HAWASSA UNIVERSITY

COLLEGE OF NATURAL AND COMPUTATIONAL SCIENCE

DEPARTMENT OF PHYSICS

OPTICAL AND STRUCTURAL STUDY OF ZINC SULFIDE THIN FILMS AT VARIOUS DEPOSITION TEMPERATURES BY CHEMICAL BATH DEPOSITION METHOD

MSc. Thesis

BY:

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IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF MASTER SCIENCE IN SOLID STATE PHYSICS

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Declaration

I **, Mengistu Mendedo Berata** ,hereby declare that the thesis entitled " Optical and Structural study of Zinc Sulfide thin films at various deposition temperatures by chemical deposition method" is my work conducted under the supervision of **Dr.Hagos Tsegaye**.

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Abbreviation and Acronyms

A	Absorbance
AlSb	Aluminium antimonide
CBD	Chemical Bath Deposition
Cd	Cadmium
CdS	Cadmium Sulfide
E_g	Band gap
GaAs	Gallium arsenide
GaN	Gallium Nitride
InAs	Indium arsenide
InP	Indium phosphide
h	Plank's constant
IC	Integrated circuit
K	Wavenumber
λ	Wavelength
S	Sulfur
UV	Ultraviolet
υ	Photon frequency
VIS	Visible Spectrum
VLSI	Very large scale integration
XRD	X-ray diffraction
Zn	Zinc
ZnO	Zinc oxide
ZnS	Zinc Sulfide

Abstract

Researcher was able to successfully deposit zinc sulfide (ZnS) thin films on glass substrates using chemical deposition method. The author employed ammonium hydroxide and hydrazine hydrate as complexing agents, which helped control the chemical reactions. Thiourea acted as the source of sulfide (S2-) ions, while zinc chloride provided the zinc (Zn2+) ions needed to form the ZnS compound. Author then characterized the structural and optical properties of the deposited ZnS thin films .The author used X-ray diffraction (XRD) to probe the crystal structure and found that the films had an amorphous (non-crystalline) nature, likely due to the very small size of the crystallites that formed. To understand the optical behavior, we performed UV-visible spectroscopy. This revealed some interesting trends - the band gap energy, which is a key property determining the material's optical abilities, decreased from 3.51eV to 3.45eV as the deposition temperature was increased from 45°C to 60°C. Interestingly, the light absorption of the films increased with higher deposition temperatures. Further analysis showed that the optimal deposition temperature for these ZnS thin films was 55°C, where the optical properties were most favorable. . Overall, this study provides valuable insights into tuning the optoelectronic characteristics of ZnS thin films by carefully controlling the deposition temperature - an important parameter in thin film fabrication. The findings could have implications for applications like solar cells, light-emitting diodes, and optical coatings.

Key words: Zinc sulfide (ZnS) thin films, Chemical bath, Deposition temperature, Optical and structural properties.

CHAPTER ONE

1. INTRODUCTION

1.1 Semiconductors

Semiconductor is composed of two words viz. semi and conductor. ‘Semi’ means not complete; ‘Conductor' refers to something which can conduct electricity. Conductor is a material with ability to conduct charge flow. Semiconductors lesser than conductors. Conduction through semiconductor depends on the type of material, its composition and size. Physical properties of semiconductors lie between a conductor like Aluminum and an insulator like Glass. In "doping process" small amount of impurities are added to pure semiconductors. It brings large changes in the conductivity of material. The basic IC materials are silicon and Germanium. [1]. Semiconductor materials presents physicochemical, electronic, electrical elastic, mechanical, magnetic, optical, and other properties of a vast group of elemental, binary, and ternary inorganic semiconductors and their solutions[2]. Semiconductor devices charge-coupled devices, field-effect transistors, unijunction transistors, thyristors, zender and avalanche diodes, and photodiodes and lasers. The current tetra transitioning from Silicon technology to gallium arsenide technology in field-effect-based electronic devices is a special feature that is also covered [2]. Semiconductor is a word that only chemists should really be using. It means a Chemical or a substance that conducts electricity, but not very well. Some materials like copper, conduct electricity quite well. That's why houses are built with copper wires. Other materials, like rubber and plastic, don't conduct electricity at all. That's why power cords are plastic on the outside: to protect us from the electricity inside [3].

A semiconductor device is an interdisciplinary subject of great industrial importance. This subject has led to the emergence of various states of art areas of engineering and technology like IC fabrication and packaging. Microelectronics, VLSI, analog digital electronics, semiconductor electronics, etc.[1]. Semiconductors are the heart of modern living. Almost everything we do, be it work, travel, communication, or entertainment, all depend on some feature of semiconductor technology [4].

Doping in semiconductor greatly increases the number of charge carriers with in the crystal.

When a doped semiconductor contains free holes, it is called "p-type", and when it contains free electrons, it is known as "n-type".

The semiconductor materials used in electronic devices are doped under precise conditions to control the concentration and regions of p- and n-type dopants.

A single semiconductor device crystal can have many p-and n-type regions; the p-n junctions between these regions are responsible for the useful electronic behavior. Using a hot-point probe, one can determine quickly whether a semiconductor sample is p-or n-type [5]. In general, depending on the level of doping, Semiconductors can be classified into two main groups such as intrinsic semiconductors and extrinsic semiconductors. The intrinsic semiconductors are pure semiconductors, and no addition is made.

In this type of semiconductor, conductivity is provided by the thermal stimulation of the electrons. At the same time, the number of excited electrons and positively charged hole is equal. The behavior here appears as the result of the carrier production and recombination steps [6].

On the other hand, extrinsic Semiconductors have low conductivity values, and an important process called doping is applied to overcome the problems encountered in applications and to increase the conductivity [7] .Two general another classifications of semiconductors are elemental and compound semiconductors. The elemental semiconductor materials are found in group IV of the periodic table and the compound semiconductor materials, most of which are formed special combinations of group III and group V elements. One of the most important characteristics of a semiconductor, which distinguishes it from metals and insulators, is its energy band gap. This property determines among other things the wave lengths of light that can be absorbed or emitted by the semiconductor [101].

1.1.1 Compound semiconductor

Semiconducting materials that are synthesized by mixing elements from groups IIIA and VA of periodic table known as the III-V Compound semiconductors. These compounds could be binary, ternary, quaternary, pentanary or higher orders depending on the number of elemental species used for synthesizing the compounds. III-V compounds have found widespread applications in electronic, optoelectronic, and Photovoltaic devices [8]. The III-V semiconductors are a family of materials developed from cations groupIIIA and anions from group VA. These materials generally form a homologous series of compounds possessing the zinc blende crystal structure (F43m). The exceptions are nitride-based materials that are of the Wurtzite crystal structure (P63mc). The binary semiconductors, such as GaAs, InAs, InP, GaN, AlSb, etc. cover a broad range of electronic Structures useful in technology. [9]. Compound semiconductor devices provides a comprehensive insight into today's standard technologies covering the vast range of semiconductor products and their possible applications. The materials covered runs from the basics of conventional Semiconductor technology through standard, power and opto-semiconductors, to highly complex memories and modules for smartcards, automotive electronics, consumer electronics and telecommunications. [10]

1.1.2 Semiconductor thin films

Thin film semiconductors have become an essential component in the manufacturing of semi-conductor devices. These devices are used in a wide range of applications, including transistors, Sensors, and LEDs(Light emitting diodes). Moreover, this technology has enabled a wide range of applications, including radio frequency identification (RFID) tags, solar cells, and thin-film batteries [11].

1.1.3 General properties of Zinc Sulfide (ZnS)

ZnS is a noteworthy semiconductor compound of the II–VI group[12,87]. It is composed of metal and sulfur atoms[5]. ZnS is typically found naturally in two crystalline structures: cubic or zinc blende (ZB) and hexagonal or wurtzite (WZ)[97, 102]. Both Zn and S have tetrahedral coordination geometry [103]. ZnS exhibits a large band gap at room temperature (300 K) and has attracted considerable interest[104]. The hexagonal phase is a polymorph at high

temperatures, while the cubic phase is formed at low temperatures[87]. Studies[]have reported a range of temperatures for crystal structure transition between ZB and WZ phases. As the ZB structure, a = b = c =5.41 Å when Z = 4, whereas for the WZ phase, a = b = 3.82 Å and c = 6.26 Å when Z=2[43]. ZnS has n-type conductivity [105] with a band gap semiconductor (3.54 eV) for cubic zinc blende (ZB) and (3.91 eV) for hexagonal wurtzite (WZ) [103]. These values imply that ZnS has a wide band gap[106]. Zinc Sulfide (also known as zinc sulfide) is a chemical compound having the formula ZnS. It appears as white, greyish-white, or yellow crystals or powder . Insoluble in water and denser than water. Density of Sphalerite: 4.04g/cm^3, Wurtzite: 4.09g/cm^3 and its optical property is refractive index with value 2.35. Boiling and melting point values are 1185^{o}C and 1850^{o}C respectively[12,103].

1.2 Statement of the problem/Justification of the research

For the last few years the investigation has been focused on the application and characterization of II-VI semiconductor nanoparticles for applications in biological field as molecular probes or boilables[107] and also have attracted much attention in photo and electroluminescence properties because of their size-dependent (which is tunable) and have promising optoelectronic applications[108]. Now as traditionally shown remarkable fundamental properties versatility, it has a promise for novel diverse applications, including light-emitting diodes(LEDs), flat panel displays, infrared windows, sensors, lasers, and bio devices, etc. Its atomic structure and chemical properties are comparable to more popular and widely known ZnO. To name a few, ZnS has a larger band gap of 3.68eV and 3.91eV for cubic zinc blende(ZB) and hexagonal wurtzite(WZ) ZnS, respectively, than ZnO(3.4eV) and therefore it is more suitable for visible-blind ultraviolet(UV)-light based devices such as sensors/photo detectors[109]. On the other hand, ZnS is traditionally the most suitable candidates for electroluminescence devices[110]. Beside this, ZnS is considered one of the best materials for the CIGS(copper indium gallium selenide) solar cells among possible alternative buffer layers. In comparison with CdS , the advantages of ZnS include its non-toxic and environmentally safe handling as well as its ability to provide better lattice matching to CIGS absorbers having energy band gaps in the range of 1.3 to 1.5eV compared with CdS and having a wider energy band gap compared with CdS, which transmits even higher energy

photons and increases the light absorption in the absorber layer[111]. ZnS in films are notable for their high transparency in the solar spectrum, fluorescence effect, and high refractive index (2.35) as well as n/p- type electrical conductivity [13]. Recently, ZnS scintillation detectors have even been used in the potential detection of dark electric matter objects[112]. These objects can catalyze the fusion of light nuclei, suggesting new ways for solving the problem of deficiency of solar neutrons and solar energetic as a whole. ZnS thin film can be prepared using several techniques such as sputtering, molecular beam epitaxy, spray pyrolysis, successive ionic layer adsorption and reaction technique, electro deposition, pulsed-laser deposition, metal-organic, chemical vapour deposition and chemical bath deposition. Among them, we used CBD method because it is well known as prevalent low temperature aqueous technique for deposing large area semiconductor thin films; the simplest and the most economic one, and it can be easily applied to a large scale deposition area [14]. Various researchers have conducted numerous investigations so far, but the band gap results have not been satisfying. As a result, the author has trying to improve the band gap value, making the material more conductive and better suitable for various applications. Because of this, the author was curious to look into the structural and optical characteristics of thin films of zinc sulfide at different deposition temperatures.

1.3 Objectives of research.

1.3.1 General objectives

The main objective of this work is to synthesize and characterize ZnS thin films using CBD technique.

1.3.2 Specific objective

- To deposit ZnS thin films at different deposition temperature
- To investigate the effect of deposition temperature on structural and optical properties of zinc sulfide thin films.
- To determine the band gap of ZnS thin films at different deposition temperatures.

1.4 Structure of the thesis

This thesis is organized in five chapters

Chapter-1 is devoted to the introduction to semiconductor and types, semiconductor thin films and general properties of ZnS

Chapter-2 is focused on literature review, thin film materials and their deposition techniques and review of related literatures on ZnS thin film by CBD techniques.

Chapter-3 discussion the methodology, the chemical bath deposition technique, the experimental procedures, thin film characterization methods, structural analysis of ZnS thin films

Chapter -4 is about result and discussion.

Chapter 5 is about conclusion and recommendations for further study are presented.

CHAPTER-TWO

2. REVIEW OF RELATED LITERATURE

This chapter introduces the general aspects of thin films and their applications in current technologies and some physical and chemical deposition techniques. In addition, a review of ZnS semiconductor thin film is presented in some details.

2.1 Thin film materials

A thin film is a layer of material ranging from fractions of a nanometer (monolayer) to several micrometers in thickness. A thin film is also a low-dimensional material created by condensing one-by-one, atomic/molecular/ionic species of matter on a substrate. The thickness is typically less than several microns. Thin films differ from thick film. A thick film is defined as a low-dimensional material created by thinning a three-dimensional material or assembling large clusters (aggregate) grains of atomic / molecular ionic species [16]. The structural, Chemical, metallurgical and physical properties of such a material are strongly dependent on a large number of deposition parameters and may also be thickness dependent. Thin films may encompass a considerable thickness range, varying from a few nanometers to tens of micrometers and thus are best defined in terms of the production processes rather than by thickness [16]. Historically, thin films have been used for more than a half century in making electronic devices, optical coatings, instrument hard coatings, and decorative parts. The thin film is a traditional well-established material technology. However, thin film technology is still being developed on a daily basis since it is a key in the twenty-first century development of new materials such as nanometer materials and for a man-made super lattice. Thin film materials and devices are also available for minimization of toxic materials since the quantity used is limited only to the surface and /or thin film layer. Thin film processing also saves on energy consumption in production and is considered an environmentally friendly material technology for the next century.

Thin film technology is both an old and a current key material technology [17]. Thin film technology is based on three foundations: fabrication, Characterization and applications. The fabrication of thin films is carried out by employing conventional physical and chemical Vapor deposition techniques and their modifications. Thin film application categories include:

electronic components, electronic displays, and optical coatings, magnetic films for data storage, optical data storage device antistatic coatings and hard surface coatings. Characterization of thin films can be investigated based on film thickness, structure and other Chemical composition. The characteristic of a thin film can be quite different from those of bulk material because thin films as a two dimensional systems have a large surface to volume ratio [18].

2.2 Application of thin films in various fields and industries

Thin film technologies are prevalent in virtually every industrial sector. For example, this technology is essential for fabricating active and passive devices, complex optical systems, and even protective coatings for tools. Typical thin film applications, including thin film batteries, optics, magnetics, resistors, solar cells, and many more. Among the modern thin film applications, thin film interference is often one of the first that comes to mind. Thin film interference is an optical illusion caused by the interaction and reflection of light on this top and bottom surfaces of a film [19]. The most common application of thin film interference is optical devices, including lenses and mirrors. It's also present on the wings of certain butter flies, on soap bubbles, and as a security feature on money, credit cards, driver’s licenses, etc. [19]. Thin film resistors widespread in modem technology and crucial among thin film applications. Its applications range from radio receivers and circuit boards to computers and radiofrequency devices. Additional applications include monitors, wireless routers, Bluetooth modules, cell phone receivers, and electronics, where they're invaluable.

For example, nickel-chromium alloy-embedded resistors are vital for manufacturing smaller, thinner electronic devices due to their high resistivity [20].

Magnetic thin films are essential components of many devices, including electronics, data storage, radio frequency identification, microwave devices, displays, circuit boards, and Optoelectronics. Beyond that, they are critical for fabricating wearable electronics, including biomedical Sensors. By far, this is one of the most uses that drive thin film applications to be so important [21]. Applications for polymer thin films range from solar cells and electronics to health care and memory chips. Advancements in Chemical deposition method (CVD) allow

greater control over polymer film coatings, including coating thickness and conformity. Certain chemical reaction allow for solvent free fabrication, ·eliminating the risk of adverse reactions to human tissue.

2.3 Thin film deposition techniques

Thin film deposition is the technology of applying a very thin film of material between a few nanometers to about 100micrometers, or the thickness of a few atoms on the to a "Substrate" Surface to be coated, or onto a previously deposited coating to form layers. Thin film deposition manufacturing processes are at the heart of today's semiconductor industry, solar Panels, disk drivers, and optical devices industries [23]. In present time, thin films can be fabricated in various ways. The techniques can be divided into physical and chemical methods as described in figure 2.1a [24].

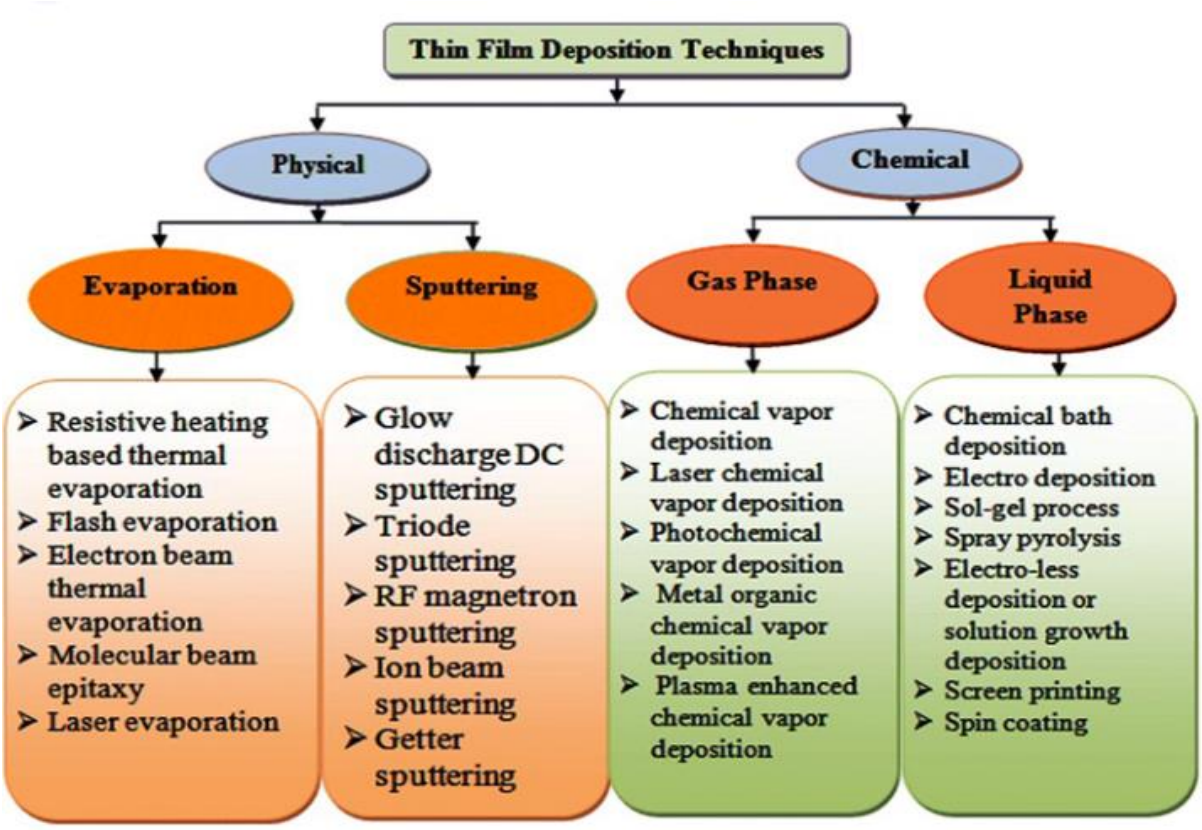

Figure 2.1(a) Classification of thin film deposition technique

Physical deposition techniques often result in good quality thin films but the necessity of vacuum, high energy and high quality target make them economically not viable. Further buffer layers synthesized by physical techniques are reported to exhibit comparatively poor photovoltaic conversion effectively [25]. Unlike the physical methods of preparation of thin films which involve evaporation or ejection of material from a source chemical reaction. In comparison, Chemical deposition techniques are less sophisticated and are most suitable for large area deposition. Cost effectiveness of Chemical techniques and their feasibility to synthesis variety of materials on different substrates has increased the research interest in there techniques in synthesizing good quality semi conducting chalcogenide thin films suitable for photovoltaic and optoelectronic applications [26-30]. Among the Chemical deposition techniques, liquid phase techniques are more suitable for large area deposition. Liquid phase chemical techniques include electro deposition, spray pyrolysis, chemical bath deposition, Solution growth deposition etc. In the present work, chemical bath deposition technique is used for preparation of ZnS thin films. Chemical solution deposition (CSD) or Chemical bath deposition (CBD) uses a liquid precursor and complexing agent. The experimental set up of this method is shown in Figure 2.1b below [98].

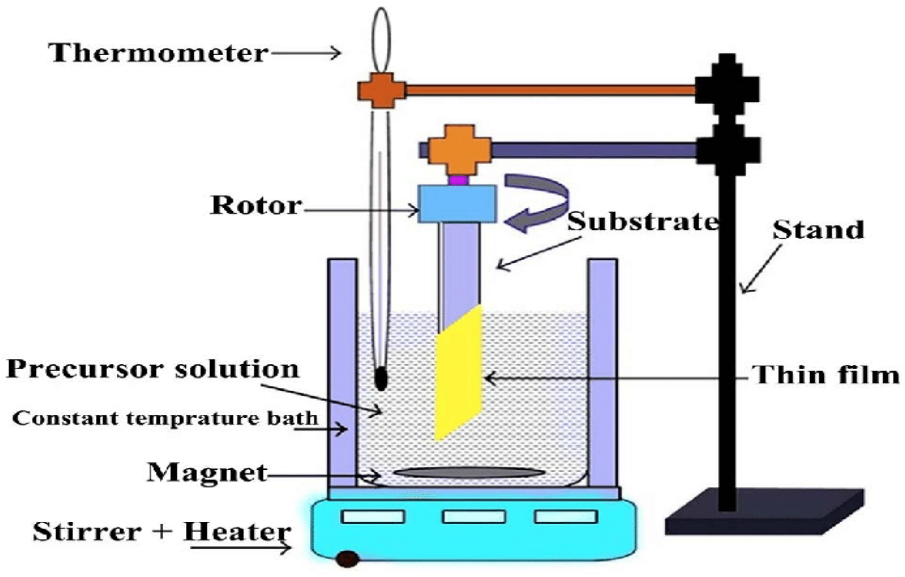

Figure 2.1b shows experimental set up of CBD method to deposition of thin film.

The main advantages of CBD method are:

Amongst the various methods available for the synthesis of thin films, the CBD method have several advantages and widely used for thin film deposition because

- It is relatively inexpensive .
- Convenient for large area deposition and ability of tuning thin film properties by adjusting and controlling the deposition parameters
- The starting chemicals are commonly available and cheap
- It gives pin hole free and uniform deposits of films since solution and substrate are in contact during deposition process [91].

The main deficiencies of CBD method are:

- The deposition of multicomponent phases with a stable composition is not possible because individual binary components precipitate at different PH or temperature
- CBD growth layers tend to contain impuries of the solution, which limit the optoelectronic performance and often reduce the corrosion ability e.g CBD-growth ZnO under moisture exposure), which necessitates a dedicated encapsulation. One of the main drawbacks is the wastage of the solution after every deposition, which require waste treatment Schemes on industrial scale [31].

2.4 Review of related literature on chemically deposited ZnS thin films

Zinc sulfide thin films were prepared and Characterized by Eid et al using CBD technique. As they did, the chemical bath was an aqueous solution of zinc chloride, thiourea, Ammonium hydroxide and hydrazine. Various process parameters such as volume of Ammonium hydroxide and hydrazine, pH, deposition time and bath temperature are optimized. The depositions were carried out in PH 11.5 structure of these films was Characterized by X-ray diffraction. X-ray diffraction analysis of the as deposited and annealed films the cubic structure (β-ZnS). It was found the crystallinity of the films decreased as the annealing temperature increased till 200° [32].

The influence of deposition temperature on the structure and optical band gap of zinc sulphide thin films deposited from acidic chemical bath were investigated by Tizazu etal. As they studied, Nano crystalline zinc sulfide (ZnS) thin films have successfully deposited on silica glass substrates from acidic Chemical baths containing tartaric acid and hydrazine as complexing agents, thioacetamide as a sulphur source and zinc acetate as the source of zinc ions. The influence of temperature on the structural, optical, morphological properties and elemental composition of the films were investigated by variety of techniques. Powder X-ray diffraction patterns of the film's exhibited the cubic structure. The deposition temperature had a significant influence on the lattice parameter and crystallite size scanning electron microscope and energy dispersive x-ray investigations have shown an improvement in morphology and stoichiometry of the films with increasing deposition temperature. The band gap of the thin films obtained by optical absorption spectroscopy showed a decrease from 3.88 eV to 3.75eV as the deposition temperature increased. Transmittance of the films increased with decreasing deposition temperature [15].

The Influence of bath temperature and deposition time on topographical and optical properties of nanoparticles ZnS thin films were investigated by Zein etal . As they did, Zinc sulfide nanoparticle (ZnS NP) thin films were deposited on the glass substrates by chemical bath deposition using zinc sulfate as cation precursor and thiourea as the anionic precursor.at bath Different temperatures (65^{o}C, 70^{o}C, 75^{o}C and 80°c) and different deposition times (20, 30, 40, and 50min) were selected to study the performance of ZnS thin films.

Topographical and optical characterizations of the films were studied using the atomic force microscope (AFM) and UV-Vis spectroscope. The best ZnS thin films were deposited at a bath temperature (70°) and a deposition time (30min) with homogeneous distribution, high density, and small average diameter (106nm). The energy gap was found to be in the range of 4.05-3.97eV for the ZnS films. Optical constants (refractive index, extinction coefficient, and dielectric constant) of the films Obtained in the wave length range 300-500nm by using spectrophotometric measurement. The dispersion of the refractive index is analyzed by using a single Oscillator model. The Oscillator energy and dispersion energy were determined using

the Wemple- Didomenico single oscillator model. Urbanch's energy increases from 0.907eV to 2.422eV with increasing of deposition time [33].

Crystalline ZnS thin films by chemical bath deposition method & its Characterization were investigated by Roy etal . As they studied, ZnS thin films have been deposited by CBD method using tartaric acid as a complexing agent. The structural and morphological characteristics of films have been investigated by X-ray diffraction (XRD), Scanning electron microscope and atomic force microscope analysis. XRD shows development of well-crystallized film with pure Wurtzite Structure after annealing. The films show good optical properties with high transmittance in the visible region and the band gap Value was estimated to be 3.69eV [34].

Effect of different complexing agents on the properties of chemical bath deposition ZnS thin films were studied by Liu,et al. As they investigated, Zinc sulfide (ZnS) thin films were deposited on glass substrates using the chemical bath deposition (CBD) technique. The effects of different complexing agents (tri-sodium citrate, hydrazine hydrate) and their concentrations on the structure, composition, morphology, optical properties and growth mechanism of ZnS thin films were investigated. The results indicated that the chemical-bath-deposited ZnS thin films exhibit poor crystallinity and a high Zn/S atomic ratio with an average transmittance of 75% in the range of visible light. The ZnS thin films prepared using hydrazine hydrate as the complexing agent present a more compact surface, a smaller average particle size, and a sharper absorption edge at 300–340 nm compared with those prepared using tri-sodium citrate. Based on their experimental observations and analysis, they concluded that the predominant growth mechanism of ZnS thin films were an ion-by-ion process. The nucleation density of $Zn(OH)_2$ nuclei on the substrate in the initial stage produces the different morphologies and properties of the ZnS thinfilms prepared using the two complexing agents [49].

Effect of substrate temperature on ZnS films prepared by thermal evaporation techniques investigated by Vishwakarma et al. As they did, The nanocrystalline ZnS semiconducting thin films of 500 nm thickness have been deposited on glass substrate at different substrate temperatures (T_s) by thermal evaporation technique. The structural property of deposited thin

films has been measured by X-ray diffraction, scanning electron microscopy, and Energy dispersive analysis of X-ray. The electrical and optical properties of thin films have been determined by D.C. two point probe and ultra-violet visible spectroscopy measurements. The X-ray diffraction patterns show that thin films have cubic structure. The electrical resistivity of thin films has decreased from 0.36×10^6 to 0.15×10^6 Ω cm as substrate temperature increases from 300 to 400 K. It shows that films have semiconducting in nature. The grain size and electrical conductivity of the thin films have increased as the deposition temperature increased while dislocation density, activation energy, and band gap decreased. The minimum band gap 3.43 eV has been found [97].

Effects of thiourea concentration in formation of ZnS thin films grown by chemical bath deposition for heterojunction solar cell investigated by Babatunde et al. As they studied, the effect of sulphur concentration was investigated on optical and morphological properties of synthesized Zinc Sulphide thin film(ZnS). The chemical bath is prepared by mixing 30ml of 0.50 M, 2.00 M and 2.5M of thiourea (SC(NH2)2) as asource of sulphur were poured in to three different beakers labelled as M1, M2 and M3 respectively and stirred for several minutes ,20ml of 3M (NH4OH) solution as a complexing agent was added to each of the beaker and 30 ml of 0.1 M of zinc sulphate ZnSO4) as the source of zinc was added to each of the beaker slowly under continuous stirring for several minutes until the solutions turned milky after which became colourless. Finally, the mixtures were poured into three different 100ml in chromatography tanks labelled M1, M2 and M3 respectively. The cleaned three samples M1, M2 and M3 were immersed vertically in the chromatography tank M1 , M2 and M3respectively. The tanks were then placed inside the preheated water bath. The deposition was allowed to stay for 1hour, the temperature of the bath (Tb) was maintained at 50^oC . There after, the glass substrates were removed and found coated with ZnS observed to have been coated with milky white deposits which the thickness varies according to the concentration of (SC(NH2)2) , then one side of the substrate was cleaned using cotton wool with HCl and annealed at constant temperatures of 100^oC for 15minutes in an oven. The mass of chemical reagent for the various molar solution was calculated from relation m=Dc*Dv*W/1000 Where m is the mass of salt required, Dc is the required concentration; Dv is the volume of distilled water required and W is the molar mass of the chemical salt. After the deposition,

thickness of the samples were determined using double weighing method. Morphological and optical prope rties of the films were determined using scanning electron microscope (SEM PHENON WORD) andUV-visible double beam spectrophotometer (ATICO) respectively.

The result shows that transmittance spectral increases in the visible region of wave length 400nm to 800nm and decreases in the infrared region at above 800nm wavelength.

The extrapolated optical band gap energy for the film deposited increases from 3.7 eV to 3.9 eV as concentration increases. The microstructural images of all the samples were rough and the grains were dense[113].

Influence of deposition temperature on structural, morphological and optical properties of ZnS thin films investigated by Temel, S. As he studied, ZnS thin films were deposited on glass substrates by chemical bath deposition(CBD) technique at different deposition temperatures, (75^{o}c 80^{o}C, 85^{o}C, 90^{o}C) using 0.15M Zinc acetate dehydrate, 0.5M nontoxic complexing agent tri-sodium citrates and 1M Thiourea. Effects of deposition temperature on structural, morphological and optical properties of thin films were investigated by using X-Ray

Diffraction (XRD), Field Emission Scanning Electron Microscopy (FESEM) and UV-Visible Spectroscopy respectively. The XRD results show that all produced ZnS thin films have cubic structure. The calculated grain size values are between 13-26 nm. It was observed that the grain size values increase and crystallization of films improve as the deposition temperature increases. The FESEM images reveal that film surfaces are formed by almost homogeneously dispersed nanostructured particles. Optical characterization results show that ZnS thin films have high transmittance of about 80% in the range of 400–800 nm with band gap energy values between 3.52 – 3.65 eV. As the deposition temperature increases the band gap energy alues increase. According to these results, it was observed that the structural, morphological and optical properties of ZnS films vary depending on the deposition temperature[114].

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CHAPTER THREE

3. METHODOLOGY

This chapter briefly discusses some commonly used thin film deposition techniques. The chapter also explained in detail about chemical bath deposition technique which is used in this work. Basic principle of CBD and concept of solubility product, experimental procedures, reaction mechanism, substrate cleaning and factors affecting the deposition process of CBD techniques are included. Basic working principles of X-ray diffraction and optical devices employed in this work are also briefly described.

3.1 Chemical Bath Deposition (CBD) Technique

Chemical Bath deposition, also called chemical solution Deposition and it is a method of thin-film deposition (Solids forming from a solution or gas), using an aqueous precursor solution.[35]. Chemical bath deposition typically forms films using heterogeneous nucleation (deposition or adsorption of aqueous ions onto a solid substrate),[36] to form homogeneous thin films of metal chalcogenides(mostly oxides,sulfides,and selenides) and less common ionic compounds[35][37]. Chemical bath deposition procedures films reliably, using simple process with little infrastructure, at low temperature (<100 degree Celsius), and at low cost.[35]. Furthermore, Chemical bath deposition can be employed for large-area batch processing or continuous deposition. Films produced by CBD are often used in semiconductors, photovoltaic cells, and super capacitors, and there is increasing interest in using Chemical Bath Deposition to create nanomaterial [35][38].

3.1.1 Basic principles of CBD and concept of Solubility product

The basic Working principle behind the CBD process is Similar to those for all precipitation reactions and it is based on relative solubility of the product. At a given temperature when the ionic product (IP) of reactants exceeds the solubility product ($\mathbf{K_{sp}}$), precipitation occurs. Whereas if the ionic product is less than the solubility product, then the solid phase produced will dissolve back to the solution resulting in no net precipitation [39]. A central concept necessary to understanding the mechanisms of CBD is that of the solubility of a sparingly

soluble ionic salt (this includes salts normally termed "insoluble"). sparingly soluble ionic salt, AB(S), When placed in Water, a Saturated Solution containing A^+ and B^- ions in contact with un dissolved solid AB is obtained and equilibrium is established between the solid phase and ions in the solution as:

$$AB(s) \rightleftharpoons A^+ + B^- \quad (3.1)$$

Applying the law of mass action,

$$K=[A^+][B^-]/[AB] \quad (3.2)$$

Where k is stability constant,

$[A^+]$, $[B^-]$ and [AB] are concentrations of A^+, B and AB in the solution, respectively. The concentration of pure solid is a constant number, ie,

$$AB(s) = \text{constant} = K^*$$

$$K=[A^+][B^-]/K^* \quad (3.3)$$

$$KK^*=[A^+][B^-] \quad (3.4)$$

Since k and k^* are constants, the product of KK* is also a constant, say Ksp, [40].

Therefore $KK^* = [A^+][B^-]$ becomes

$$Ksp=[A^+][B^-] \quad (3.5)$$

The constant, Ksp, is called solubility produce (SP) and [A] [B] is called the ionic product (IP). When the solution is saturated, the ionic product is equal to the solubility product. But when the ionic product exceeds the solubility product (IP/SP=S>1), the solution is supersaturated (Where S is degree of super saturation) precipitation occurs and ions combine on the substrate and in the solution to form nuclei. There are three main factors which affect the solubility product these and temperature, solvent and particle size[41]. The equilibrium between a precipitate and its ions in solution will shift according to whether the heat of solution is endothermic or exothermic [42]. Using a solvent of lower dielectric constant, the solubility of

moderately insoluble substance in water is reduced by the addition of alcohol or some other water miscible solvent. As particle size decreases, solubility appears to increase. Solubility constants have been reported by using different methods which includes calorimetric, cation exchange, conductivity, ion exchange, polarography, thermodynamic data, rate of reaction etc [40]. A complexing agent acting as a catalyst is usually employed in a bath to control the reaction otherwise spontaneous reaction and sedimentation of material will be obtained [39]. The more soluble salt is, the greater the ion product and the greater the Ksp. However, K_{sp} also depends on the number of ions involved, for any formation of thin film there is some minimum number of ions or molecules, which produce a static phase in contact with solution, called nucleus. Nucleation on the substrate of surface starts at local homogeneity. The rate at which nuclei forms on the surface of the substrate, depends on the degree of super saturation [43].

3.1.2 Factor affecting the Chemical Bath Deposition Method

The various factors that affect the deposition process in CBD techniques are:

Effect of chemical bath solution pH, effect of complexing agent, effect of bath temperature, effect of deposition time , effect of concentration cation and anion sources, effect of type of precursors source, nature of substrates and their separation.

3.1.2.1 Effect of Chemical Bath solution PH

The reaction rate as well as rate of deposition on the super saturation condition and rate of the formation of MX(Where M and X is the number of metals and O^-/ OH^- ions respectively). If the concentration of OH^- ions in the solution is higher, the M ions concentration will lower and the react ion rate will be slow [44]. At a certain pH, the concentration of M ion decreases to a level such that the ionic product of M and X becomes less than the Solubility of MX and a film will not be formed. For the growth of good quality thin films, the hydroxide ions in precursor solution are necessary. The thin film formation depends on the pH of the reaction mixture and PH depends on OH^- ions. The decrease in PH results in porous, non-reflecting, powdery and weakly adhered thin films on the substrates. At higher pH metal ion concentration will be lower and the reaction rate will be slow. When an increase in pH make

the metal ion concentration decreased, as a result the rate of film formation will be decreased [44,45]. T. Ben Nasr etal [46] deposited ZnS thin films using CBD method by changing the pH of the bath solution fixing the other deposition parameters constant. Their results suggested that the PH contributes had noticeably effects on the growth and crystal Structure of deposited ZnS thin films. It was particularly observed that the best crystallinity of the ZnS thin films was obtained at pH of 10. The decreasing of the PH value from 10.99 to 10 is related with the increasing of the (111) diffraction peak intensity. The optical transmission coefficient was found to increase when the PH increased from 10 to 11.5.

This may be interpreted by the decrease of the film thickness. ZnS film prepared at PH 11.5 shows a high transmission coefficient (70%) and a wide band gap of 3.67eV. The influence of PH (9, 10.5, 11 and 12.5) on an aqueous alkaline chemical bath deposition of PbS thin films were studied by A-N.Chattarki, etal[47]. They reported that the film growth is found to be dependent on the pH of the reaction bath.

3.1.2.2 Effect of complexing Agent.

Complexing agents, also known as ligands, are typically added to the chemical bath to control the availability of the free cation through thermodynamic equilibrium. The concentration of the complexing agent is typically tuned together with that of the metal salt to achieve desired film properties such as deposition rate, adhesion, and roughness [46] . It is also greatly influences the structural, electrical, morphological and optical properties of thin films [48, 49]. In CBD technique the process depends on the slow release of chalcogenide ions into an alkaline/acidic Solution in which the free metal ion is buffered at a low concentration [50]. The free metal ion concentration is controlled by the information of complex species according to the general reaction:

$$M(A)^{+2} \longleftrightarrow M^{+2} + A \qquad (3.6)$$

Where M is the metallic ion sources and A is the complexing agent; here concentration of the free metal ions at a particular temperature is represented by the relation:

$$K = [M^{+2}][A]/[M(A)^{+2}] \qquad (3.7)$$

Where K being the instability constant of the complex ion. The instability constant is different for different complexing agents.

As the instability constant increases, more number of ions will be released. The stability of the complex also depends on temperature and pH of the reaction bath. Increase in temperature of the solution will make the complex less stable; whereas an increase in PH generally makes it more stable [51]. Film formation occurs by combination of released metal ions from complex metal ion source and chalcogen source. It helps to limit the hydrolysis of the metal ion and important and impart some stability to bath otherwise it undergoes rapid hydrolysis and precipitation [45]. In general complexing agents usually form complexes with metal ions used to increase the bath stability, control deposition rate and good quality films, it also greatly influence the structural electro-optical properties of the thin film [51,52].

3.1.2.3 Effect of Bath Temperature

The rate of chemical reaction in the bath can also be influenced by the bath temperature. As temperature increases dissociation of the complex increases hence the kinetic energy of the molecules also increases leading to greater interaction between ions and subsequent deposition at Volume nucleation centers of the Substrate [53]. This will result in increase or decrease of terminal thickness, depending on the extent of supper Saturation of the solution of the bath. Stirring basically brings fresh parts of the solvent into contact with solute and particles are forced to connect and the presence of temperature assists the entire process for effective desired results [54]. The experimental data verified that a better bath temperature has an important effect on a crystal size.

In most cases higher temperatures allow more grain whereas, lower temperatures gives very small nuclei in Solution that are thermodynamically unstable.

3.1.2.4 Effect of Deposition Time

Deposition time is one of the parameter which affects thin film deposition in CBD method. In most cases it has a great influence on structural, morphological and optical properties of thin films. F.G Hone etal [55], showed that deposition time strongly influenced the preferred

orientations of the crystallites as well as structural parameters such as average crystallite size, strain and dislocation density for PbS thin films. In this study the optical band gap of PbS thin films also decreased from 1.32eV to 1.10eV with increasing deposition time. O'Brien and Saeed, used ethylenediamine as complexing agent,higher deposition temperatures and glass as a substrate and found that the thickness of the CdS thin film increased linearly with deposition time [51]. In general, the growth. of good quality semiconductor thin film by the Chemical "bath deposition technique proceeds at a slow pace. Higher deposition rates and higher films thickness are usually accompanied by powdery deposits and a lack of specular reflection.

3.1.2.5 Effect of concentration of cation and Anion sources

Chemical bath composition is critical for synthesis of good quality of thin films. The nature of the reactants influences the whole physical and chemical properties of the deposited thin film. By changing the composition of the reactive solution, competition between the processes of homogeneous and heterogeneous nucleation could be altered to favor thin film growth [51].

Nature of the reactants influence the composition it the products. The deposition of good quality, adherent, specular and crystalline CdSe has usually been associated with supersaturated bath with respect to the precipitation of cadmium hydroxide species irrespective of the substrate according to p.p. Hankare et al. [44] the growth under these circumstances give Se^{-2} ions into an alkaline solution, where the free metal ions are buffered. Thus concentration of bath ingredients usually favors the nucleation in the first stage. Indeed, the bath concentration plays an important role in the substrate interaction with growing particles. For high concentrations, the films formed were the thicker, indicating stronger interaction.

3.1.2.6 Effect of Types of precursor sources

Varies studies Verified that using different types of cat ion and anion precursor sources during film deposition play a vital role on the final physical and chemical properties of thin films. In the preparation of cadmium sulphide ,[56] investigated the effect of different cadmium salts. The results have shown tangible difference in growth kinematics and properties of thin films. Hanikhallaf et al [57] Studied effect of four differ cadmium Sources on physical properties of

CdS thin films deposited by chemical bath deposition method. The result revealed that film thickness was found to decrease in the order $CdSO_4$, Cd $(CH_3COO)_2$, $CdCl_2$,CdI_2. However, the band gap was found to decrease in the order $CdSO_4$, $Cd(CH_3COO)_2$ /CdI_2, $CdCl_2$.

3.1.2.7 Nature of substrates and their separation

The nature of the substrate is another important factor that plays a major role in the reaction kinetics; moreover, nucleation and crystal growth also takes place on it during thin film deposition [58]. Substrate should be cleaned properly with a standard procedure before being immersed in the reactant mixture. One of the advantages of CBD is that thin films can be deposited on any surface. Moreover, shape and electrical conductivity of the substrates are usually not important very irregularly shaped substrates can be used. However, the nature of the substrate is usually important in order to obtain an adherent film [40,59]. Glass is one of the most commonly used substrates with different adhesion in CBD, however, metals make good substrates in general, either because chalcogenides tend to adsorb strongly on many metals, or the non-noble metals are covered with a (hydroxylated in the deposition solution) oxide layer. If the metal in the deposition solution has a sufficiently negative potential, an internal electrochemical reduction may occur[51]. A large variety of CBD thin films have been also deposited on different polymer surfaces. Deposition sometimes is satisfactory on the clean polymer with Various activation treatments, such as treatment with permanganate, have been used to improve the adhesion and homogeneity [60]. Apart from adhesion, the crystallographic properties of chemically deposited films are sometimes dependent on the nature of the substrate. One examples is epitaxial deposition on a crystallographic ally-ordered substrate [61].

3.1.3 Thin film Deposition Mechanism in CBD

There are three main mechanisms leading to compound thin film formation, whose operation depends on these specific process and reaction parameters.

3.1.3.1 Ion-By-Ion mechanism

In Ion-By-Ion deposition, aqueous precursor ions react directly to form the thin film. The conditions are controlled such that few hydroxide ions form to prevent deposition (not on the

substrate) or precipitation of insoluble metal hydroxide. Sometimes a complexing agent is used to prevent the formation of metal hydroxide.[35]. The metal salt and the Chalcogenide salt disassociate to form precursor metal cations and chalcogenide anions, Which are attracted to and adhere to the substrate by Van der Waals forces. [63] · Ions adhere to the substrate, and aqueous ions attach to the growling crystals, forming larger crystals. Thus, this method to deposition results in larger and less uniform crystals than the hydroxide-cluster mechanism [35]. An example of the reaction, depositing Cadmium sulfide, is shown below:

$Cd^{2+}+S^{2-}$---------CdS (deposition)[62] (3.8)

3.1.3.2 Hydroxide-Cluster Mechanism

Hydroxide-cluster deposition occurs when hydroxide ions are present in the solution and usually results in smaller and more uniform crystals than ion-by-ion deposition. When hydroxide ions are present in the solution in quantity, metal hydroxide ions form. The hydroxide ions act as ligands to the metal cations, forming insoluble colloidal clusters which are both dispersed throughout the solution and deposited on to the substrate. These clusters are attacked to the substrate by Van der Waals forces.

The chalcogenide anions react with the metal hydroxide clusters, both dispersed and deposited, to form metal chalcogenides crystals. These crystals form the thin film, which has a structure similar to crystallite. In essence, the hydroxide ions acts as an intermediaries between the metal ions and the Chalcogenide ions. Because each hydroxide cluster is a nucleation site, this deposition method usually results in smaller and more uniform crystal than ion-by-ion deposition. [62] [63]

An example of the chemical reaction, depositing Cadmium sulfide, is shown below:

$nCd^{2+}_{(aq)}+2nOH^{-}_{(aq)} \longrightarrow [Cd(OH_2)](s)$ (Formation of cadmium hydroxide cluster)

$[Ca(OH)2]n+ns \longrightarrow nCdS+2nOH^{-}$ (replacement reaction) [63]. (3.9)

3.1.3.3 Complex-decomposition ion-by-ion Mechanism

As an example, let us take the decomposition of CdS thin film in alkaline medium using thiourea as S ion source. In this mechanism, complexion of free metal cations (M^{n+}) by thiourea gives M thiourea complex ion. This is illustrated by the example of CdS deposition.

$$Cd^{2+}+CS\ (NH_2)_2 = [CS\ (NH_2)_2\ -Cd]^{2+} \quad (3.10)$$

This ion is hydrolyzed by breaking the S-C bond to form CdS.

$$[(NH_2)_2CS\text{-}Cd]_2+2OH \rightarrow CdS+CN_2H_2+2H_2O \quad (3.11)$$

This would lead to CdS formation is solution. If Cd^{2+} is absorbed on the substrate (either directly or indirectly through a hydroxide linkage) then above reaction occurs and CdS is formed on substrate, the result would be the film growth by ion-by-ion.

This mechanism is also useful in acidic solution; thioacetamide decomposition at intermediate pH values, particularly in weakly acidic solution (PH $\geq$ 2) has been suggested to occur through a thioacetamide complex rather than through intermediate formation of sulfide [64].

3.2 Thin film characterization Methods

Once a thin film is synthesized, it is essential to characterized them in order to check the practical feasibility, material confirmation by a wide array of test. Advancement in characterization techniques made possible to study the material properties at atomic scale. The characterization typically has as a goal to the performance of the material

As such, much characterization technique should ideally be linked to the desirable properties of the material such as physiochemical, electrical, surface related properties etc. characterization techniques are typically used to determine molecular structure, morphology, crystal size, particle size, film thickness etc. [65]. An important step in the development of superior materials is film characterization the complete characterization of any material consists of phase analysis, compositional characterization, structural elucidation, micro structural analysis and surface characterization, which have strong bearing on the properties of materials. This has led to the emergence of a variety of advanced techniques in the field of thin film tech technology. The structural and optical properties of thin films are found to be

highly sensitive to the technique adopted, the substrate chosen, deposition conditions, the presence of defects and impurities and. film thickness. In the next sub sections a short Summary of commonly used characterization techniques in thin film technology. It is not intended to provide a complete discussion of the methods.

3.2.1 Structural Analysis

The analysis of crystal structure is a great importance in the description of materials; such an analysis is typically performed by employing X-ray diffraction techniques (other techniques include electron and neutron diffraction method)[73]. XRD measurements were performed by to study the crystal structure of ZnS thin film and complement the electron diffraction studies.

3.2.1.1 X-ray diffraction

X-ray diffraction (XRD) is a powerful nondestructive technique for characterizing crystalline materials. It provides information on structures, phases, preferred crystal orientations (texture), and other structural parameters, such as average grain size, Crystallinity, strain, and crystal defects. X-ray diffraction peaks are produced by constructive interference of a monochromatic beam of X-rays scattered at specific angles from each set of lattice planes in a sample. The peak intensities are determined by the distribution of atoms within the lattice. Consequently, the X-ray diffraction pattern is the fingerprint of periodic atomic arrangements in a given material [92].

The basic law involved in the diffraction method of structural analysis is the Bragg's law. X-ray diffraction methods have very convincingly demonstrated the crystallinity of solids by exploiting the fact that the spacing between atoms is comparable to the wavelength of radiation. This results in easily detected emitted beams of high intensity along certain directions when incident X-rays impinge at critical diffraction angles. Under these conditions the well-known Bragg relation [67], shows in equation3.12 holds, where n is the order of diffraction, λ is the wavelength of the X-rays, d is the spacing between consecutive parallel planes and θ is the glancing angle.

$$n\lambda = 2d\sin\theta \qquad (3.12)$$

If beams diffracted by two different layers are in phase, constructive interference occurs appear and the diffraction pattern shows a peak, however if they are out of phase, destructive interference occurs appear and there is no peak. Diffraction peaks only occur if $\sin\theta =$

n λ/2d. Since a highly regular structure is needed for diffraction to occur, only crystalline solids will diffract; amorphous materials will not show up in a diffraction pattern [74, 93].

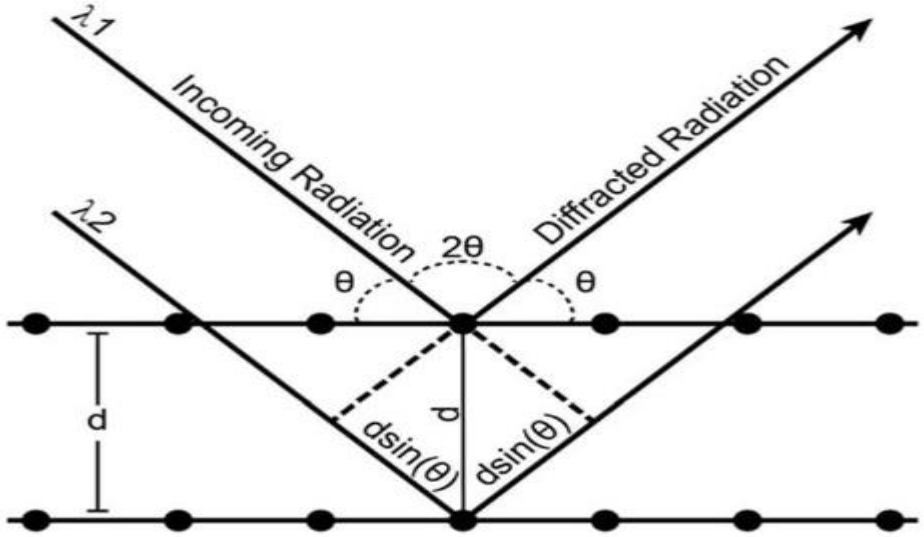

Figure 3.1: Schematic representation of Bragg's law [99]

X-ray diffraction studies gives a whole range of information about the crystal structure, orientation, average crystalline size and stress in the films[68]. Experimentally obtained diffraction patterns of the sample are compared with the standard Powder Diffraction Files published by the Joint Council of powder Diffraction Standards (JCPDS).

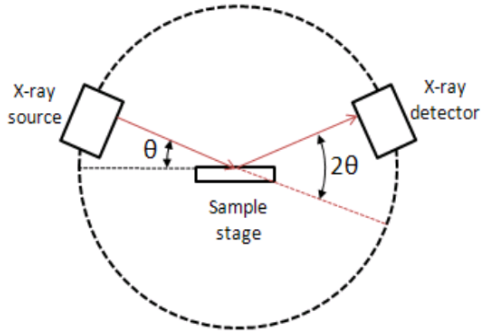

Figure 3.2: Schematic power x-ray diffraction diagram [74,93]

The power X-ray diffract meter consists of an X-ray source(usually an X-ray tube),a sample stage, a detector and a way to vary angle θ .The X-ray is focused on the sample at some angle θ, while the detector opposite the source reads the intensity of the X-ray it receives at 2θ away from the source path. The incident angle is than increased over time while the detector angle always remains 2θ above the source path.

3.2.1.2 Microstructural parameters analysis

The size of crystals and micro strain plays a crucial role in the behavior of the material and its physical properties, especially the microstructural properties. Their importance is due to their specific characteristics and potential uses in advanced technological applications. The X-ray diffraction line profile analysis considered to be one of the most accurate techniques to determine the crystallite size[75].

3.2.1.2a Crystallite size (D)

The average grain size of the film can be calculated using the Scherer's formula [66,69],

$$D=0.94\lambda/\beta\cos\theta \qquad (3.13)$$

where, λ is the wavelength of the X-ray and β is the full width at half maximum intensity in radians.

3.2.1.2b Lattice parameters

The lattice parameter values for cubic and hexagonal crystallographic systems associated in the present investigation can be calculated from the following equations using the (h k l) parameters and the interplanar spacing 'd'. Cubic system, Hexagonal system,

Cubic system,

$$1/d^2=(h^2+k^2+l^2)/a^2 \qquad (3.14)$$

Hexagonal system, $1/d^2=4/3a^2\ (h^2+hk+k^2)+l^2/c^2$ (3.15)

3.2.1.2c Micro strain (ε)

The presence of strain in the films is inevitable irrespective of the deposition techniques. The strain can be uniform or non-uniform. In the case of uniform strain, the inter-planar lattice spacing 'd' shift to the lower or higher values depending upon the nature of the strain (tensile

or compressive) [66,70,71]. Non-uniform strain changes from one region of the grain to another within the same grain. The presence of non-uniform strain is manifested by the broadening of the X-ray diffraction lines [72] . Information of the particle size are obtained from full width at half maximum of diffraction peaks. The FWHM (β) can be expressed as a linear combination of the contributions from the strain (ε) and crystallite size (D) by the following relation [76],.

$$\beta\cos\theta/\lambda=1/D+\varepsilon\sin\theta\lambda \quad (3.16)$$

The micro strain (ε) can be determined using the tangent formula [77],

$$\varepsilon=\beta/4\tan\theta \quad (3.17)$$

3.2.2 Optical Analysis

Optical properties of a material change or affect the characteristics of light passing through it by modifying its propagation vector or intensity. Measurement of the absorption of light is one of the most important techniques for optical measurements in solids [78]. In optical absorption spectroscopy, electromagnetic radiation in the near –Ultraviolet, visible or near infrared regions are used to excite transitions between the electronic states. Optical measurements have many unique and attractive features for studying and characterizing semiconductor properties. They are contactless, nondestructive, and compatible with any transparent ambient including high-vacuum environments.

3.2.2.1 UV/VIS Spectrometer

UV/Vis Spectrometers collect the data over the required range and generate the spectrum of the compound under analysis as a graph representing the transmittance (or absorbance) as a function of wavelength along the abscissa, given in nanometers, the recommended unit in this region. The region of the spectrum is conventionally divided into three sub-domains termed near UV(185-400nm), visible(400-700) and very near infrared (700-1100nm) [79]. One of the defining features of semiconductor is the band gap, which separates the conduction band valance band. The wavelength of the light absorbed and emitted from this material is determined by the width of the band gap. The UV-Vis absorption spectroscopy is frequently

used to characterize semiconductors thin films and to determine the band gap of nanoparticles [80].

In the present study, optical characterization was carried out to determine the nature of absorption and energy band gap of ZnS thin films. These properties have dependence on grain size and chemical composition of the thin films. During this study the optical absorption measurement was carried out in the wave length range from 200-800nm by using TBO UV/VIS spectrometer at the room temperature. A clean glass substrate was used for base line correction.

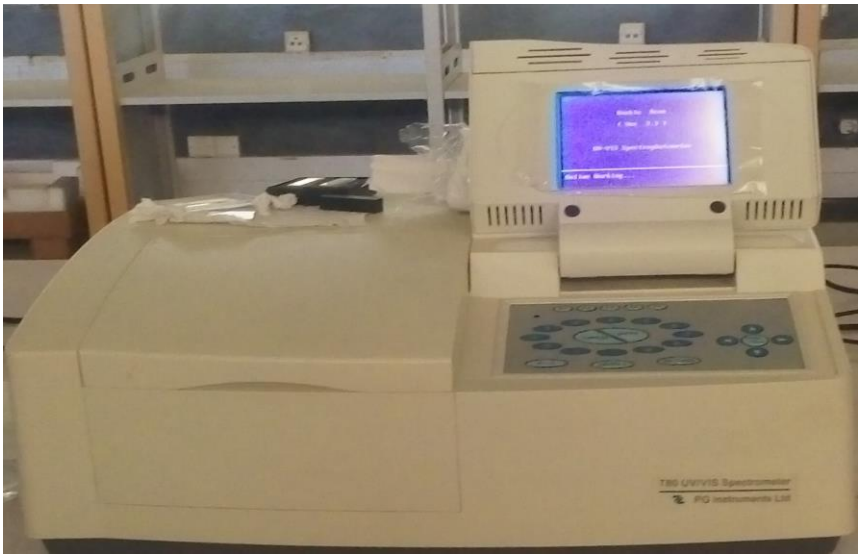

Figure 3.3. TBO UV/Vis Spectrometer

3.2.2.2 Energy band gap calculation from absorbance spectra

One the basis of their optical properties there are two types of optical transition that occur at the fundamental edge of crystallite semiconductors: direct and indirect transitions. Both involve the interaction of an electromagnetic wave with an electron in the valance band, which is raised across to the band gap to the conduction band. However, indirect transitions also involve simultaneous interaction with lattice vibrations see (Figure 3.4b). Thus the wave vector of the electron can change in the optical transition, the momentum change being taken or given up by the phonons [81]. Phonons are quantum of lattice vibration having a small

amount of energy and a large amount of momentum, and one or more phonons can take part the transition process if they have the required amount of momentum and energy[82].

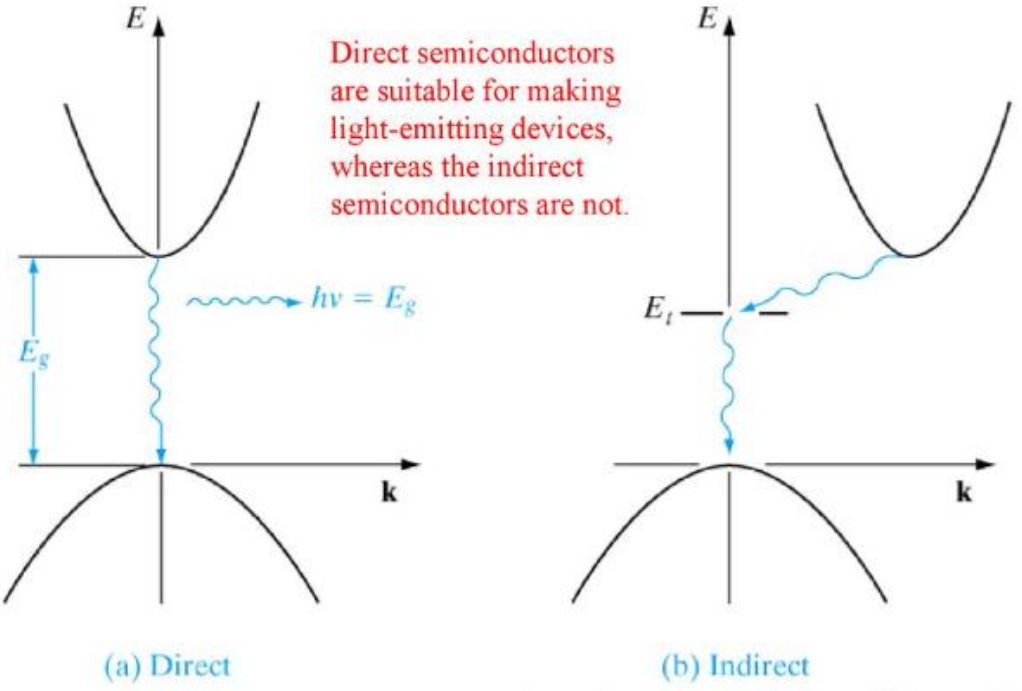

Fig 3.4: direct and indirect energy band diagram [100].

The direct inter-band optical transitions involves a vertical transition of electrons from the valance band to the conduction band such that there is no change in the momentum of the electron remains unchanged in E-K space shown in figure 3.4a. The optical transition is denoted by a vertical up ward narrow [83]. The energy band gap and transition type can determine from mathematical treatment of data obtained from optical absorbance versus wave length, with the Stern (1963), relationship of near edge absorption which is given as [84]:

$$A=[k(hv-E_g)]^{n/2}/hv \quad (3.18)$$

Where A is absorbance , hv is the incident photon energy, k is constant, and the exponent ‘n’ assumes the values 1,4,3 and 6 for allowed direct , allowed indirect , forbidden direct and forbidden transitions, respectively. The energy band gap can be obtained by extrapolating the linear portion of (Ahv)^2 versus hv to the energy axis at (Ahv)^2 = 0 [73].

3.3 Experimental procedures

3.3.1 Materials used

To Synthesize ZnS thin film the experimenter used the following materials:

- Beakers with different sizes
- Spoon
- Electronic beam balance
- Distilled water
- Wash bottle
- Chemical and reaction bath
- Magnetic Stirrer
- Heat supplier
- Ordinary glass substrates
- Temperature reading instrument
- Stand
- Magnetic stirrer rod
- Substrate holder in the laboratory.

3.3.2 Chemical Precursors used

For the Synthesization of ZnS thin film the experimenter used the following commercially purchased chemical in the laboratory:

- Zinc Chloride($Zncl_2$), 98 % purity
- Thiourea($Sc(NH_2)_2$) ,99 % purity,
- Ammonium hydroxide($NH_4(OH)$),25% purity.
- Hydrazine($N_2H_4(H_2O)$) ,98 % purity

3.3.3 Substrate cleaning

The substrate used in the deposition process was microscope glass slide because the surface glass can be very reactive towards species in solution [74]. For deposition of films, highly polished and thoroughly cleaned substrates are required. A variety of cleaning processes are

available [85]. Substrates were cleaned using liquid detergent. Then it was kept in dilute nitric acid for a day .After this the substrates were cleaned using distilled water. Then the substrates were agitated in ethanol for about 30 min.to eliminate grease and other oily substances. They were then rinsed in the distilled water dried under open air for about 15 min.

3.3.4 Solution preparation of precursors

Before preparing the stoke solution metallic precursor and complexing agents were properly prepared. Thus 13.36gm of solid zinc chloride was weighed using an electronic beam balance and then placed in a cylinder and carefully stirred. 1M Zinc Chloride solution for the use of metallic precursor was prepared. 7.54gm thiourea was weighted and then placed in cylinder and 100ml of deionized water was added and carefully stirred. 1M thiourea solution for the use of nonmetallic precursor was prepared. Finally, the required amount of Ammonium hydroxide and hydrazine was prepared and placed in a separate cylinder. All the four solutions were shacked to made homogenous (uniform) solutions. All the separate cylinders were cleaned using de-ionized water.

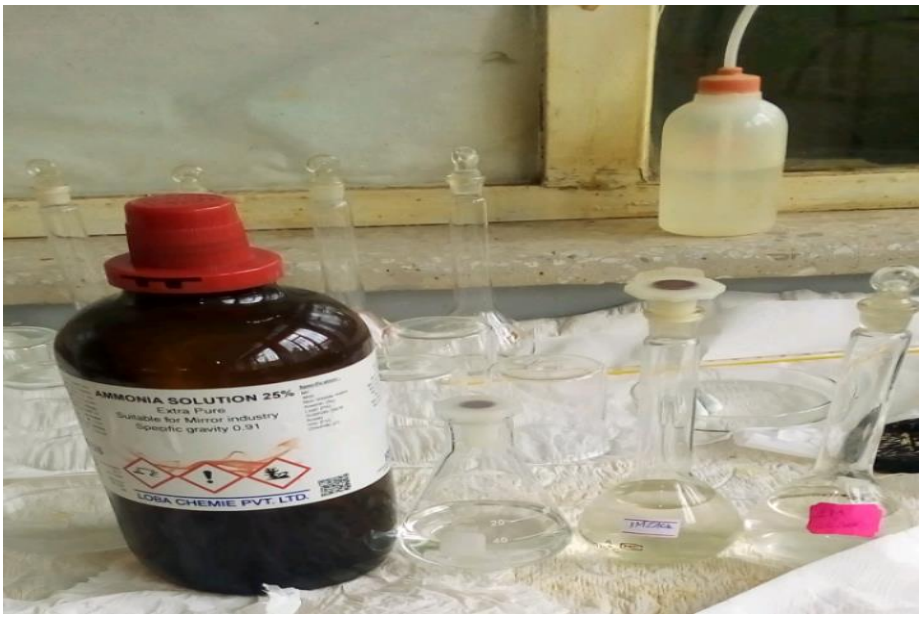

Figure 3.5 photos of prepared solution in the laboratory

3.3.5 Preparation of mother solution and synthesized of ZnS thin film

The preparation condition of ZnS thin films were optimized by adjusting concentration of dissolved chemicals bath temperature , as well as deposition time to obtain homogenous films with good adherence to the substance .The chemical bath contained Zinc Chloride ($ZnCl_2$) of 98 purity which provided Zinc ions ,Thiourea ($Sc(NH_2)_2$) 99 Percent purity which provided sulfur ion, Ammonium hydroxide($NH_4(OH)$), 25 Percent purity used as complexing agent and hydrazine ($N_2H_4(H_2O)$) 98 Percent purity were used as complementary complexing agent and adjust the PH of the aqueous solutions. All the solution were prepared using de-ionized water and all the chemicals used were analytical graded without the further purification .The concentration of metal ions was controlled by complexing agent .

The following procedures were used for the deposition of zinc thin films

The chemical bath was prepared as follows:

10ml of 1M Zinc Chloride ($ZnCl_2$) and 5ml de-ionized water placed in 100ml beaker to which 5ml hydrazine ($N_2H_4(H_2O)$) and 10ml de-ionized water was added and stirred very well , and 10ml Ammonium hydroxide ($NH_4(OH)$) and 5ml de-ionized water added and stirred. And also 10ml thiourea($Sc(NH_2)_2$) and 5ml de-ionized water was added. Then the solution was stirred thoroughly for a few seconds with magnetic stirrer. The cleaned substrate was then placed in pair vertically with a cork to prevent impurities in to the reaction bath. Finally, temperature meter was used to record the temperature of the solution. The reaction was stirred and maintained at a time of 2hr for deposition. The deposition is carried out at five deposition temperature of 40^oC, 45^oC, 50^oC, 55^oC, 60^oC in separate reaction bath.

Figure 3.6 Photo shows the preparation of Zinc sulfide thin film deposition in the laboratory

Figure 3.7 shows thin films after taken out from the reaction

The pre cleaned glass substrates with a special holder made in our laboratory were then immersed vertically In the stock solution. The stock solution was placed temperature in a water bath kept at constant temperature as shown in figures (3.6) .The stock solution was continuously stirred for the whole deposition time. Initially the solution was cleaned. As the temperature of the bath increases gradually to the value of interest, the color changed to grey-white (Figure 3.6) for the whole deposition time. The effects of deposition duration on the

structural and optical properties of ZnS thin films were studied. To investigate the effect of deposition temperature on the properties of the zinc thin films, depositions were carried out at 40°C, 45°C, 50°C, 55°C, and 60°C at time of 2 hr. The deposition process was then repeated to increase the thickness of the thin films in order to obtain good x-ray signal în Bragg Brentano diffraction geometry. After each deposition cycle, the thin films were taken out from the reaction vessel and cleaned with de-ionized water to remove powdery and less-adherent particles. The as-deposited films were grey-white in color, transparent and cell adherent to the substrate samples were dried in ambient conditions and kept in the desired place as shown in figure 3.7 until they were characterized by various techniques.

CHAPTER FOUR

4. Result and Discussion

This chapter basically includes the final reports of the result and discussions carried out in the previous chapter.

4.1 Reaction Mechanism for Zns Thin film deposition

Decomposing a zinc salt, thiourea, and complexing agent that permits the formation of soluble Zn^{2+} and S^{-} species in the solution [86,89]. $Zn^{2+}$and S^{-} ions in solutions release steadily during deposition, Condensing on appropriately mounted substrates to yield ZnS thin films [90] .The chemical equations for the reactions are as follows;

$$ZnCl2 + 2NH3 \longrightarrow Zn\,(NH3)2C12 \qquad (4.1)$$

$$CS(NH2)2 + OH^{-} \longrightarrow CH2+H2O+SH \qquad (4.2)$$

$$Zn(NH3)2Cl2 + CS(NH_2)2+2OH \longrightarrow Zns+CH_2N_2+2NH_3+2H_2O+Cl \qquad (4.3)$$

CBD's Methodology is dependent on the product's. It is critical to know CBD mechanisms in terms of its solubility product. The solubility product and the ionic product values for ZnS are 10^{-25} [87,88]. Ionic product equals the solubility product when the solution is saturated. super saturation, precipitation and ionic nuclei on the substrate and in the Solution emerge whenever the insolubility product exceeds the solubility product [87, 91] Therefore, formation ZnS thin film takes place$[Zn^{2+}][S^{-2}]$ exceeds [ZnS]. The solubility product is affected by three primary factors: temperature, solvent, and Particle size [91]. Solubility is the spontaneous interaction between two or more compounds to produce a uniform molecular dispersion.

When the solute and solvent are in equilibrium, the solution is considered to be saturated. The equilibrium between a precipitate and its ions in the solution will vary in terms of temperature depending on whether the heat of solution is endothermic or exothermic [91].

4.2 Studies of Optical properties of the ZnS thin films

Optical parameters, like absorbance, transmittance and band gap are very important parameters

to be considered while study in the optical properties materials. The optical properties of ZnS thin films were determined from absorption measurements in the wave length range of 400-800nm.

Figure 4.1(a-e) Shows UV-Vis absorption spectra of ZnS thin films prepared at different deposition temprature

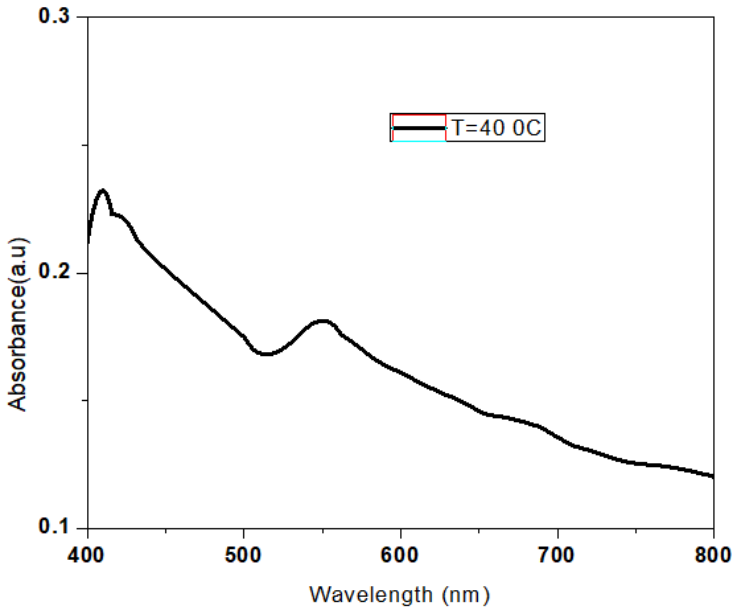

Figure 4.1a The plot of absorption versus wavelength of the ZnS thin film sample at deposited T=40^{o}C

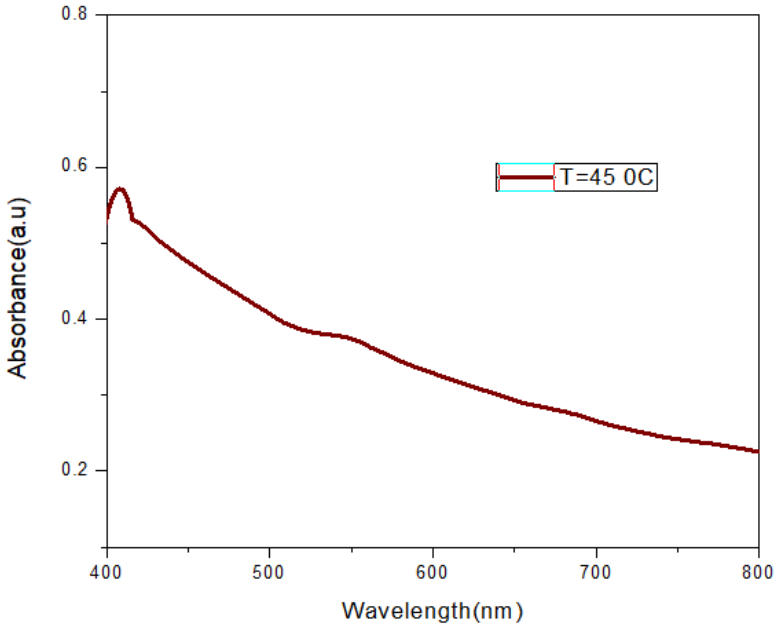

Figure 4.1b The plot of absorption vesus wavelength of the ZnS thin film sample at deposited T=45^{o}C

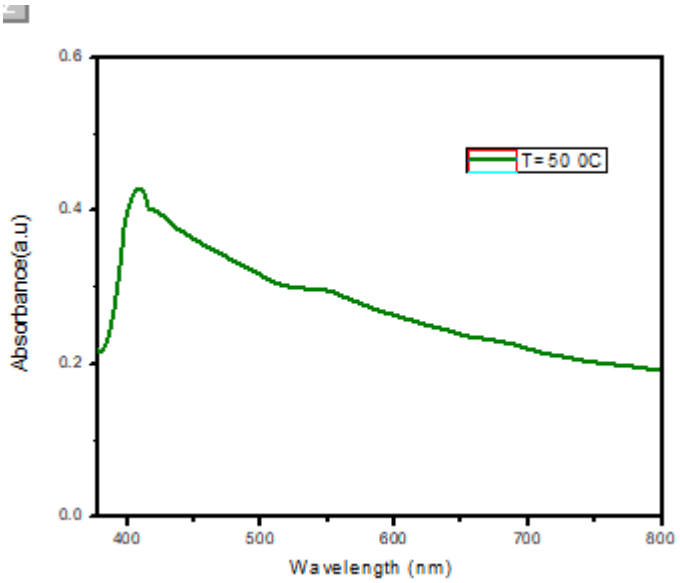

Figure 4.1c The plot of absorption vesus wavelength of the ZnS thin film sample at deposited T=50^{o}C

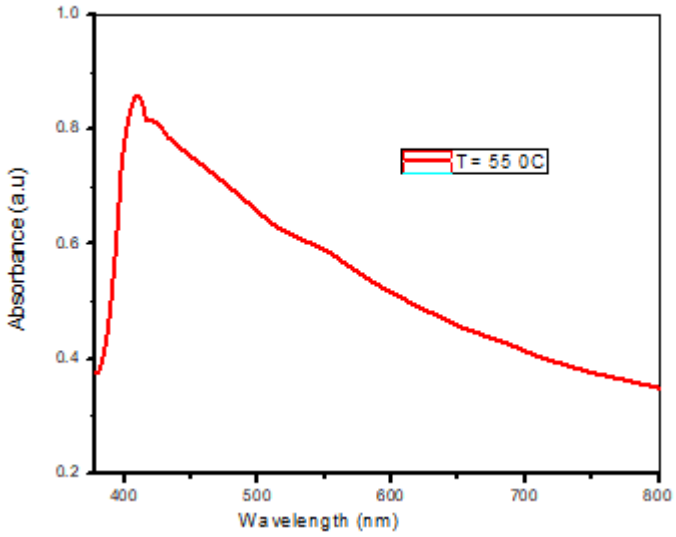

Figure 4.1d The plot of absorption vs wavelength of the ZnS thin film sample at deposited T=55^{o}C

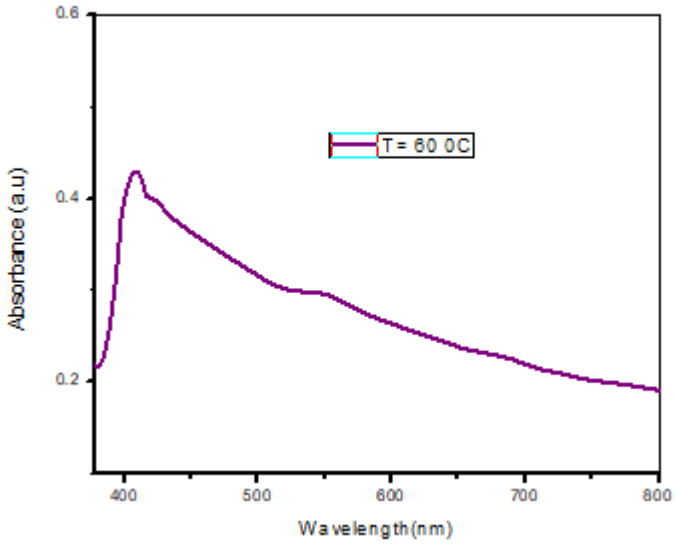

Figure 4.1e: The plot of absorbance of ZnS thin film at T=60^{o}C

As shown in the figure 4.1a at the maximum peak of the graph the wave length of the deposition temperature 40^{o}C was 410nm which is the highest value from other sample and also at this peak the absorbance value is 0.23 which was the smallest value from the others. The sharp peak or high intensity peak attributes to the excited electron (make them high energy). This causes an electronic transition from ground state (none excited) to an excited state. A narrow grain size distribution and the existence of below concentrations defects in the films at this condition [94,49]. Figure 4.1d shows optimal deposition temperature and the absorbance was most favorable from others samples. The highest absorbance of the films was found to be in the visible region at the maximum peak around 408nm which observed at the deposition temperature 55^{o}C. The estimated wave lengths of colors in the visible light region are violet (340-450nm). So in our study the absorbed color is violet. Hence it is applicable for different purposes including electroluminescent devices, displays, sensors, light-emitting diodes, optical laser coatings, and solar cells.

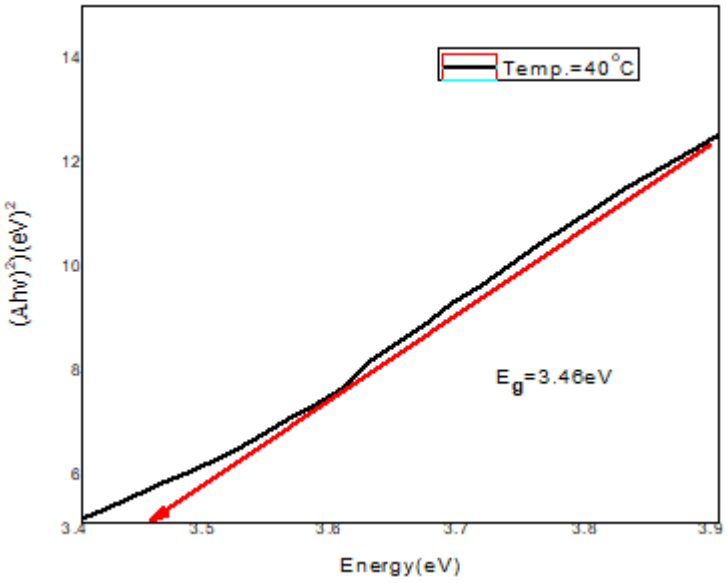

Figure 4.2 (a) Energy bandgap of ZnS thin films at T = 40 ^{0}C

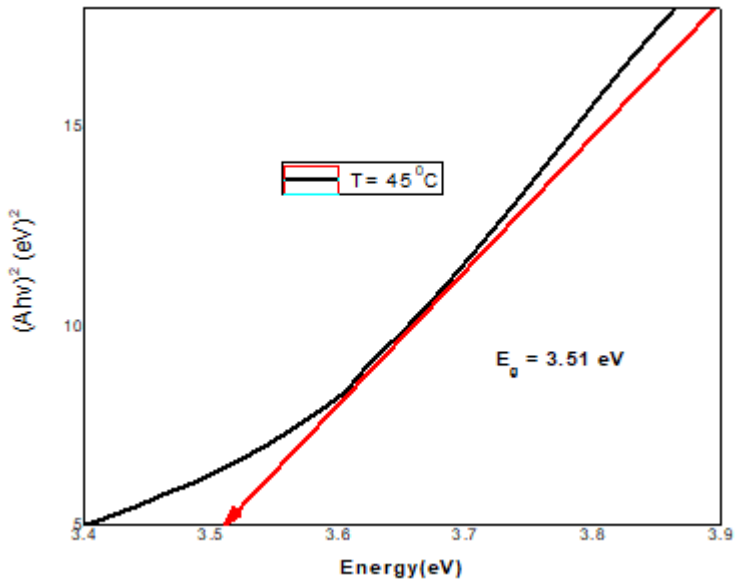

Figure 4.2 (b) Energy bandgap of ZnS thin films at T = 45 ^{0}C

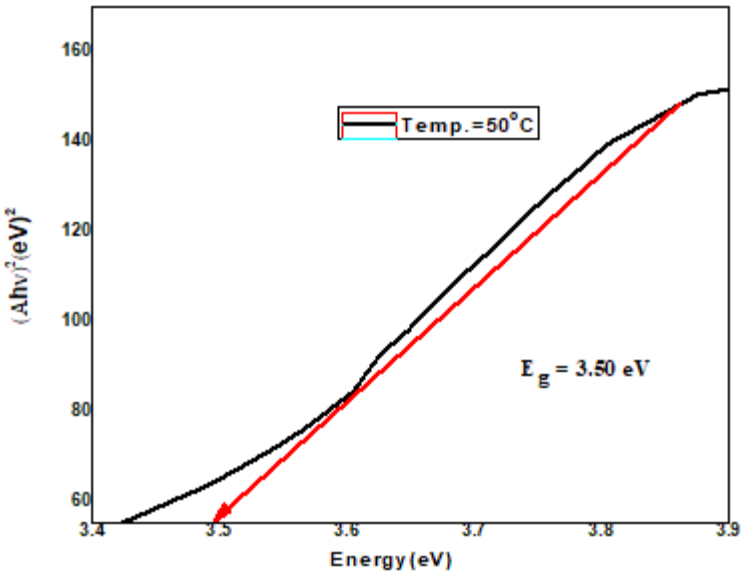

Figure 4.2 (c) Energy bandgap of ZnS thin films at T = 50 ^{0}C

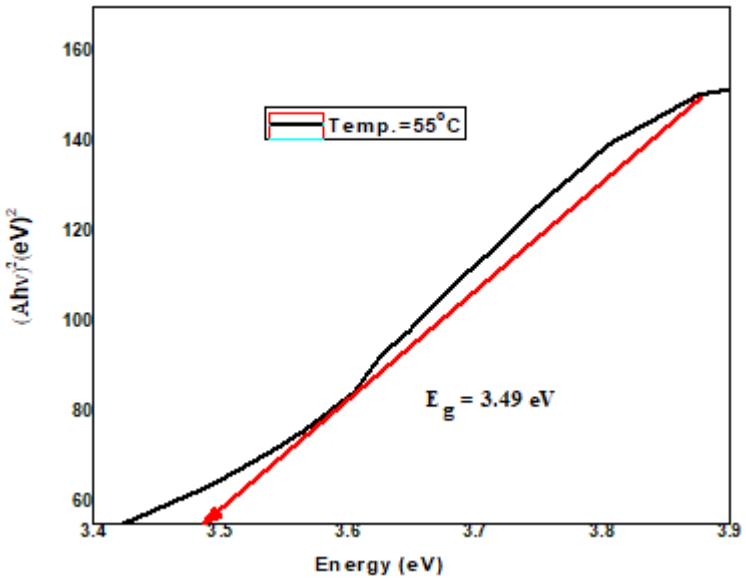

Figure 4.2 (d) Energy bandgap of ZnS thin films at T = 55 ^{0}C

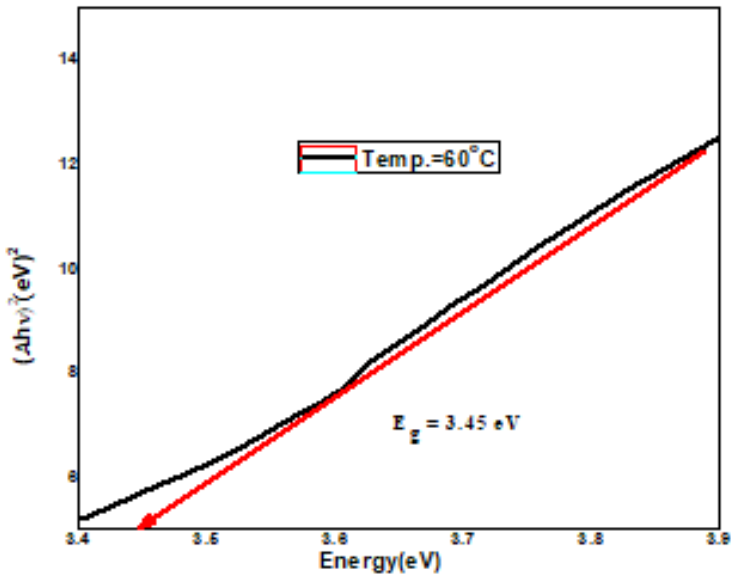

Figure 4.2 (e) Energy bandgap of ZnS thin films at T = 60 ^{0}C

The band gaps (E_g) of ZnS thin films were obtained by plotting the square of the product of absorbance and photon energy $(Ahv)^2$ against photon energy (hv) as shown figure 4.2(a-e).

The band gap energy (E_g) can be obtained by extrapolating the linear portion of the curve towards zero absorption $(Ahv)^2 = 0$.

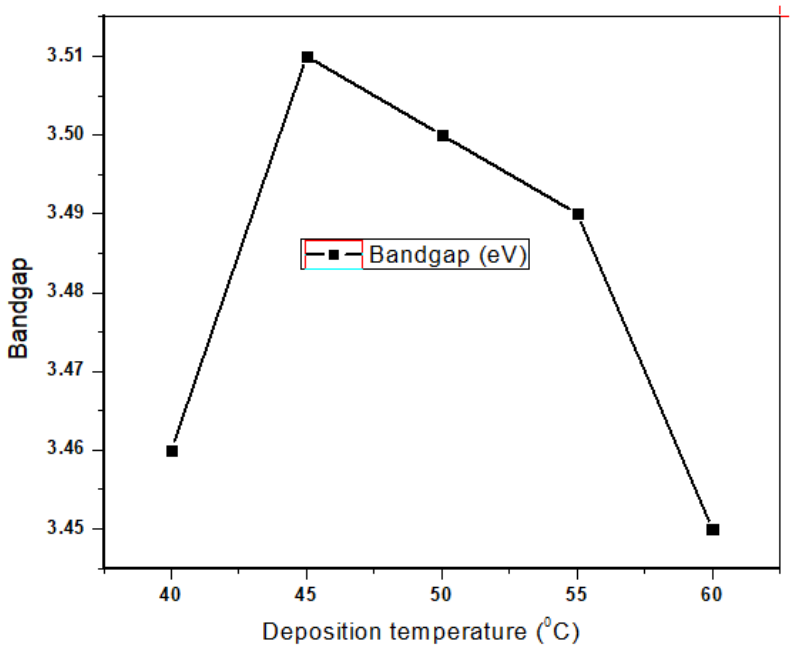

Fig 4.3: The relationship between deposition temperature and energy band gap

As Shown in the figure 4.2(a-e) and 4.3 the range of band gaps were 3.46eV, 3.51eV, 3.50eV, 3.49eVand 3.45eV at 40°C, 45°C, 50°C, 55°C and 60°C deposition temperature respectively. The maximum and minimum band gap energy observed at 45°C and 60°C respectively. This showed that the band gap energy decreased as the deposition temperature increased from 45°C to 60°C. The reason for this, as the temperature is increased, the mobility of electrons and lattice distortions increase resulting in narrower band gaps are created. In addition to this, when temperature increases, the amplitude of atomic vibrations increase, leading to larger inter atomic spacing. An increased inter atomic spacing decreases the potential seen by the electrons in the material, which turn reduces the size of energy band gap. The obtained values of band gap are somewhat smaller than the typical value of the bulk ZnS(3.68eV) [95]. As observed above figure 4.2(a-b) ,the band gap has been widened as the deposition on the temperature increases from 40°C to 45°C. This is due to the thickness and grain size of thin films are not increased sufficiently at this temperature. Such kinds of band gap effects have been studied by various researchers [78,114].

4.3 Structural Analysis of ZnS samples

Structural analysis is one of the common techniques in the characterization of thin films. XRD measurements were carried out to investigate the crystal structure and microstructural parameters of the thin films at the deposition temperature were varied in the range of interest.

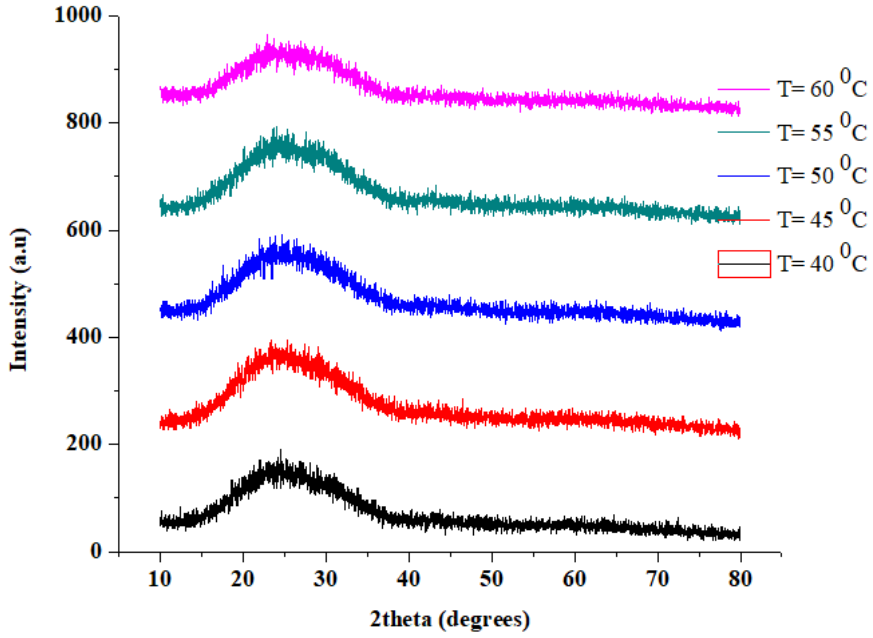

Figure 4.4: XRD patterns of the ZnS thin films deposited at different deposition temperature

The ZnS thin films deposited at all temperatures were almost amorphous in structure. As shown figure 4(a-e) the peaks were not clearly observed. Non crystalline of the films indicate that irregular arrangement of the particles. This might be ascribed for the small size crystalline of the film. Different researchers annealed the film in the range of 300^{o}C-400^{o}C and they had observed a crystalline thin film [96]. In our work, the films were annealed at the temperature of 200^{o}C for two hours. But if we could have annealed above 200^{o}C, the expected crystallite film might be observed. There are also various factors that can contribute for the ZnS thin film to be amorphous, like the nature of the complexing agent, concentration, the range of deposition time and others.

CHAPTER FIVE

5.1 Conclusion

ZnS thin films were successfully deposited on macroscopic glass substrates from a basic chemical bath using ammonium hydroxide and hydrazine as complexing agents. The films were adherent to the substrate and transparent. The effects of temperature on the structural and optical properties were investigated. Optical characterizations in the UV-Visible range indicated that ZnS thin film absorption is dependent on the deposition temperature. The results of XRD examinations showed that the films prepared the CBD method have an amorphous structure. The UV-Visible measurement also showed that the optimum condition from the prepared ZnS thin films at 55°C. The band gap decreases as deposition temperature increases from 45^{o}C to 60^{o}C. The maximum and minimum energy band gaps 3.51eV and 3.45eV were observed at deposition temperatures of 45°C and 60°C respectively. The decreasing of band gap shows that the deposition temperature has a direct impact on the optical properties of the ZnS thin films. The band gaps were increased as deposition temperature increase from 40^{o}C to 45^{o}C.

5.2 Recommendation

Further studies on this thesis could yield valuable information and move the process and materials closer to commercial application. Moreover, the author recommends and suggests the following key points that have to be improved for the synthesis and characterization of ZnS thin films:

1. Study the morphological and electrical characterization of ZnS thin films.
2. Investigate the impact of using the current materials as a buffer on the efficiency of different thin film solar cells.
3. Optimize the deposition parameters, such as temperature, pH, and precursor concentrations, to further improve the structural, optical, and electrical properties of the ZnS thin films.

Reference

1. Singh, Y. (2013). *Semiconductor devices*. IK International Pvt Ltd.
2. Berger, L. I. (2020). Semiconductor materials. CRC press.
3. Turley, J. L. (2003). The essential guide to semiconductors. Prentice Hall Professional
4. Bhattacharya, P., Fornari, R., & Kamimura, H. (2011). Comprehensive semiconductor science and technology. Newnes
5. Golan, G., Axelevitch, A., Gorenstein, B., & Manevych, V. (2006). Hot-probe method for evaluation of impurities concentration in semiconductors. Microelectronics journal, 37(9), 910-915.
6. Nuwal, Anuj, Shubhra Kakani, and S. L. Kakani. "Two band model for the iron based superconductors." Indian Journal of Pure & Applied Physics (IJPAP) 52, no. 6 (2015): 411-422.
7. Pham, V.P., & Yeom. G.Y. (2016). Recent advances in doping of molybdenum disulfide: Industrial applica toons and future prospects. Advanced Materials, 28141), 9024-9059
8. Dutta, p.5. (2011). Bulk growth of crystals of 111-V compound semiconductors.
9. Kuech, T. F. (2016). III-V compound semiconductors: Growth and structures. Progress in crystal growth and characterization of materials, 62(2), 352-370.
10. Jackson, k.A(Ed.). (2008). Compound semiconductor devices: structures and processing. John Wiley & Son
11. Butt, M. A. (2022). Thin-film coating methods: A successful marriage of high-quality and cost-effectiveness—A brief exploration. Coatings, 12(8), 1115..
12. Shobana, T., Venkatesan, T., & Kathirvel, D. (2020). A Comprehensive Review on Zinc Sulphide Thin Film by Chemical Bath Deposition Techniques. J. Environ. Nanotechnol, 9(1), 50-59.
13. Gençyılmaz, O., Akyüz, İ., & Atay, F. (2024). Binary ZnS–ZnO films as an alternative buffer layer for solar cell applications. Applied Physics A, 130(4), 227.

14. Pawar, S. M., Pawar, B. S., Kim, J. H., Joo, O. S., & Lokhande, C. D. (2011). Recent status of chemical bath deposited metal chalcogenide and metal oxide thin films. Current Applied Physics, 11(2), 117-161.
15. Abza, T., Ampong, F. K., Hone, F. G., Nkrumah, I., Nkum, R. K., & Boakye, F. (2016). The influence of deposition temperature on the structure and optical band gap of zinc sulphide thin films deposited from acidic chemical baths. Elixir, 93, 39511-14.
16. Poortmans, J., & Arkhipov, V. (Eds.). (2006). Thin film solar cells: fabrication, characterization and applications (Vol. 18). John Wiley & Sons
17. Seshan, K. (2012). Scaling and its Implications for the Integration and Design of Thin Film and Processes. Handbook of Thin Film Deposition, 19-40.
18. Moshfegh, A. Z. (2004). PVD growth method: physics and technology. Physics And Technology Of Thin Films: IWTF 2003, 28-53.
19. Ling, S. J., Sanny, J., Moebs, W., Friedman, G., Druger, S. D., Kolakowska, A., ... & Wheelock, K. (2016). University Physics Volume 2.
20. Wang, J., & Clouser, S. (2001, April). Thin film embedded resistors. In Proc. IPC Expo (pp. S08-1).
21. Sheng, P., Wang, B., & Li, R. (2018). Flexible magnetic thin films and devices. Journal of Semiconductors, 39(1), 011006.
22. Khlyustova, A., Cheng, Y., & Yang, R. (2020). Vapor-deposited functional polymer thin films in biological applications. Journal of Materials Chemistry B, 8(31), 6588-6609
23. Brown, P. R., Kim, D., Lunt, R. R., Zhao, N., Bawendi, M. G., Grossman, J. C., & Bulovic, V. (2014). Energy level modification in lead sulfide quantum dot thin films through ligand exchange. ACS nano, 8(6), 5863-5872.
24. George, J. (1992). Preparation of thin films. CRC press.
25. Abou-Ras, D., Kostorz, G., Romeo, A., Rudmann, D., & Tiwari, A. N. (2005). Structural and chemical investigations of CBD-and PVD-CdS buffer layers and interfaces in Cu (In, Ga) Se2-based thin film solar cells. Thin Solid Films, 480, 118-123.

26. Rumberg, A., Sommerhalter, C., Toplak, M., Jäger-Waldau, A., & Lux-Steiner, M. C. (2000). ZnSe thin films grown by chemical vapour deposition for application as buffer layer in CIGSS solar cells. Thin Solid Films, 361, 172-176
27. Johnston, D. A., Carletto, M. H., Reddy, K. T. R., Forbes, I., & Miles, R. W. (2002). Chemical bath deposition of zinc sulfide based buffer layers using low toxicity materials. Thin Solid Films, 403, 102-106.
28. Sankapal, B. R., Sartale, S. D., Lokhande, C. D., & Ennaoui, A. (2004). Chemical synthesis of Cd-free wide band gap materials for solar cells. Solar energy materials and solar cells, 83(4), 447-458.
29. Hankare, P. P., Chate, P. A., Chavan, P. A., & Sathe, D. J. (2008). Chemical deposition of ZnSe thin films: Photoelectrochemical applications. Journal of alloys and compounds, 461(1-2), 623-627.
30. Shin, S. W., Agawane, G. L., Gang, M. G., Moholkar, A. V., Moon, J. H., Kim, J. H., & Lee, J. Y. (2012). Preparation and characteristics of chemical bath deposited ZnS thin films: Effects of different complexing agents. Journal of Alloys and Compounds, 526, 25-30.
31. Fuchs, P., Romanyuk, Y. E., & Tiwari, A. N. (2018). Chemical Bath Deposition. Transparent Conductive Materials: Materials, Synthesis, Characterization, Applications, 81-103.
32. Eid, A. H., Salim, S. M., Sedik, M. B., Omar, H., Dahy, T., & Abou-Elkhair, H. M. (2010). Preparation and characterization of ZnS thin films. J. Appl. Sci. Res, 6(6), 777-784.
33. Zein, R., & Alghoraibi, I. (2019). Influence of bath temperature and deposition time on topographical and optical properties of nanoparticles ZnS thin films synthesized by a chemical bath deposition method. Journal of Nanomaterials, 2019.
34. Roy, P., Ota, J. R., & Srivastava, S. K. (2006). Crystalline ZnS thin films by chemical bath deposition method and its characterization. Thin Solid Films, 515(4), 1912-1917..
35. Hodes, (2007). Semiconductor and ceramic nanoparticle films deposited by chemical bath to position. physical chemistry chemical physics ,9(18),2181-2196.

36. Guire, M. R. D., Bauermann, L. P., Parikh, H., & Bill, J. (2013). Chemical bath .deposition. Chemical solution deposition of functional oxide thin films, 319-339.
37. Nair, P. K., Nair, M. T. S., Garcıa, V. M., Arenas, O. L., Pena, Y., Castillo, A., ... & Rincon, M. E. (1998). Semiconductor thin films by chemical bath deposition for solar energy related applications. Solar Energy Materials and solar cells, 52(3-4), 313-344.
38. Switzer, J. A., & Hodes, G. (2010). Electrodeposition and chemical bath deposition of functional nanomaterials. MRS bulletin, 35(10), 743-75
39. Chopra, K. (2012). Thin film device applications. Springer Science & Business Media
40. Mane, R. S., & Lokhande, C. D. (2000). Chemical deposition method for metal chalcogenide thin films. Materials Chemistry and physics, 65(1), 1-31.
41. Pietrzyk, D. J., & Marcus, Y. (1976). Ion exchanger-solvent interactions: properties and methodology.
42. Skoog, D. A., & West, D. M. (1982). Fundamentals of analytical chemistry (persisk): Bd. 2. Saunders.
43. Pathan, H. M., & Lokhande, C. D. (2004). Deposition of metal chalcogenide thin films by successive ionic layer adsorption and reaction (SILAR) method. Bulletin of Materials Science, 27, 85-111.
44. Hankare, P. P., Delekar, S. D., Asabe, M. R., Chate, P. A., Bhuse, V. M., Khomane, A. S., ... & Sarwade, B. D. (2006). Synthesis of Cadmium Selenide thin films at low-temperature by simple Chemical route and their Characterization. Journal of Physics and Chemistry of Solids, 67(12), 2506-2511
45. Barote, M. A., Yadav, A. A., & Masumdar, E. U. (2011). Effect of deposition parameters on growth and characterization of chemically deposited Cd1-XPbXS thin films. Chalcogenide letters, 8(2), 129-138.
46. Opasanont, B., & Baxter, J. B. (2015). Dynamic speciation modeling to guide selection of complexing agents for chemical bath deposition: Case study for ZnS thin films. Crystal Growth & Design, 15(10), 4893-4900.
47. Chattarki, A. N., Kamble, S. S., & Deshmukh, L. P. (2012). Role of pH in aqueous alkaline chemical bath deposition of lead sulfide thin films. Materials Letters, 67(1), 39-41.

48. Carrillo-Castillo, A., Lázaro, R. A., Jimenez-Pérez, A., Pérez, C. M., De la Cruz Terrazas, E. C., & Quevedo-López, M. A. (2014). Role of complexing agents inchemical bath deposition of lead sulfide thin films. Materials Letters, 121, 19-21.
49. Liu, J., Wei, A., & Zhao, Y. (2014). Effect of different complexing agents on the properties of chemical-bath-deposited ZnS thin films. Journal of alloys and compounds, 588, 228-234.
50. O'Brien, P., & McAleese, J. (1998). Developing an understanding of the processes controlling the chemical bath deposition of ZnS and CdS. Journal of Materials Chemistry, 8(11), 2309-2314
51. Hodes, G. (2002). Chemical solution deposition of semiconductor films. CRC press..
52. Prabukanthan, P., Soukup, R. J., Ianno, N. J., Sarkar, A., Kment, Š., Kmentova, H., ... & Darveau, S. A. (2010, June). Chemical bath deposition (CBD) of iron sulfide thin films for photovoltaic applications, crystallographic and optical properties. In 2010 35th IEEE Photovoltaic Specialists Conference (pp. 002965-002969). IEEE.
53. Arsad, A. Z., Zuhdi, A. W. M., Abdullah, S. F., Chau, C. F., Ghazali, A., Ahmad, I., & Abdullah, W. S. W. (2023). Effect of chemical bath deposition variables on the properties of zinc sulfide thin films: a review. Molecules, 28(6), 2780.
54. AGUIRRE-TOSTADOC, F. S. (2013). Characterization of CdS thin films deposited by chemical bath deposition using novel complexing agents. Chalcogenide letters, 10(10), 421-425.
55. Hone, F. G., Ampong, F. K., Abza, T., Nkrumah, I., Nkum, R. K., & Boakye, F. (2014). Investigating the effect of deposition time on the morphology, structure and optical band gap of PbS thin films synthesized by CBD technique. Elixir Thin Film Tech, 76, 28432-28437.
56. Cao, M., Sun, Y., Wu, J., Chen, X., & Dai, N. (2010). Effects of cadmium salts on the structure, morphology and optical properties of acidic chemical bath deposited CdS thin films. Journal of alloys and compounds, 508(2), 297-300
57. Ernits, K., Muska, K., Danilson, M., Raudoja, J., Varema, T., Volobujeva, O., & Altosaar, M. (2009). Anion effect of zinc source on chemically deposited ZnS (O, OH) films. Advances in Materials Science and Engineering, 2009.

58. Kumaran, S. S., & Banu, T. P. (2013). Investigation on structural and optical properties of chemically deposited Pbs thin films. Int. J. Recent Sci. Res, 4, 1685-1687.
59. Moreno, O. P., Ávila, G. A., Cerna, J. R., Tecorralco, J. H., Portillo, M. C., Juárez, J. M., ... & Ángel, O. Z. (2011). Characterization of chemical bath deposited CdS, CdSe and PbS. Journal of Materials Science and Engineering A: Structural Materials: Properties, Microstructure and Processing, 1(5), 692-704.
60. Pramanik, P., & Bhattacharya, S. (1987). Deposition of chalcogenide thin films by solution growth technique on polymer surfaces. Journal of materials science letters, 6(9), 1105-1106.
61. Furlong, M. J., Froment, M., Bernard, M. C., Cortès, R., Tiwari, A. N., Krejci, M., ... & Lincot, D. (1998). Aqueous solution epitaxy of CdS layers on CuInSe2. Journal of crystal growth, 193(1-2), 114-122.
62. Froment, M., & Lincot, D. (1995). Phase formation processes in solution at the atomic level: Metal chalcogenide semiconductors. Electrochimica Acta, 40(10), 1293-1303.
63. Aida, M. S., & Hariech, S. (2020). Cadmium Sulfide Thin Films by Chemical Bath Deposition Technique. Advances in Energy Materials, 49-75
64. Visoly-Fisher, I., Dobson, K. D., Nair, J., Bezalel, E., Hodes, G., & Cahen, D. (2003). Factors affecting the stability of CdTe/CdS solar cells deduced from stress tests at elevated temperature. Advanced Functional Materials, 13(4), 289-299.
65. *Kumar, R., Singh, S., & Yadav, B. C. (2015). Conducting polymers: synthesis, properties and applications. International Advanced Research Journal in Science, Engineering and Technology, 2(11), 110-124.*
66. *Cullity, B. D., & Stock, S. R. (2001). Elements of x-ray diffraction, Prentice Hall. Upper Saddle River, NJ, 388.*
67. *Kittel, C., & McEuen, P. (2018). Introduction to solid state physics. John Wiley & Sons.*
68. *Dorn, J. E. (1953). Structure of Metals: Crystallographic Methods, Principles, and Data. Charles S. Barrett. New York-London: McGraw-Hill, 1952. 661 pp. $10.00. Science, 117(3042), 421-422.*

69. He, B. B. (2018). *Two-dimensional X-ray* Diffraction. John Wiley & Sons.
70. Fell, C. R., Chi, M., Meng, Y. S., & Jones, J. L. (2012). In situ X-ray diffraction study of the lithium excess layered oxide compound Li [Li0. 2Ni0. 2Mn0. 6] O2 during electrochemical cycling. *Solid State Ionics*, *207*, 44-49.
71. Kril, C. E., & Birringer, R. (1998). Estimating grain-size distributions in nanocrystalline materials from X-ray diffraction profile analysis. *Philosophical Magazine A*, *77*(3), 621-640.
72. Mazher, J., Shrivastav, A. K., Nandedkar, R. V., & Pandey, R. K. (2004). Strained ZnSe nanostructures investigated by x-ray diffraction, atomic force microscopy, transmission electron microscopy and optical absorption and luminescence spectroscopy. *Nanotechnology*, *15*(5), 572.
73. Fekadu, G. H. (2015). *Synthesis and characterization of cadmium selenide (CdSe) and lead sulphur selenide (PbS1-xSex) thin films by chemical bath deposition method* (Doctoral dissertation).
74. Skoog, D. A., Holler, F. J., & Crouch, S. R. (2019). Textbook "principles of instrumental analysis". *Cengage learning*.
75. Eisermann, S., Kronenberger, A., Laufer, A., Bieber, J., Haas, G., Lautenschläger, S., ... & Meyer, B. K. (2012). Copper oxide thin films by chemical vapor deposition: Synthesis, characterization and electrical properties. *physica status solidi (a)*, *209*(3), 531-536.
76. Qadri, S. B., Skelton, E. F., Hsu, D., Dinsmore, A. D., Yang, J., Gray, H. F., & Ratna, B. R. (1999). Size-induced transition-temperature reduction in nanoparticles of ZnS. *Physical Review B*, *60*(13), 9191.
77. Klug, H. P., & Alexander, L. E. (1974). *X-ray diffraction procedures: for polycrystalline and amorphous materials* (p. 992).
78. Göde, F. A. T. M. A., Gümüş, C. E. B. R. A. İ. L., & Zor, M. (2007). Investigations on the physical properties of the polycrystalline ZnS thin films deposited by the chemical bath deposition method. *Journal of Crystal Growth*, *299*(1), 136-141.

79. Rouessac, F., & Rouessac, A. (2022). *Chemical analysis: modern instrumentation methods and techniques*. John Wiley & Sons.
80. Shibu, E. S., Muhammed, M. H., Tsukuda, T., & Pradeep, T. (2008). Ligand exchange of Au25SG18 leading to functionalized gold clusters: spectroscopy, kinetics, and luminescence. *The Journal of Physical Chemistry C*, *112*(32), 12168-12176.
81. Kim, E., Jiang, Z. T., & No, K. (2000). Measurement and calculation of optical band gap of chromium aluminum oxide films. *Japanese Journal of Applied Physics*, *39*(8R), 4820.
82. Lancry, O., Farvacque, J. L., Pichonat, E., & Gaquière, C. (2011). Indirect interband transition in hexagonal GaN. *Journal of Physics D: Applied Physics*, *44*(7), 075105.
83. Streetman, B. G., & Banerjee, S. (2000). *Solid state electronic devices* (Vol. 4, pp. 202-203). New Jersey: Prentice hall.
84. Kassim, A., WeeTee, T., Abdullah, D. K., Sharif, A. M., SoonMin, H., Yong, G. S., & Nagalingam, S. (2010). Preparation and characterization of iron sulphide thin films by chemical bath deposition method. *Indonesian Journal of Chemistry*, *10*(1), 8-11.
85. Doha, M. H., Alam, M. J., Rabeya, J., Siddiquee, K. A. M. H., Hussain, S., Islam, O., ... & Sarkar, S. H. (2015). Characterization of chemically deposited ZnS thin films on bare and conducting glass. *Optik*, *126*(24), 5194-5199.
86. Nasr, T. B., Kamoun, N., Kanzari, M., & Bennaceur, R. (2006). Effect of pH on the properties of ZnS thin films grown by chemical bath deposition. *Thin solid films*, *500*(1-2), 4-8.
87. Sinha, T., Lilhare, D., & Khare, A. (2018). Effects of various parameters on structural and optical properties of CBD-grown ZnS thin films: a review. *Journal of Electronic Materials*, *47*, 1730-1751.
88. Abou-Ras, D. (2005). *Structural and chemical analyses of buffer layers in Cu (In, Ga) Se2 thin-film solar cells* (Doctoral dissertation, ETH Zurich).
89. Vidal, J., Vigil, O., De Melo, O., Lopez, N., & Zelaya-Angel, O. (1999). Influence of NH3 concentration and annealing in the properties of chemical bath deposited ZnS films. *Materials Chemistry and Physics*, *61*(2), 139-142.

90. Dona, J. M., & Herrero, J. (1994). Process and film characterization of chemical-bath-deposited ZnS thin films. *Journal of the Electrochemical Society*, *141*(1), 205.
91. Hone, F. G., & Abza, T. (2019). Short review of factors affecting chemical bath deposition method for metal chalcogenide thin films. *Technology*, *8*(2), 3.
92. Bunaciu, A. A., UdriŞTioiu, E. G., & Aboul-Enein, H. Y. (2015). X-ray diffraction: instrumentation and applications. *Critical reviews in analytical chemistry*, *45*(4), 289-299.
93. Dann, S. E. (2000). *Reactions and characterization of solids* (Vol. 2). Royal Society of Chemistry.
94. Goudarzi, A., Aval, G. M., Park, S. S., Choi, M. C., Sahraei, R., Ullah, M. H., ... & Ha, C. S. (2009). Low-temperature growth of nanocrystalline Mn-doped ZnS thin films prepared by chemical bath deposition and optical properties. *Chemistry of Materials*, *21*(12), 2375-2385.
95. Lee, H. J., & Lee, S. I. (2007). Deposition and optical properties of nanocrystalline ZnS thin films by a chemical method. *Current Applied Physics*, *7*(2), 193-197.
96. Arsad, A. Z., Bahrudin, M. S., Arzaee, N. A., Abd Rahman, M. N., Chau, C. F., Abdullah, S. F., & Zuhdi, A. M. (2024). Zinc sulfide thin films deposited by chemical bath: Tuning consideration of structural, optical band gap, and electrical properties for CIGS solar cells application. *Ceramics International*.
97. Vishwakarma, R. (2015). Effect of substrate temperature on ZnS films prepared by thermal evaporation technique. *Journal of Theoretical and Applied Physics*, *9*, 185-19
98. https://www.researchgate.net/figure/Experimental-setup-of-CBD-method-to-deposition-of-thin-film_fig3_354147679
99. https://www.researchgate.net/figure/Figure-A1-Schematic-representation-of-Braggs-law-conditions_fig16_322664978
100. https://www.researchgate.net/figure/Schematic-showing-the-difference-in-direct-and-indirect-band-gaps-in-semiconductors_fig2_341043505
101. Tyagi, M. S. (2008). *Introduction to semiconductor materials and devices* John Wiley & Sons

102. Yang, K., Li, B., & Zeng, G. (2019). Effects of temperature on properties of ZnS thin films deposited by pulsed laser deposition. Superlattices and Microstructures, 130, 409-415.

103. Kaur, N., Kaur, S., Singh, J., & Rawat, M. (2016). A review on zinc sulphide nanoparticles: from synthesis, properties to applications. J Bioelectron Nanotechnol, 1(1), 1-5.

104. Salim, S. M., Eid, A. H., Salem, A. M., & Abou El-khair, H. M. (2012). Nanocrystalline ZnS thin films by chemical bath deposition method and its characterization. Surface and interface analysis, 44(8), 1214-1218.

105. Djelloul, A., Adnane, M., Larbah, Y., Sahraoui, T., Zegadi, C., Maha, A., & Rahal, B. (2015). Properties study of ZnS thin films prepared by spray pyrolysis method. Журнал нано-та електронної фізики, (7,№ 4), 04045-1.

106. Kennedy, J., Murmu, P. P., Gupta, P. S., Carder, D. A., Chong, S. V., Leveneur, J., & Rubanov, S. (2014). Effects of annealing on the structural and optical properties of zinc sulfide thin films deposited by ion beam sputtering. Materials science in semiconductor processing, 26, 561-566.

107. Goldman, E. R., Balighian, E. D., Kuno, M. K., Labrenz, S., Anderson, G. P., Mauro, J. M., & Mattoussi, H. (2002). Luminescent Quantum Dot-Adaptor Protein-Antibody Conjugates for Use in Fluoroimmunoassays. physica status solidi (b), 229(1), 407-414.

108. Wang, L., Xu, X., & Yuan, X. (2010). Preparation and photoluminescent properties of doped nanoparticles of ZnS by solid-state reaction. Journal of Luminescence, 130(1), 137-140.

109. Kasap, S., Capper, P., Wang, J., & Isshiki, M. (2007). Wide-bandgap II-VI semiconductors: growth and properties. In Springer Handb. Electron. Photonic Mater..

110. Fang, X., Zhai, T., Gautam, U. K., Li, L., Wu, L., Bando, Y., & Golberg, D. (2011). ZnS nanostructures: from synthesis to applications. Progress in Materials Science, 56(2), 175-287.

111. Hwang, D. H., Ahn, J. H., Hui, K. N., Hui, K. S., & Son, Y. G. (2012). Structural and optical properties of ZnS thin films deposited by RF magnetron sputtering. Nanoscale research letters, 7, 1-7.
112. Drobyshevski, E. M. (2000). In searches for daemons. Physics of Atomic Nuclei, 63, 1037-1041.
113. Babatunde, R. A., & Bolanle, Y. I. (2019). Effects of Thiourea Concentration in Formation of Zns Thin Films Grown By Chemical Bath Deposition for Heterojunction Solar Cell.
114. Temel, S. (2018). Influence of deposition temperature on structural, morphological, and optical properties of ZnS thin films. Canadian Journal of Physics, 96(7), 826-830.