Studying The Effect Of Metallic Precursor Concentration On The Structural And Optical Properties Of Zinc sulfide Thin Films Synthesized By Chemical Bath Deposition Method

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BY

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Abstract

Zinc sulfide (ZnS) thin films with different concentrations of zinc chloride (0.3M, 0.5M, 0.7, 0.9M and 1.1M) have been deposited on a glass substrate made by chemical bath deposition technique in basic medium. Zinc chloride, thiourea, ammonia, and hydrazine hydrate were used to synthesize ZnS thin films. The films were annealed at 200°c. This study investigates how the concentration of metallic precursor affect the crystal structure and optical properties of Zinc sulfide thin films. The XRD result shows that no sharp peak which indicates the samples is amorphous nature. UV-Vis spectroscopy was used to analyze the optical characteristics of the deposited thin films. The absorbance increase with increasing of the zinc sulfide concentration and the band gap energy for the films prepared in different concentration of zinc chloride decrease from 3.53 to 3.42 eV with increasing of zinc sulfide concentrations. The results demonstrated that concentration of metallic precursor have distinct effects on optical absorbance and band gap energy.

***Keywords**: ZnS thin film, Chemical bath deposition, X- ray diffraction (XRD), Optical properties.*

Contents

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List of Abbreviations

Abs	Absorbance
a.u	Arbitrary unit
ZnS	Zinc sulfide
CBD	Chemical Bath Deposition
ZnCl2	Zinc chloride
N2H4(H2O)	Hydrazine hydrate
NH4(OH)	Ammonia solution
SC(NH2)2	Thoreau
d	Atomic spacing
D	Crystalline size
Eg	Band gap energy
g	gram
FWHM	Full Width at Half Maximum
hv	photon energy
IR	Infrared
LEDs	Light emitting diode
VB	Valence band
XRD	X-ray diffractometer
UV-VISS	Ultra-violet visible spectroscopy
FTIR	Fourier transform infrared
SEM	Scanning electron microscopy
FESEM	Field emission scanning electron microscope
nm	Nanometer
PL	Photoluminescence
TEM	Transmission electron microscopy
H2O	water
ml	milliliter
K	proportionality constant

SYMBOLS

α	Alpha
β	Beta
^{o}C	degree Celsius
λ	Lambda
h	Planck constant
θ	theta
M	mole

CHAPTER ONE

1. INTRODUCTION

1.1 Background

Zinc sulphide belongs to the II-IV family of semiconducting material. It has ever increasing attention due to the wide variety of applications such as UV light emitting diodes [1], efficient Phosphor in flat panel displays [2], etc. ZnS has a wide band gap (3.7 eV), high refractive index (2.35) and is a direct transition semiconducting material [3] .It is widely used as antireflection coatings in the solar cells [4, 5]. As it is electroluminescent, used in opto-electronic devices, photo synthetic coating, blue light emitting laser diodes [6] etc. Because of its non-toxicity character experimental researches are going on to replace CdS by ZnS [7]. The nano and polycrystalline ZnS thin films have attracted the attention of scientists and researchers as it plays a very crucial role in the optoelectronic and photovoltaic devices. Various techniques have been used to make ZnS thin film such as closed space sublimation [8], chemical bath deposition [9], vacuum evaporation [10], magnetron sputtering [11], spray pyrolysis [12] Thermal evaporation, chemical pyrolysis deposition and metal organic chemical vapor deposition [13-14] and each method has its own characteristic merits and demerits in producing homogeneous and defect free ZnS thin films.

Among these techniques, chemical bath deposition technique is chosen for the present study, due to its easy, economical, and reproducible quality. Thin film properties are sturdily dependent on the method of deposition, concentration of precursor, the substrate materials, temperature, rate of deposition and the background pressure. The films were characterized using X-ray diffraction analysis (XRD) and UV-Visible spectrometry. In present work, the effect of zinc chloride concentration (0.3M, 0.5M, 0.7M, 0.9M and 1.1M) on the structural and optical properties of ZnS is studied at a constant deposition temperature of 80°C using CBD technique in basic medium.

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1.2 Semiconductors

A semiconductor material is one whose electrical properties lie in between those of insulators and good conductors. Examples are: *germanium* and *silicon*. In terms of energy bands, semiconductors can be defined as those materials which have almost an empty conduction band and almost filled valence band with a very narrow energy gap (of the order of 1 eV) separating the two. Semiconductors can conduct electricity under preferable conditions or circumstances. This unique property makes it an excellent material to conduct electricity in a controlled manner as required. The electronic and optical properties of semiconductor materials are strongly affected by impurities, which may be added in precisely controlled amounts. Such impurities are used to vary the conductivities of semiconductors over wide ranges. This process of controlled addition of impurities is called doping [15].

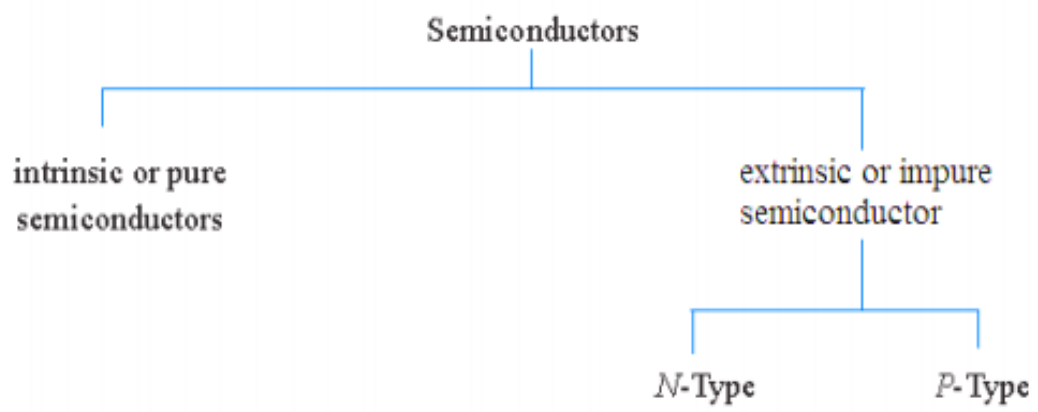

Figure 1.1: types of Semiconductor

1.2.1 Intrinsic semiconductors

An intrinsic semiconductor is one which is made of the semiconductor material in its extremely pure form. The energy gap is so small that even at ordinary room temperature; there are many electrons which possess sufficient energy to jump across the small energy gap between the valence and the conduction bands. Alternatively, an intrinsic semiconductor may be defined as one in which the number of conduction electrons is equal to the number of holes. Fermi level is the term used to describe the top of the collection of electron energy levels at absolute zero Fermi level lies in the mid of forbidden gap in intrinsic semiconductor[16].

1.2.2 Extrinsic semiconductors

The conductivity of an intrinsic semiconductor depends on its temperature, but at room temperature its conductivity is very low. As such, no important electronic devices can be

developed using these semiconductors. Hence there is a necessity of improving their conductivity. This can be done by making use of impurities. When a small amount, say, a few parts per million (ppm), of a suitable impurity is added to the pure semiconductor, the conductivity of the semiconductor is increased manifold. Such materials are known as extrinsic semiconductors or impurity semiconductors. The deliberate addition of a desirable impurity is called doping and the impurity atoms are called dopants. Such a material is also called a doped semiconductor. The dopant has to be such that it does not distort the original pure semiconductor lattice. It occupies only a very few of the original semiconductor atom sites in the crystal. A necessary condition to attain this is that the sizes of the dopant and the semiconductor atoms should be nearly the same [17].

1.2.3 Energy band gap of Semiconductor

The respective conduction and valence bands can be thermally populated with both electrons and holes, respectively as the Fermi energy level is near enough to both bands. There are two types" band structures in semiconductors: direct or indirect band. A direct band semiconductor is distinguished by having the minimum conduction band and maximum valence band edges aligned in at the same wave vector value, k, so that an electron can easily transit from the maximum edge of the valence band to the minimum edge of the conduction band. On the other hand, in the indirect band semiconductors, the band edges are not aligned at the same value of k, so that the electron does not transit directly to the conduction band minimum edge, both a photon and a phonon production mechanism are involved. In crystalline solids, the energy band gap, Eg between the valence band maximum, EV and conduction band minimum, EC is referred to as energy band gap [18].

$$Eg=EC-EV$$

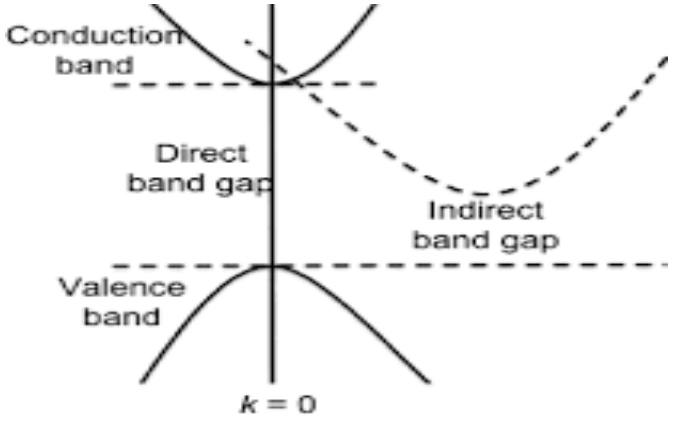

Figure 1.2: Direct and indirect band gap semiconductors.

1.3 Semiconductor thin films

Semiconductor thin films are produced in one or more thin layers. Common applications of such structures include many electronic materials such as transistors, sensors, and photovoltaic devices. Numerous semiconductor materials, both in bulk crystal form and thin film for found to be the pillars of the electronic industry. The continuously growing field of optoelectronic applications increases the demand of semiconducting materials with specific properties and there is a great demand for high speed and high functional devices. Thin film science has received tremendous attention because of numerous applications of films in diverse fields such as electronic industries, solar energy utilization, military weapon systems, space science, high memory computer elements, sensors, microelectronic and hybrid circuits and in others. Rapid developments in thin film technologies have been spurred by the growing importance of microelectronics. The development of semiconductor science and technology has been increasingly in the direction of devices utilizing thin film materials, which offer the advantages over bulk crystals in many aspects and in terms of material requirements [19].

1.4 Doping a semiconductors

Doping means the introduction of impurities into a semiconductor crystal to the defined modification of conductivity. Two of the most important materials silicon can be doped with, are boron (3 valence electrons) and phosphorus (5 valence electrons). Other materials are aluminum, indium (3-valent) and arsenic, antimony (5-valent) [20].

The dopant is integrated into the lattice structure of the semiconductor crystal, the number of outer electrons define the type of doping. Zinc oxide is an intrinsic n-type semiconductor because of native defect such as oxygen vacancy and zinc interstitials. While the electronics devices need to use junction between p-type and n-type semiconductor. Making p-type ZnCl2 is one of effective ways to enhance performance of the device that can improve carrier transport by interface modification at p-n junction. Elements with 3 valence electrons are used for p-type doping, 5-valued elements for n-doping [20].

1.5 General properties of Zinc sulfide (ZnS)

Figure: 1.3 Zinc Sulfide

Zinc sulfide ZnS is one of the direct II–VI semiconductor compounds with large band gap energy of ~3.65 eV at room temperature. Solid zinc sulfide is found in two different crystal forms, alpha (wurtzite) and beta (sphalerite), which have hexagonal and cubic structures, respectively. The beta crystalline (sphalerite) is the more stable form of ZnS. The wurtzite form exists as white or yellowish-white crystals, while the sphalerite form exists as greyish white crystals. It has a density of 4.09 g/mL, and melting point of 1,185 °C. Zinc sulfide is completely insoluble in water. It decomposes in the presence of acids and strong oxidizing agents. At temperatures higher than 900 °C, it decomposes with the release of zinc and sulfur fumes, and it also reacts with strong acids to release hydrogen sulfide gas. When heated to a temperature of 102 °C, the stable beta crystalline form of ZnS (sphalerite) changes into the alpha form (wurtzite). ZnS is a luminescent material, and exhibits phosphorescence when illuminated with UV light.

1.6 Statement of the problem

ZnS thin films have attracted the attention of scientists and researchers as it plays a very crucial role in the optoelectronic and photovoltaic devices. It can also be used in a variety application, including light-emitting diodes (LEDs), optical coatings, electroluminescence, flat panel displays, infrared windows, sensors, lasers, biodevices and etc. Zinc sulfide thin films prepared using various techniques such as hydrothermal, sputtering thermal oxidation of Cu foil, Spraying Pyrolysis, and a chemical bath deposition (CBD) method. In this research chemical bath deposition (CBD) technique was used to synthesize zinc sulfide thin film using zinc chloride as precursor concentration, thiourea, hydrazine hydrate and ammonia solution as complexing agents. The resulting zinc sulfide thin film could be characterized for their structural and optical properties using XRD and UV-VIS spectrophotometer. Many researchers have studied the effect of solution PH, deposition time and bath temperature on zinc sulfide thin film. However, the study on effect of metallic precursor concentration by CBD method using zinc chloride as precursor is not sufficient. Therefore, in this work the effect of zinc chloride concentration on the structural and optical properties of zinc sulfide thin films deposited by CBD method is studied.

1.7 Objective

1.7.1 General objective

The general objective of this research is to study the effect of metallic precursor concentration on the structural and optical properties of zinc sulfide thin films by CBD.

1.7.2 Specific objectives

- To synthesize ZnS by CBD method
- To Characterize the crystalline structure and optical properties of the synthesized ZnS thin film using X- ray diffraction (XRD) and Optical Absorption Study.

1.8 Significance of the study

The findings of this research could be used in technologies that use ZnS thin films and benefit for the researchers who are studying the properties of zinc sulfide synthesized by CBD method for different applications such as light-emitting diodes (LEDs), optical coatings, electroluminescence, flat panel displays, infrared windows, sensors, supper conductors, photovoltaic devices, optoelectronic devices and etc.

2. Review of Literature

2.1. Thin films

Thin film is a layer of material ranging from fractions of a nanometer (monolayer) to several micrometers in thickness. The controlled synthesis of materials as thin films (a process referred to as deposition) is a fundamental step in many applications. A familiar example 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. These layers serve in both reflective and refractive systems. Large-area (reflective) mirrors became available during the 19th century and were produced by sputtering of metallic silver or aluminum on glass. A well-known example for the progress in optical systems by thin-film technology is represented by the only a few mm wide lens in smart phone cameras. Other examples are given by anti-reflection coatings on eyeglasses or solar panels. Physical deposition uses mechanical, electromechanical or thermodynamic means to produce a thin film of solid. An everyday example is the formation of frost [21].

2.3 Applications of thin films

While some of the films show very high absorption in the UV-VIS-NIR region, the absorption of the films was found to increase with increasing thickness, suggesting potential applications as solar absorbers for cell applications. The property of high transmission across the UV-VIS-NIR makes the film a suitable material for poor thermal control window coatings and anti-reflection coatings in cold climates. The moderate transmittance makes this film a suitable material for anti-glare coatings on car windshields, and the transmittance makes the film a suitable material for absorption material in solar cells. Chemical bath-deposited films are currently being developed for use in converting solar radiation into electricity.

The key material properties of these films are the optical properties in the UV-VIS and NIR regions, which strongly depend on the thin film band gap and the nature of the film material properties. Other uses for this type of film relate to use in decorative and protective coatings. These properties determine the film's absorption, transmission, reflection, and photoconductivity properties. Thus, studying the solid-state properties of thin films gives an idea of their properties resulting from the interaction between the photon energy and the structure of the thin film, or between the energy configuration and other optical constants (n, k) of materials. Some films have a large band gap and high dielectric strength. Some wide-gap semiconductors have applications in light-emitting diodes, photodetectors, gas detector sensors, etc.

2.4 Review of Synthesis and Characterization of ZnS Thin Films

In this section some works done by different researchers to synthesis and characterize zinc sulfide thin film by different techniques such as; chemical bath deposition method, sol-gel technique, and successive immersion have been reviewed. Recently, numerous researcher synthesized ZnS thin films by chemical bath deposition method (Biswas *et al.* 2005; Roy *et al.* 2006; Prabahar *et al.* 2009a; Prabahar *et al.* 2009b; Kathirvel *et al.* 2011; Srikanth *et al.* 2011; Jeyachitra *et al.* 2014; Gallanti *et al.* 2016).

Gilbert et al. combined real space Pair Distribution Function (PDF) analysis of nanoparticle structure with the particle size analysis (zetasizer) and FTIR to point out that the nature of surface solvent or ligand interactions will have an effect on the interior crystallinity of nanoparticles. The availability of particles with a variety of crystallinity provides a model system during which it's possible to see the interior disorder effects of nanoparticle, where properties like mechanical stiffness and fluorescent quantum yield are affected. PDF analysis showed that samples of ZnS nanoparticle with similar mean diameters (3.2-3.6 nm) however synthesized and treated differently possess a dramatic range of interior disorder [21].

Vacassy et al. fabricated ZnS nanoparticles in the powder form by using precipitation method from homogeneous solutions of various zinc compounds, with S2- as precipitating anion, formed by decomposition of thioacetamide. Also, the complexing-attachment phenomena of the ZnS particles with acetate and acetylacetonate anions leading to the seize of particle growth processes. The presence of complexed Zn2+ species in the acidic solution is demonstrated both theoretically (using a model based on the calculations of the solubility isotherms of the soluble species) and experimentally by Fourier-transform infrared techniques [22].

Ghosh et al. synthesized Polyvinyl Pyrrolidone (PVP) encapsulated Zinc Sulphide (ZnS) nanoparticles by adding measured amount of zinc acetate, thiourea and PVP into N, N- Dimethyl Formamide (DMF) medium with consistent stirring at 150 rpm. The resulted TEM image of ZnS NPs explained the effect of capping on size separation. It exhibited that PVP capped ZnS nanoparticles were mono dispersed in nature. Their size ranging within 2-3 nm matches with of XRD results. Whereas uncapped nanoparticles on the other hand were aggregated and were larger in sizes than capped ones. This explains the use of PVP as capping agent. Also Blue shift in absorption edge as compared to bulk ZnS clearly explained the quantum confinement effect within ZnS nanoparticles [23].

Kanemeto et al. have reported the photo-physical and photocatalytic properties of ZnS nanoparticles and explained the role of defect levels in influencing the luminescence characteristics of quantum particles. PL studies revealed a peak at 325 nm (3.82 eV) which was due to transition of trapped electrons to valence levels. Thus it was concluded that capping agents are important in removing Zn dangling orbitals (electron traps) from the gap. Observation of broad red shift in luminescence and absence of band edge luminescence is due to unsaturated

sp3 hybridized orbitals of surface S atoms. In this paper they have measured PL emission for various excitation wavelengths. They observed a broad peak at about 363 nm (3.41 eV) for all samples in the PL spectra for all organic passivating agents at 220 nm excitation wavelength [23].

Sarika Pandey et al. prepared Manganese doped ZnS nanoparticles capped with histidine molecule by co-precipitation reaction from the homogenous solution of zinc and manganese salts. The PL spectrum shows the emission peak of doped nanoparticles at around 590 nm. The XRD results calculated the average particle size of ZnS nanophosphor by Debye Scherrer's formula to be of the order of 5-6 nm. A small angle X-ray study shows the maximum uniform particle size distribution of 3.5 nm for the prepared sample [24].

Vacassy et al. fabricated ZnS nanoparticles in the powder form by using precipitation method from homogeneous solutions of various zinc compounds, with S2- as precipitating anion, formed by decomposition of thioacetamide. They observed that nucleation is enhanced by the use of acetic acid but restricted particle growth occurs due to formation of complex with zinc cations that lowers the concentration of free cations in the solution. Also, the complexing-attachment phenomena of the ZnS particles with acetate and acetyl acetonate anions leading to the seize of particle growth processes. The presence of complexed Zn2+ species in the acidic solution is demonstrated both theoretically (using a model based on the calculations of the solubility isotherms of the soluble species) and experimentally by Fourier-transform infrared techniques [25].

Ram Kripal et al., prepared ZnS: Mn+2 by co-precipitation method and conducted their photo luminescent and photoconductivity properties. UV- visible spectra shows blue shift as compared to bulk counterpart. PL spectra show orange emission that varies with Mn+2 concentrations. The XRD studies estimated the size of nanoparticles to be around 2-4 nm. The TEM images over estimates the larger nanoparicle size due to drying step in sample preparation. The time resolved rise and decay of photocurrent indicates the anomalous behavior during steady state illumination [26].

As the above review indicates the researcher's synthesis zinc sulfide thin film by different methods, chemicals and characterization techniques. But in this research chemical bath deposition (CBD) technique can be used to synthesize zinc sulfide by using zinc chloride as precursor concentration, ammonia solution and hydrazine hydrate as complexing agents. The resulting zinc sulfide thin films can be characterized for their structural and optical properties using XRD and UV-VIS spectrophotometer.

CHAPTER THREE

3. Methodology

3.1 Thin Film Deposition And Characterization Techniques

3.1.1 Thin film deposition methods

Thin film deposition is an act of preparing a thin film onto a surface called substrate or onto previously deposited layers. There are many techniques available for researchers in the deposition of thin film of different material on the layer, like evaporation, sputtering, chemical bath deposition (CBD), sol gel etc. The chemical bath deposition (CBD) method is greater commercial value than either thermal evaporation or sputtering.

3.1.2 Chemical Bath deposition technique

Chemical bath deposition (CBD) is a method to deposit nano materials; it can be employed for large area batch processing or continues deposition. Chemical bath deposition methods are based on the controlled precipitation of compounds from solution onto suitable substrates. The substrate is immersed in an alkaline or basic solution containing metal ions, chalcogenide sources, and complexing agents. Chemical bath deposition has proven to be a simple and inexpensive thin film deposition method with many advantages (Biswas *et al.* 2005; Roy *et al.* 2006; Prabahar *et al.*

CBD method has significant advantages over the other methods as follows:

✓ CBD is the simplest and cost effective method.

✓ It is possible to deposit multi compound chalcogenide thin films over a wide range of stoichiometry with this technique.

✓ Chemicals do not require high vacuum and it can be carried out even at room temperature

✓ Large area deposition is possible by carefully lying down the substrate on a shallow tray containing the deposition bath.

✓ Produces uniform well adherent and reproducible thin films for photovoltaic applications.

✓ An inexpensive method for large scale industrial applications

✓ The material consumption is low and minimizes the loss.

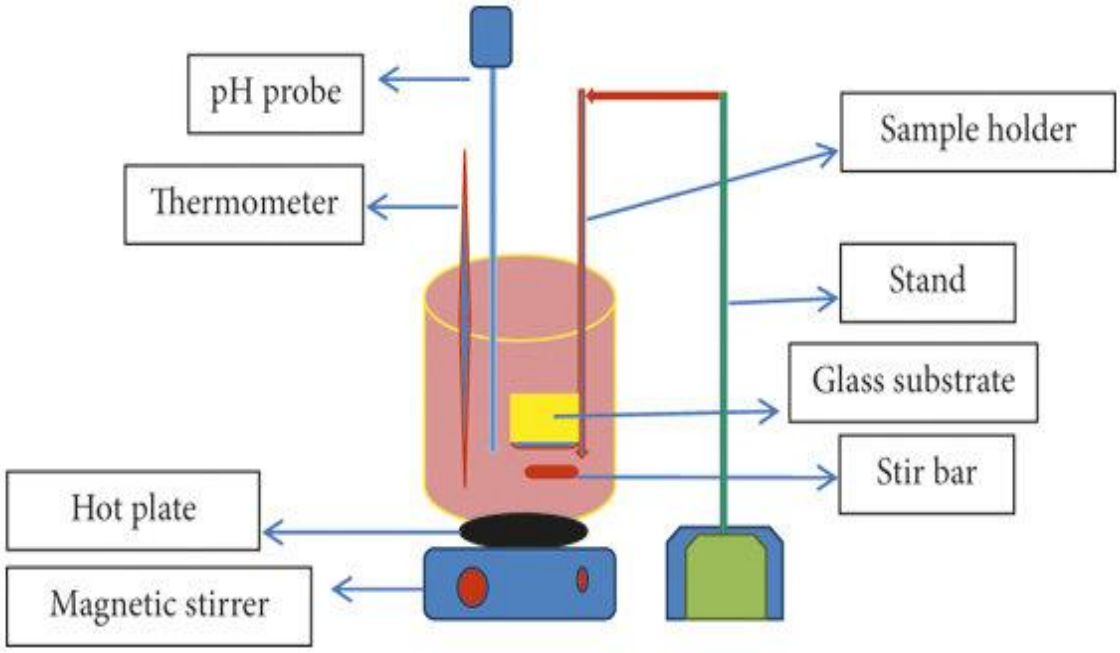

Figure 3.1: chemical bath deposition set up

In chemical bath deposition, complexing agents are used to bind metal ions to avoid uniform precipitation of the corresponding compounds. Formation of complex ions is important to control reaction kinetics and avoid immediate precipitation of compounds in solution. Metal complexes hydrolyze slowly to produce cations in solution. A solution containing a metal complex was mixed with a solution that generates negative ions by hydrolysis. Compound deposition occurs when the ionic product exceeds the solubility product of the compound being deposited. Both uniform and non-uniform deposits can occur. The homogenous process is faster and adsorbs the powder particles onto the substrate with a large amount of sedimentation. Therefore, metal complex formation is essential to minimize the homogenization process. In heterogeneous processes, the slow release of ions by metal complexes leads to preferential adsorption of ions, resulting in uniform nucleation and growth of thin films. The quality of the deposited film depends on bath parameters such as temperature, deposition time, concentration of reactants, and pH of the chemical bath [27].

3.2 Thin film characterization techniques

Measurements and characterization of the film thickness, micro-structure and composition can be carried out using various techniques. They include X-ray diffraction (XRD), UV-Vis spectrophotometer, scanning electron microscopy, energy dispersive x-ray diffraction, transmission electron microscopy (TEM).

3.2.1 X-Ray Diffraction (XRD)

X- ray diffraction (XRD) is a very powerful experimental technique for studying crystal structures of solids and thin films. The crystal structures of the samples were examined by X-ray diffraction. The X-Ray Diffraction follows the principles of Bragg's law (Bo et al., 1978).

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

Where, d is perpendicular distance between lattice planes of miller indices, λ is wavelength of the incident X-ray and θ is glancing angle.
The crystallite sizes of the particles were calculated by using Scherer's equation (Ahmad and Mehrnaz, 2012)

$$D = 0.9\lambda/\beta\cos\theta$$

Where; d is the crystallite size of the particles, 0.9 is a shape factor, λ is the wavelength of the incident X-ray (1.5418 Å, Cu Kα), θ is the diffraction angle and β is the full width half maximum [28].

3.2.2 Ultraviolet-Visible Spectroscopy (UV-VISS)

UV-Vis absorption spectrophotometer being utilized to analyze how much light the ZnS thin film is capable of absorbing. The initial absorption which conforms with the electron excitation from the valence band to the conduction band is adopted to deduce the optical band gap value of the manufactured film. This method consists of a deuterium or tungsten lamp for the ultraviolet and visible region wavelengths, respectively, sample and reference beams, a detector, and a monochromator. Exposing the sample to UV light will give the UV spectrum. Cuvettes are used for sample holding and are kept inside the instrument for introducing samples to the light path.
Glass, plastic, silica, or quartz cells can be used as cuvettes. Plastic and glass cuvettes absorb wavelengths below 310 nm, so they cannot be used for absorbance studies below that wavelength. Therefore, quartz cuvettes are used for absorption measurements in the ultraviolet range as they are transparent to the wavelengths above 180 nm [29].

3.3 Experimental details

3.3.1 Material used

The instruments and apparatus used in this study included:
UV/Visible spectrophotometer, X-ray diffractometer (XRD), furnace, glass substrates, beakers, substrate holders, beam balances, graduated cylinders, heaters, water baths, magnetic stirrers, volumetric flasks and stirrer holders are used.

3.3.2 Chemicals and Solvents

The chemicals used in the production of zinc sulfide thin films are zinc chloride (ZnCl2), thiourea (SC(NH2)2), hydrazine hydrate (N2H4(H2O)) and ammonia solution (NH4(OH)). Distilled water also used to clean glass substrates and devices.

3.3.3 Substrate cleaning procedures

Substrate cleaning is the process of breaking the bond between the substrate and contaminants. Due to the variety of processes involved in manufacturing substrates, extreme cleanliness is required to remove common contaminants such as dust particles, some adsorbed water and other debris. Glass substrates were used for film deposition. The ZnS thin films were growing on 7.5 × 2.5cm microscope glass slides. Before the deposition the substrates must be cleaned with ordinary water and soup. Substrate cleaning plays an important role in forming smooth, uniform, and adherent films. After washing the glass substrate with ordinary water and soup, it was immersed in nitric acid for 24 hours. Then were washed with fresh water and immersed in ethanol alcohol for 30 minutes. Finally they were washed with distilled water and dried in air for 30 min.

3.3.4 Preparation of zinc chloride and thiourea solution

There are 5 different concentrations of ZnCl2 (0.3M, 0.5M, 0.7M, 0.9M, 1.1M). In order to measure the above concentrations of ZnCl2 in gram we use a beam balance. The mass of zinc chloride is calculated by multiplying the concentration (moles), the volume in liters, the molar weight (grams), and the percentage (percent).
Mass=concentration*volume*molar weight*percentage purity

i. For the first concentration of ZnCl2 the mass is calculated as 0.3 x 0.1 x 36.28 x 0.98 = 1.1 g. Then the salt was dissolved in a small amount of distilled water and then transferred to a 100 ml volumetric flask using a funnel. The solution was then made up to the 100 ml mark with distilled water and shaken well to completely dissolve the salts. The concentration of the metallic precursor ZnCl2 was 0.3M. By following the same procedure the mass of other samples were calculated as 1.8g, 2.5g, 3.2g and 3.9 g respectively. The concentrations of the metallic precursor ZnCl2 were 0.5M, 0.7M, 0.9M and 1.1M. Finally five different solutions were prepared for five different concentrations of ZnCl2.

ii. The mass of 0.2M concentration of thiourea calculated as 0.2 x 0.1 x 76.12 x 0.98 = 1.5 g
Then the salt was dissolved in a small amount of distilled water and then transferred to a 100 ml volumetric flask using a funnel. The solution was then made up to the 100 ml mark with distilled water and shaken well to completely dissolve the salts. The concentration of the metallic precursor ZnCl2 was 0.2M.

3.3.5 Synthesize of zinc sulfide thin film

Many trails were conducted for optimizing the deposition parameters to obtain good quality of zinc sulfide thin films. The adsorption, reaction, and rinsing times were experimentally optimized to ensure uniform deposition of zinc sulfide thin films. The first samples were made by mixing 10 ml (0.3M) of zinc chloride aqueous solution as precursor concentration then 5ml of distilled water, 5ml of hydrazine hydrate solution then 10ml of distilled water, 10ml of ammonia solution as complexing agent then 5ml of distilled water, 10ml of thiuorea (0.2M) then 5ml 0f distilled water. Total volume of distilled water was 25ml and total volume solution was 35ml.The total volume of solution and distilled water were 60ml.Then the solution is continuously stirred to completely dissolve the chemicals. The prepared glass substrate was immersed in the solution. This solution was also placed in a water bath with the temperature set at 80°C for 2hour. Initially, the solution was looks like water. After 5minute the color began to change and turned golden. Finally, a thick, white zinc sulfide thin film was deposited, and then the film was washed with distilled water to remove precipitates, air dried, and finally annealed at 200°C for 2hour.

The same procedure was taken for the rest of four samples in order to synthesize zinc sulfide thin film only by varying the concentration of zinc chloride (0.5M, 0.7M, 0.9M and 1.1M). Finally, a thick, white zinc sulfide thin film was deposited, and then the film was washed with distilled water to remove precipitates, air dried, and finally annealed at 200°C for 2hour.

Figure.3.2: Deposition processes of zinc sulfide thin films.

Figure .3.3: Samples of zinc thin films as deposited.

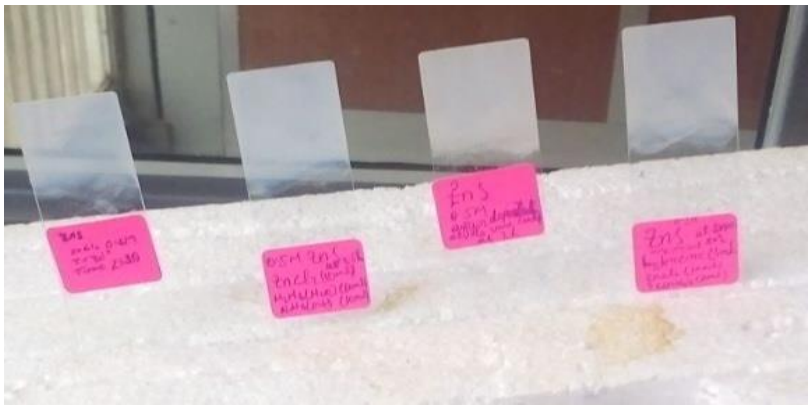

Figure 3.4: Samples of zinc chloride thin films after annealing at 200^{o}c for 2 hour.

CHAPTER FOUR

4. Results and Discussion

4.1 X-Ray Diffraction (XRD)

X- ray diffraction (XRD) is a very powerful experimental technique for studying crystal structures of solids and thin films. The crystal structures of the samples were examined by X-ray diffraction. In this study, the XRD pattern of the nano crystals powder were recorded with the ray diffracttometer using Cu (Kα) radiation (λ = 1.5418 Å). The X-Ray Diffraction follows the principles of Bragg's law (Bo et al., 1978).

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

Where, d is perpendicular distance between lattice planes of miller indices, λ is wavelength of the incident X-ray and θ is glancing angle. The measurement was carried out at room temperature, and the accelerating voltage and the applied current was 40 kV and 30 mA, respectively. The instrument was operated under step scan type with step time and degree (2θ) of 60 s and 0.020°, respectively over the range: 20° to 80°. The crystallite sizes of the particles were calculated by using Scherer's equation (Ahmad and Mehrnaz, 2012)

$$D = 0.9\lambda/\beta\cos\theta$$

Where; D is the crystallite size of the particles, 0.9 is a shape factor, λ is the wavelength of the incident X-ray (1.5418 Å, Cu Kα), θ is the diffraction angle and β is the full width half maximum.

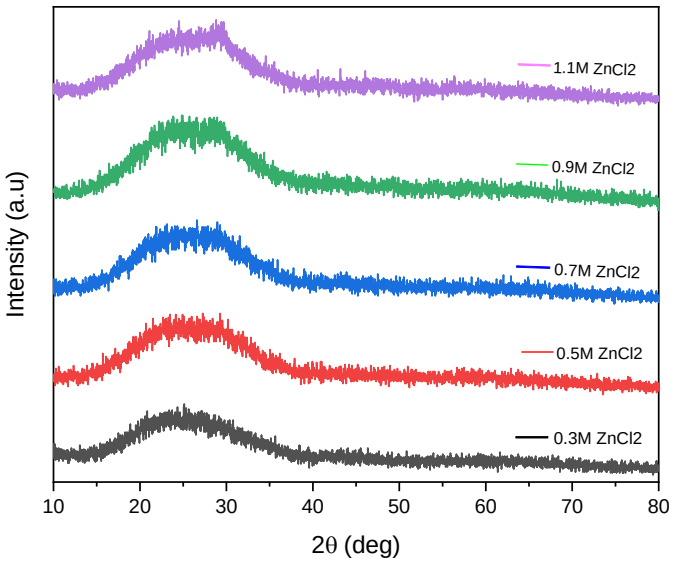

Figure 4.1: XRD patterns of deposited ZnS thin film at different zinc chloride concentrations.

Generally, the crystal structures of ZnS exist in two forms, that is, the cubic (zincblende) and hexagonal (wurtzite) phases. The cubic ZnS is stable at room temperature, while the hexagonal ZnS is formed as the temperature is above1020∘C [32]. The crystalline structure of ZnS thin films has been investigated by the X-ray diffraction measurements. All films deposited on glass substrate has no sharp peak which indicates the samples are in amorphous nature as illustrated by the X-ray scattering curves. The XRD spectra are obtained by scanning of intensity versus 2θ. Figure 4.1 shows the results of XRD scan for different concentration of ZnCl2 samples (0.3M, 0.5M, 0.7M, 0.9M and 1.1M).There is no visible diffraction peak found except for a broad hump appeared in the wide angle (2θ) region from 10-80° indicating the film is amorphous. Therefore, it is not possible to evaluate grain size using Scherrer's formula from XRD data for those films. As the concentration of ZnCl2 precursor increased, relatively small sharp peak which is around 29 degree had observed on 1.1M of ZnCl2 precursor. The presence of small peaks in the X- ray diffractogram reveals the formation of nanocrystalline ZnS thin films. The peaks are not sharp indicating that the average crystallite size is small. Due to size effect the peaks in the diffraction pattern broaden and their widths become large as the particles become smaller and also similar trend was observed by Jafarov et al. [14]. XRD patterns of ZnS thin film annealing with small amount of temperature (200°C) has no diffraction peaks, which shows that in this condition ZnS cannot crystallize reported by Jiankang.

4.2 Optical Absorption Analysis

UV-Visible spectroscopy is an important characterization study to analyze the optical absorption and band gap of semiconductors. Optical properties of materials depend on different parameters like doping, their interaction with the surrounding environment, as well as, their preparation conditions and preparation methods. The optical absorption spectrum of synthesized ZnS sample is shown in fig.4.2. The optical absorption of zinc sulfide thin films formulated from various zinc

chloride concentrations was calculated throughout the range of wavelength of 370 to 800 nm. The absorbance of the films significantly increased with increasing of the zinc chloride concentration within the considered range of wavelength. The apparent wavelength spectrum is where the films maximum absorption is observed. The maximum absorption (λ max) peaks were observed around 404nm and the lowest absorption peaks were observed around 529nm. All ZnS thin films for different concentrations of zinc chloride have high absorbance in the visible light area that make them candidate materials for absorber layers in thin-film solarcells as well as effective visible light photocatalysts [33–35]. The absorption result shows that concentration of a ZnCl2 has clearly observable effect on the optical properties of the films.

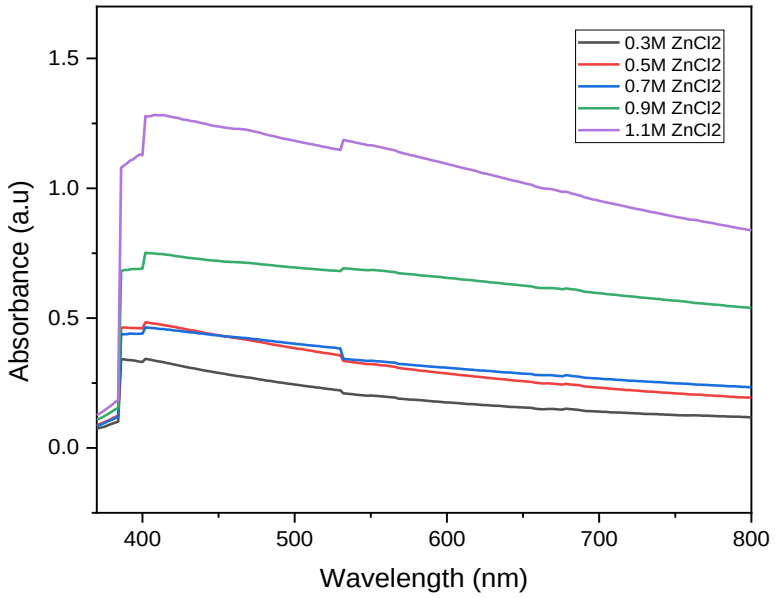

Figure 4.2: Plots of variation of optical absorption versus wavelength of ZnS films using different concentrations 0.3M, 0.5M, 0.7M, 0.9M and 1.1M of ZnCl2.

The band gap energy was calculated using the Stern relation which is given by

$$(Ahv)^{2} = [\mathrm{k}\ (hv - Eg)]^{n}$$

Where *n* is a constant either 4 for indirect transition or 1 for direct transition and *k* is a constant; n was taken the value 1 because ZnS has direct transition. Figure 4.2 displays the Stern plot of $(Ahv)^2$ versus (hv) for ZnS thin films at different ZnCl2 molar concentration. The intercept of the interpolation of the linear region of the $(Ahv)^2$ versus (hv) plot with the x-axis gives the band gap of the thin films and the estimated values. The optical band gap values are found to vary from 3.53 eV to 3.42 eV with increasing ZnCl2 concentration (see Fig.4.3). This result verified that band gap was decreased when ZnCl2 concentration was increased.
The observed variation of optical band gap ascribed to the change of microstrain, annealing temperature and dislocation density of the samples with complexing agent molar concentration.

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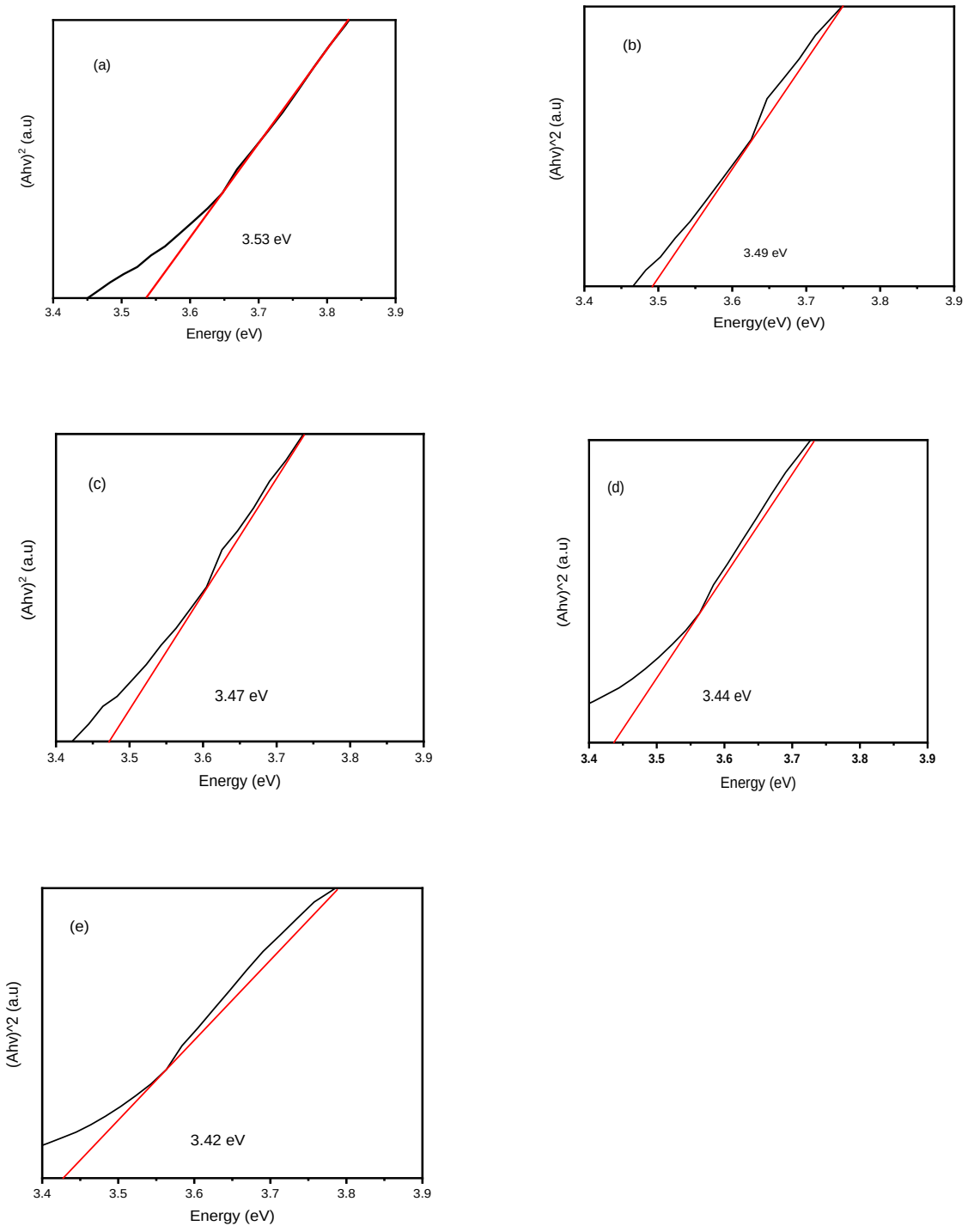

Figure. 4.3 : Plot of (Ahν)^2 versus (hν) of ZnS thin films with 0.3M, 0.5M, 0.7M, 0.9M and 1.1M of ZnCl2.

5. Conclusions

Zinc sulfide has great potential as a useful material for nanoscale devices due to its non-toxicity and wider band gap. In this work, wide band gap ZnS is obtained by chemical bath deposition method (CBD). The X-ray diffraction reveals that there is no sharp peak which indicates the samples is amorphous nature. The optical absorption study reveals that absorption of ZnS thin film increases as the concentration of ZnCl2 precursor increases and the optical band gap decreases as the zinc chloride concentration in the reaction mixture increases.The results demonstrated that concentration of metallic precursor have distinct effects on optical absorbance and band gap energy.

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RECOMMENDATION

In this study we investigated that concentration zinc chloride has great effect on the structure and optical properties of zinc sulfide thin films deposited by CBD method. In present work only two characterization techniques (XRD and UV-VISS) were used to charachterize the synthesized ZnS thin film. There are further characterizations techniques such as SEM, EDX, Hall Effect measurement, FTIR spectroscopy and so on. Zinc sulfide thin films has wide applications therefore; more characterizations were advisable to broaden its applicability.

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