EFFECT OF DEPOSITION TIME ON STRUCTURAL AND OPTICAL PROPERTIES OF CdS THIN FILM PREPARED BY CHEMICAL BATH DEPOSITION METHOD IN ALKALINE MEDIUM

MSC IN SOLID STATE PHYSICS

ABERASH BEKENA

HAWASSA UNIVERSITY, HAWASSA, ETHIOPIA

JUNE, 2024

EFFECT OF DEPOSITION TIME ON STRUCTURAL AND OPTICAL PROPERTIES OF CdS THIN FILM PREPARED BY CHEMICAL BATH DEPOSITION METHOD IN ALKALINE MEDIUM

BY

ABERASH BEKENA

A THESIS SUBMITTED TO THE DEPARTMENT OF PHYSICS,

COLLEGE OF NATURAL AND COMPUTATIONAL SCIENCE,

SCHOOL OF GRADUATE STUDIES

HAWASSA UNIVERSITY HAWASSA, ETHIOPIA

IN PARTIAL FULFILLMENT OF THE REQUIREMENTS

FOR THE DEGREE OF

MASTER OF SCIENCE IN PHYSICS

(SPECIALIZATION: SOLID STATE PHYSICS)

JUNE, 2024

Advisor approval sheet -1

The undersigned certify that have read and recommend to the College of school of Graduate Studies for acceptance MSc Thesis entitled **"Effect of Deposition Time on Structural and Optical Properties of CdS Thin Film in Alkaline Chemical Bath Deposition Method"** by author ABERASH BEKENA in partial fulfillment of the requirements for the Degree of Masters in Solid state physics.

Approved by:

Main Advisor	signature	Date
Dr; Abebe Getachew	_____	_____
Department head	signature	Date
Dr; Abebe Getachew	_____	_____

EXAMINER'S APPROVAL SHEET-2

SCHOOL OF GRADUETE STUDIES

HAWASSA UNIVERSITY EXAMINER'S APPROVAL SHEET-2

We, the undersigned, members of the Board of Examiners of the final open defense by Aberash Bekena Atsebi have read and evaluated her thesis entitled "**EFFECT OF DEPOSITION TIME ON STRUCTURAL AND OPTICAL PROPERTIES OF CdS THIN FILM IN ALKALINE CHEMICAL BATH DEPOSITION METHOD**", and examined the candidate. This is, therefore, to certify that the thesis has been accepted in partial fulfillment of the requirements for master's degree.

_____	_____	_____
Name of Major Advisor	signature	Date
_____	_____	_____
Name of Internal Examiner-I	signature	Date
_____	_____	_____
Name of Internal Examiner-II	signature	Date
_____	_____	_____
Name of external Examiner	signature	Date
_____	_____	_____
SGS Approval	signature	Date

Final approval and acceptance of the thesis is contingent upon the submission of the final copy of the thesis to the school of Graduate Studies (SGS) through the Department/School Graduate Committee (DGS/SGS) of the candidate's department.

Stamp of SGS Date: _____

Declaration

I hereby declare that this submission is my own work towards the Master of Science and that, to the best of my knowledge, it contains no material previously published by any person nor material which has been accepted for the award of any other degree of the University, except where due acknowledgment has been made in the text.

Name: Aberash Bekena signature; ……

ACKNOWLEDGEMENT

First and foremost, I would like to thank the **ALMIGHTY GOD** endowing me with courage and strength to accomplish this work and for every stage of entire life. I would like to express my sincere gratitude and acknowledgement to my respected Advisor Dr. Abebe Getachew. I am very much grateful to him for his able supervision, good guidance, constant encouragement, constructive discussion, valuable suggestions and continuous support during this work. I am especially thankful to him for allowing me to work under his supervision. Next I would like to thanks Werabe University for giving this chance to study my graduate studies and also thanks Department of physics Hawassa University allowing me to use the instrument facilities of his laboratory for this work as well. I also like to thank all the respected teachers and office workers of Physics department at Hawassa University.

Lastly; I would like to convey my deep gratitude and love to my family who has been continuous support during each and every phase of my educational career. I am grateful to my parents, brothers, sisters especially my beloved and respectful father Bekena Atsebi and my mother Demekech mirgeda and other relatives for their blessings and encouragement throughout my entire life.

Table of contents

List of tables

List of figures

Acronyms and Abbreviation

AR	anti-reflective
XRD	X-ray Diffraction
CBD	Chemical Bath Deposition
CdS	Cadmium sulfide
Cd^{2+}	Cadmium ion
Se^{2-}	Selenium ion
S^{2-}	sulphur ion
M^{2+}	metal ion
IR	infrared
NIR	near infrared
GaAs	gallium arsenide
InP	indium phosphide
CdTe	Cadmium telluride
ZnSe	zinc selenide
ZB	zinc blend
WZ	wurtzite
CdCl2	Cadmium chloride
SC (NH2)2	Thiourea
NH4 (OH)	ammonium hydroxide
SEM	scanning electron microscopy
DIW	deionized water
PL	photoluminescence
a.u	arbitrary unit
eV	electro volt

K	proportionality constant
SILAR	successive ionic layer adsorption reaction
LEDs	light emitting diode
FESEM	Field emission scanning electron microscope
JCPDS	Joint Committee for Powder Diffraction Standards

Symbols

Å	Angstrom
α	Alpha
β	Beta
^{o}C	degree Celsius
λ	Lambda
h	Planck constant
(^{o})	Degree
M	mole

ABSTRACT

Cadmium Sulfide thin films were prepared by chemical bath deposition (CBD) technique at bath temperature of 80^0C for various deposition time. The bath solution was a mixture of cadmium chloride and thiourea as source of Cd^{2+} and S^{2-} respectively and ammonia hydroxide was used as complexing agent in basic medium. After deposition the film were annealed at temperature of 300^0C for 90min. The effect of deposition time on the structural and optical properties of CdS thin film were investigated by XRD, FT-IR and Uv-Vis spectroscopy characterization technique. The XRD analysis revealed CdS thin film were cubic (Hawleyite) structure. The diffracted peaks are indexed (111),(200), (220) and (311) planes and with preferred orientation along the (111) plane. Estimated crystallite size and optical band gap was found in range of 11.7nm to 16.12nm and 1.8ev to 2.06ev respectively for deposition time 30min to 60min in 10min interval. The functional group of CdS thin films were proposed based on FTIR result obtained. The absorbance generally decreased with increase in wavelength and has relatively low values in the infrared region of the spectrum. A strong absorption was observed at wavelength range of 400 nm to 600 nm.

Key words: CBD; CdS thin film; XRD studies and optical studies

CHAPTER ONE

1. INTRODUCTION

1.1. Thin film material

The characteristics of materials differ significantly when examined in thin-film form. Because of their distinct optical, electrical, magnetic, or fix resistance qualities, the majority of functional materials are often employed in thin layers. Thin film technology depends on the controllable features, particularly with respect to the thickness parameter. Both crystalline and amorphous are essential in technological sector. Among them are temperature controllers in satellites, solar cells, polarizers, AR coatings, photoconductors, IR detectors, magnetic thin films in microelectronic devices, recorders, magnetic sensors, gas sensors, anti-corrosion, and decorative coatings[1].

Thin films are especially appropriate for applications in microelectronics and integrated optics. However the physical properties of the thin films like electrical resistivity do not substantially differ from the properties of the bulk material. For a thin film the limit of thickness is considered between tenths of nanometer and several micrometers. The properties of semiconducting thin films are not general in nature, but, rather, unique to the material and the technique of deposition.

The deposition technique and its associated process parameters have a characteristic effect on the nucleation and growth of a thin film and thereby on its physical properties. Thin films are directly or indirectly useful for new areas of research in solid state physics and in the field of chemistry, which are based on the unique characteristics of the thickness, geometry, and structure of the films [2].

In recent years, the development of Nano structured materials in the form of thin films occupy a prominent place in basic research and solid state technology due to their expanding range of potential applications in the diverse field such as photovoltaic cells, electronic components, fabrication of large area photodiode arrays, photoconductors, sensors, antireflection coatings, optical filters, surface acoustic wave devices, solar selective coatings and solar cells etc.

The Nano structured material has high surface area to volume ratio and hence shows different structural, optical, electrical, magnetic and dielectric properties than bulk. A Nano structured thin films material layer can be grown on a substrate by controlled condensation of the individual atomic, molecular or ionic species either directly by a physical process or through a chemical and/or electrochemical reaction. The application of Nano structured thin films can be utilized to enhance the efficiency of semiconductor or photovoltaic devices. In this regard many Nano-structured materials are now being investigated for their potential applications in photovoltaic [3].

Thin film deposition manufacturing processes are at the core of today's semiconductor, solar panel, hard disk drive and optical device industries. Thin films can now be made in a variety of ways. The techniques can be divided into physical methods (top down approach) and chemical methods (bottom-up approach) [4].

Due to their exceptional optical and electrical characteristics, semiconductors can be used in a variety of devices, including field effect thin-film transistors, light emitting diodes, and single electron transistors. Most of semiconductor belongs easy to synthesis and their extensive preparation as particles or thin films, the majority of studied semiconductors in according to the II-VI and IV-VI groups [3].One of a well-known semiconductor from the II–VI group is cadmium sulfide (CdS) is a good material for optoelectronic and electrical applications. Due to its strong photoconductivity in the visible spectrum, low resistivity, simple ohmic contact, high absorption coefficient, and high electron affinity, CdS thin film has received an extensive attention. Due to its direct and wide band gap energy (2.42eV) at ambient temperature, this material's thin film finds extensive application in numerous devices, including gas sensors, light emitting diodes, photo sensors, and logic circuits. It is an n-type semiconductor by nature [5].

Group II–VI semiconductor like (CdS, ZnS) thin films have attracted considerable attention from the research community because of their wide use in the fabrication of solar cells and other opto-electronic devices. CdS thin film window layer absorbs the blue portion of the solar spectrum, which causes decrease in the efficiency of solar cells [6].

However, these properties depend on the condition of crystal growth and the nature of substrates. Because of these reasons, many researchers have been attracted a great interest in the study of

this material with different deposition technique. The commonly employed techniques are electro deposition [7] spray pyrolysis [8] vacuum evaporation[9] and chemical bath deposition[10]. Among those various methods for the preparation of CdS thin films, the chemical bath deposition method is a good and suitable one because of its advantages, such as low cost, low temperature requirement, and easy to control growth rate. the ability to deposit thin films on different types of substrates suitable for large scale deposition areas and the controllable properties of thin films through adjustable deposition parameters[11]. In this paper, we report the effect of deposition time for (30, 40, 50 and 60) min with constant Temperature and pH values on structural and optical properties of CdS thin films obtained by CBD method using NH_3 as a complexing agent.

1.1.1. Semi-Conductor Materials

The magic word semiconductor is composed of two words Semi and Conductor. Semi means not completely while conductor mean something, which can conduct electricity. A semiconductor is a material that has intermediate conductivity between a conductor (such as aluminum and copper) and an insulator (some glasses and plastics). The electrical characteristics of these materials are extremely sensitive to the presences of small concentrations of impurity atoms, for which the concentrations may be controlled very smalls partial regions. Semiconductors have made possible the arrival of combined motherboard that has totally revolutionized the electronics and computer industries [12].

Some of the valence electrons in semiconductors can be excited from the highest occupied energy band to the valence band, where they are situated energetically to the conduction band by thermal, optical, or alternative sources of energy because the energy gap between the top and bottom of the valence band and the conduction band is sufficiently small [12].

Two general 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 from special combinations of group III and group V elements [13].

Additionally, group IV and group VI elements as well as combinations of group II and group VI elements can create semiconductors. Due to their single-species atomic character, group IV

semiconductors such as silicon and germanium are referred to as elemental semiconductors. Additional classifications for semiconductors include extrinsic (impure) and intrinsic (pure).

An intrinsic semiconductor as a material with no impurity atoms present in the crystal. An extrinsic semiconductor is defined as a semiconductor in which controlled amounts of specific dopant or impurity atoms have been added so that the thermal equilibrium electron and hole concentrations are different from the intrinsic carrier concentration. One type of carrier will predominate in an extrinsic semiconductor [13].

In terms of energy bands, semiconductors can be defined as those materials which have almost an empty conduction band and almost filled valence band with a very narrow energy gap (of the order of 1 eV). 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 wavelengths of light that can be absorbed or emitted by the semiconductor. For example, the band gap of GaAs is about 1.43 eV, which corresponds to light wavelengths in the near infrared [14].

1.1.2. compound semiconductor

A compound semiconductor is a semiconductor made from two or more elements. Most compound semiconductors are from combinations of elements from Group III and Group V of the periodic table of the elements (GaAs, GaP, InP and others). Other compound semiconductors are made from Group II and VI (CdTe, ZnSe and others). It is also possible to use different elements from the same group to make compound semiconductors such as SiC (silicon carbide)[15].

1.1.3. Semiconductor thin film

The thickness of semiconductor thin films, which can range from a few nanometers to hundreds of micrometers, is directly correlated with the fabrication method. Typically, one or more thin layers are created when producing semiconductor thin films. Transistors, sensors, and photovoltaic devices are just a few of the electronic materials that frequently use these kinds of architectures[16]. In recent year, Due to its wide range of features, semiconductor thin films have become increasingly attractive as a potential ideal applicant in the electronic material

industry, particularly as compared to the use of bulk materials. The low cost fabrication of semiconductor material on huge areas with the necessary geometry and structure is made possible, by a variety of chemical, electrochemical, and physical deposition processes. Also modifying the technique, temperature, substrate, and additional production factors according to the approach can readily provide single or multi-crystalline structures with complicated geometry and even nanocrystalline thin-film microstructures. Using various connection types between various semiconductor materials to improve the electrical characteristics of thin films brings electronic materials' industrial uses to reality. Modern electronic devices like mobile phones, LED displays, and solar cells depend heavily on semiconductor thin film technologies[17].

1.1.4. General Properties of cadmium sulphide

Cadmium sulfide is an in organic compound with the formula CdS and yellow solid. And it is yellow salt and insoluble hot and cold water but soluble in acid (slightly in ammonium hydroxide). CdS has good potential industrial application including electronics and optoelectronics devices. Cadmium sulphide has been successfully utilized as buffer layer in the most advanced thin film solar cell such as CdTe and CIGS based devices. It is an II-VI semiconductor compound which has been used in making heterojunction thin film solar cell. Mostly because it has a wide band gap of 2.42 eV CdS exhibits good thermal stability and can be used as light dependent resistor sensitive to visible region and near infrared light. this indicates that it is capable of absorbing light that has a wavelength less than or equal to 510 nm, or the visible spectrum's blue end. B/c of this characteristic CdS very essential compound different fields, such as photodetectors, solar cells, and light-emitting diodes (LEDs)[18]

CdS thin films are n-type semiconductors, meaning that they have an excess of electrons. This makes them good conductors of electricity, with a resistivity of about 10 ohm-cm which is good electrical conductivity. Cadmium sulfide has, like zinc sulfide, two crystal forms (fig.1), the more stable hexagonal(wurtzite) structure and the cubic (zinc blende) structure [19].

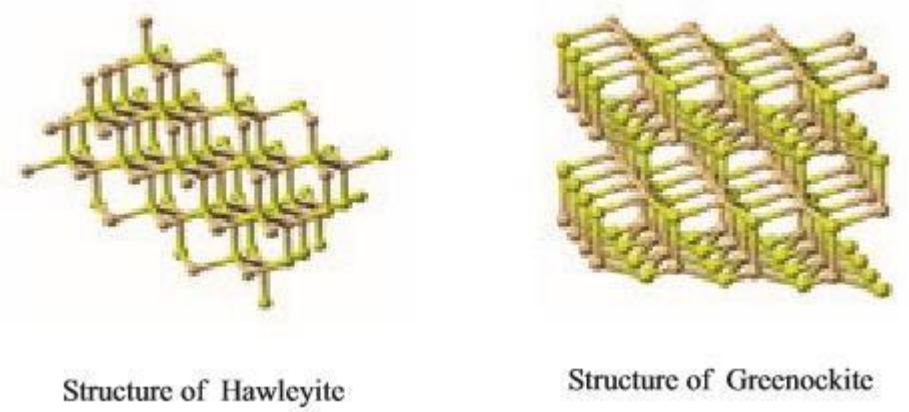

Figure 1 structure of cadmium sulfide [19]

A brief summary of the physical and chemical properties of CdS are:

- Melting point 1750 (0C)
- Boiling point 980 (0C)
- Appearance yellow-orange solid
- Energy band gap Eg 2.42eV
- Bond length (2.530x10-6m (ZB))
- Structure (ZB/WZ)
- Thermal conductivity (0.2w/cmk)
- Electron mobility at R.T (350cm2 /v.s)
- Solubility in water 0.013g/100ml(20^0c) etc.[20].

1.2. Statements of the problem

Metal sulfide semiconductor thin films have received intensive attention due to their very important role on the photovoltaic technology, optoelectronic devices and solar cell fabrication[21].

Especially group II-VI binary semiconducting compounds belonging to the cadmium chalcogenide family (CdS, CdSe, and CdTe) have been considered very important materials for photovoltaic applications. CdS also metal semiconductor with a wide range of applications. Particularly in optoelectronic devices like solar cells LEDs and photodetectors. Its thin-film form exhibits unique properties that make it suitable for these applications. Because of its high absorption coefficient, nearly optimum band gap energy for the efficient absorption of light and conversion into electrical power [23]. Many researchers have studied the effect of solution PH, complexing agent, metallic precursor and bath temperature on the properties of CdS thin film. The researcher is motivated to study the effect variation of time on the properties of CdS thin film by using CdCl2 and SC(HN2)2 as a precursors . Furthermore the film was annealed at 300^0 C for 90 minutes which significantly would change the crystllinty the material. Therefore, the present study demonstrate the influence of deposition time on the structural and optical properties of CdS thin film by using optimized proportion of CdCl2 and SC(HN2)2 as cationic and anionic source respectively. The bath temperature is kept constant at 80^0C in alkaline medium.

1.3. General objectives

The general objective of this research is

- To study the influence of deposition time on the structural and optical properties of CdS thin films prepared by chemical bath deposition method.

1.3.1. Specific objective

The specific object of this research is:

- To synthesis CdS thin films by using chemical bath deposition method in alkaline medium.
- To investigate the properties of CdS thin films by using XRD, UV-VIS Spectroscopy and FT-IR.

1.4. Significance of the study

The results of this study were useful in examining the optical characteristics of cadmium sulfide thin films produced using the CBD method for a variety of uses, including gas sensors for solar cells, super conductors, photovoltaic devices, batteries, and more especially the study will have its own contribution in the production of solar cell. Solar cell converts solar energy or light energy to electrical energy. The importance of solar energy is to avoid global warming and environmental pollution. Additionally the thesis also used for a reference source for future study.

1.5. Thesis structure

The thesis is organized in four chapters: Chapter One gives an introduction about thin film and semiconductor research over the years and some properties of CdS thin film. It also talks about the objectives, Statement of the problem and the reasons for interest in semiconducting materials such as CdS. The Second chapter deals with the literature review. This chapter also reviews literature on the deposition of CdS thin films by chemical bath deposition technique. Chapter Three gives the important theory leading this research. The methods and materials used in this research were presented. Chapter four then deals with the results in graphical representation attached with a considered discussion of the results and also conclusion and recommendation discussed in this chapter

CHAPTER TWO

2. LITERATURE REVIEW

In this chapter a review of some thin film solar cell presented as particular thin film technology materials and some theory about chemical bath deposition were described in this chapter and in addition to related work on the deposition of Cadmium sulphide thin films prepared by chemical bath deposition method has been reviewed.

2.1. Thin Film materials

Individual atoms are deposited on a substrate to create thin films. An atomic, molecular, or ionic species of matter condensing one by one to form a low-dimensional material is known as a thin film. Usually, the thickness is less than a few microns. Thick and thin films are not the same. This method a three-dimensional material or constructing large clusters, aggregates, grains of atomic, molecular, or ionic species results in a low-dimensional material known as a thick film. [24]. Several new fields of solid state physics and chemistry study that are based on phenomena that are specific to their fields have been directly or indirectly advanced by thin film investigations. Other thin-film technologies, such as organic, dye-sensitized, and polymer solar cells, as well as quantum dot, copper zinc tin sulfide solar cells, are often categorized as resulting of third generation photovoltaic cells because they are still in the early stages of ongoing research or have limited commercial availability [22].

Thin films are crystalline or non-crystalline and play vital role in all optoelectronic devices. They have been used as electroplated films for decoration and protection [25].

Thin film materials are the key elements of continued technological advances made in the fields of optoelectronic, photonic and magnetic devices. Thin film technologies make use of the fact that the properties can particularly be controlled by the thickness parameter. Thin film technology is the basic of outstanding development in solid state electronics and also the usefulness of the optical properties of metal films and scientific interest about the behavior of two dimensional solids has been responsible for the immense interest in the study science and technology of the thin films. Thin film studies have directly or indirectly advanced many new areas of research in solid state physics and chemistry which are based on phenomena unique

characteristic of the structure of the film [26]. In the past years, II-IV semiconductor thin films have attracted considerable attention from the research community because of their wide range of application in the fabrication of solar cells and other optoelectronic devices with much interest in the use of CdS window layer in solar cell.

Thin film materials have a wide range of applications across various industries due to their unique properties and versatility. Some of the general applications of thin film materials include; Optoelectronics, Semiconductors, Coatings, Energy Storage, Sensing and Detection, Microelectronics, Optical Coatings and Photovoltaic [27].

2.2. Chemical bath deposition

Chemical Bath Deposition (CBD) is a widely used technique for the synthesis and deposition of thin films onto solid substrates. It is most popular and inexpensive low-temperature, solution-based method that allows for the growth of various materials, including semiconductors, metal oxides, and chalcogenide compounds. The CBD technique achieves thin layer deposition by precipitation through a controlled chemical reaction. The structural, surface morphological and compositional characteristics of the as-deposited films are described. For the film with the best crystal quality, electrical and optical properties are reported [10, 38].

Additionally, the use of CBD makes it possible to deposit nanostructured thin films because it involves low processing temperatures of up to 100 °C, or the boiling point of water, which is much lower than the temperatures required for more conventional deposition techniques like vacuum evaporation, plasma deposition, and sputtering. According to Mane et al. (2012), reduced processing temperatures are also another benefit of CBD.The stoichiometry, structure, microstructure, optical absorption, electrical transport characteristics, and surface morphology of the thin films achieved through chemical bath deposition [39].

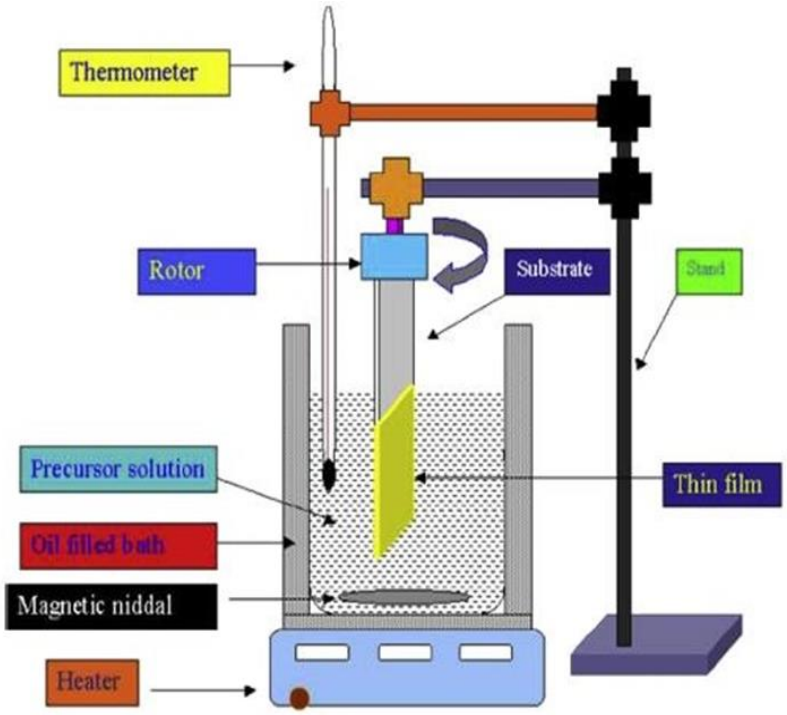

Figure 2.1 Experimental set up of chemical bath deposition technique [49].

The basic setup for CBD involves immersing the substrate into a chemical bath containing the appropriate precursor solution. This precursor solution consists of metal salts, complexing agents, and other chemicals necessary for the film growth. The substrate acts as a nucleation site, and as the reaction proceeds, a thin film gradually forms on its surface. The growth mechanism in CBD involves the controlled nucleation and subsequent growth of the desired material. The chemical reactions occurring in the bath solution lead to the formation of colloidal nanoparticles or complexes that then deposit onto the substrate surface. These nanoparticles or complexes act as building blocks, which aggregate and form a coherent film during the deposition process [10].

2.2.1. Basis of Chemical bath deposition

Chemical bath deposition is used to deposit thin films of a wide-range of materials. The deposition mechanism is largely the same for all such materials. A soluble salt of the required metal is dissolved in an aqueous solution, to release cations. The non-metallic element is provided by a suitable source compound, which decomposes in the presence of hydroxide ions, releasing the anions. The anions and cations then react to form the compound. This technique is based on the controlled release of metal ion (M^{2+}) and sulphide (S^{2-}) or selenide (Se^{2-}) ions in an

aqueous bath in which the substrates are immersed. In this process, release of metal ion (M^{2+}) is controlled by using a suitable complexing agent. The deposition begins with nucleation phase followed by growth phase in which the thickness of film increases with duration up to the terminal phase where film depletion into constituent ions occurs after a certain time. Typical CBD processes for sulphide utilize an alkaline medium containing the chalcogenide source, the metal ion and added base few reports of the CBD of the binary CdS [40].

The basic principle behind the CBD process is based on the solubility product of the compounds. At a given temperature when the ionic product (IP) of reactants exceeds the solubility product (KSP), 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[41]. The solubility product provides the solubility of an ionic salt that is properly soluble, including salts that are usually referred to as insoluble. When the relatively soluble salt AB(S) is dissolved in water, a saturated solution with A+ and B-ions that interact with the undissolved solid AB exists. This equilibrium between the ions in the solution and the solid phase results in as follows:

$AB(S) \longleftrightarrow A^{+} + B^{-}$…… (3.1) Applying the law of mass action,

$$K = \frac{[\mathbf{A+}][\mathbf{B-}]}{[\mathbf{AB}]} \text{……} (3.2)$$

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, i.e.

$$CAB(S) = \text{constant} = K^{*} \text{……} (3.3)$$

$$K = \frac{[A^{+}[B^{-}]]}{K^{*}} \text{……} (3.4)$$

$$KK^{*} = [A+]\,[B^{-}] \text{……} (3.5)$$

Since K and K* are constants, the product of is also a constant, say Ksp. Therefore equation (3.5), becomes

$$Ksp = [A+]\,[B^{-}] \text{……} (3.6)$$

The constant, KSP, is called solubility product (SP) and [A+][B] is called the ionic product (IP). When the solution is saturated, the ionic product is equal to the solubility product [55 ,42] 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.

2.2.2. Nucleation and crystal growth

Nucleation is the process by which formation of new phases begins. Condensation evaporation, crystal growth, and deposition of thin films all involve nucleation processes. Nucleation is the first critical step in the formation of crystals from a solution, liquid, or vapour. In this initial stage, small clusters of ions, atoms, or molecules come together and arrange themselves in a specific, ordered pattern that's characteristic of the crystal structure. These tiny, ordered clusters are called nuclei or embryos. Film growth can involve continuous nucleation powerful of mixture & growth of individual crystal in the film [43,44].

The process of film growth can occur through ion-by-ion condensation of materials or by adsorption of colloidal particles from the solution on the substrate, depending on the specific deposition parameters, which include bath temperature, stirring rate, pH, and solution concentration.

Nucleation and crystal growth are two interrelated processes that occur during the formation of crystals in a liquid or solid state [44].

The growth of crystals can proceed through different mechanisms, depending on factors such as temperature, super saturation, and the presence of impurities. The two primary modes of crystal growth are termed as "dislocation-controlled growth" and "layer-by-layer growth."

In dislocation-controlled growth, atoms or molecules are added to the crystal lattice through the movement of crystal defects known as dislocations. Dislocations are line defects in the crystal structure that allow for the rearrangement of atoms and the incorporation of additional units. This mechanism leads to the growth of crystals with irregular shapes and surface imperfections[45].

In layer-by-layer growth, atoms or molecules are added to the crystal surface in a well-ordered, step-by-step manner. Each layer grows on top of the previous one, resulting in the formation of flat, smooth crystal surfaces. Layer-by-layer growth is typically observed under conditions of

low super saturation and when the crystal lattice structure is compatible with the growth mode. The rate and extent of crystal growth are influenced by the availability of nuclei. The number and size of nuclei formed during nucleation affect the density and size distribution of the resulting crystals[46].

Depending on the deposition mechanism crystal growth can take place either by initial homogeneous nucleation in solution or by hetero nucleation on a substrate [43].

i. **Homogenous nucleation;** refers to the formation of nuclei within the bulk of the deposition material itself. When there are no crystals or foreign particles in the solution, homogeneous nucleation occurs [22]
ii. **Heterogeneous nucleation** these nucleation can be formed in the presence of impurities, container walls, or other solid surfaces. The presence of foreign particles reduces the degree of super saturation or super cooling required for nucleation to occur [47].

2.2.3. Thin film deposition mechanism in chemical bath deposition method

The specific film deposition mechanism in CBD can vary depending on the film material, bath composition, and process conditions. Various CBD methods exist, including metal sulfide deposition, oxide deposition, and semiconductor deposition, each with its own unique mechanisms and considerations semiconductor thin films are grown on substrates using the chemical bath deposition technique, which involves immersing the substrates into diluted solutions that containing metal ions and a source of hydroxide, sulfide, or selenide ions.

The fundamental idea behind chemical deposition technique is that nucleation and particle growth are the two processes that lead to the formation of a solid phase from a solution. the chemical bath deposition approach continues to be one of the most simple, successful, and inexpensive means to achieve the desired outcome, such as deposition on number of substrates that come in various shapes and dimensions [48,41].

In CBD, deposition of thin films takes place from aqueous solutions at low temperatures by a chemical reaction between dissolved precursors, with the help of a complexing agent (or ligand). In general semiconductor thin films are deposited by immersing substrates in diluted solutions containing metal ions and a source of a hydroxide, sulphide or selenide ions [48 ,10].

There are four main mechanisms leading to compound formation, whose operation depends on the specific process and reaction parameters.

The precipitation is observed in solution only when the ionic product exceeds the solubility product. The concept of ionic product and solubility product are described below. Wisely soluble salt AB, when placed in water, a saturated solution containing A and B ions in contact with un dissolved solid AB is obtained and an equilibrium established between the solid phase and in the solution as,

$$AB(s) \rightarrow A^{+} + B^{-} \quad \text{Applying law of mass action}$$

In the chemical bath deposition of the CdS thin film semiconductor can be obtained by direct reaction between Cd^{2+} and S^{2-} precursor species in solution.

The cadmium ion is complexed by ammonia to control the slow release of Cd^{2+} to avoid sudden precipitation of CdS.

The cadmium chloride decomposed as follow:

$$(CdCl_2).2H2O \Leftrightarrow Cd^{+2} + Cl^{2-} + 2H2O \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots.. (3.7)$$

The cadmium ion (Cd^{+2}) is released from cadmium chloride and sulfide ion (S^{2-}) is released from thiourea.

The direct interaction of the Cd^{+2} and S^{2-} by ion by ion mechanism:

$$Cd^{+2} + S^{2-} \Leftrightarrow CdS \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3.8)$$

When the ionic product exceeds the solubility product of CdS, i.e. $[Cd^{+2}]\,[S^{2-}] \geq Ksp$ CdS precipitated as a thin film on the substrate.

The thin film growth in CBD occurs via the following four possible mechanisms[49].

i. Simple Ion by ion mechanism

In most of the CBD's the ion-by ion conceptually simplest mechanism often assumed to be the operative one in general.

$$Mn^{+} + Xm^{-} \rightarrow MmXn \text{ (absorbed on the substrate)}$$

The formation of solid MmXn is based on the principle that when the ion product [Mn+][Xm-] exceeds the solubility product Ksp of MmXn then MmXn can form as a solid phase although a larger ionic product may be required if super saturation occurs. If the ion product does not exceeds Ksp no solid phase will form. Local fluctuation in the solution and the small solid nuclei

will re-dissolve before growing to a stable size. For that reason the precipitation process is an equilibrium rather than as a one-way reaction.

ii. Simple Cluster (Hydroxide) mechanism

Metal hydroxide production should be prevented in the majority of CBD due to specially selected preparative conditions. This might seem to imply that a precipitate of metal hydroxide [M (OH) n] is formed at that a precipitate of metal hydroxide formed is either as a colloid rather than a precipitate or as an adsorbed species on the substrate but not in the bulk of the solution.

In this case metal chalcogenide (MmXn) is formed by reaction of Xm- ion with the M (OH) n.

$$Mn^{+} + OH^{-} \rightarrow M(OH)n$$

Followed by,

$$M(OH)n + Xm^{-} \rightarrow MmXn + nOH^{-}$$

The deposition of the thin film takes place through the condensation of the metal and sulfide/selenide ions on this initial layer, which acts as a catalytic surface.

iii. Complex decomposition ion by ion mechanism

In this mechanism complexation of free metal cations ($M^{n+)}$ by thiourea gives M-thiourea complex ion. This is illustrates by the examples of Cadmium sulfide deposition.

$$Cd^{2+} + (NH_2)_2CS \rightarrow [(NH_2)_2CS\text{-}Cd]^{2+}$$

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

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

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

iv. Complex decomposition cluster mechanism

The complex-decomposition cluster mechanism is based on the formation of solid phase instead of reacting directly with a free anion it forms an intermediate complex with the anion- producing chemical reagent. Continuing with Cadmium sulfide deposition from a thiourea bath by considering example gives as:

Cd(OH)2 + (NH2)2CS → Cd(OH)2.SC(NH2)2 is one molecule in the solid phase cluster.

This complex or similar one if contains ammine ligands then decomposes to Cadmium sulfide.

Cd (OH) 2.SC (NH2)2 → CdS + CN2H2 + 2H2O

The S-C bond of the thiourea breaks leaving the S bond to Cd. It is suggested that Cd (OH) 2 forms initially on the substrate and catalyzes the thiourea decomposition. The catalytic effect of the solid surface could be to decompose thiourea to sulfide ion and not necessarily to catalyze the complex-decomposition mechanism[50].

2.3. Factor that affecting chemical bath deposition

Factor that the formation of thin film by chemical bath deposition such as

- Bath temperature
- Nature and concentration of the precursors
- Nature and concentration of complexing agent
- pH of the solution
- Deposition time
- Nature of the substrate
- Effect of Types of Precursor Sources

2.3.1. Effect of Deposition Time

Deposition time is one of the parameter which affects thin film deposition in CBD method. Deposition time can affect the film's crystal structure and morphology. Increased time can lead to larger crystallite sizes and denser, more homogeneous films. The growth mechanism might also shift from ion-by-ion to cluster-by-cluster deposition at longer times. In general, the growth of good quality semiconductor thin films by the chemical bath deposition technique proceeds at a slow rate. Higher deposition rates and higher films thicknesses are usually accompanied by powdery deposits and a lack of specular reflection [55].

Nair *.et a*l. (1998) has studied intensively the effect of deposition period on film thickness by fixing all the other parameters for different semiconductor thin films and for most cases (not always) the film thickness increase with deposition time.

2.3.2. Effect of Bath Temperature

Temperature of deposition is another factor that influences the rate of reaction. In CBD it is generally necessary to raise the temperature of the deposition. As temperature increases, dissociation of the metal complex to release free metallic ions and hydrolysis of the chalcogenide source increases. The kinetic energy of the molecules also increases leading to greater interaction

between ions. These effects will result in increase or decrease of terminal thickness, depending on the extent of super saturation of the solution[51].

2.3.3. Effect of Complexing Agent

Complexing agents (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 adjusted together with that of the metal salt to achieve desired film properties such as deposition rate, adhesion, and roughness. It is also greatly influences the structural, electrical, morphological and optical properties of the thin films[52].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. The free metal ion concentration is controlled by the formation of complex species according to the general reaction:

$$M\,(A)^{+2} \leftrightarrow M^{+2} + A \text{……………………………………..} \quad (3.9)$$

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:

$$K = \frac{[M^{+2}][A]}{[M(A)^{+2}]} \text{………………………………} \quad (3.10)$$

where K being the instability constant of the complex ion. The instability constant is different for different complexing agent. The instability constant increases the 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 [53].

2.3.4. Effect of concentration of cat ion and anion sources

The reactant concentration affects the overall chemical and physical characteristics thin film thin film growth could be increased by changing the reactive solution's composition to equilibrium the competition between homogeneous and heterogeneous nucleation processes. The products' composition is influenced by the reactant nature.

When it comes to the precipitation of cadmium hydroxide species, the deposition of high-quality, adherent, specular, and crystalline CdS is usually related to supersaturated baths. For high concentrations, the films formed were thicker, indicating stronger interaction. Under these circumstances, the growth process becomes cluster-by-cluster rather than ion-by-ion nucleation.

On the other hand, at low concentration, the films formed were too thin and non-uniform. This may be attributed to the fact that the required number of ionic species is not available in the solution to get better quality film. In the preparation of lead sulphide thin films by using different cationic precursors[54].

2.3.4. Effect of Types of Precursor Sources

Various studies verified that using different types of cation and anion precursor sources during film deposition play a vital role on the final physical and chemical properties of the thin films. In the preparation of cadmium sulphide investigated the effect of different cadmium salts. The results have shown tangible difference in growth kinematics and properties of the thin films. Hani Khallaf et *al* studied the effect of four different 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 CdSO4, Cd (CH3COO)2, CdCl2, CdI2. However, the band gap was found to decrease in the order CdSO4, Cd (CH3COO)2/CdI2, CdCl2. The grain size decreases in the order CdSO4, CdCl2, Cd(CH3COO)2, CdI2. Using CdCl2 and CdI2 source results in highly stoichiometric films (S:Cd ratio = 1:1). More Cd was detected when CdSO4 and Cd (CH3COO)2 were used. The S: Cd ratio and carrier concentration were found to decrease in the order CdSO4, Cd(CH3COO)2, CdI2/CdCl2. CdCl2-based films were found to have a better transmission and much smoother surfaces than other films [55].

2.3.5. Nature of Substrates

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. 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[56].

2.4. Thin film Characterization techniques

Characterization is an important step in the development of better-quality materials. The complete characterization of any material consists of phase analysis, structural explanation, com positional characterization, surface characterization, and micro structural analysis, which have strong bearing on the properties of materials. This has led to the rise of variety of advanced techniques in the field of materials science. In this section different analytical instrumental techniques are used to characterize our thin films described with relevant principles of their working and operation.

2.4.1. X-ray diffraction (XRD) technique

The crystal structure and phase of a material can be investigated using X-ray diffraction. The discovery by von Laue in 1912 that crystals scatter x-rays, with the method of diffraction disclosing the crystal's structure, served as the instinct for this technique. X-rays are reflected from the many crystallographic planes of materials in the process of X-ray diffraction. and Bragg's law governs it,

$2d\sin\Theta = n\lambda$…….. (3.1)

Where,

d – Inter planer spacing,

Θ- Bragg's angle or diffraction angle,

λ- Wavelength of x-ray used,

and n - Order of diffraction.

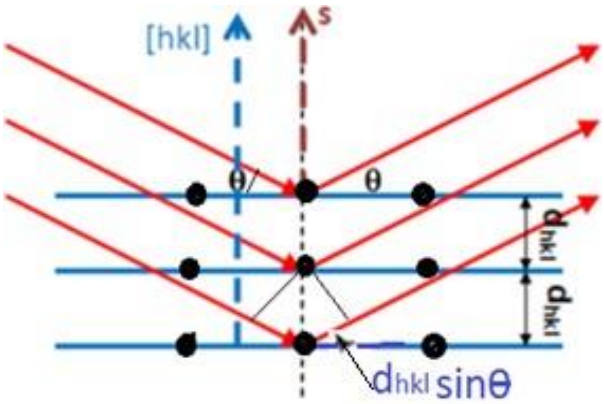

Figure 2.2 Schematic representation of Bragg's law [57]

The Debye-Scherer formula is derived assuming that a diffraction peak is associated with a family of crystal planes in a size limited crystal [58]. The sample used may be powder, single crystal or thin film The Debye-Scherer formula is mathematically given as:

$$D = \frac{0.94\lambda}{\beta \cos\theta} \quad \text{..... (3.2)}$$

Where, D is crystallite size, λ is wavelength of X-ray used, β is full width at half maxima of the peak (FWHM) in radians, θ is Bragg's angle. The X- ray diffraction data can also be used to determine the dimension of the unit cell. X-ray diffraction is the most convenient tool for crystallographic structural analysis like phase identification, phase quantification and lattice parameter refinement.

2.4.2. Optical properties

2.4.2.1. UV-Vis spectrophotometer

There are several processes that can happen when radiation interacts with matter: absorbance, phosphorescence (absorption and re-emission), reflection, scattering, and photochemical reactions (absorbance and bond breakage).

When optical photons are incident on any material, they can be transmitted, reflected, or absorbed. The equilibrium situation in semiconductors can be disturbed by the generation of carriers due to optical photon absorption. The absorption by the first type of electrons is very important in the study of the fundamental properties of semiconductors.

Since the valence band of a perfect semiconductor would be entirely filled with electrons at absolute zero temperature, no electron could be prompted from the valence band to a higher energy state. Electrons tend to move from the valence band into the conduction band upon absorption of significantly high in energy quanta. Because the excitation of electrons from the valence band to the conduction band occurs, semiconductor optical absorption spectra typically show a sharp rise at a particular value of the input photon energy.

A Spectrophotometer is an instrument used to measuring the transmittance or absorbance of the sample as a function of a wavelength of incident of electromagnetic radiation.

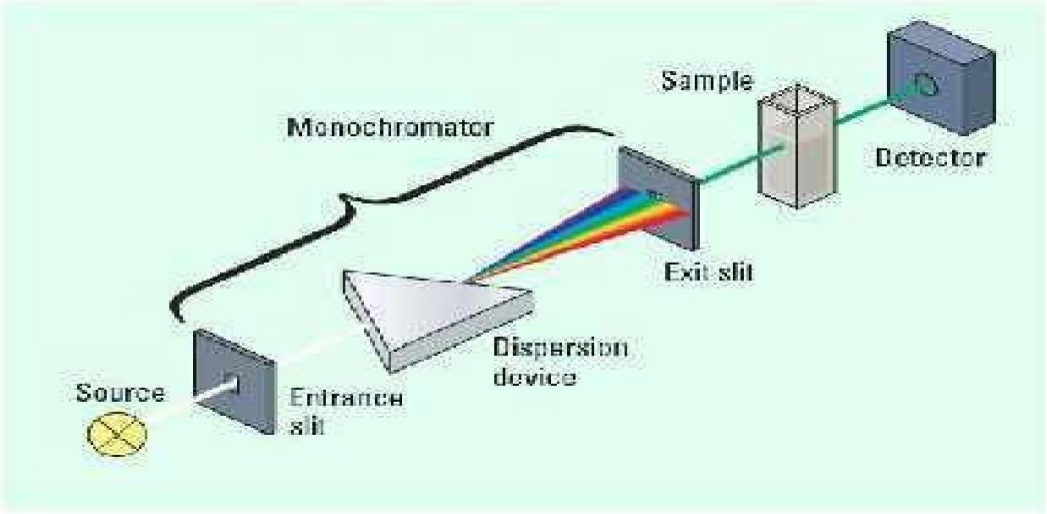

Figure 2.3 Schematic of a conventional spectrophotometer [59]

A source sends a broad band of light towards a sample and a detector, as shown in Figure 3.4. At some wavelengths, the intensity of the incident ray will transmit through the sample, but at other wavelengths, the intensity will be absorbed[59]. When light passes through or is reflected from a sample, the amount of light absorbed is the difference between the incident radiation (*I*o) and the transmitted radiation (*I*). The absorbance of a sample is determined by measuring the intensity of light reaching the detector without the sample (the blank) and comparing it with the intensity of light reaching the detector after passing through the sample.

From the absorption spectra, the optical band gaps of the films were estimated using the Stern (1963) relation for near edge absorption given as:

$$(\mathrm{A}h\nu) = \mathrm{K}\left(h\nu - E_g\right)^{n/2} \quad \text{..... (3.2)}$$

Where K is constant, Eg is the energy separation between the valence and conduction band that called band gap, A is absorbance, ν is the frequency of the radiation, h is the Planck's constant and n carries the value of either 1 or 4. The value of n is 1 for the direct transition and 4 for indirect transition; respectively is a pure number. Since most of compound semiconductors including CdS have a direct band gap, the value of n was taken to be 1 the energy band gap can be obtained by extrapolating the linear portion of $(\mathrm{A}h\nu)^2$ versus hν to the energy axis at $(\mathrm{A}h\nu)^2 = 0$[29].

2.4.3. FT-IR spectroscopy

FTIR is a technique used to obtain an infrared spectrum of absorption or emission of a solid, liquid or gas. An FTIR spectrometer simultaneously collects high-spectral-resolution data over a wide spectral range. The electromagnetic spectrum is composed of energy that may behave both as a particle and as a wave. When we describe energy as a wave, we use the terms frequency (v) and wavelength (λ). Frequency is the number of wave troughs that pass a given point in a second and wavelength is the distance from one crest of a wave to an adjacent crest. According to the equation $E = hv = hc / \lambda$. Therefore, as frequency increases, wavelength decreases. When we discuss IR spectroscopy, we introduce a new unit of measurement called the wavenumber (v). The wavenumber is the number of waves in one centimeter and has the units of reciprocal centimeters (cm^{-1}). Since the wavenumber is inversely proportional to wavelength, it is directly proportional to frequency and energy which makes it more convenient to use. Infra-red spectroscopy is particularly applicable to the study of orientation in polymers [60].

Different alignment of the molecules results in changes in the intensity of a number of infra-red modes and therefore is an indicator of crystalline nature, because each interatomic bond may vibrate in several different modes (stretching or bending). Individual bond may absorb at more than one IR frequency. Stretching absorptions usually produce stronger peaks than bending, however the weaker bending absorptions can be useful in differentiating similar type of bonds (e.g. aromatic substitution). It is also important to note that symmetrical vibration do no cause absorption of IR radiation. In general, the most important factors determining where a chemical bond will absorb or not are the bond order and type of atoms joined by the bond. Conjugation and nearby atoms shift the frequency to a lesser degree. Therefore, the same or similar functional group in different molecules will typically absorb within the same and specific frequency range. Hooke's law states that the IR frequency at which a chemical bond absorbs is inversely proportional to the square root of the reduced mass of the bonded atoms[61].

2.5. Review of Related literature on Effect of deposition time on CdS Thin film prepared by chemical bath deposition technique.

M. Maghouli and H. Eshghi (2019). Reported that prepared cadmium sulfide (CdS) thin films on glass slide substrates using the chemical bath deposition (CBD) technique on the effect of

deposition time at 90°C temperature for various minutes. In Aqueous solutions of 0.03M cadmium acetate Cd(CH3COO) 2.2H2O) 0.1M ammonium acetate (CH_3COONH_4) and 0.067M thiourea (SC_2 (HN_2)$_2$. Ammonia solution (NH_4OH) was also added in order to achieve pH were used to prepare thin films. Surface morphology and structure of the films was studied by scanning electron microscopy (SEM) and XRD respectively. The FESEM images indicated the formation of spherical Nano-grains in such a way that with increasing the deposition time the grain diameters are decreased from about 100 to 60 nm. The XRD patterns showed all layers have cubic phase along (111) direction, and as the deposition time increased the crstalinity of the layers are gradually degraded, consistent with the Raman spectra optical properties revealed that band gap of the films are gradually increased from 2.41 to2.47 eV[28].

A. El-Shaer *et al* (2023).Reported that Cadimium sulfide (CdS) thin films were deposited on glass substrates using chemical bath deposition technique. Studied on Effect of Deposition Period on CdS thin films deposited by Chemical Bath Deposition Method. The films growth was 20 ml of DIW was used to dissolve 0.08 M of (3 $CdSO_4.8H_2O$) and 0.2 M of Thiourea and potassium hydroxide is added used to pH stabilizers and complexing agents respectively. The effect of deposition time on the fabricated sample's properties was investigated by XRD, Raman, UV-vis spectrophotometry, and PL spectroscopy. XRD results indicate the formation of cubic and hexagonal structures of CdS thin films. And Raman study confirmed that the fabricated thin films have two distinct peaks that are centered at 298 cm^{-1} and 599 cm^{-1}, which are characteristic vibration modes for CdS thin film. UV-vis absorption spectra indicate absorption band edges near 500 nm, which are related to the band gap values of Eg of CdS thin films was reduced from 2.4 to 2.22 eV as the deposition time increased from 5 to 60 min. PL results show the main peak centered at 537 nm, its intensity decreasing as deposition time increases. Our results reveal that CdS thin films are an excellent candidate for optoelectronic application[29].

H. Moualkia *et al* (2012). Studied the structural, optical and electrical properties of CdS thin films prepared by chemical bath deposition (CBD) under the effect of solution temperatures vary between 55 and 75 °C. Using aqueous solution of cadmium acetate Cd(CH3COO)2 .2H2O ($5x10^{-3}$ M), Thiourea SC(NH2)2 ($2x10^{-2}$ M) and ammonia NH4OH (2M). The XRD patterns show that the films have a hexagonal phase with a preferential (002) orientation. The transmission spectra, recorded in the UV visible range, reveal a high transmission coefficient

(85%) of the prepared films and optical band gap values of 2 to 2.4 eV. And Structural, optical, and electrical properties of the CdS thin films have been investigated as a function of solution temperature in order to optimize their optoelectronic properties and prepare promising films for window layer applications in photovoltaic solar cells. From these results we inferred that the elaborated CdS thin films exhibit good properties intended for solar cell window layers[30].

A. Kariper *et al* (2012). Reported that in aqueous solutions containing 10 ml of CH_3CSNH_2 (thioacetamide) 0.1 M, 10 ml of Cd $(NO_3)2•4H_2O$ (cadmium nitrate) 0.1 M, and NH_4OH (ammonium hydroxide) were used to make CdS thin films. The same bath composition but with varying pH levels was used for the film deposition process. The chemical bath's pH levels were adjusted by adding various amount of NH_4OH, in that order. Each deposition required three hours, and a temperature of 70°C.The Resulting Investigations were conducted into how pH affects the structural, optical, and electrical characteristics of CdS thin films. The thin films are characterized by energy dispersive X-ray analysis, scanning electron microscopy, ultraviolet-visible absorption spectroscopy, and X-ray diffraction. X-ray diffraction measurements show that the cubic phase is growing with a preferential orientation along the (1 1 1) direction, and that as the pH of the chemical bath increases from 9 to 12, the samples' band gap increases from 2.29 to 2.40 eV. According to these findings, CBD produced films with a wide band gap, low resistivity, high mobility, and high carrier concentration at pH 11. After all of the investigation, it was concluded that the chemical bath deposition method produces CdS thin films best at a pH of 11. The resulting film adhered to the substrate well and was transparent and homogeneous. These findings suggest that films produced by CBD at pH 11 are suitable for use in a variety of optoelectronic devices [31].

S. Rondiya *et al* (2017). As deposited CdS thin film Using CdCl2 asCd^{2+} , thiourea as an S^{2-}ion source and ammonia as a complexing agent produced by the chemical bath deposition (CBD) process. A systematic investigation has been conducted into the effects of bath temperature on structural, morphological, and optical properties. The produced CdS films, according to XRD examination, are nanocrystalline with a hexagonal structure and a (002) preferred orientation. The crystallite size was estimated to be between 16 and 32 nm. The films have a high transmission (>70%) in the visible and near-infrared regions of the solar spectrum, according to the UV-visible spectroscopic investigation. The optical band gap was determined to be > 2.3 eV.

According to the SEM study, CdS thin films are uniformly sized, smooth, and randomly oriented spherical Nano crystallites. With a band gap greater than 2.6 eV, the CdS thin films exhibit strong transmission in the 600–1200 nm region. As expected from quantum size effects, there is an inverse relationship between the band gap energy values and crystallite sizes. It has now been determined that thin film solar cells may benefit from the usage of CBD-grown CdS films as a buffer layer[32].

R. Demir and F. Gode (2015). Reported that Cadmium sulfide thin films were prepared on glass substrates using chemicals cadmium chloride ($CdCl_2.H_2O$), thiourea [$CS(NH_2)_2$], ammonia as buffer solution at 82 °C for 1 hour by chemical bath deposition. After deposition, the films are annealed at 480 °C for 1 hour in air atmosphere. Both as-grown and annealed films are characterized by X-ray diffraction, scanning electron microscopy, energy dispersive spectroscopy, optical absorption spectroscopy and their structural, morphological, compositional, optical and electrical properties are investigated. The X-ray diffraction patterns of deposited films show the formation of polycrystalline of CdS with both cubic and hexagonal structure. However, by annealing effect at 480 °C in air preserves the same structural hexagonal phase and results in transformation of CdS phase to CdO. After the thermal treatment of 480 °C, they mostly turn into Polycrystalline CdO with cubic structure the grain size of the deposited film decreases approximately from 10−20 nm to 3.5−5.5 nm by annealing. The band gap energy of the films is determined for the direct transitions of 2.15 eV and increased to 2.25 eV by the thermal treatment. It could be concluded that annealing process changes the structural, optical and electrical properties of the CdS films [33].

A.Z. Shaikh *et al* (2023). Cadmium sulphide (CdS) thin films were deposited on commercial glass substrates by the chemical bath deposition (CBD) method using cadmium chloride (CdCl2.H2O), thiourea (SC(NH2)2), ammonium chloride (NH4Cl), ammonium hydroxide (NH4OH), and deionized water. The optical, structural, morphological, and photoelectric properties of these prepared CdS thin films were studied at different deposition temperatures, which varied between 50 to 80 °C. Optical spectra showed the transmittance, up to 70 to 85%, and a band-gap of 2.83 to 2.4 eV within the temperature range. X-ray diffraction patterns revealed the hexagonal phase of all synthesized CdS thin films with a (002) orientation and temperature-dependent intensity variation. The measured crystallite size ranged from 42 to 63 nm. The distribution of spherical grains throughout the substrate was seen in Field Emission

Scanning Electron Microscopy (FESEM) micrographs. As the deposition temperature increased from 60 to 80°C, the photoelectric resistance of the CdS film under light illumination significantly decreased from 108 to 107 Ω. With rise and decay time constants, the CdS film deposition at 80°C demonstrated a considerable photo response, making it appropriate for photo sensor applications. Band gap values of the CdS thin films were significantly. CdS thin film deposited at 80℃ showed good crstalinity, high optical transmission, and significant photo response, which makes the film suitable in solar cells as a window layer and photo sensor device[34].

The above reviewed literature CdS thin film were prepared by chemical bath deposition method at different precursor and other deposition parameter reported, the present study using CdCl2 as Cd ion source and SC (NH2)2 as S ion source, and all the films were annealed at 300^0C for 1:30hr and characterized using XRD, UV-VIS spectrophotometer and FT –IR spectrophotometer. The bath temperature was kept constant at 80^0C. NH4OH was used as a complexing agent and pH adjuster. There is no literature directly same with all of the present study conditions. Therefore, the present study on the influences of deposition time on the structural and optical properties of the film were investigated by varying the time from 30 minute to 60 minute in the interval of 10min.

CHAPTER THREE

3. Methodology

There are many techniques available for researchers in the deposition of thin film of different material on the layer, like evaporation, sputtering, chemical bath deposition (CBD), sol gel etc. The chemical bath deposition (CBD) method is greater commercial value than either thermal evaporation or SILAR method because it easy and cost effective.

3.1. Thin film deposition techniques

Methods for the deposition of thin films can be conveniently divided into two classes

1. Physical deposition is a commonly working technique in complex thin films, where atoms or molecules of the source material are evaporated through physical processes such as thermal evaporation or bombardment of the source by an intense beam of electrons, photons, or ions.
2. Chemical deposition is a technique that creates a desired composition of film by reacting chemically with vapor species that include the film elements when they are incident on a substrate. It is widely used for the deposition of various metal chalcogenide thin films. It produces good deposits on suitable substrates by the controlled precipitation of the compounds from the solution.Chemical film fabrication method involves chemical reaction and the precursors are mostly undergoing reaction at the substrate surface or in the area of the substrate[35].

The three basic steps of any thin-film deposition process are as follows:

1. Production of the proper species of atoms, molecules, or ions.

2. These species' transfer via a medium to the substrate.

3. Condensation to form a solid deposit on the substrate, either directly or by an electrochemical or chemical reaction [36].

Thin film deposition techniques play a major role in the physical and chemical characteristics of thin films. As a result the thin films growth technique has received major research and engineering emphasis and has advanced dramatically over the last few decades. The rapid growth of deposition technology is also the improved understanding of the physics and chemistry of

films, surfaces, interfaces, and microstructures made possible by the remarkable advances in analytical instrumentation. A better fundamental understanding of materials leads to expanded applications and new designs of devices that incorporate these materials [37].

Thin films can be fabricated in various ways. The techniques can be divided into physical methods (Top-down approach) and chemical (Bottom-up approach) method

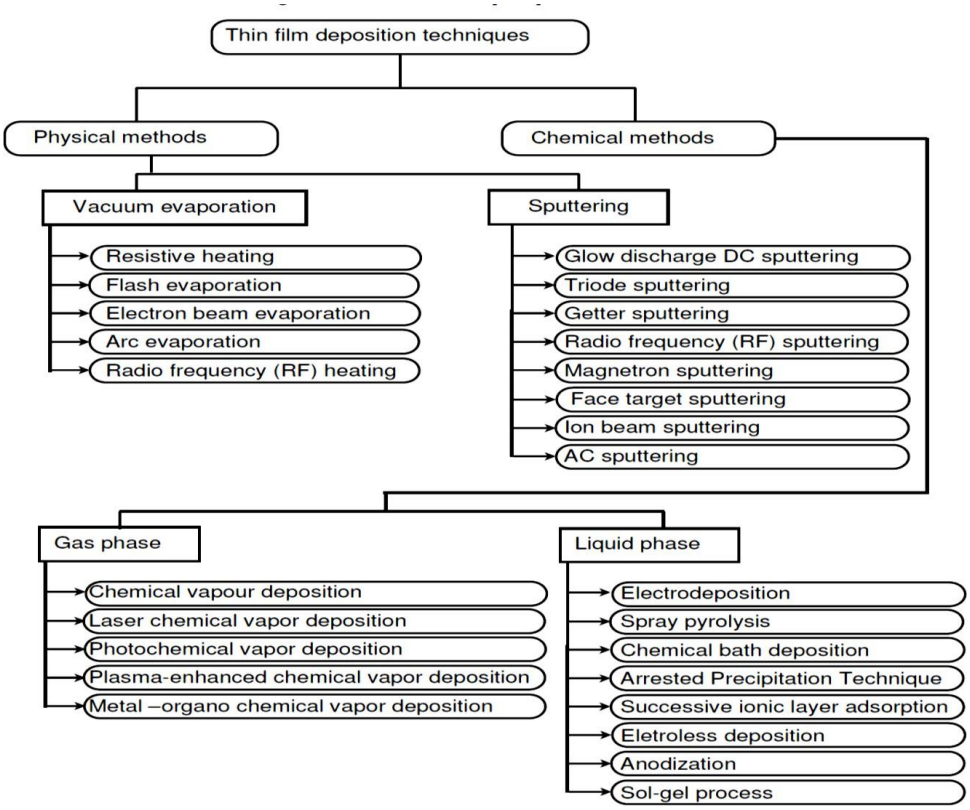

Figure 2 Classifications of thin film deposition techniques [35]

3.2. Experimental procedure

3.2.1. Material used

- Beaker used to measure the solution
- Magnetic stirrer used to stir the solution
- Heat supply is a main source of energy and to adjust temperature
- Electrical beam balance used to measure the mass of solution.
- Thermometer used to measure temperature.
- Distilled water to clean materials and prepare solution.
- Substrate used as deposited thin films.

3.2.2. Reagents/chemicals used.

During synthesizing CdS thin film the researcher used the following commercially obtained chemicals;

Cadmium chloride dehydrate ($CdCl_2.2H_2O$), 99.0%PP

Thiourea [CS (NH2)2], 99%PP

Ammonia or ammonium hydroxide ((NH3/NH_4OH), 99%PP

Pure Acetone $(CH_3)_2CO$), 96%PP

Nitric acid (NHO3), 36.38%PP

3.2.3. Reagents solution preparation.

3.2.3.1.Preparation of 0.2M Cadmium chloride dehydrate ($CdCl_2.2H_2O$)

Mass=concentration*volume*molar weight*percentage purity

0.2M/L*0.1L*228.35M/g*0.99PP =4.5213g

4.5213g of $CdCl_2$ was measured in electronics beam balance and then weighed into a beaker. The salt was dissolved in a small amount of distilled water then filled up to the 100 ml mark with distilled water and thoroughly shaken to dissolve the salt completely. The resulting solution had a concentration of 0.2 M.

3.2.3.2. Preparation of 0.2M Thiourea ([CS (NH2)2])

Mass=concentration*volume*molar weight*percentage purity

0.2M/L*0.1L*76.128M/g*0.99PP =1.507176g

1.507176g of CS (NH2)2] was measured in electronics beam balance and then weighed into a beaker. It was dissolved in small amount of distilled water and then transferred in to 100 ml volumetric flask using funnel. The Resulting solution was then concentration of 0.2 M

3.2.4. Substrate cleaning procedure.

The essential things in the deposition of thin films were cleaning substrate. Generally most cleaning surface can use as substrates. Glass is one of the most commonly used substrate in chemical bath deposition in spite of the fact the glass is relatively inert materials, the surface of

the substrate can be reactive towards species in solution .Procedures for cleaning the substrate is important, as it is one of the factors determining the composition and grain size of the film. One can used different method due to the nature of substrate, before deposition the microscope glass substrate would be immersed in a beaker contained Nitric acid for 24 hours and then it can be immersed in beaker containing Acetone for 30minute, after that ultrasonically cleaned with distilled water and dried under ambient condition.

3.2.5. Sample preparation/ Deposition of CdS thin film

In the present study CdS thin film were deposited onto the substrates by CBD using CdCl2,SC(NH2)2 , NH4OH and deionized water as precursor materials.

The preparation conditions of CdS thin films were optimized by adjusting concentration of dissolved chemicals, bath temperature, and bath solution pH as well as deposition time to obtain homogeneous films with good adherence to the substrate. The chemical bath contained cadmium Chloride [CdCl2 .2H2O] of 99 % purity and thiourea (CS (NH2)2) of 99% purity, which provided cadmium ions and Sulfur ions respectively, while ammonium hydroxide (NH4OH) was used as a complexing agent. All the solutions were prepared using deionized water and all the chemicals used were analytical graded without further purification. The complexing agent in the chemical bath deposition technique prevents spontaneous precipitation and reduces the concentration of free metal ions. The following procedures were used for the deposition of cadmium sulfide thin films :(0.2) M of10 ml of cadmium Chloride (CdCl2). 2H2O] was poured into 100 ml beaker then 10 ml distilled water added and complexed with 8ml ammonium hydroxide (NH4OH) solution was added slowly in order to adjust the pH of the solution. Then (0.2) M 10ml thiourea (CS (NH2)2) and 22 ml distilled water added, the total volume is 60ml.

Finally the temperature kept at 80^0C deposited at (30, 40, 50 and 60) min. The color change initially at room temperature the solution was no color and after 11 minute colors changed to light yellow and finally deep yellow in color. After each deposition cycle, the thin film were taken out from the reaction vessel after deposition minute and cleaned with de-ionized water to remove powdery and less-adherent particles.

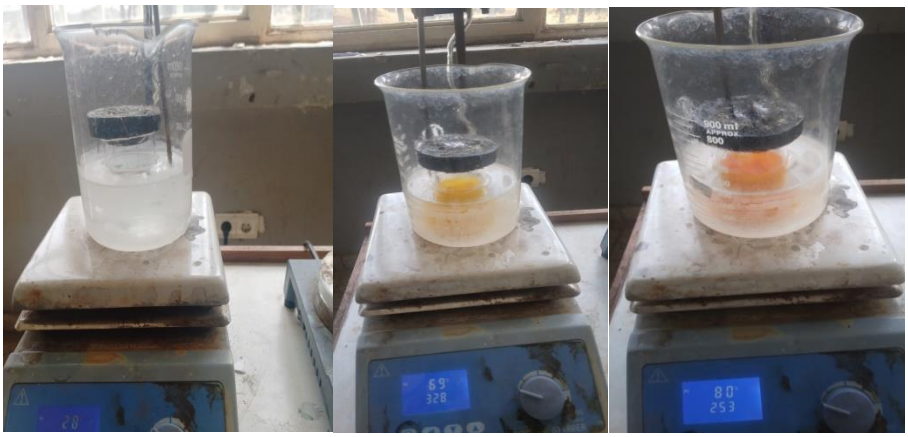

Figure 3.2 The color change of CdS thin films during deposition

The chemical reaction to deposit CdS films may be written as follows:

Cd $(NH3)_4{}^{2+} \leftrightarrow 4NH_3 + Cd^{2+}$ ..... (1)

N$H_3 + H_2O \leftrightarrow NH_4 + OH^-$ ..... (2)

Cd $(NH_2)_2 + OH^- \leftrightarrow SH^- + CH_2N_2 + H_2O$ ..... (3)

S$H- + OH- \leftrightarrow S^{2-} + H_2O$ ..... (4)

C$d^{2+} + S^{2-} \leftrightarrow CdS$ ..... (5)

3.2.6. Annealing of CdS thin film

Annealing can be defined as heat treatment of materials at elevated temperature to investigate or improve their properties. It helps to improve the crystalline structure of the film, reducing defects and overall crystllinty. These enhance the optical and electrical properties of the material. And also it increase photosensitivity of the CdS thin film ,making them more responsive to light particularly important for application such as photoconductors ,photodetectors ,and solar cells .the annealing temperature play a crucial role in determining the final properties of a material. Proper selection of the annealing temperature is essential to achieve the desired improvements in the material's structure and properties. So in order to improve the whole properties of the film The present study, deposited cadmium sulfide (CdS) thin films were annealed a temperature of 300^0C for 1:30hr then due to annealing effect the CdS film were the film were physically more adherent after annealing.

CHAPTER FOUR

4.1. RESULT AND DISCUSSION

4.1.1. Optical properties

Using a UV-VIS beam spectrophotometer, optical absorbance investigations were conducted for films with varying deposition times in the 400–800 nm wavelength range. The optical band gap energy was determined using the wavelength and optical absorbance data. Figure 4.1 indicated absorbance vs wavelength graph of Cadmium sulfide thin-films produced at different deposition times. The Figure shows the optical absorbance decreases with an increase in wavelength. The spectrum also showed that high transmittance (low absorbance) in visible region.

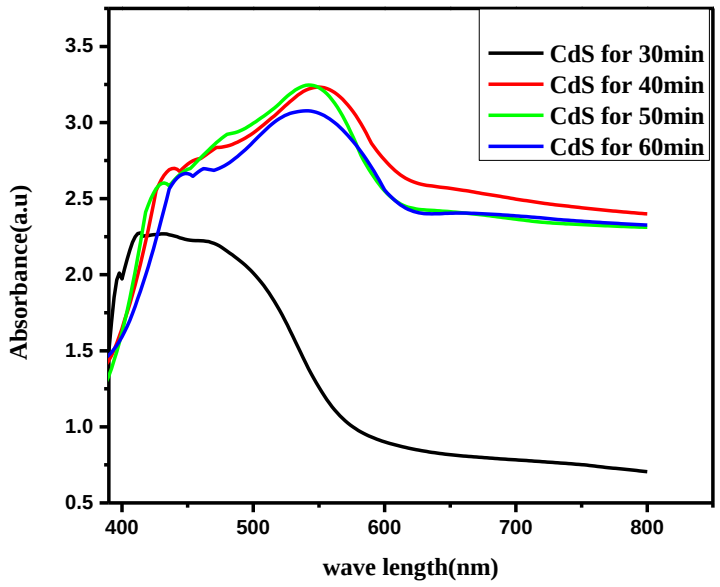

Figure 4.1 Plot of absorbance versus wave length for CdS thin film deposited by various time.

4.1.2. Optical Band gap Determination

The absorbance data were examined to determine the optical band gap of the semiconductor by using the classical Stern formula for near edge optical absorption of semiconductors (see equation 3.2). According to optical absorption measurement, the optical band gap of the present study has been determined were range from 1.8 eV to 2.06 eV at different deposition time. In most case (not always) the film thickness increases with deposition time. Increasing the

deposition time resulted in thicker films and more material being deposited onto the substrate. The estimated band gaps of the present study were closer to earlier report [29]. The observed band gap was less than the typical value of bulk CdS. Hence when the deposition time increase the optical band gap slightly decrease.

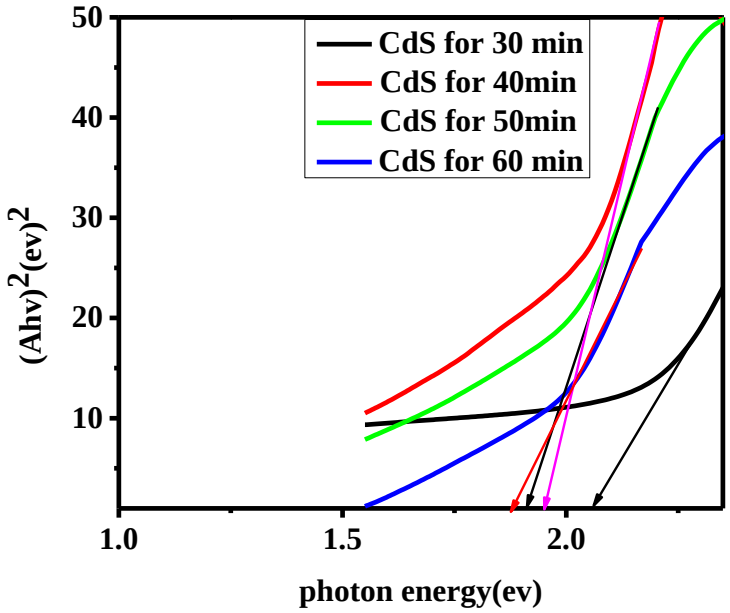

Figure 4.2 A plot of $(Ahv)^2$ versus (hv) of CdS thin films deposited at (30,40,50,60)min.

Table 4.1: Optical band gap with difference deposition time.

Deposition time (min)	Band gap (eV)
30	2.06
40	1.95
50	1.91
60	1.8

4.1.3. Structural analysis

In the field of material characterization, X-ray diffraction is a crucial technique for obtaining atomic-scale information from both crystalline and non-crystalline (amorphous) materials.

The Structural properties of CdS thin films were carried out using X-ray diffractometer, with Cu K (λ =1.54060Å) and energy incidence 40kv, 30 mA. The graph's horizontal plane is 2θ, which

corresponds to twice the Bragg angle, and its vertical axis represents the overall intensity rate. As shown in figure 9 below.

The Figure shows X-ray diffraction patterns of CdS thin films, deposited at 30, 40, 50 and 60 min). All films diffraction patterns exhibit the intensity of the peak at position 26.54 2theta indicate that the grains have preferred orientation along the line (111).

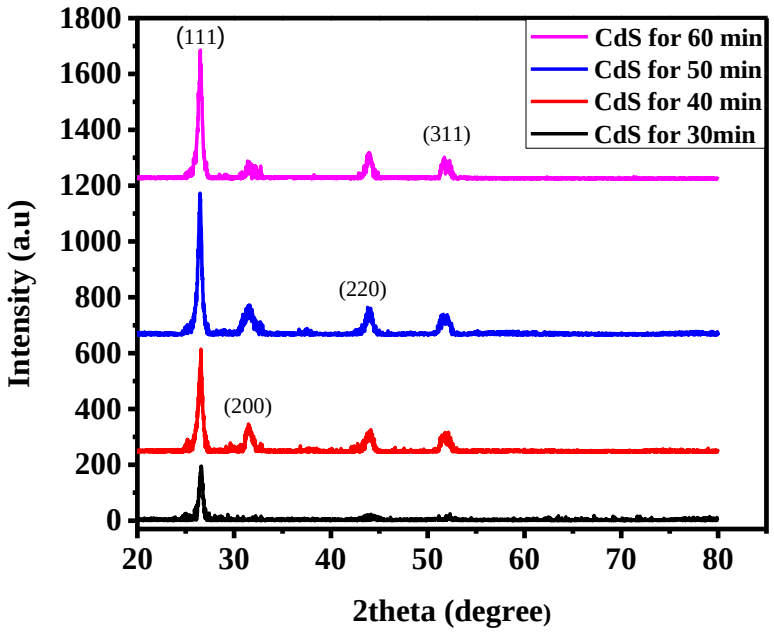

Figure 4.3 XRD patterns of CdS thin films deposited at 30, 40, 50 and 60 min at 80^0C.

The x-ray pattern showed four well defined peaks at 2θ position at 26.5, 31.42, 43.6and 51.9 an angle of 2θ corresponds with the diffracted peaks are indexed at the (111), (200), (220) and (311) planes respectively and with preferred orientation along the (111) plane .The above XRD results showed that as the deposition time increased the intensity also increased this is a consequence of thickness increasing which leads to better crystalline of CdS thin films. It is best application for solar cell fabrication. The peaks are in good agreement with the standard JCPDS data file reference code: 00-010-0454 of the cubic (Hawleyite) structure. The XRD analysis agreed well with earlier report [62, 63]. The CdS thin film deposited in CBD at a constant temperature of 80^0C and different deposition time were found with crystallite size 11.7nm, 13.2nm, 15.5nm and 16.1nm for (30, 40, 50, and 60) min respectively. The grain size is continuously increased as increase deposition time. The reason may be related with thickness of the film. The lattice constant for cubic phase structure (hkl) are given by equation:

$$a_{hkl} = d_{hkl}\sqrt{h^2 + k^2 + l^2} \text{ .....(4.3)}$$

The lattice constant (a) of CdS thin film can be calculated from the preferred orientation of the crystal along (111) plane at 2Θ =26.54 the value of a=5.8 obtain from Bragg's law. The crystalline size (D) was obtained from the X-ray diffraction pattern using the Scherer (1918) formula which is given:

$$D = \frac{0.94\lambda}{\beta \cos\theta} \text{ ..... (4.2)}$$

Table 4.2: Comparison of standard structural parameters with the calculated XRD value

Deposition time (min)	2Θ in (deg)	hkl plane	d-space in (Å)		FWHM (deg)		Lattice constant(a)in (nm)
			standard	observed	standard	observed	
30	26.70	111	3.3459	3.3356	0.6220	0.5967	5.77
40	26.53	111	3.3527	3.3570	0.5841	0.6579	5.78
	31.56	200	2.830	2.8319	1.0200	1.0482	
	43.97	220	2.0013	2.0575	0.8934	0.9793	
	51.57	311	1.6530	1.7623	1.332	1.2001	
50	26.46	111	3.3595	3.3656	0.4990	0.5391	5.79
	31.56	200	2.8324	2.8320	1.6800	1.4628	
	43.94	220	2.8135	2,0586	0.9455	0.8545	
	51.76	311	1.7743	1.7645	1.0576	1.0824	

60	26.48	111	3.3597	3.3629	0.5460	0.5944	5.77
	31.71	200	3.02561	2.8190	0.9100	1.5910	
	43.94	220	2.0576	2.0586	0.8477	0.9577	
	51.85	311	1.701	1.7617	1.0847	1.0947	

From table 4.2 summarized that all of the observed data that has been calculated in the XRD analysis were mostly closer to the standard value of standard JCPDS data file reference code: 00-010-0454.

The origin of strain is related to lattice misfit which is in turn depends upon the growing conditions of the films. The micro strain (ε) developed in the thin films can be calculated from the relation.

$$\varepsilon = \frac{\beta \cos\theta}{4} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (4.3)$$

A dislocation is an imperfection or error in a material's crystal lattice structure. It arises when individual atoms or groups of atoms shift off of the crystal lattice's optimal positions. Dislocations are not equilibrium errors, distinction to vacancies and intermediate atoms. The Williamson and Smallman's relationship offers the thin-film dislocation density in relation [45].

$$\delta = \frac{1}{D^2} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (4.4)$$

Table 4.3: The grain size, dislocation density and micro strain calculated from XRD result.

Deposition time(min)	2Θ in degree	hkl plane	Grain size(nm)	Dislocation density in(line/m^2) $\delta \times 10^{15}$	Strain ($\boldsymbol{\varepsilon}$)in $\times 10^{-3}$
30 min	26.70	111	11.7nm	7.2	3.0
40 min	26.53	111	13.2nm	5.8	2.7
50 min	26.46	111	15.5nm	4.1	2.3
60 min	26.48	111	16.1nm	3.8	2.2

From the table 4.3 one can observed that, the average crystalline size increased when deposition time increased. The result revealed that as the deposition time increased from 30min to 60 min in 10min interval the crystalline size also increased from 11.7 nm to 16.1 nm. Increased time can lead to larger crystallite sizes and denser, more homogeneous films. The reason may be related with thickness of the film [63]. It also observed that the microstructural parameters like the dislocation density (δ) and micro strain (ε) calculated from the preferred orientation (111) plane were decreased.

4.1.4. FT-IR spectroscopy

FTIR spectroscopy is most useful for identifying chemicals that are either organic or inorganic functional groups. It can be used to determine the nature and the structure of compounds. In this work it is used to identify the chemical reactions leading to the formation of the CdS thin film [65]. The wavelength of light absorbed is characteristic of the chemical bond. Infrared (IR) spectroscopy is a chemical analytical technique, which measures the infrared intensity versus wavenumber of light. Based upon the wavenumber, infrared light can be categorized as far infrared (4 ~ 400cm-1), mid infrared (400 ~ 4,000cm-1) and near infrared (4,000 ~ 14,000cm-1). It identifying how certain atom is bonded to each other or how they are grouped in a molecule [66]. So Stretching and Bending are types of vibrations that cause absorptions in an IR spectrum

[65, 64] .Bending vibration generally require less energy and occur at long wave lengths than stretching vibrations. Stretching vibrations are found to occur their band strength.

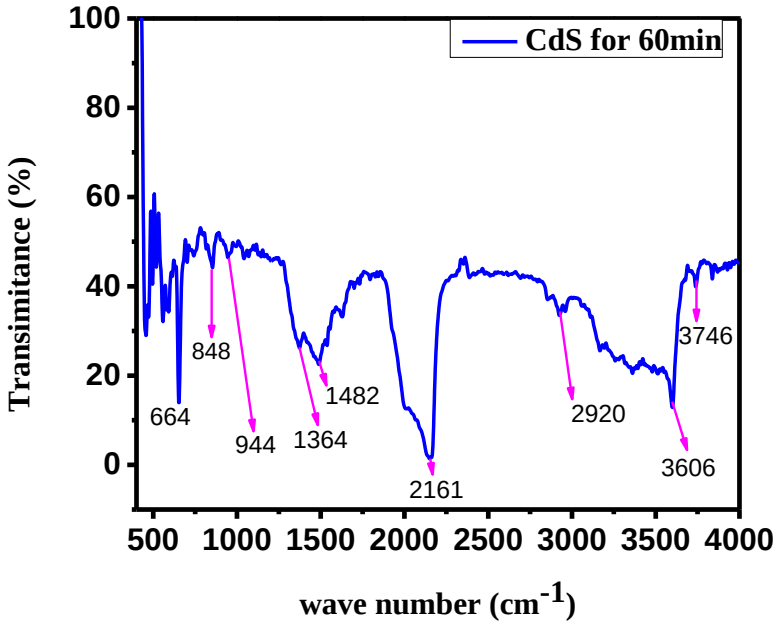

Figure 4.4 FT-IR spectra of CdS thin film for 60min

The FTIR spectroscopy studies were effectively used to identify the functional groups present in the synthesized compound and to determine the molecular structure [60]. The FTIR spectroscopy studies were conducted by PerkinElmer FTIR spectrometer. The sample were scanned from 400cm^{-1} to 4000cm^{-1}[64]. The characteristic vibrational frequencies of the functional groups have been presented in Figure 4.4. The figure shows that the wave number 3606cm^{-1} is due to - OH stretching. The wave number 3746cm^{-1} is N-H stretching mode due to ammine group in ammonium hydroxide source. The peaks at 1482cm^{-1}and 1364cm^{-1} correspond to C-N and N=O respectively[63 , 67] in the presence thiourea source. The wave number of 944cm^{-1} due to stretching mode of S=O present sulphate compound. Cd-S stretching are assigned in the region between 664cm^{-1} and 848cm^{-1} [63].

4.2. CONCLUSION

In this research, a well adherent cadmium sulfide thin film has been successfully deposited on glass substrate by using chemical bath deposition technique and the thin films were deposited from chemical bath contains cadmium chloride, thiourea and ammonia hydroxide at deposition time 30, 40, 50 and 60min and after deposition the film were annealed at a temperature of 300^0C for 90minutes. According to the XRD investigation, the CdS thin films exhibit a face centered cubic crystal structure with (111), (200), (220), and (311) diffraction planes. From those planes, the preferred orientation plane is (111).

The films were deposition time increased the crystalline size of CdS thin films also increase from 11.7nm to 16.1 nm at deposition time from (30 to 60) min in 10min interval respectively. This means when the deposition time increase the atom more arranged in their structure. The Uv-vis spectroscopy result also showed that absorbance was low in visible region. This leads the CdS thin film was used for thin film material for solar cell. The optical band gap determined from optical absorption spectroscopy was found in the range of 1 .8 eV to 2.06 eV which is less than the typical value of bulk CdS. When the deposition time increase the optical band gap decrease and the crystllinty increase.

4.3. Future work

The research conducted in this paper focused on the characteristics of the CdS thin film formed by CBD on the effect of deposition time. However the investigation focused on only the structural and optical characteristics of the film using XRD and UV-Vis spectroscopy technique were employed. In order to study effective characteristics of the film in the future should be further characterization techniques will be required to study the morphology, electrical and photoluminescence properties of the film.

Reference

[1] Rao, M. C., & Shekhawat, M. S. (2013). A brief survey on basic properties of thin films for device application. In *International Journal of Modern Physics: Conference Series* (Vol. 22, pp. 576-582). World Scientific Publishing Company.

[2] Abou-Ras, D., Kirchartz, T., & Rau, U. (Eds.). (2011). *Advanced characterization techniques for thin film solar cells* (Vol. 2). Weinheim, Germany: Wiley-Vch.

[3] Abza, T., Ampong, F. K., Hone, F. G., Nkrumah, I., Nkum, R. K., & Boakye, F. (2017). A new route for the synthesis of CdS thin films from acidic chemical baths.

[4] Geremew, T. (2022). Thin film deposition and characterization techniques. *J. 3D Print. Appl*, *1*, 1-24.

[5] Alekseev, P. S. (2013). Anisotropy of the electron g factor in quantum wells based on cubic semiconductors. *Semiconductors*, *47*, 1241-1245.

[6] Mahdi, M. A., Kasem, S. J., Hassen, J. J., Swadi, A. A., & Al-Ani, S. K. J. (2009). Structural and optical properties of chemical deposition CdS thin films. *Int. J. Nanoelectronics and materials*, *2*(2), 41-52.

[7] Lu, C., Zhang, L., Zhang, Y., Liu, S., & Liu, G. (2014). Fabrication of CdS/CdSe bilayer thin films by chemical bath deposition and electrodeposition, and their photoelectrochemical properties. *Applied surface science*, *319*, 278-284.

[8] Ikhmayies, S. J., & Ahmad-Bitar, R. N. (2010). The influence of the substrate temperature on the photovoltaic properties of spray-deposited CdS: In thin films. *Applied Surface Science*, *256*(11), 3541-3545.

[9] Tomakin, M. U. R. A. T., Altunbaş, M., Bacaksiz, E. M. İ. N., & Çelik, Ş. (2012). Current transport mechanism in CdS thin films prepared by vacuum evaporation method at substrate temperatures below room temperature. *Thin Solid Films*, *520*(7), 2532-2536.

[10] Shaikh, S. U., Siddiqui, F. Y., Desale, D. J., Ghule, A. V., Singh, F., Kulriya, P. K., & Sharma, R. (2015). Effect of swift heavy ion irradiation on structural and opto-electrical properties of bi-layer CdS–Bi2S3 thin films prepared by solution growth technique at room temperature. *Radiation Physics and Chemistry*, *106*, 193-198.

[11] Devi, R. A., Latha, M., Velumani, S., Oza, G., Reyes-Figueroa, P., Rohini, M., ... & Yi, J. (2015). Synthesis and characterization of cadmium sulfide nanoparticles by chemical precipitation method. *Journal of nanoscience and nanotechnology*, *15*(11), 8434-8439.

[12] Yacobi, B. G. (2003). Semiconductor materials: an introduction to basic principles. Springer Science & Business Media.

[13] Chen, Y., Wang, Y., Wang, R., Hu, X., Tao, J., Weng, G. E., ... & Akiyama, H. (2020). Importance of Interfacial Passivation in the High Efficiency of Sb2Se3 Thin-Film Solar Cells: Numerical Evidence. *ACS Applied Energy Materials*, *3*(11), 10415-10422.

[14] Tyagi, V. V., Rahim, N. A., Rahim, N. A., Jeyraj, A., & Selvaraj, L. (2013). Progress in solar PV technology: Research and achievement. *Renewable and sustainable energy reviews*, *20*, 443-461.

[15] Khallaf, H., Oladeji, I. O., & Chow, L. (2008). Optimization of chemical bath deposited CdS thin films using nitrilotriacetic acid as a complexing agent. *Thin solid films*, *516*(18), 5967-5973.

[16] Hariech, S., Aida, M. S., Bougdira, J., Belmahi, M., Medjahdi, G., Genève, D., ... & Rinnert, H. (2018). Cadmium sulfide thin films growth by chemical bath deposition. *Journal of Semiconductors*, *39*(3), 034004.

[17] Verlaak, S., Arkhipov, V., & Heremans, P. (2003). Modeling of transport in polycrystalline organic semiconductor films. *Applied physics letters*, *82*(5), 745-747.

[18] Clark, L. (1965). The preparation and properties of large single crystals of cadmium sulphide (Doctoral dissertation, Durham University).

[19] Traill, R. J., & Boyle, R. W. (1955). Hawleyite, isometric cadmium sulphide, a new mineral. *American Mineralogist: Journal of Earth and Planetary Materials*, *40*(7-8), 555-559.

[20] Rockett, A. (2008). Physical vapor deposition. *The materials science of semiconductors*, 505-572.

[21] Ali, N., Hussain, A., Ahmed, R., Wang, M. K., Zhao, C., Haq, B. U., & Fu, Y. Q. (2016). Advances in nanostructured thin film materials for solar cell applications. *Renewable and Sustainable Energy Reviews*, *59*, 726-737.

[22] Machlin, E. S. (2006). Materials Science in Microelectronics: The relationship between thin film processing and structure. Amsterdam, The Netherlands: Elsevier.

[23] Orori, M. C. (2012). Electrical and optical characterization of CdxZn1-xS and PbS thin films for photovoltaic applications. *Department of Electronics and instrumentation, Kenyatta University School of pure and Applied Sciences*.

[24] Andriesh, A. M., Iovu, M. S., & Shutov, S. D. (2002). Chalcogenide non-crystalline semiconductors in optoelectronics. *Journal of Optoelectronics and Advanced Materials*, *4*(3), 631-647.

[25] Sanap, V. B., & Pawar, B. H. (2011). Study of chemical bath deposited nanocrystalline CdZnS thin films. *Journal of Optoelectronics and Biomedical Materials*, *3*(2), 39-43.

[26] Poortmans, J., & Arkhipov, V. (Eds.). (2006). Thin film solar cells: fabrication, characterization and applications (Vol. 18). John Wiley & Sons.

[27] Manivannan, R., & Victoria, S. N. (2018). Preparation of chalcogenide thin films using electrodeposition method for solar cell applications–A review. *Solar Energy*, *173*, 1144-1157.

[28] Maghouli, M., & Eshghi, H. (2019). Effect of deposition time on physical properties of nanostructured CdS thin films grown by chemical bath deposition technique. *Superlattices and Microstructures*, *128*, 327-333.

[29] Ebrahimiasl, S., Yunus, W. M. Z. W., Kassim, A., & Zainal, Z. (2011). Synthesis of nanocrystalline SnOx (x= 1–2) thin film using a chemical bath deposition method with improved deposition time, temperature and pH. *Sensors*, *11*(10), 9207-9216.

[30] Moualkia, H., Attaf, N., Hadjeris, L., Herissi, L., & Abdelmalek, N. (2012, March). Preparation and characterization of CdS thin films. In *2012 First International Conference on Renewable Energies and Vehicular Technology* (pp. 66-73). IEEE.

[31] Kariper, A., Güneri, E. M. İ. N. E., Göde, F., & Gümüş, C. E. B. R. A. İ. L. (2012). effect of ph on the physical properties of cds thin films deposited by cbd. *Chalcogenide letters*, *9*(1).

[32] Rondiya, S., Rokade, A., Gabhale, B., Pandharkar, S., Chaudhari, M., Date, A., ... & Jadkar, S. (2017). Effect of bath temperature on optical and morphology properties of CdS thin films grown by chemical bath deposition. *Energy Procedia*, *110*, 202-209.

[33] Demir, R. A. M. A. Z. A. N., & Gode, F. (2015). Structural, optical and electrical properties of nanocrystalline cds thin films grown by chemical bath deposition method. *Chalcogenide letters*, *12*(2), 43-50.

[34] Shaikh, A. Z., Satpute, S. D., Gadde, J. R., Hawaldar, R. R., & Mohite, K. C. (2023). Influence of chemical bath deposition temperatures on cadmium sulphide thin film and photosensor application. *ES Materials & Manufacturing*, *20*, 819.

[35] Jilani, A., Abdel-Wahab, M. S., & Hammad, A. H. (2017). Advance deposition techniques for thin film and coating. *Modern technologies for creating the thin-film systems and coatings*, *2*(3), 137-149.

[36] Frey, H. (2015). Applications and developments of thin film technology. *Handbook of Thin-Film Technology*, 1-3.

[37] Torres-Castanedo, C. G., Márquez-Marín, J., Castanedo-Pérez, R., Torres-Delgado, G., Aguilar-Frutis, M. A., Arias-Cerón, S., & Zelaya-Ángel, O. (2020). Optical properties of CdS nanocrystalline thin films in the abrupt phase transition from zinc blende to wurtzite. *Journal of Materials Science: Materials in Electronics*, *31*, 16561-16568.

[38] Ampong, F. K. (2012). Synthesis and Characterization of Cadmium zinc sulphide (Cd1-xZnxS) thin films from acidic chemical baths .

[39] 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).

[40] Gebre, T.D. (2017). Effect Of Temperature On Morphological, Structural And Optical Properties Of Cadmium Selenide (Cdse) Thin Films Deposited By Chemical Bath Deposition Method.

[41] Debele, T., & Gashaw, F. (2018). Effect of temperature on morphological, structural and optical properties of cadmium selenide (CdSe) thin films deposited by chemical bath deposition method. *Advances in Life Science and Technology*, *67*, 12-16.

[42] Ullah, S., Ullah, H., Bouhjar, F., Mollar, M., Marí, B., & Chahboun, A. (2018). Influence of zinc content in ternary ZnCdS films deposited by chemical bath deposition for photovoltaic applications. *ECS Journal of Solid State Science and Technology*, *7*(8), P345.

[43] Velevska, J., Pecovska-Gjorgjevich, M., Najdoski, M., & Stojanov, N. (2011). Studies on electrochromism of chemically deposited nickel oxide thin films. *Science, Engineering and Health Studies*, 34-42.

[44] Vekilov, P. G. (2010). Nucleation. *Crystal growth & design*, *10*(12), 5007-5019.

[45] Le Boulbar, E. D., Priesol, J., Nouf-Allehiani, M., Naresh-Kumar, G., Fox, S., Trager-Cowan, C., ... & Shields, P. A. (2017). Design and fabrication of enhanced lateral growth for dislocation reduction in GaN using nanodashes. *Journal of Crystal Growth*, *466*, 30-38.

[46] De Yoreo, J. J., Orme, C. A., & Chernov, A. A. (2006). In situ atomic force microscopy of layer-by-layer crystal growth and key growth concepts. *Crystallography Reports*, *51*(6).

[47] Kathalingam, A., Ambika, N., Kim, M. R., Elanchezhiyan, J., Chae, Y. S., & Rhee, J. K. (2010). Chemical bath deposition and characterization of nanocrystalline ZnO thin films. *Materials Science-Poland*, *28*(2), 513-522.

[48] Seshan, K. (2002). Handbook of thin film deposition techniques principles, methods, equipment and applications, second editon. CRC Press.

[49] 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.

[50] Orava, J., Kohoutek, T., & Wagner, T. (2014). Deposition techniques for chalcogenide thin films. In *Chalcogenide glasses* (pp. 265-309). Woodhead Publishing.

[51] Rathinamala, I., Pandiarajan, J., Jeyakumaran, N., & Prithivikumaran, N. (2014). Synthesis and physical properties of nanocrystalline CdS thin films-influence of sol aging time & annealing temperature. International Journal of Thin Films Science and Technology, 3(3), 113-120.

[52] 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.

[53] Eslamian, M. (2017). Inorganic and organic solution-processed thin film devices. *Nano-micro letters*, *9*(1), 3.

[54] Preetha, K. C., Murali, K. V., Ragina, A. J., Deepa, K., Dhanya, A. C., & Remadevi, T. L. (2013, May). The role of cationic precursors in structural, morphological and optical properties of PbS thin films. In *IOP Conference Series: Materials Science and Engineering* (Vol. 43, No. 1, p. 012009). IOP Publishing.

[55] Hone, F. G., & Abza, T. (2019). Short review of factors affecting chemical bath deposition method for metal chalcogenide thin films. *Technology*, *8*(2), 3..

[56] Zhong, Z. Y., Li, Z. H., Cho, E. S., & Kwon, S. J. (2011). Effect of [Zn2+] concentration on the formation of zinc sulfide film as a buffer layer of Cu (In, Ga) Se2 thin film solar cells. *ECS Transactions*, *41*(4), 199.

[57] Metin, H., Erat, S., Emen, F. M., Kafadar, V., Yazici, A. N., Ari, M. E. H. M. E. T., & Kulcu, N. (2010). The thermoluminescence properties of CdS films under nitrogen atmosphere. *Journal of Luminescence*, *130*(8), 1531-1538.

[58] Mane, R. S., & Lokhande, C. D. (2000). Chemical deposition method for metal chalcogenide thin films. *Materials Chemistry and physics*, *65*(1), 1-31.

[59] Zhang, T. W., Zhu, C. J., Wang, C. Z., & Li, J. (2013). Preparation and characterization of Cd 1− x Zn x S buffer layers for thin film solar cells. *Rare Metals*, *32*, 47-51.

[60] Mohamed, M. A., Jaafar, J., Ismail, A. F., Othman, M. H. D., & Rahman, M. A. (2017). Fourier transform infrared (FTIR) spectroscopy. In *Membrane characterization* (pp. 3-29). elsevier.

[61] Y. Karuta, synthesis and characterization of pbcds thin films by using chemical bath deposition method, 2018.

[62] Samanta, S. S., Shinde, M. S., & Patil, R. S. (2015). Studies on Characterization of Cadmium Sulphide Thin Films Deposited by Chemical Bath Deposition (CBD) and Successive Ionic Layer Adsorption and Reaction (SILAR) Method. *International Journal of Thin Films Science and Technology*, *4*(2), 97.

[63] Haile, A. (2020). Fourier transform infrared spectroscopy (ftir) study of cadmium sulfide (cds) thin film prepared by chemical rute. *Int J Sci Eng Res*, *11*.

[64] M. Muthusamy, S. Muthukumaran, M. Ashokkumar, (2014), Composition dependent Optical, structural and photoluminescence behavior of CdS: Al thin films by chemical bath Deposition method, *Ceramics International* 40, 10657 10666

[65] Mishra, A., Dwivedi, J., Shukla, K., & Malviya, P. (2014, September). X-Ray diffraction and Fourier transformation infrared spectroscopy studies of copper (II) thiourea chloro and sulphate complexes. In *Journal of Physics: Conference Series* (Vol. 534, No. 1, p. 012014). IOP Publishing.

[66] Eldin, A. B., & Akyar, I. (2011). Near infra red spectroscopy. *Wide spectra of quality control. InTech, Rijeka, Croatia*, 237-248.

[67] Cao, G., Yan, Y., Zou, X.M., Zhu, R.S. and Ouyang, F. (2018). Applications of Infrared Spectroscopy in Analysis of Organic Aerosols, Spectral Analysis Reviews, 6, 12-32