important: for instance, the purification of copper by electroplating and the deposition of silicon and enriched uranium by a CVD - like process after gas phase processing .

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 conformal, rather than directional.

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

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 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. The speed at which the solution is spun and the viscosity of the sol determine the ultimate thickness of the deposited film. Repeated deposition can be carried out to increase the thickness of film as desired. Thermal treatment is often carried out in order to crystallize the amorphous spin coated film. Such crystalline films can exhibit certain preferred orientations after crystallization on single crystal substrates.

Chemical vapor deposition (CVD) generally uses a gas- phase precursor, often a halide or hybrids of the element to be deposited. In the case of MOCVD, an organ metallic 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.

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 store these energies, commercial physical deposition systems tend to require a low-pressure vapor environment to function properly; most can be classified as physical vapour deposition(PVD). The material to be deposited is placed in an energetic, entropic environment, so that particles of material escape its surface. Casing 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 freely as possible. Since particles tend to follow a straight path, films deposited by physical means are commonly directional, rather than conformal.

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. Molecular beam epitaxy is a particularly sophisticated form of thermal evaporation.
- An electron beam evaporator fires 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 270° in order to ensure that the gun filament is not directly exposed to the evaporant flux. Typical deposition rates of 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. The beam of material can be generated by either physical means (that is, by a furnace) or by a chemical reaction (chemical beam epitaxy).
- 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.

2.1.3 COATING PROCESS

a) Spin Coating

Spin coating is a procedure used to deposit uniform thin film to flat substrates . Usually small amount of coating material is low speed or not spinning at all. The substrate is then rotate at high speed in order to spread the coating is called a spin coater or simply spinner.

Rotation is continued while the fluid spins off the edge of the substrate, until the desired thickness of the film is achieved. The applied solvent is usually volatile, and simultaneously evaporates. So, the higher the angular speed of spinning the thinner film. The thickness of the film also depends on the viscosity and concentration of the solution and the solvent. A widely studied phenomenon in spin – coating is the coffee ring effect.

Spin coating is widely used in micro fabrication of oxide layers using sol-gel precursors, where it can be used to create uniform thin films with nanoscale thickness. It is used intensively in photolithography, to deposit layers of photoresist about 1 micrometer thick. Photoresist is typically spun at 20 to 80 revolution per seconds.

The thickness of the thin film is depends on the concentration of the film. The largest substrate, theoretically would be a 9” (229mm) diagonal measurement. Some space must be allowed between the wall of the bowl and the substrate to avoid splash back, this being the reason for the maximum size being led than the maximum bowl diameter.

b) Dip Coating

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 were 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 up on withdrawal from bath with a layer of semi-fused polymers. The amount of 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 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 the 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.!

2.1.4 FEATURES AND BENEFITS OF DIP COATING

- User independent. High resolution motorized movement and software control, simply precision dipping experiments.
- Flexible programming of dipping sequences. 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.
- Versatile and robust. The range of products and accessories enable various configurations fitting a wide range of experimental requirements. The accessories offer the capability for in-built temperature and pH control and magnetic stirring. The Dip Coaters are safe long-term investments that are made from durable materials.
- 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
- 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.



Fig: Dip Coating Unit With Hot Chamber

- 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. To further enhance the dip coating process, a primer can be applied to the metal prior to coating to gain a virtually non removable bonds

2.1.5 APPLICATIONS OF DIP COATING

Applications for dip coating are extensive and include:

- Amusement Park Lab Bars
- Seat belt tongues
- Hand tools
- Toys
- Medical Instruments
- Plumbing Fittings
- Electrical Equipment
- Exercise Equipment
- Timeline to Production

Dip coating can be applied to a large variety of materials from the inorganic sols and inorganic nanoparticles to self-assembling biochemical systems. Applications include deposition electrical- and electro-optical layers, anti- reflective coatings, creating super hydrophobic surfaces and depositing biologically compatible coatings.

The following surface coatings can, for example, be created:

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

CHAPTER 3

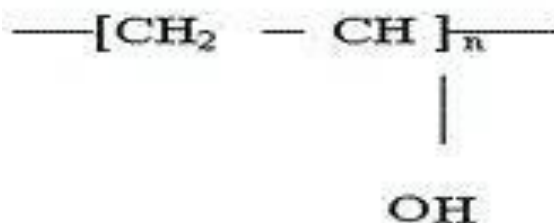
ZINC SULPHIDE AND POLYVINYL ALCOHOL

3.POLYVINYL ALCOHOL

Polyvinyl alcohol was placed on the agenda of the 61stJECFA. Polyvinyl alcohol was first prepared by Hermann and Haehnel in 1924 hydrolyzing poly vinyl acetate in ethanol with potassium hydroxide. Poly(vinyl alcohol) (PVOH, PVA, or PVAI) is a water-soluble synthetic polymer. It has the idealized formula $[\text{CH}_2\text{CH}(\text{OH})]_n$. It is white (colourless) and odorless. It is sometimes supplied as beads or as solutions in water.

Polyvinyl alcohol (PVA), a colourless, water-soluble synthetic resin employed principally in the treating of textiles and paper. PVA is unique among polymers (chemical compounds made up of large, multiple-unit molecules) in that it is not built up in polymerization reactions from single-unit precursor molecules known as monomers. Instead, PVA is made by dissolving another polymer, polyvinyl acetate (PVA), in an alcohol such as methanol and treating it with an alkaline catalyst such as sodium hydroxide. The resulting hydrolysis, or “alcoholysis”, reaction removes the acetate groups from the PVA molecules without disrupting their long-chain structure.

The chemical structure of the resulting vinylalcohol repeating unit is



When the reaction is allowed to proceed to completion, the product is highly soluble in water and insoluble in practically all organic solvents. Incomplete removal of acetate groups yields resins less soluble in water and more soluble in certain organic liquids

PVA is used in sizing agents that give greater strength to textile yarns and make paper more resistant to oils and greases. It is also employed as a component of adhesives and emulsifiers, as a water-soluble protective film, and as a starting material for the preparation of other resins

Polyvinyl alcohol is produced commercially from polyvinyl acetate, usually by a continuous process. The acetate groups are hydrolysed by ester interchange with methanol in the presence of anhydrous sodium methylated or aqueous sodium hydroxide. The physical characteristics and its specific functional uses depend on the degree of polymerization and the degree of hydrolysis. Polyvinyl alcohol is classified into two different classes namely: partially hydrolysed. Partially hydrolyzed PVA is used in foods. Polyvinyl alcohol is an odorless and tasteless, translucent, white or cream colored granular powder. Polyvinyl alcohol is not known to occur as a natural product.

Polyvinyl alcohol for food use is an odorless and tasteless, translucent, white or cream colored granular powder. It is soluble in water, slightly soluble in ethanol, but insoluble in other organic solvents. Typically a 5% solution of polyvinyl alcohol exhibits a pH in the range from 5.0 to 6.5. Polyvinyl alcohol has a melting point of 180 to 190°C. It has a molecular weight of between 26,300 and 30,000 and a degree of hydrolysis of 86.5 to 89%.

3.1 STRUCTURE AND PROPERTIES OF PVA

PVA is a tactic material that exhibits crystallinity. In terms of microstructure, it is mainly composed of 1,3-diol linkages $[-CH_2-CH(OH)-CH_2-CH(OH)-]$ but a few percentages of 1,2-diols $[-CH_2-CH(OH)-CH(OH)-CH_2-]$ occur, depending on the conditions for polymerization of the vinyl ester precursor.

Polyvinyl alcohol has excellent film forming, emulsifying and adhesive properties. It is also resistant to oil, grease and solvents. It has tensile strength and flexibility, as well as high oxygen and aroma barrier properties. However these properties are dependent on humidity, in other words, with higher humidity more water is absorbed. The water, which acts as a plasticiser, will then reduce its tensile strength, but increase its elongation and tear strength.

PVA has a melting point of 230°C and 180-190°C (356-374 degrees Fahrenheit) for the fully hydrolysed and partially hydrolysed grades, respectively. It decomposes rapidly above 200° as it can undergo pyrolysis at high temperatures. PVA is close to incompressible. The Poisson's ratio is between 0.42 and 0.48

3.1.1 Physical Properties Of Polyvinyl Alcohol

PVA sponge is a synthetic sponge essentially composed of Polyvinyl Alcohol. It possesses a three dimensional open cell structure similar to that of natural sea sponges. All of its cells are interconnected, not independent. Major advantages of this physical structure are its high filtering efficiency, its ability to be reused after cleaning (non medical uses only) , and its impressive retention and wicking properties.

PVA sponge will be absorb up to 12 times dry weight in water. When saturated with water, it becomes flexible and soft like natural sea sponge. The wet volume is about 20% greater than any other synthetic sponge material. Pore size and shape can vary to meet specific applications. Wet PVA sponge will with standard temperatures to 90° C without plastic deformation. PVA in its raw state is pure white. It can be pigmented in any colour and to a high degree of colour fastness.

3.2.1 Chemical Properties Of Polyvinyl Alcohol

During the manufacture of PVA sponge, water soluble porous structure is chemically in solubalized. The material will withstand the action of dilute acids, strong alkalies and solutions of common detergents. Some detergents of the “sulphonate” category(over 5% strength) will slowly swell and weaken the sponge. Organic solvents do not as a rule, affect the sponge unless they are water-

miscible and are applied mixed with 30%-60% of water through washing in water will return the sponge to its original state a PVA is also incompactable with nickel-sulphate solutions

3.2 USES OF POLYVINYL ALCOHOL

Polyvinyl alcohol is used as an polymerization aid, as protective colloid, to make polyvinyl acetate dispersions. This is the largest market application in China. In Japan its major use is vinyl on fiber production

Some other uses of Polyvinyl alcohol include:

- Paper adhesive with boric acid in spiral tube winding and solid broad production
- Thickener, modifier, in polyvinyl acetate glues
- Textile sizing agent
- Paper coatings, release liner
- As a water – soluble film useful for packaging. An example is the envelope containing laundry detergent in “liquid-tabs”.
- Feminine hygiene and adult incontinence products as a biodegradable plastic backing sheet
- Carbon barrier in polythene terephthalate (PET) bottles
- As a film used in the water transfer printing process
- Movie practical effect and children's play plutty or slime when combined with borax
- Used in eye drops (such as artificial tears to treat dry eyes) and hard contact lens solution ASA lubricant
- PVA fiber,as reinforcement in concrete
- Used in protective chemical resistant gloves
- When doped with iodine, PVA can be used to polarize light
- As an embolization agent in medical procedures
- Used in 3 D printing as support structure that can then be dissolved away.

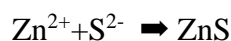
3.3 ZINC SULPHIDE

Zinc sulphide 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 sulphide can be transparent, and it is used as a window for visible optics and infrared optics.

Zinc sulphide is usually produced from waste materials from other applications. Typical sources include smelter, slag, and pickle liquors. It is also a by-product of the synthesis of ammonia from methane where zinc oxide is used to scavenge hydrogen sulphide impurities in the natural gas:



It is easily produced by igniting a mixture of zinc and sulphur. Since zinc sulphide is insoluble in water, it can also be produced in a precipitation reaction. Solutions containing Zn^{2+} salts readily form a precipitate ZnS in the presence of sulphide ions (e.g., from H_2S).



3.3.1 Structure Of ZnS

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 PS also known as zinc blend or sphalerite. The hexagonal form is known as the mineral wurtzite, although it can be produced synthetically. The transition from the sphalerite to the wurtzite form occurs at around 1020 Celsius. A tetragonal form is also known as the very rare mineral called polhemusite.

3.3.2 Applications of ZnS

a) Optical materials

Zinc is also used as an infrared optical material, transmitting from visible wavelengths to just over 12 micrometers. 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 (HIPed) can be converted to a water-clear form known as "Cleartran".

b) Luminescent material

Zinc sulfide, with addition of few parts per ppm of suitable activator (phosphor)|activator, is used as phosphor in many applications, from cathode ray tubes through X-ray screens to phosphorescence 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 nanometers. 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 electroluminescence panels.

c) Catalyst

Fine ZnS powder is an efficient photocatalyst, which produces hydrogen gas from water upon illumination. Sulfur vacancies can be introduced in ZnS during its synthesis; this gradually turns the white-yellowish ZnS into a brown powder, and boosts the photocatalytic activity through enhanced light absorption.

CHAPTER 4

PREPARATION AND CHARACTERIZATION

4. PREPARATION OF ZnS THIN FILM

Materials used in present synthesis are :

- Zinc acetate as zinc source
- Sodium sulphide as sulphur source
- Polyvinyl Alcohol (PVA) as capping and dispersing agent

ZnS thin films were deposited on a glass plate using dip coating method. Thin films were prepared for three different molarities of zinc acetate and sodium sulphide. Steps in this method are:

1) Preparation of zinc acetate solution:

Solutions are prepared in 30 ml distilled water.

a) 1 molar solution

1 molar solution = molecular mass/litre

i.e , $W = 219.5 \times 30 \times 1 / 1000 = 6.585 \text{ gm}$

b) 1.5 molar solution i.e. , $W = 219.5 \times 30 \times 1.5 / 1000 = 9.8775 \text{ gm}$

c) 2 molar solution i.e. , $W = 219.5 \times 30 \times 2 / 1000 = 13.17 \text{ gm}$

2) Preparation of Sodium sulphide

(a) 1 molar solution i.e. , $W = 78.04 \times 30 \times 1 / 1000 = 2.3412 \text{ gm}$

(b) 1.5 molar solution i.e. , $W = 78.04 \times 30 \times 1.5 / 1000 = 3.5118 \text{ gm}$

(c) 2 molar solution i.e. , $W = 78.04 \times 30 \times 2 / 1000 = 4.682 \text{ gm}$

(3) Preparation of Polyvinyl alcohol matrix

1gm of PVA is dissolved in 50 ml of distilled water by stirring for 2 hours using a magnetic stirrer at 50°C .

Now 10 ml PVA, 10 ml, 1M zinc acetate solution and 10 ml, 1 M sodium sulphide solutions are mixed and stirred for 3 hours. After mixing the solution is deposited on a glass plate as thin film using a dip coating apparatus with hot chamber. The program for the dip coating is as follows:

Start position. –0mm

Dip length– 146mm

Dip speed –3mm

Retrieval speed – 3mm

Dip duration – 1min

Dry duration – 3min

No. of dips – 4

Temperature – 75°C

This process is repeated for 1.5 and 2 molar solutions and the samples are annealed at 3 different temperatures such as; 300°C, 350°C, 400°C for 1 hour and then cooled.

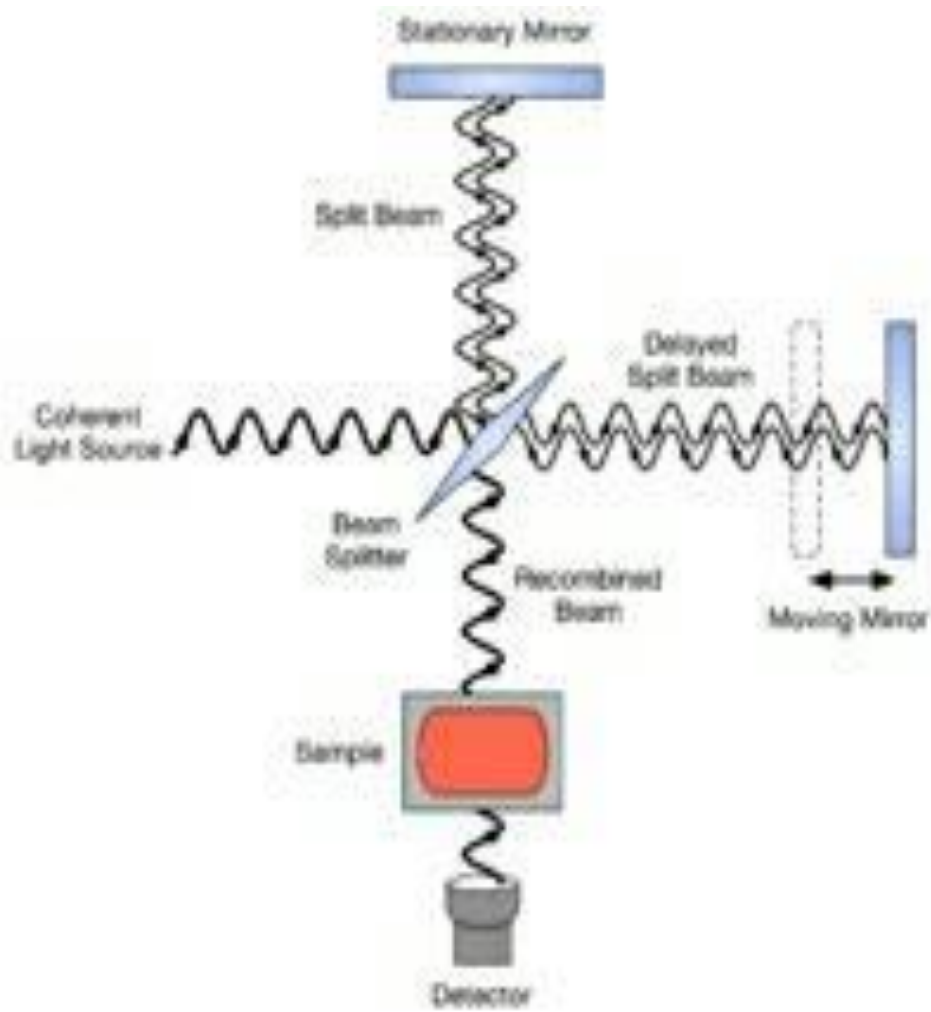
Dip coating unit is manufactured as a table top device with entire electronics and servo motor housed in a compact unit. A number of substrate can be held to the holder at the same time. Height of the substrate holder can be adjusted with respect to the level of the solution during the experiment. Servo motor is used as actuator for vibration free doping and withdrawal

4.2.1 FOURIER TRANSFORM INFRARED SPECTROSCOPY

FTIR is a technique which is used to obtain an IR spectrum of absorption or emission of a solid, liquid or gas. An FTIR spectrometer simultaneously collects high spectral resolution data over a wide spectral range. This confers a significant advantage over a dispersive spectrometer which measures intensity over a narrow range of wavelengths at a time.

FTIR is a method of measuring an infrared absorption spectrum. Fourier transform inverts the dimension, so the FT of the interferogram belongs in the reciprocal length domain, that is the wave number domain. The spectral resolution in wavenumbers per cm is equal to the reciprocal of the maximum retardation in cm. Thus a 4cm^{-1} resolution will be obtained if the maximum retardation is 0.25 cm; this is typical of the cheaper FTIR instruments. Much higher resolution can be obtained by increasing the maximum retardation. This not easy as the moving mirror must travel in a near perfect straight line.

The use of corner-cube mirrors in place of the flat mirrors is helpful as an outgoing ray from a corner-cube mirror is parallel to the incoming ray, regardless of the orientation of the mirror about axes are perpendicular to the axis of the light beam. Michelson himself attempted to resolve the hydrogen $\text{H}\alpha$ emission band in the spectrum of a hydrogen atom into its two components by using his interferometer. A spectrometer with 0.001 cm^{-1} resolution is now available commercially. The through put advantage is important for high resolution FTIR as the monochromator in a dispersive instrument with the same resolution would have very narrow entrance and exist slits.



Schematic diagram of a Michelson interferometer, configured for FTIR

4.2.4 Advantages Of FT-IR Spectroscopy

There are two principal advantages for an FT spectrometer compared to a scanning (dispersive) spectrometer.

1. The multiplex or Fellgett's advantage. This arises from the fact that information from all wavelengths is collected simultaneously. It results in a higher Signal- to-noise ratio for a given scan time or a shorter scan time for a given resolution.
2. The throughput or Jacquinot's advantage. This results from the fact that, in a dispersive instrument, the monochromator has entrance and exit slits which restrict the amount of light that passes through it. The interferometer throughput is determined only by the diameter of the collimated beam coming from the source.

4.2.3 UV SPECTROSCOPY

UV spectroscopy is an important tool in analytical chemistry. The other name of UV spectroscopy is Electronic spectroscopy as it involves the promotion of the electrons from the ground state to the higher energy of excited state.

UV spectroscopy is a type of absorption spectroscopy in which light of ultraviolet region (200-400nm) is absorbed by the molecule. Absorption of the ultraviolet radiations results in the excitation of the electrons from the ground state to higher energy states.

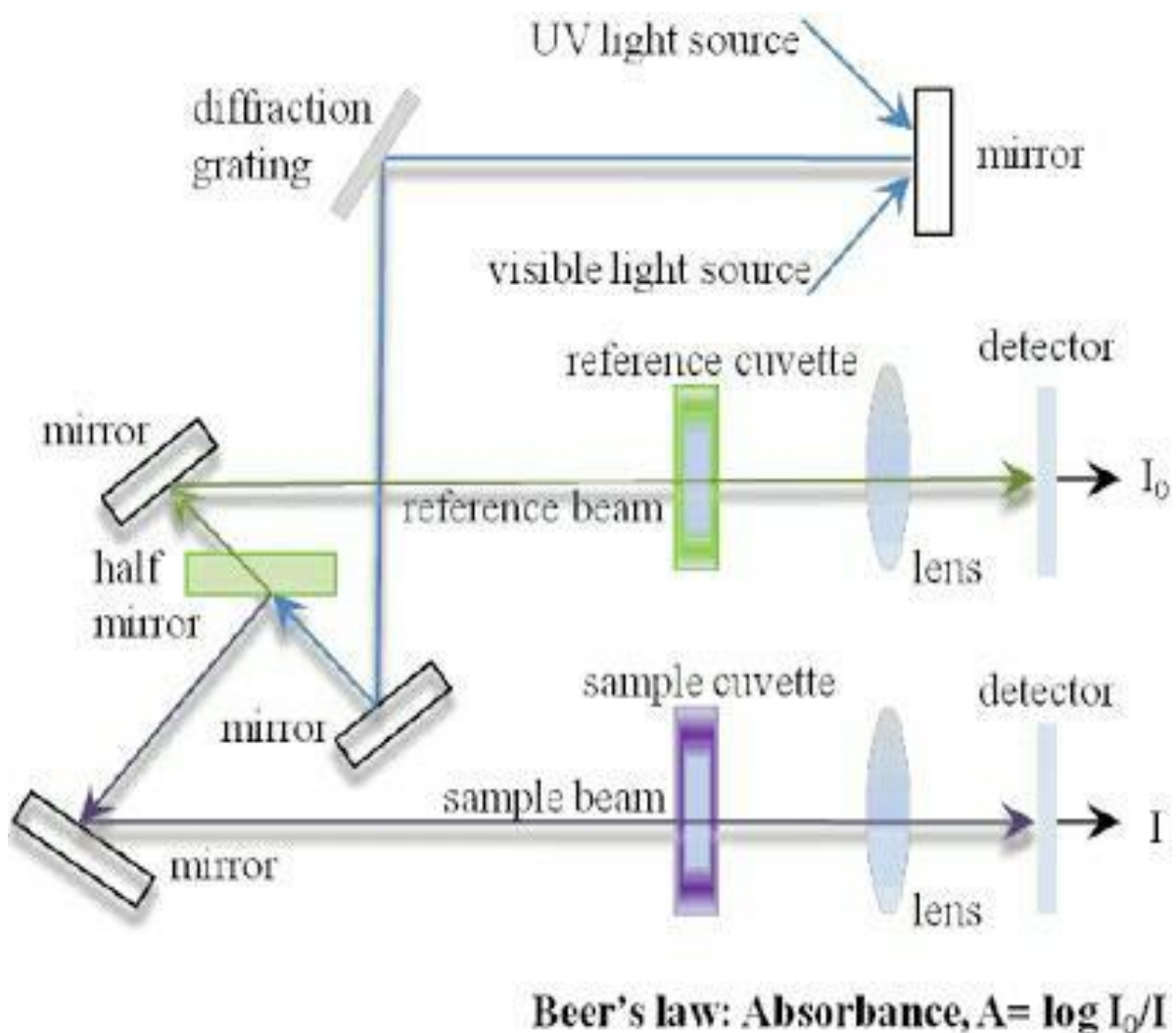
Electromagnetic radiation can be considered a combination of alternating electric and magnetic fields that travel through space with a wave motion. Because radiation acts as a wave, it can be classified in terms of either wavelength or frequency, which are related by the following equation:

$$\nu = c/\lambda$$

Where: ν is frequency (in seconds), c is the speed of light (3×10^8 m/s), and λ is wavelength (in meters). In UV visible spectroscopy, wavelength usually is expressed in nanometers. In UV visible spectroscopy, the low wavelength UV light has the highest energy.

When radiation interacts with matter, a number of processes can occur, including reflection, scattering, absorbance, fluorescence/phosphorescence (absorption and reemission), and photochemical reaction (absorbance and bond breaking). In general, when measuring UV-visible spectra, we want only absorbance to occur. Because light is a form of energy, absorption of light by matter causes the energy content of the molecules (or atoms) to increase. The total potential energy of a molecule generally is represented as the sum of its electronic, vibrational, and rotational energies:

$$E_{\text{Total}} = E_{\text{electronic}} + E_{\text{vibration}} + E_{\text{rotation}}$$



Schematic diagram of UV spectrophotometer

4.2.4 BAND GAP

In solid state physics a bandgap also called an energy gap is an energy range in a solid where no electron states can exist. In graphs of the electronic band structure of solid, band gap is the energy difference between the top of the valence band and bottom of the conduction band in insulators and semiconductors. This is equivalent to the energy required to free an outer shell electron from its orbit about the nucleus to become a mobile charge carrier, able to move freely within the solid material. So the bandgap is a major factor determining the electrical conductivity of a solid. Substances with large band gaps are semiconductors while conductors either have very small band gaps or none, because the valence and conduction band overlaps.

Determination of band gap energy

Optical absorption studies of the thin film are made using UV-VIS-NIR spectrometry. From the absorption spectra optical parameters like absorption coefficient (α), optical bandgap (E_g) have been evaluated. The absorption coefficient (α) is calculated from the equation

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

Where d is the thickness and is measured using an air wedge arrangement. A is absorbance of thin film. The direct optical band gap (E_g) was determined by fitting absorption data to the equation

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

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 bandgap amorphous material, therefore the value of $n = 2$. Then,

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

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

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 $(\alpha h\nu)^2$ versus $h\nu$ graph. β = bandwidth, λ = wavelength of light used

4.2.5 THIN FILM THICKNESS-AIR WEDGE

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 inferometer. The theory of the methods are presented and their applications to measurement of film thickness and refractive index are given. The accuracy of the measured film thickness is calculated .The three interference method proved that they could be transformed in to valuable technological tools . The study established that , estimation of film thickness by air wedge interference method is more simple and more accurate than others. Thickness can be calculated using the formula

$$t = \lambda l / 2\beta$$

where , t =thickness
plates

l = distance of wire from line of contact of two

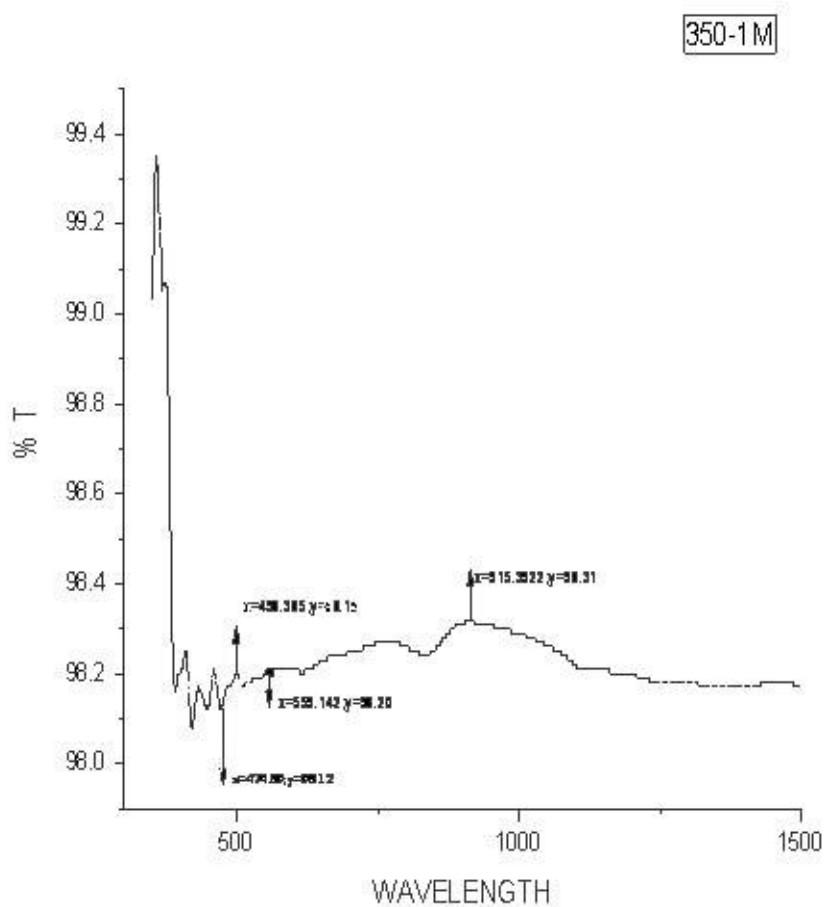
CHAPTER 5

RESULTS AND DISCUSSION

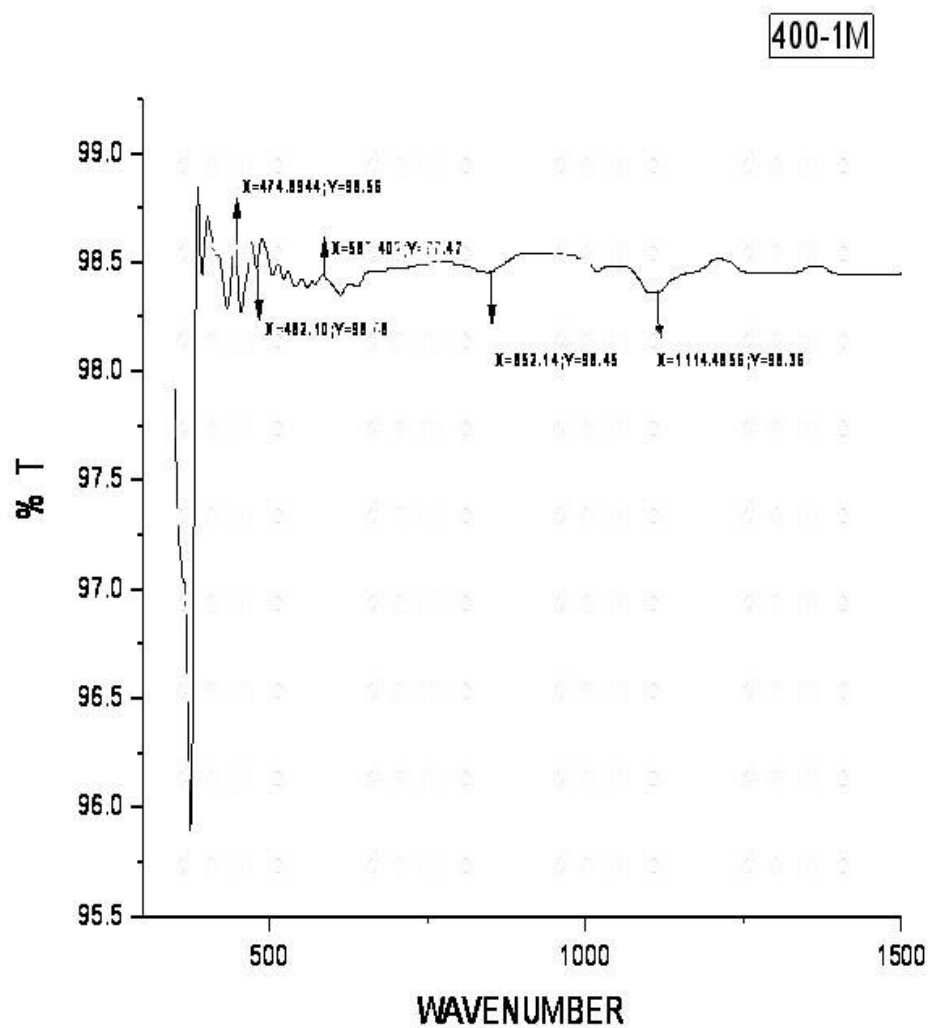
5.1 FOURIER TRANSFORM SPECTROSCOPY CHARACTERISATION

a) FT-IR Studies Of ZnS Thin Film

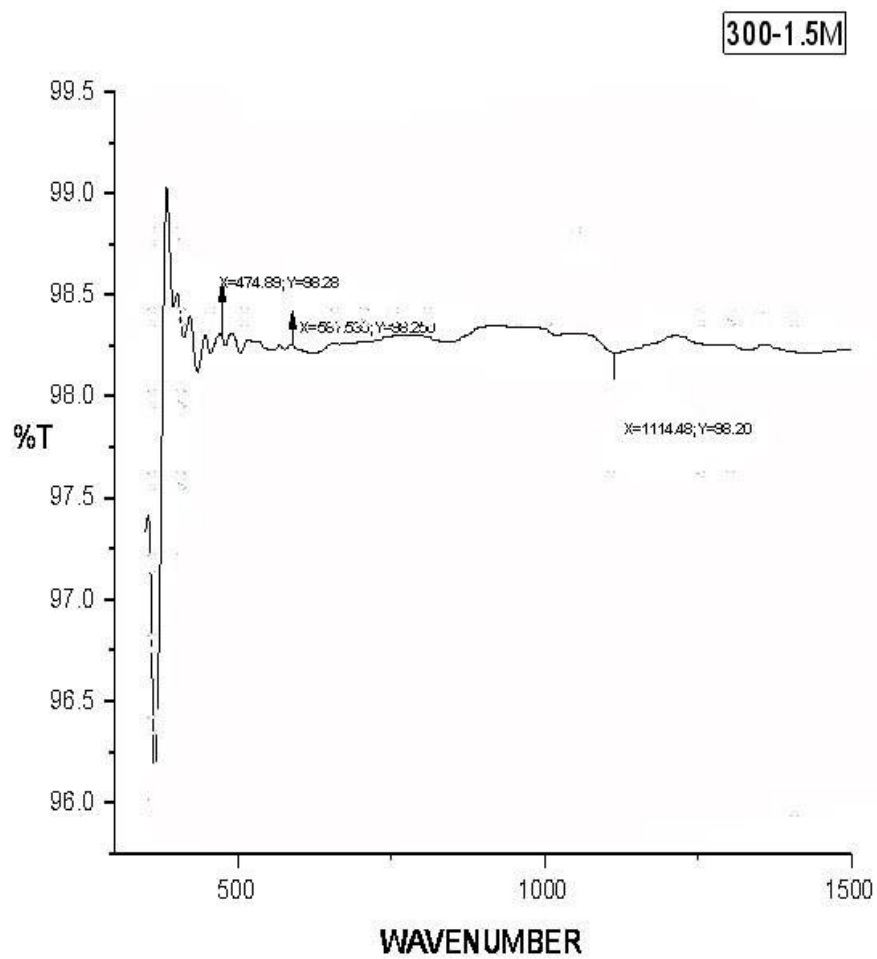
- Annealed at 350°C and molarity 1



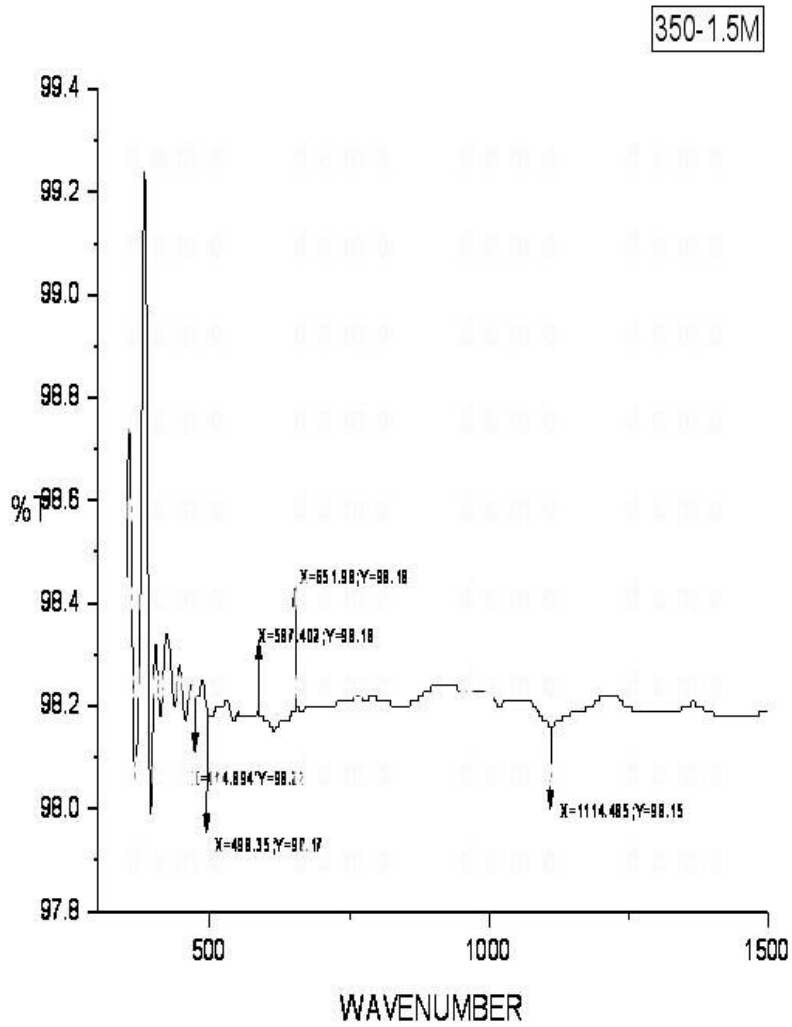
- **Annealed at 400°C and molarity 1**



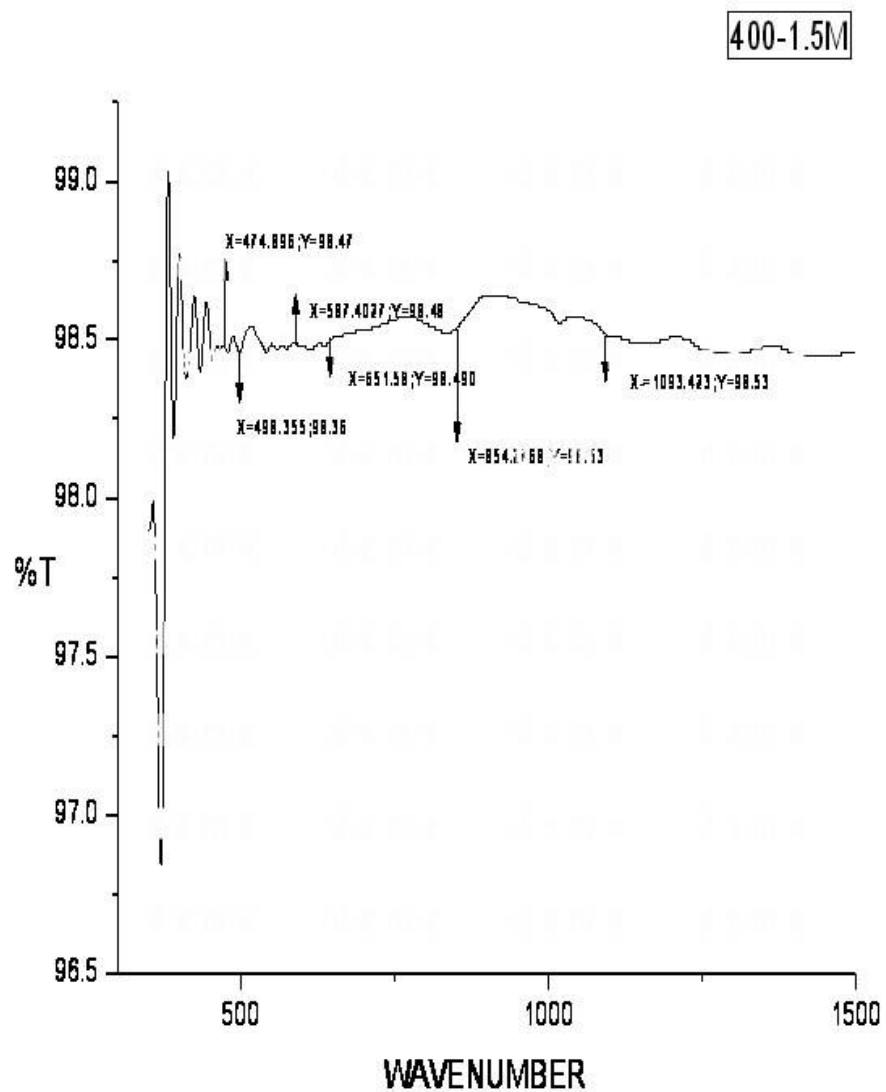
- Annealed at 300°C and molarity 1.5



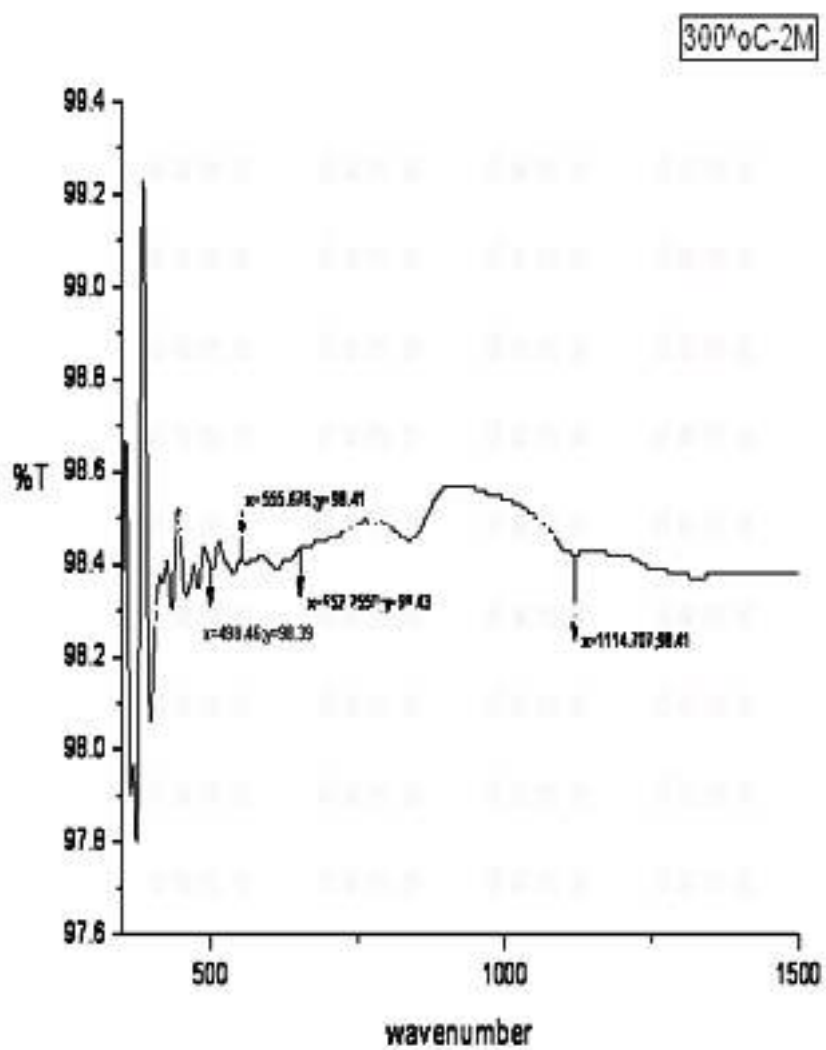
- Annealed at 350°C and molarity 1.5



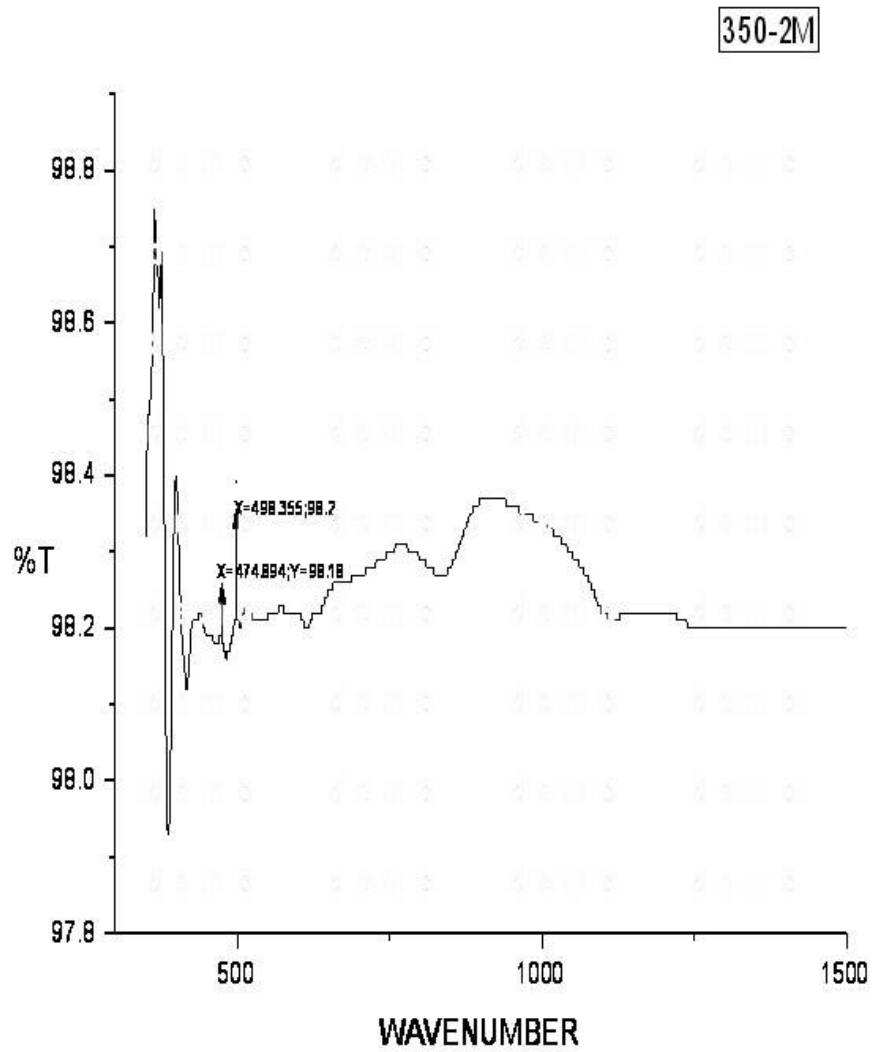
- Annealed at 400°C and molarity 1.5



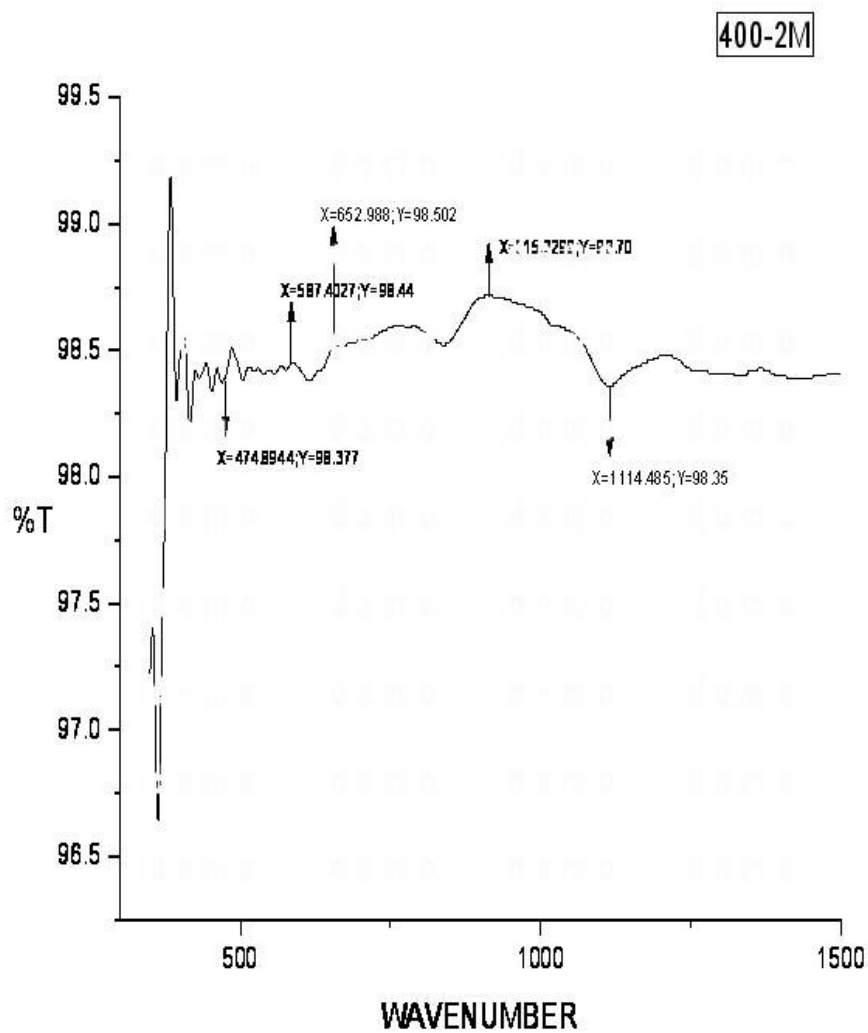
- Annealed at 300°C and molarity 2



- Annealed at 350°C and molarity 2



- Annealed at 400°C and molarity 2



Above given are the FTIR spectra of ZnS thin film samples. The peaks and corresponding vibrational modes are given below.

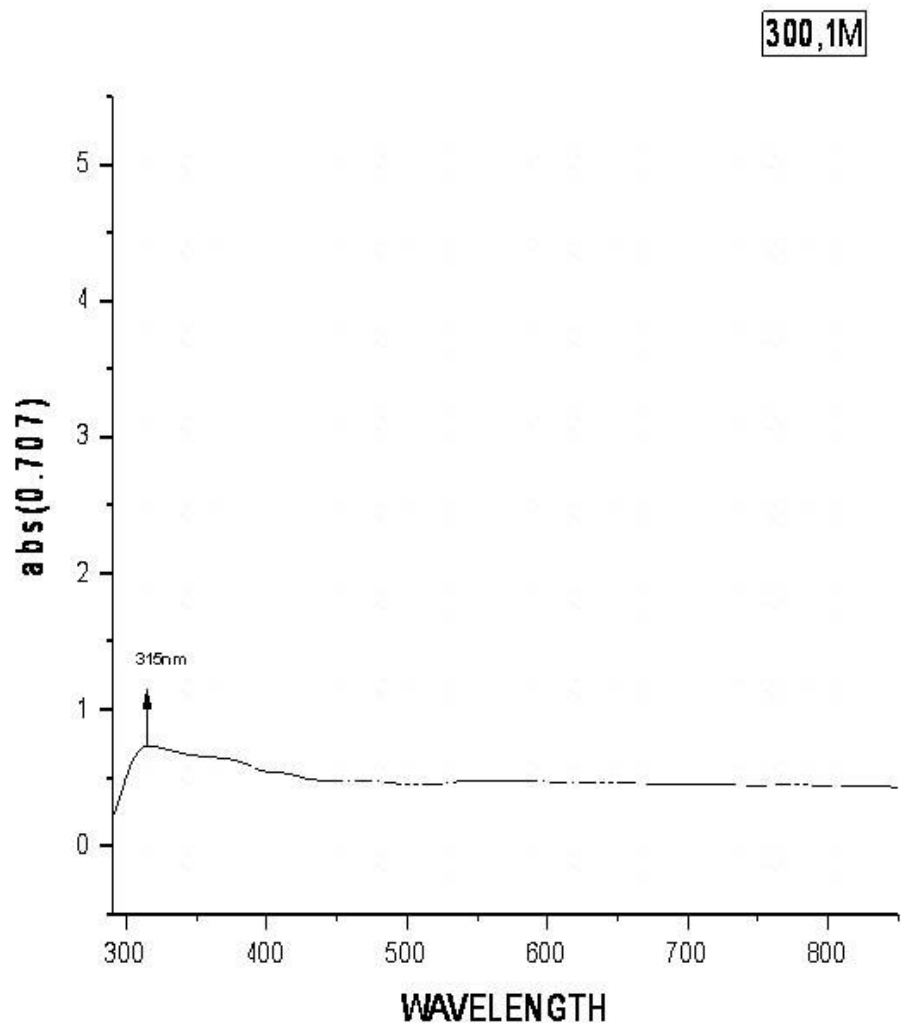
WAVELENGTH(cm⁻¹)	ASSIGNMENT
474	C-H
498	C-H
587	C-O-H
852	CH₂ STREACHING
1114	C-O-H STREACHING
1093	HYDROXY C-O STREACHING BAND
551-666	C-O-H STRETCHING
1639	C=O CARBONYL STRETCH
390	ZnS NANO PARTICLES

Samples annealed at 400°C shows maximum number of peaks which corresponds to different vibrational modes as compared to samples annealed at 350 and 300°C.

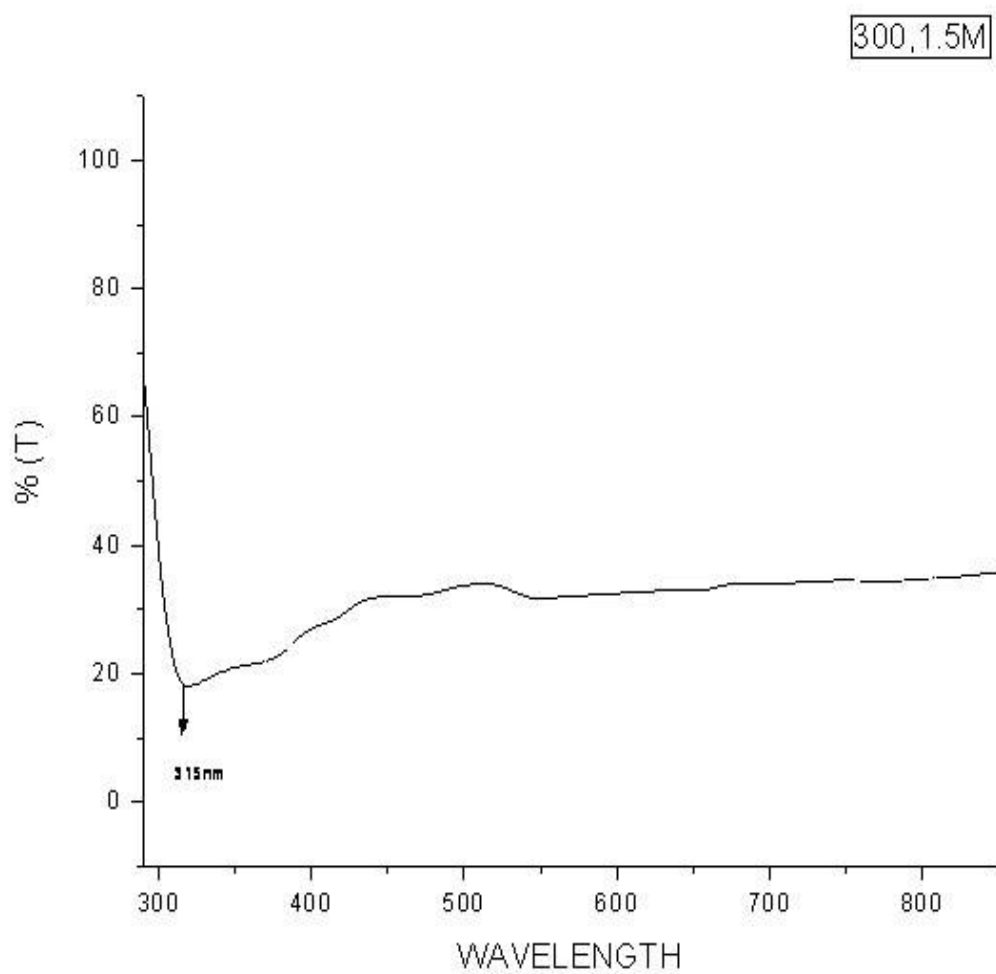
5.2 UV STUDIES OF ZnS THIN FILM

- Annealed at 300°C and molarity 1

a) absorbance

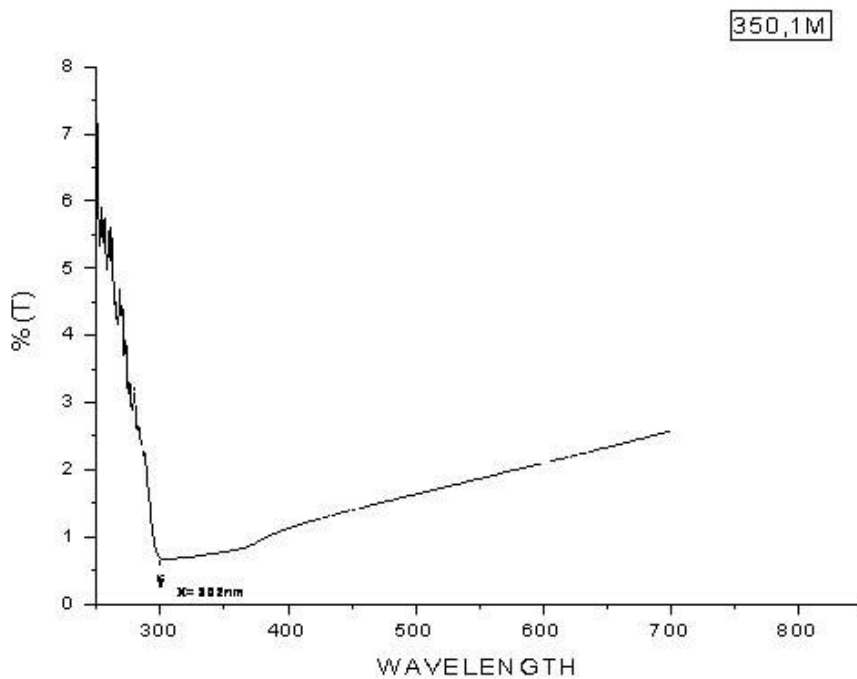
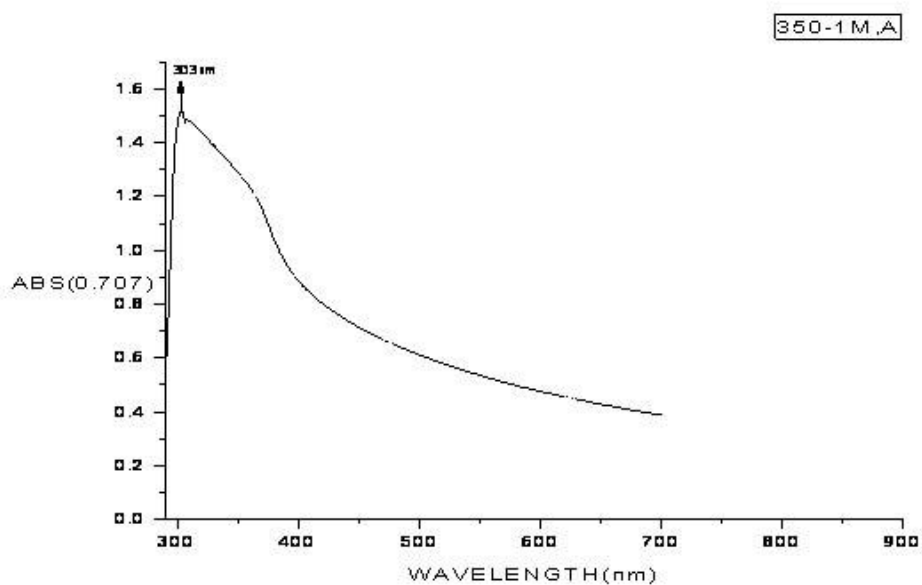


b) transmittance



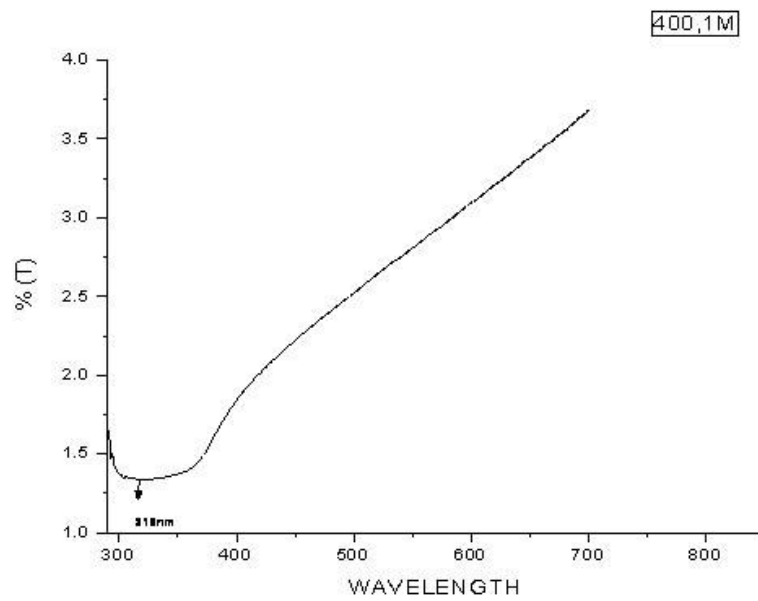
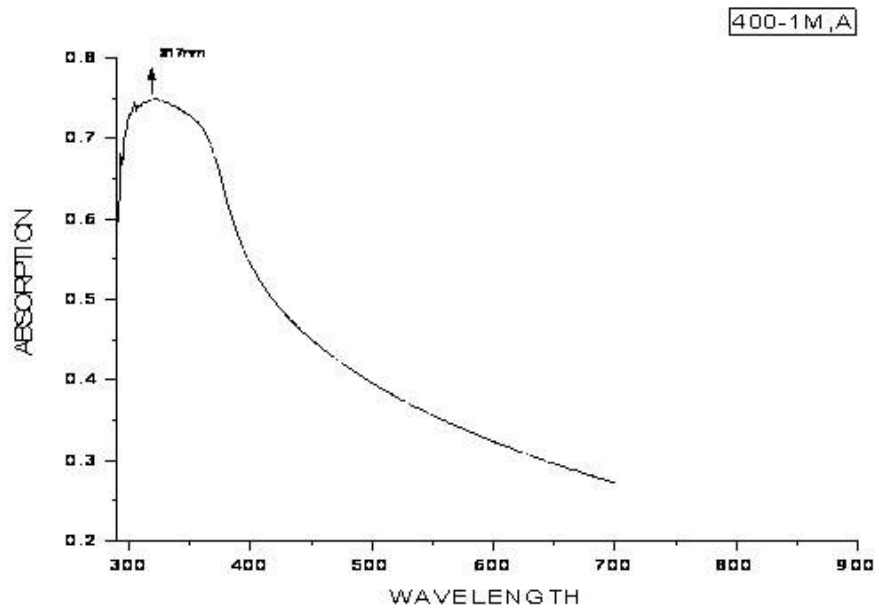
- annealed at 350°c and molarity 1

absorbance and transmittance



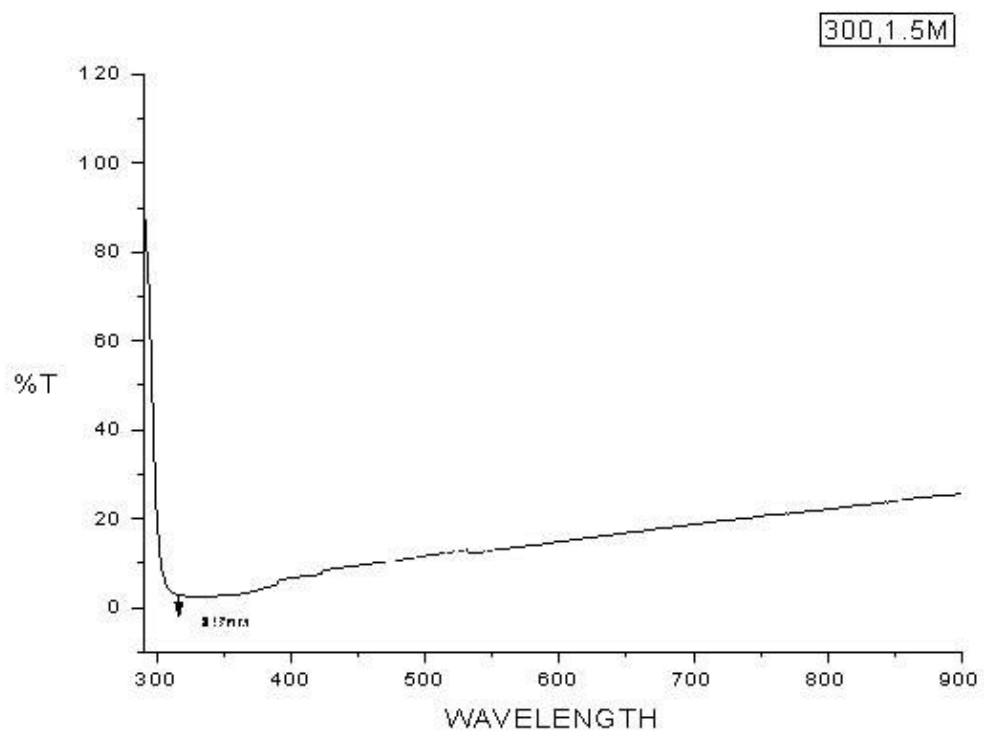
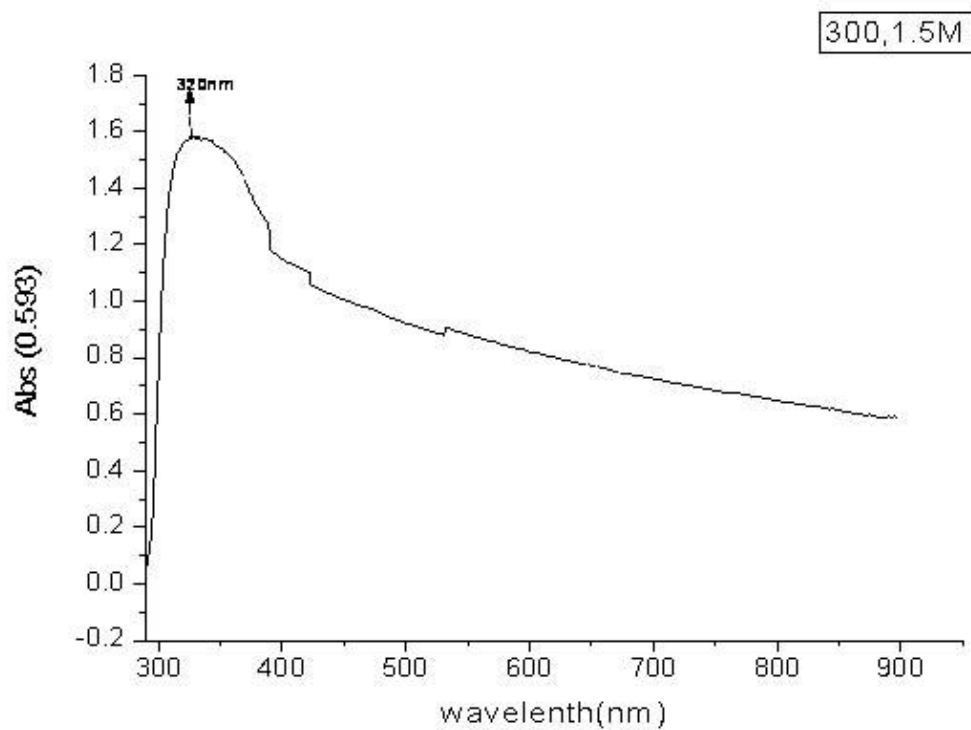
- annealed at 400°C and molarity 1

absorbance and transmittance



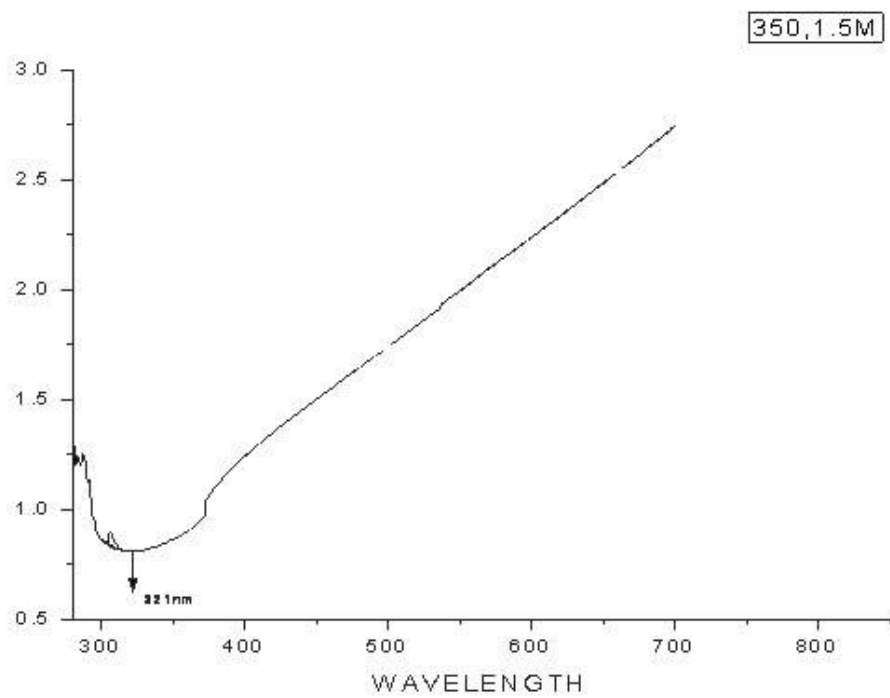
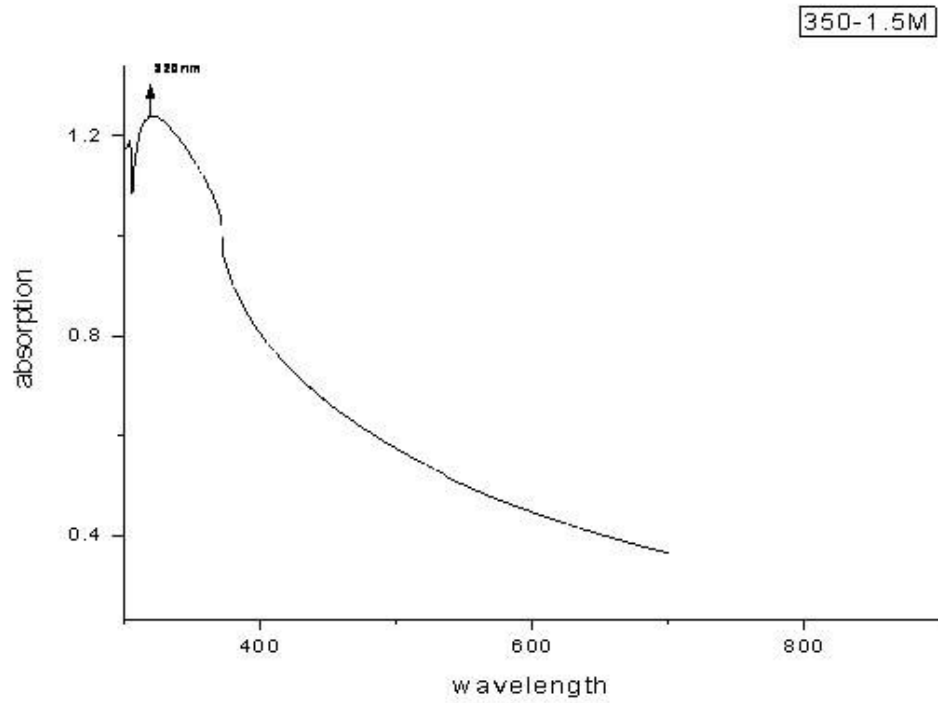
annealed at 300°c and molarity 1.5

absorbance and transmittance

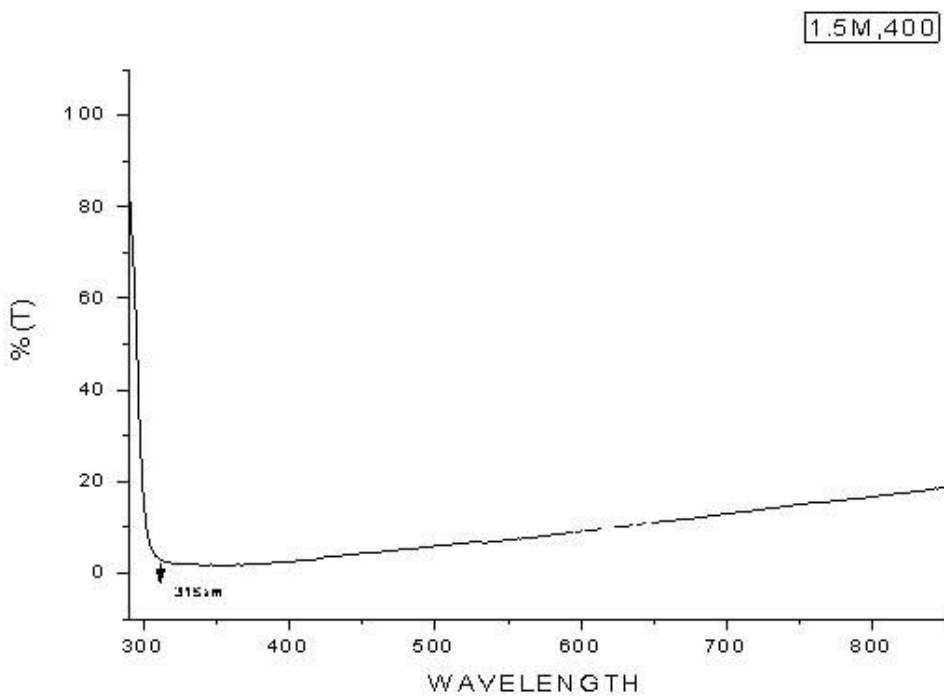
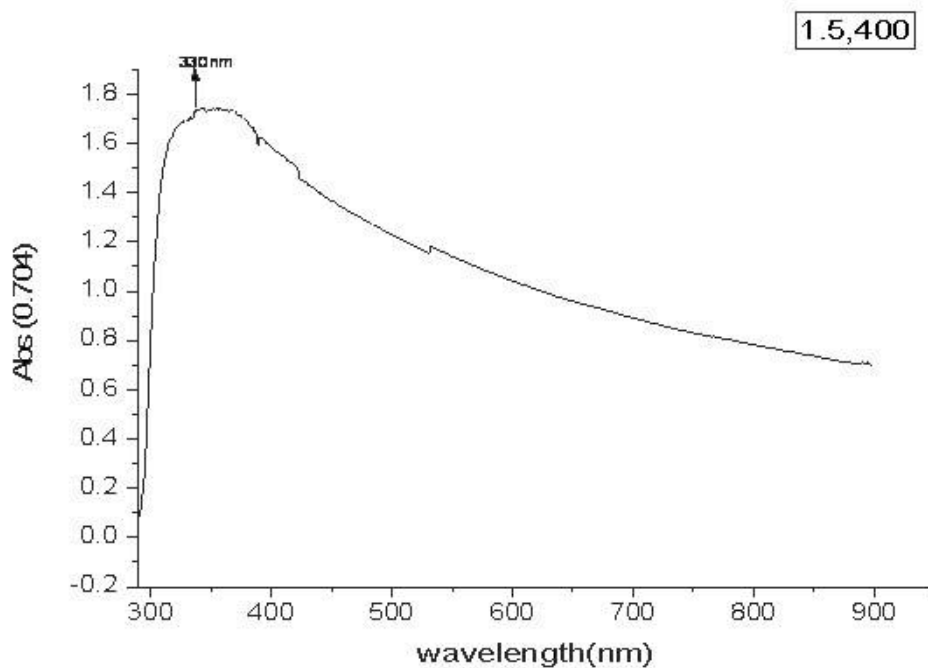


annealed at 350°c and molarity 1.5

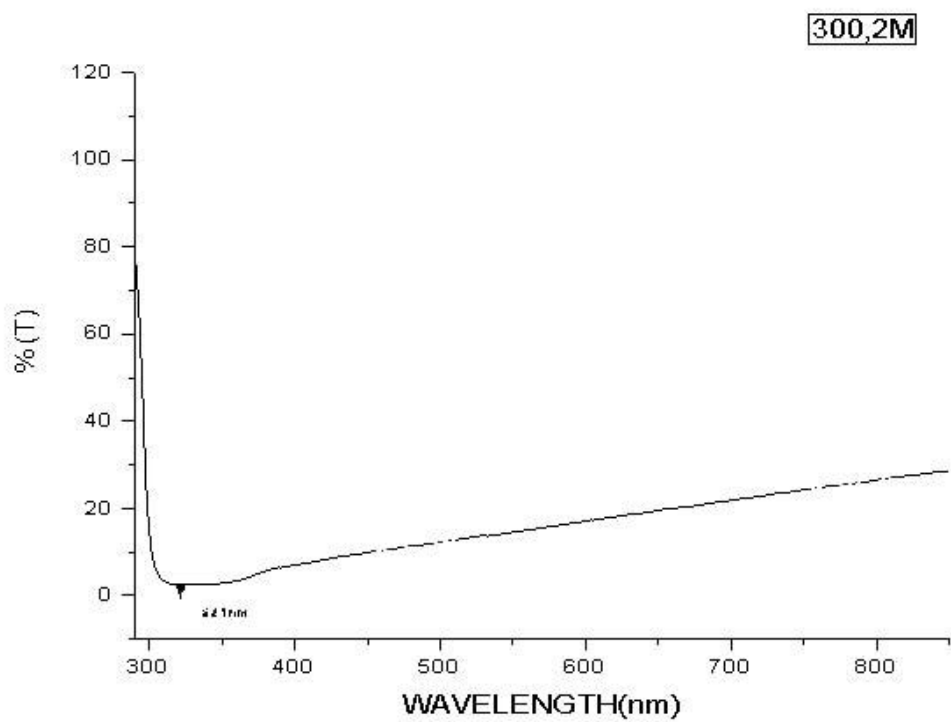
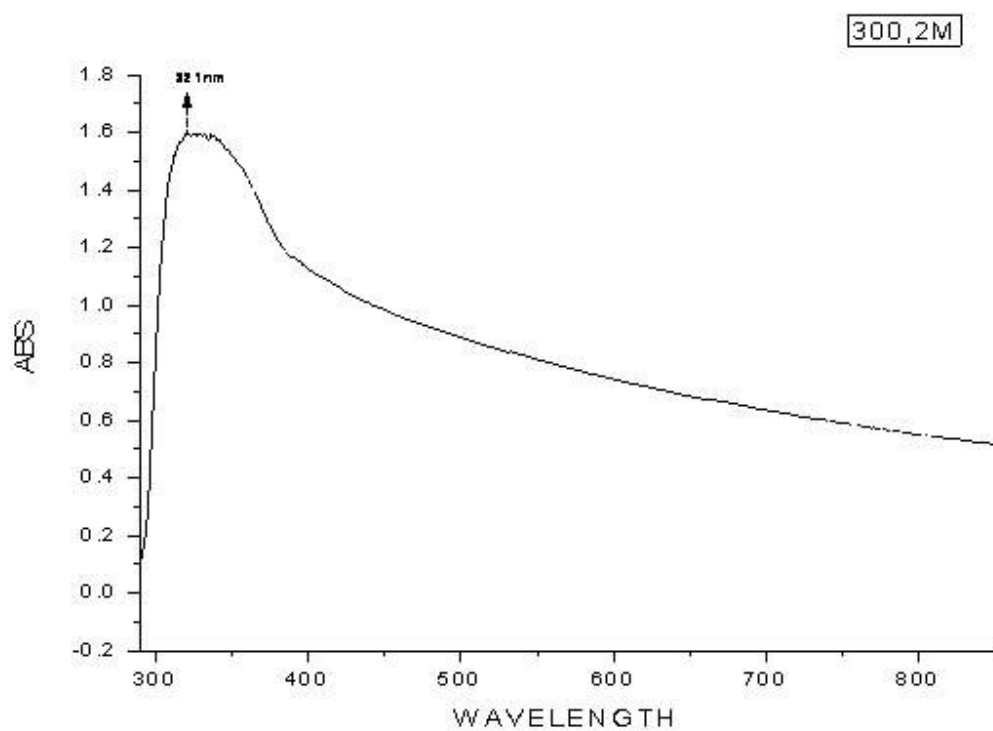
absorbance and transmittance



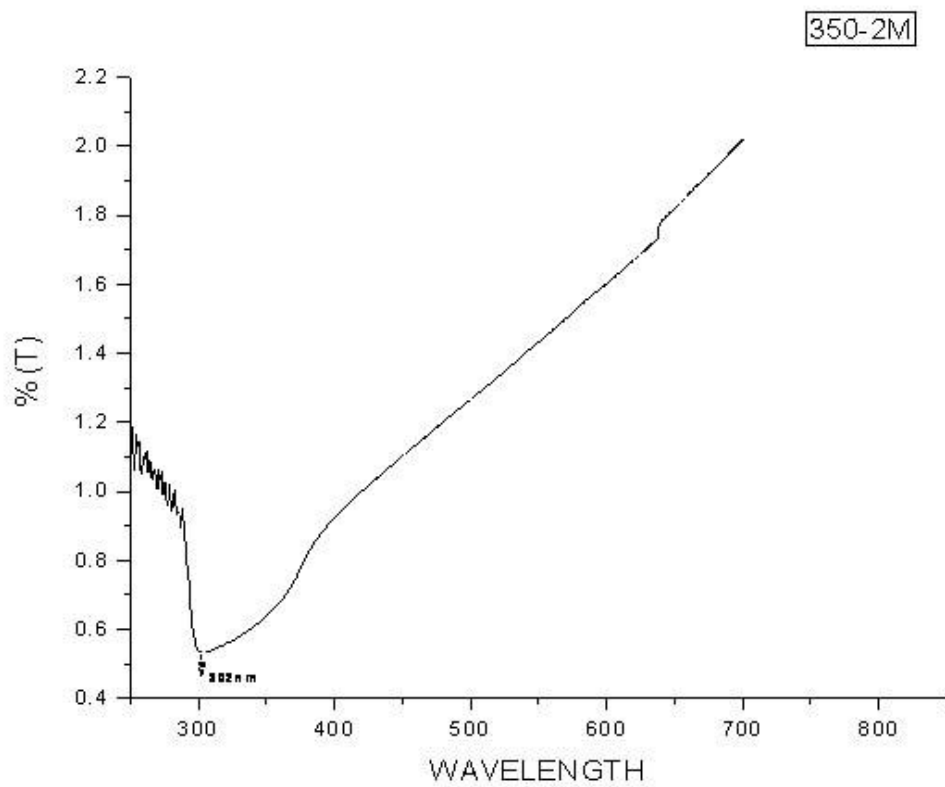
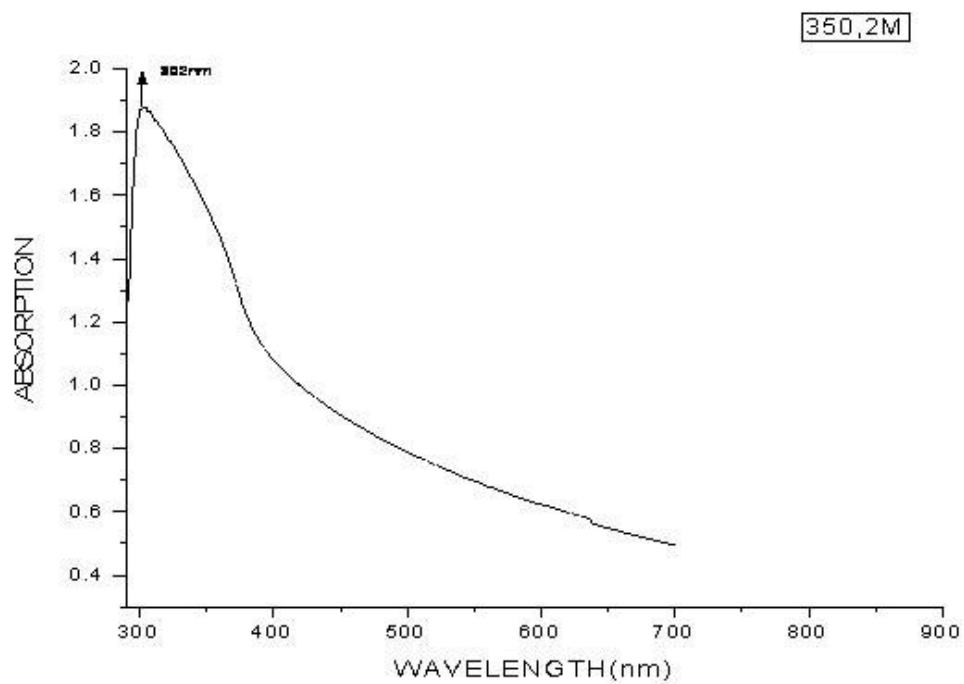
annealed at 400°C and molarity 1.5



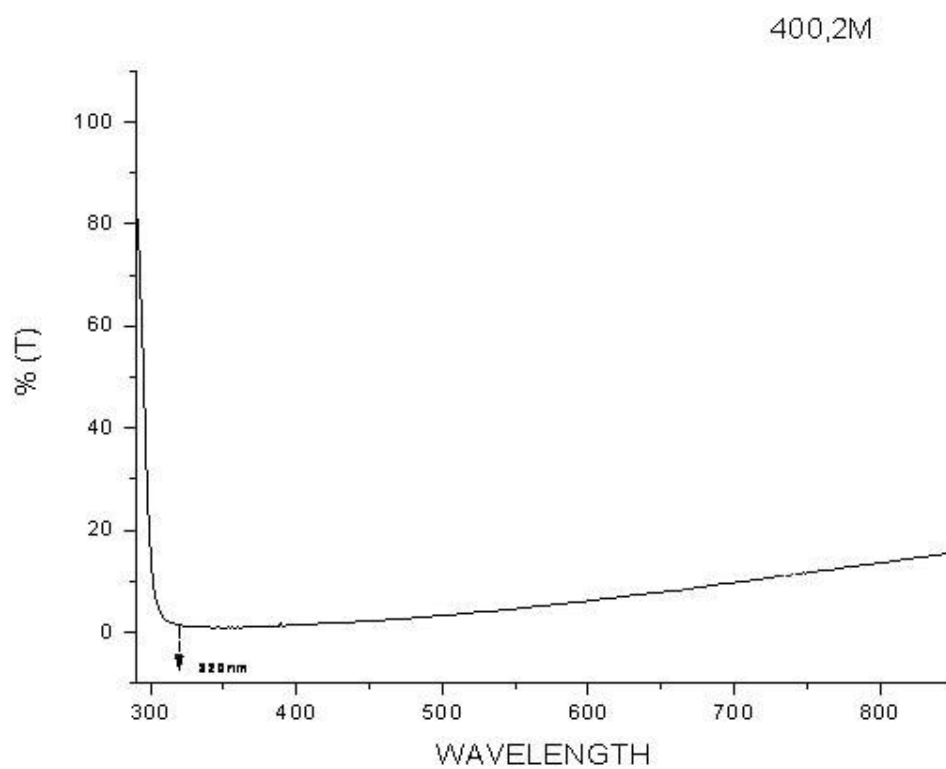
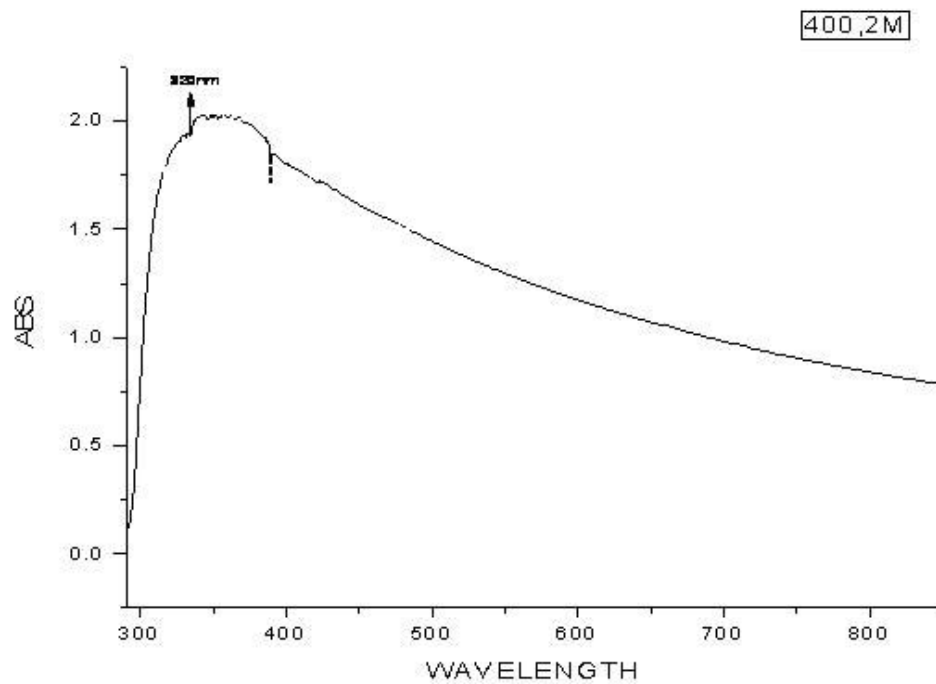
annealed at 300°c and molarity 2



annealed at 350°c and molarity 2



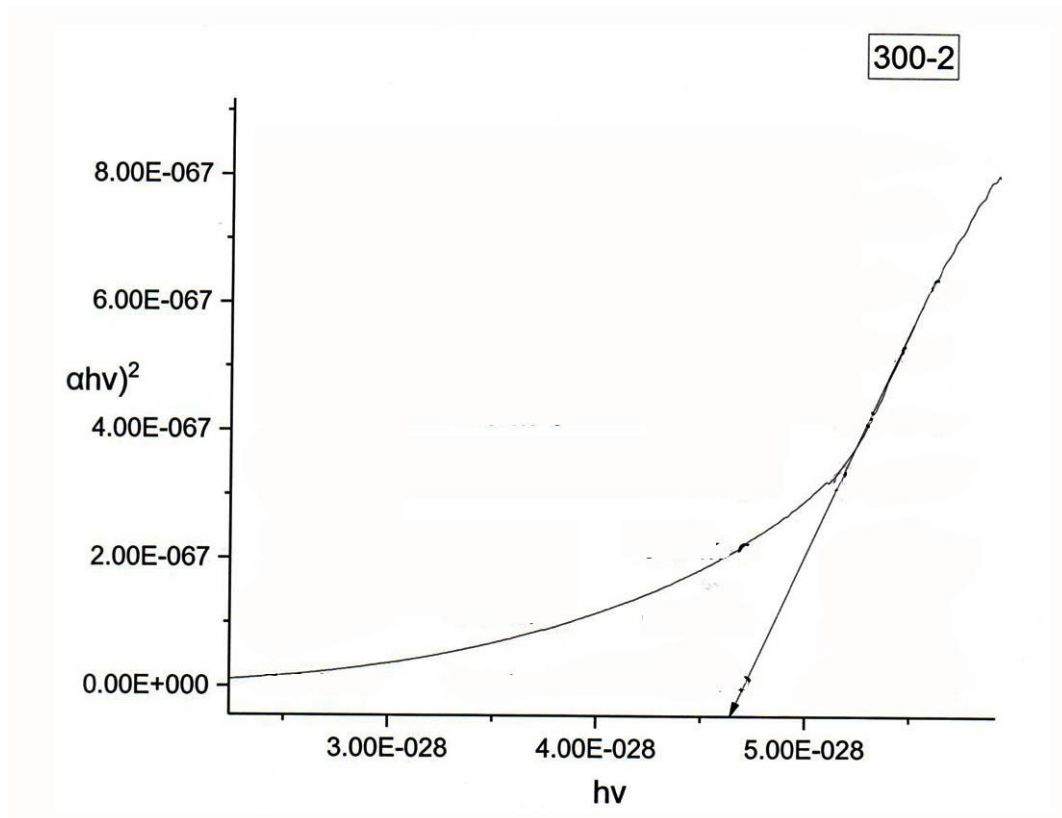
annealed at 400°C and molarity 2



- ZnS shows absorption and emission peaks between 300 and 330 nm.

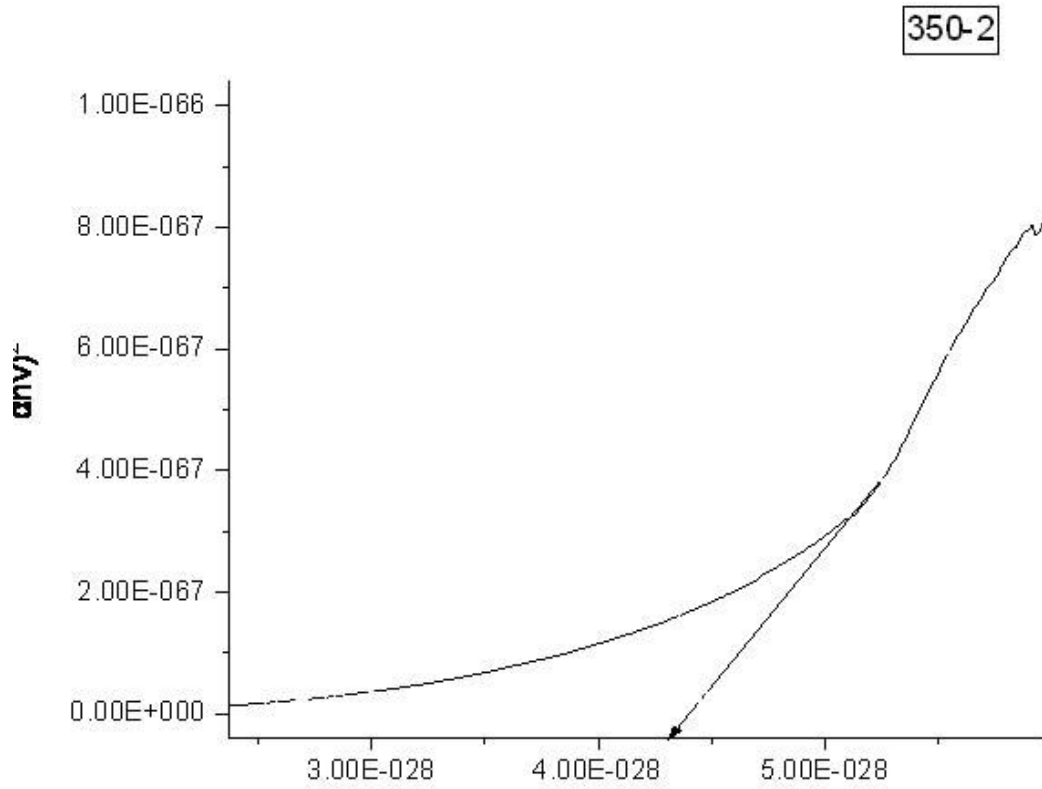
5.3 OPTICAL BAND GAP

- annealed at 300°C and molarity 2



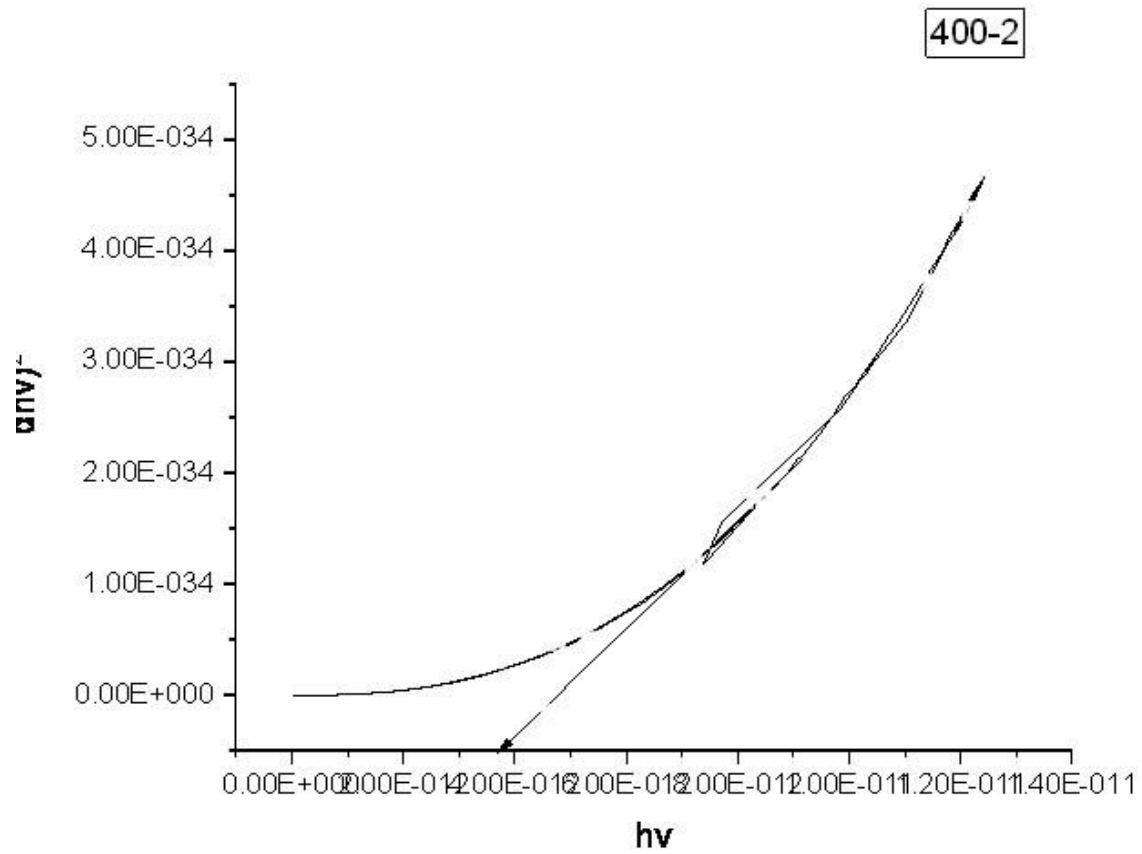
BAND GAP ENERGY =4.59eV

- annealed at 350°C and molarity 2



BAND GAP ENERGY=4.29eV

- **annealed at 400°C and molarity 2**



BAND GAP ENERGY= 3.69eV

- From the band gap energies determined it is found that it decreases with increase in annealing temperature and at 400°C it becomes equal to the band gap energy of ZnS single crystal(3.6eV).

5.4 THINFIL THICKNESS-Air Wedge Method

Least count=0.001cm At 400°C, 2M

Order	Microscope Reading(cm)	Width of 3 fringes	Mean(cm)
M	9.5154		
M+3	9.3371	0.6083	0.5946
M+6	9.1484	0.5913	
M+9	8.9071	0.5844	
M+12	8.7458		
M+15	8.5640		

Fringe width $\beta = 0.1988 \times 10^{-2} \text{m}$

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

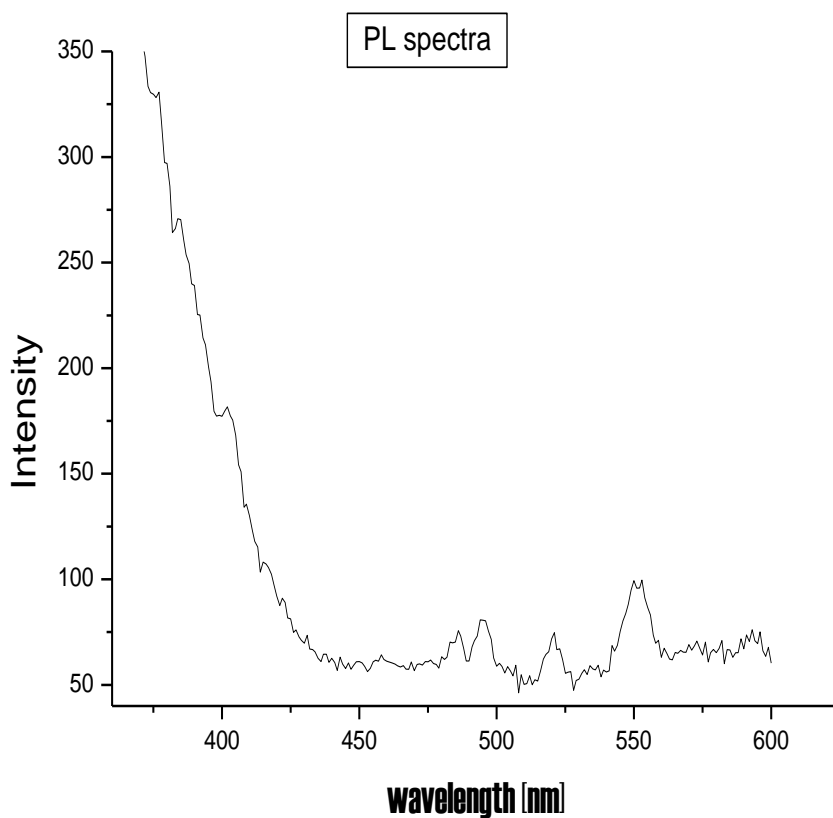
Distance of film from the line of contact of the glass plate = $2.1 \times 10^{-2} \text{m}$

Thickness of film = $\lambda/2\beta$

$$= 3.112 \text{ micrometers}$$

- Similarly found film thickness for samples annealed at 300 and 350°C are 2.42 and 2.69 micrometers respectively. That is film thickness increases as annealing temperature increases.

5.5 PHOTOLUMINESCENCE STUDIES OF ZnS THIN FILM



The plot contains three peaks centered at 485, 520 and 550 nm. 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.

5.6 CONCLUSION AND RESULTS

- ZnS thin films are prepared for three different molarities and annealed at three different temperatures.
- FTIR spectral studies were carried out and structural properties of ZnS thin films were studied.

It is found that sample annealed at 400°C has the maximum number of peaks. That is as annealing temperature increases number of vibrational modes which are expressed also increases.

- FTIR results shows the several modes of ZnS such as C-O-H, C-H, CH₂ stretching \ modes and C-O, C-H, C-O-H modes.
- UV Spectroscopic studies shows that the absorption of ZnS around 300nm. From samples mentioned above it is found that emission and absorption peaks occurs at 300,315,320nm approximately. It is also inferred from the graphs that sample annealed at 400°C shows the highest absorption peak (330nm) of all.
- Band gap energy is obtained from the uv study data. From absorption α is determined and hence energy ($h\nu$) and hence $(\alpha h\nu)^{1/2}$. By plotting a graph between $h\nu$ on x axis and $(\alpha h\nu)^{1/2}$ on y axis, then by extrapolating the straight line of the curve to x-axis we get the band gap energy
- From the band gap energy so obtained it is found that as annealing temperature increases band gap energy decreases, at 400°C (3.69eV) it becomes equal to the band gap energy of ZnS single crystal (3.6eV). For 350°C it is (4.29eV) and for 300°C it is 4.59eV.
- Film thickness is obtained using air wedge arrangement. For 400, 350, 300 film thickness is found to be 3.112, 2.69, 2.42 micrometers respectively. That is thickness increases with annealing temperature
- From the PL studies of the ZnS thin film different peaks are observed.

- The plot contains three peaks centered at 485, 520 and 550 nm. Appearance of these peaks in this region is due to the presence of Sulphur vacancies in the lattice (Beeker and bard, 1983; Rabani, 1989; Dhas et al.1999). This emission results from the recombination of photo generated charge carriers in shallow traps.

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