EFFECT OF THIOUREA CONCENTRATION ON THE STRUCTURAL AND OPTICAL PROPERTIES OF PbS THIN FILMS SYNTHESIZED BY CHEMICAL BATH DEPOSITION METHOD

MSc. IN SOLID STATE PHYSICS

BY

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NOVEMBER, 2024

DECLARATION

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

Name: **Addisu Minayehu** Signature: _____ Date: _____

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We undersigned hereby certify that the thesis entitled **''*effect of thiourea concentration on the structural and optical properties of PbS thin films synthesized by CBD method*'',** submitted in partial fulfilment of the requirements for the Degree of Masters in Solid State Physics, the Graduate Program of the Department of Physics and has been carried out by author: **Addisu Minayehu Engida** Id No **GPPhys K/002/11**, under our supervision. Therefore we recommend that the student has fulfilled the requirements and hence hereby can submit the thesis to the department.

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We the undersigned members of the Board of Examiners of the final open defense by **Addisu Minayehu Engida** have read and evaluated his thesis entitled "**effect of thiourea concentration on the structural and optical properties of PbS thin films synthesized by CBD method**", and examined the candidate. This is, therefore, to certify that the thesis has been accepted in the partial fulfilment of the requirements for the degree of **Masters of Physics (Solid state physics)**.

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ACRONYMS AND SYMBOLS

Å	Angstrom
a	Lattice parameter
A	Absorbance
BD	Bath deposition
CBD	Chemical bath deposition
C_B	Conduction band
CdS	Cadmium sulfide
CdSe	Cadmium selinid
CSD	Chemical solutions deposition
CSP	Chemical Spray Pyrolysis
CVD	Chemical vapour deposition
d	Inter – planer spacing
D	Crystalline size
EDXR	Energy dispersive X-ray analysis
E_g	Energy band gap
eV	Electron volt
FCC	Face centered cubic
FTIR	Fourier Transforms Infra – Red Spectroscopy
FWHM	Full width at half maximum
GaAs	Gallium Arsenic
Ge	Germanium
JCPDS	Joint Committee for Powder Diffraction Standards
K	Extinction, wave vectors
M	Molar concentration
min	Minuets
mL	Millilitres

n	Refractive index
NaOH	Sodium hydroxide
nm	Nano meter
NH_3	Ammonia
Pb	Lead
$Pb(CH_3COO)_2. 3H_2O$	Lead acetate tri – hydroxide
PbS	Lead Sulphide
PbSe	Lead selinid
PV	Photovoltaic
PVD	Physical vapour deposition
S	Sulphur
$SC (NH_2)_2$	Thiourea
SEM	Scanning electron microscopy
Si	Silicon
SILAR	Successive ionic layer adsorption reaction
TGA	Thermal Gravimetric Analysis
UV	Ultra violet
V	Photo frequency
V_B	Valance band
Vis	Visible spectrum
XRD	X-ray diffraction
β	Beta
γ	Gamma
ρ	Dislocation density
θ	Theta
λ	Wave length
μm	Micrometre
ε	Lattice strain

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ABSTRACT

In the present work lead sulfide (PbS) thin films were synthesized on glass substrate by chemical bath deposition method as material employing lead acetate as a source of Pb^{2+} and thiourea as a source of precursor S^{2-} and sodium hydroxide as complexing agent in the solution of distilled water. The thin film have been deposited at constant bath temperature of 80^0c and the deposition time was 20 minute for different samples in the various 0.2M thiourea concentrations of 8, 9, 10, 11 and 12 mL respectively. The thin films were characterized by using X – ray diffraction and UV – Vis spectrophotometer. X-ray diffraction analyses revealed that all the films were polycrystalline in nature with the diffraction peaks indices to the face centred cubic structure. For as the deposited thin films, it revealed that PbS nanocrystalline with preferred orientation along the (111) for 8 mL which changes to (200) for 9 – 12 mL in per set of 1 mL for various thiourea concentration due to the change of the total system free energy during the film growth. The structural parameters, such as the lattice constant (a), crystallite size (D), dislocation density (ρ) and micro strain (ε) were evaluated from the XRD spectra. The average crystalline size was calculated using the Debye – Scherer's formula and found to decrease from 35.71 to 29.64 nm with an increase thiourea concentration in the case of increasing the growth rate, at fast deposition rate and growing species has no enough time to be organized. The dislocation density and micro strain were found to vary inversely with the crystallite size, whereas the lattice constant was found to decrease with a decrease of in crystallite size. The UV – Vis spectroscopy characterization of the sample revealed that the optical band gap of energy was increased from 1.55 to 1.61 eV with increasing thiouera concentration due to the quantum size effect of polycrystalline PbS thin film.

Keywords: Chemical bath deposition, Lead sulphide, thin films.

CHAPTER ONE

1. INTRODUCTION

1.1 Background of the study

In recent years, properties of nano-materials have gained a great deal of interest. At the nanometer scales, quantization and surface effects begin to play an important role, leading to radical changes in the measured properties of the semiconductor nanoparticle [1]. Nanostructured materials and in particular semiconductor nano structures of thin films may be exploited for their novel electronic and optical properties. These structures are a great interest since they have potential applications in future quantum and photonic devices [2]. Thin films have been growing importance in the field of technology and particular in the semi-conductors industry. New properties different from those observed in the bulk appear in the films states. Generally, those properties are linked to film thickness and preparation method [3].

The interest in the synthesis and application of semiconductor nano materials is increased since their properties are size and shape dependent [4]. Lead sulfide (PbS) is an important direct narrow gap semiconductor material with a band gap of 0.41 eV and has a cubic structure. Due to their suitable band gaps, PbS thin films are extensively used in IR detectors. Thin film of lead sulphide was establish to have very significant application in the manufacture of photoconductive infra – red detectors, transistors, contact rectifiers, prisons, lenses, windows and other components of optical system [5]. This material has also been used in many fields such as humidity, photography, solar absorption, photo resistance, diode lasers, temperature sensors, decorative and solar control coatings [6].

1.2 Semiconductor Materials

Semiconductors are a group of materials having electrical conductivities intermediate between metals and insulators. It is significant that the conductivity of these materials can be varied over orders of magnitude by changes in temperature, optical excitation, and impurity content. This variability of electrical properties makes the semiconductor materials natural choices for electronic device

investigations. Semiconductor materials are found in column IV and neighbouring columns of the periodic table. The column IV semiconductors, silicon and germanium, are called elemental semiconductors because they are composed of single species of atoms. In addition to the elemental materials, compounds of column III and column V atoms, as well as certain combinations from II and VI and from IV make up the compound semiconductors.

One of the most important characteristics of a semiconductor, which distinguishes it from metals and insulators, is its energy band gap. The energy band gap determines 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. In contrast GaP has a band gap of about 2.3 eV, corresponding to wavelengths in the green portion of the spectrum. As a result of the wide variety of semiconductor band gaps, light – emitting diodes and lasers can be constructed with wavelengths over a broad range of the infrared and visible portions of the spectrum. The electronic and optical properties of semiconductor materials are strongly affected by impurities, which may be added in precisely controlled amounts. Such impurities are used to vary the conductivities of semiconductors over wide ranges and even to alter the nature of the conduction processes from conduction by negative charge carriers to positive charge carriers. For example, an impurity concentration of one part per million can change a sample of Si from a poor conductor to a good conductor of electric current. This process of adding controlled amount of specific impurities, called doping. To investigate these useful properties of semiconductors, it is necessary to understand the atomic arrangements in the materials. The basic crystal structure for many important semiconductors is the face centered cubic lattice with a basis of two atoms, giving rise to the diamond structure, characteristic of Si, Ge, and C in the diamond form. In many compound semiconductor atoms are arranged in a basic diamond structure, but are different on alternating sites. This is **called a zinc blende structure** and is typical of the III – V compounds [7].

1.3 IV – VI Compound Semiconductors

Elements of groups IV and VI can also form semiconducting compounds. Examples are PbS, PbSe, PbTe and SnTe, which all crystallize into the **rock salt structure**. Important semiconducting alloys of such compounds are (Pb, Sn)Te and Pb(S, Se). These semiconductors are now used primarily for the generation and detection of radiation in the medium near- infrared spectral region. In addition, there is a second group of semiconducting IV – IV compounds which display an orthorhombic structure, including GeS, GeSe, SnS and SnSe. GeTe is an exception as it crystallizes into a rhombohedral structure [8]. Lead chalcogenides are narrow – gap semiconductors PbX (X = S, Se and Te) and their alloys have been applied in long-wavelength imaging in diode lasers. IV – VI semiconductors present one of the rare naturally occurring semiconductors and the name lead salts for the IV – VI semiconductors is in common use in infrared optoelectronics. Lead chalcogenides (PbS, PbSe and PbTe) exhibit some unusual and unique properties such as high dielectric constant, narrow band gap energy, direct optical transition type and high mobility [9].

1.4 Basic Properties of Lead Sulphide (PbS)

Lead sulphide (II) is an inorganic compound with the formula PbS. Bulk PbS is an important IV – VI semiconductor with cubic rock salt structure of NaCl type with lattice parameter a = 5.9362 Å, $\alpha = \beta = \gamma = 90^{o}$ and a narrow direct band gap of 0.41 eV at room temperature and 0.29 eV at liquid N_2 temperature. Pb^{2+} and S^{2-} ions occupy the lattice sites in the rock salt crystal structure alternatively. The size of the ions is: Pb^{2+} = 1.21 Å, S^{2-} = 1.84 Å. The $K_{Sp} = 1.3 \times 10^{-28}$; enthalpy of formation: $\Delta H_f{}^{0}{}_{solid}$ = - 98.32 kJ/mol, entropy: $S^{o}{}_{solid}$ = 91.34 $Jmol^{-1}K^{-1}$ and its optical density: $n_{D2}{}^{0}$ = 3.921. The dielectric constant and density of bulk PbS is 17.3 and 7.596 g/cm^3 respectively. It also possesses high carrier mobility 0.44 cm^2V^{-1} S^{-1} [10].

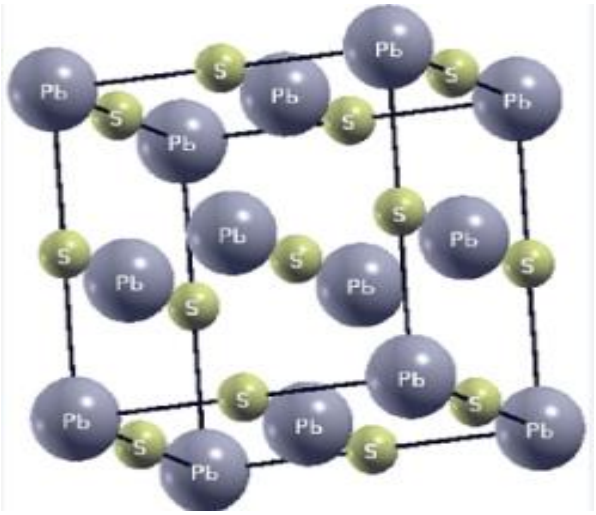


Figure 1.1 Structure of lead sulphide (PbS) [11].

The band gap of lead sulphide depends on the applied temperature, pressure and the nano crystal size. This material has also been used in many fields such as humidity, photography, solar absorption photo resistance, diode lasers, temperature sensors, decorative and solar control coatings [12].

PbS thin films can be deposited by various methods such as, electro deposition, spray pyrolysis, successive ionic layer adsorption method, sol-gel and chemical bath deposition method. Among aforementioned methods, chemical bath deposition has its own advantages such as simplicity, reproducibility, non-hazardous, cost effective and well suitability for large area deposition. The dimensions of the crystallites can be controlled by varying the deposition parameters; reaction time, temperature, annealing temperature and the presence of impurities in the solution. Chemical bath deposition (CBD) is a very attractive method for deposition of polycrystalline thin films such as PbS thin films with properties and it requires relatively mild conditions, scalable and technically straight forward [13].

Chemical bath deposition (CBD) method is attracting considerable attention, as it does not require sophisticated instrumentation. It is relatively cheap, simple to handle, convenient for large area deposition and capable of yielding good quality thin films. This paper deals with the preparation of lead sulfide (PbS) thin films, by chemical bath deposition (CBD) technique. The PbS thin films characterizes with X-ray diffraction and UV analysis.

1.5 Statement of the problem

The majority of types IV – VI thin film compounds are made of elements from groups IV and VI of the periodic table. Numerous researches have provided valuable insights into these compounds' general characteristics like structural features and optical properties of their energy gaps at room temperature. Group type of IV – VI semiconductor compounds, lead sulphide (PbS) thin films have attracted a lot of attention for a variety of useful applications; particularly for photovoltaic cells, photoconductive materials, optical detectors, photoelectron chemical cells, thin film transistors, and other optoelectronic devices. The characteristics of chemical bath deposited PbS thin films strongly depends on the growth condition by changing the deposition parameters like bath temperature, deposition time, concentration of reactants and nature of the glass substrate etc. It is difficult to adjust the thickness size, transmittance, and absorbance of chemically deposited PbS thin films because of its applicability in microelectronic devices. As a result, the researcher motivates to the study of lead sulphide thin films preparing at different thiourea concentration by CBD method to improve the structural and optical qualities of PbS thin film.

1.6 Research Objective

1.6.1 General objective

The general objective of this research is to study the effect of thiourea concentration on the structural and optical properties of lead sulphide thin film by CBD method.

1.6.2 Specific objectives

- To synthesis PbS thin films at different thiourea concentration.
- To investigate the structural and optical properties of PbS thin film using various characterization technique.

1.7 Significance of the study

The findings of this research could be used in technologies that use PbS thin film is an important material due to its structural and optical properties. PbS thin films has increased their future application like luminescent devices, photoconductive infrared detectors, transistors, contact rectifiers, lenses, diode lasers, temperature sensors, photochemical cells, solar cell absorption, solar control coating, photography and they have received

much attention because of their potential application in optical electric devices. A direct narrow band gap semiconductor are interest for photovoltaic solar energy conversion as they can absorb the IR detector of the solar spectrum, which is not absorbed by commonly used photo voltaic materials. Lead chalcogenides of their binary compounds have band gaps that are too low, but the large Bohr radius of exciting in PbS compounds make them strongly confined in crystallites. The low band gap values exhibited by PbS nano crystal thin film together with high absorbance in the UV – Vis region also make the film ideal for use as absorber material; specially for solar cell application.

1.8 Structure of the Thesis

The thesis is organized in five chapters:

Chapter one gives an introduction of the background to the importance of semiconductor group compound research over the years and some properties of PbS thin films. It also talks about the objectives of the research, statement of the problem and the reasons for interest in semiconducting materials such as PbS thin film.

Chapter two deals with the literature review, that reviews literature on the depositions of PbS thin films by chemical bath deposition technique.

Chapter three treats the relevant theory of governing research that is methods and materials, chemical bath deposition method of characterized techniques, factors affect the chemical bath deposition process and experimental procedures of materials used.

Chapter four describes the result and discussion in all structural and optical properties of detail discussion with graphical representation of parametrical factors for the researcher.

Finally chapter five deals with conclusion and recommendation were included.

CHAPTER TWO

2. LITERATURE REVIEW

In this chapter the general aspects of thin films and its application in various electronics devices have been presented. In addition, some related Literature Review of lead sulphide thin films deposited with thiourea concentration by CBD methods are also included.

2.1 Thin Film Materials

A thin film is a layer of material ranging from fractions of a nanometer (monolayer) to several micro meters in thickness. It is prepared by depositions of the film materials (metals, semi – conductors and insulators) atom by atom on a substrate through a phase transformation. In thin films there are deviations from the properties of the corresponding bulk materials that arise because of their small thickness, large surface – to – volume ratio and their unique physical structure which is a direct consequence of the growth process [14].

PbS thin films are semiconductor compounds of the type IV – VI that have developed great interests for many practical purposes especially for photovoltaic cells, photo conductive materials, optical detectors, photoelectron chemical cells, thin film transistors and other optoelectronic devices. Most of type IV – VI thin films compounds includes compounds formed from elements of group IV and VI of periodic table and a lot of studies have revealed much about their general nature, features of their chemical stability and their energy gaps at room temperature. Most of the new thin film technologies coming up are based on the use of materials with very thin film geometry because they tend to lower costs and also lower material consumption. A semiconductor material is said to be in thin film form only when it is built up as a thin layer on a solid support called substrate by a controlled condensation of the individual atomic, molecular, or ionic species. It is currently known that a relatively small group of elements and compounds have an important electrical property called semi – conduction. This is a property where they are neither good electrical conductors nor good electrical insulators but instead their ability to conduct electricity is intermediate and that is why these materials are called semiconductors

[15].

Poortmans *et al*. (2006), define a thin film as a material created by the random nucleation and growth processes of individually condensing/reacting atomic/ionic/molecular species on a substrate. The structural, chemical, metallurgical and physical properties of such materials are strongly dependent on a number of deposition parameters and thickness. Thin films encompass a considerable thickness range, varying from few nanometres to tens of micrometres and thus are best defined in terms of birth processes rather than by thickness [16].

Thin films are also regarded as two dimensional materials fabricated by the process of condensation of atoms, molecules or ions. This is what makes them have unique properties significantly different from their corresponding bulk materials. These unique properties are as a result of the changes that occur in their physical dimensions, geometry and micro structure. Thick films are prepared either by a direct application of solution dispersion or by a paste of the material on a substrate and then letting them dry irrespective of their thickness [17].

The thin films are characterized by the crystalline orientation, strain energy and multilayer aspects. Electronic semiconductor devices and optical coating are the main applications benefiting from thin films constrictions. Some of the advantages of thin films are listed below:

i. There are many deposition techniques for thin films from the same material.
ii. The structure of the films can vary from amorphous to micro/nano crystalline, depending on the substrate, the technique and parameters of deposition.
iii. Can be deposited on many substrates of different forms and surfaces.
iv. Doping and alloys/compounds in different proportions can be obtained due to relaxation of the solubility conditions.
v. The grain limits and the surfaces can be passivity with suitably chosen materials.
vi. Several types of electronic junctions can be fabricated: single junction, in tandem, etc.
vii. It is possible to fabricate materials with desired and/or graded energy gaps/

compositions/lattice constants/reflection coefficients

viii. The surfaces and interfaces can be modified to obtain suitable diffusion barriers at interfaces/electric fields [18].

2.2 Review of Lead Sulphide (PbS) Thin Films prepared by CBD Method

Growth of PbS by CBD is attracting considerable attention as it does not require Sophisticated instrumentation and it is relatively inexpensive, easy to handle, convenient for large area deposition and capable of yielding good quality thin films [19].

Ubale *et al.* (2007), deposited PbS thin films onto glass substrate by the method of chemical bath deposition (CBD) using lead acetate ($Pb(CH_3COO)_2.3H_2O$) as Pb^{2+} and thiourea ($SC(NH_2)_2$) as S^{2-} ion source in an alkaline medium. For this, 45 ml solutions of 0.05 M lead acetate, and 0.05 M thiourea were mixed together at pH of 10 adjusted by drop-wise addition of ammonia and heated at 330 K temperature for 10 minutes, and then kept at room temperature for further deposition. The results of XRD and SEM revealed that the deposited PbS thin films consists of nano – sized grains and the grain size increases with increasing film thickness. The XRD and optical analysis showed that PbS thin films had nano crystalline structure with cubic phase (galena) and direct allowed transitions in the range 2.28 – 1.88 eV with film thickness vary from 65 – 168 nm, respectively. The electrical resistivity and therefore activation energy are observed to be decrease with increase in grain size. The thermo – emf measurements revealed that deposited films were p-type in nature [20].

Chouldrury and Sarma, (2008) synthesized nano crystalline PbS thin films on glass substrate using CBD with precursor solutions containing different molarities of lead acetate ($Pb(CH_3COO)_2.3H_2O$) (0.25 to 1.00 M), polyvinyl alcohol (PVA) and thiourea ($SC(NH_2)_2$). XRD analysis showed that crystal sizes are found to vary from 2.0 – 4.4 nm but the average grain size of films are found to vary from 48 to 93 nm as observed by SEM and the x – ray diffraction of samples show preferred orientation along (111) and (200) planes. Moreover, the band gap determined from

UV spectrograph is found in the range of 1.9 – 2.6 eV [21].

Abbas, M. *et al.* (2011) synthesized PbS thin films on ordinary glass slide substrates by CBD technique. Lead acetate ($Pb(CH_3COO)_2.3H_2O$) and thiourea ($SC(NH_2)_2$) were used as sources of Pb^{2+} and S^{2-} respectively and triethanolamine ($N(CH_2CH_2OH)_3$) used as complex agent. The deposition was made at 30^0C during deposition time (30, 120, and 210 min) and kept at pH of 12. The results of AFM and XRD tests showed that the deposited PbS thin films consist of nano size grains and the grain size increases with increasing film thickness. The optical properties of these films have been studied and show that PbS thin films have allowed direct transition and the values of energy gap varied between 1.88 – 1.55 eV with increasing film thickness. It is observed that the highest absorbance values are obtained from the annealed samples and optimally from samples with 600 and 660 nm thickness annealed at 150 ^{0}C and 100 ^{0}C respectively. A dense surface composed of multilayer grains of films was obtained with the crystal size around 37.67 nm [22].

S. Zaman *et al.* (2014), deposited PbS thin films by CBD method onto chemically cleaned glass substrates using thiourea ($SC(NH_2)_2$) as a source of sulphur ions and lead acetate ($Pb(CH_3COO)_2.3H_2O$) as Pb^{2+} precursors in alkaline medium and hydrazine hydrate as base instead of commonly used basis such as sodium hydroxide (NaOH). Chemical bath was prepared by mixing aqueous solutions of thiourea and hydrazinehydrate in 1 M: 7 M respectively while lead acetate concentration was varied from 1.2 M to 0.6 M and the starting solution had pH 12 at deposition time of 30 minutes. After deposition, films were rinsed in de-ionized water and dried in oven at 60 - 80^0C and the annealing of films was done at 100^0C for 7 hours. Optical studies revealed that by lowering the lead ion concentration decreases the optical band gap of PbS thin films. The optical band gap decreases for annealed thin films which is responsible for the enhanced photosensitivity of annealed films. Thickness of the film increased as a result of decreasing Pb ion concentration, it is due to the fact the nucleation phenomena of PbS growth became more dominant and more time was available for the reaction to complete as a result thickness of PbS films enhanced. Dark resistance increased as a result of decreasing

lead ion concentration, it is due to fact that with the decreasing lead content in the deposited PbS thin films, the carrier type is shifted from n to p-type, as a result the net dark resistance of PbS films increases [23].

Rajathi, S. *et al.* (2015), prepared transparent and nano crystalline lead sulfide (PbS) thin films by chemical bath deposition (CBD) technique onto glass substrates deposited at 80^0C using aqueous solution of 100 ml beaker containing lead acetate ($Pb(C_2H_3O_2)_2.3H_2O$), which concentration range 0.1 M, thiourea ($SC(NH_2)_2$) at concentration 0.1 M and the alkalinity is set using sodium hydroxide (NaOH) at concentration 0.5 M. The pH of the solution was adjusted by adding a small amount of triethanolamine (TEA) was used as a complex agent. The distilled water was added to the solution to achieve a total volume of 100 ml. The X – ray diffraction pattern revealed that the best crystallinity and the great adhesion of PbS on glass substrate are obtained by employing lead acetate, sodium hydroxide, thiourea and triethanolamine formed only by lead sulfide compound with the centred cubic structure preferentially oriented according to the (200) perpendicular direction to the plane of the substrate. The high transmittance and low reflectance properties make the film good materials for house heating for solar chick brooding and antireflection in flat – plat collectors. The band gap of nano crystalline PbS thin films is found to be 1.8 eV which is higher than the bulk due to quantum confinement of PbS nano crystalline. Photoluminescence spectroscopy shows the emission at 355 – 490 nm [24].

S. Zaman *et al.* (2016) deposited PbS thin films of onto chemically cleaned glass substrates using analytical reagent grade chemicals by CBD process. Thiourea ($SC(NH_2)_2$) was used as a source of sulfur ions and lead acetate ($Pb(C_2H_3O_2)_2.3H_2O$) as Pb^{2+} precursors in alkaline medium, using hydrazine hydrate as base instead of commonly used basis such as sodium hydroxide (NaOH). Chemical bath was prepared by mixing aqueous solutions of thiourea, lead acetate and hydrazine hydrate in 0.7 M: 0.7 M: 5 M respectively. The starting solution had 12 pH and at different temperature (60 – 80^0C). AFM analysis revealed that increasing deposition temperature and time leads to growth of crystallites and film thickness that increases the surface roughness and average surface roughness increase from 59.55

nm to 103.54 nm. XRD spectra indicated preferred growth of cubic phase of PbS films in (200) direction with increasing deposition time. The UV – Vis spectra analysis revealed that the band gap of PbS films decreases from 0.649 eV to 0.636 eV while going from $30\,^{0}C$ to $100\,^{0}C$ as a result of increasing grain size [25].

L. Beddek *et al.* (2016) were synthesized Lead sulphide (PbS) thin films by using chemical bath deposition (CBD) method. Bath solutions were formed of various concentrations of thiourea, ranged from 0.1 to 1.2 M and two different salts as Pb source (lead acetate and lead nitrate). The thin film deposition was done in a reactive bath prepared in a 50 mL beaker. The XRD analysis revealed the whole peaks of intensities are enhanced with increasing thiourea concentration in bath solution, when lead acetate was used as lead source. The crystallite size was also decreased with increasing of thiourea concentration in bath solution. It varied in the range from 16 to 4 nm. The measured optical band gap was varied in the range from 0.5 to 0.9 eV [26].

The literature reviewed above indicates that limited research has been conducted on the effects of structural and optical properties of lead sulfide thin films, highlighting gaps in the field. Therefore, the present study focuses on the deposition of lead sulfide thin films using the chemical bath deposition (CBD) method, with sodium hydroxide (NaOH) acting as a complexing agent. Various concentrations of thiourea [$SC(NH_2)_2$] are used, while other parameters such as temperature, deposition time, and concentration of lead acetate [$Pb(CH_3COO)_2 \cdot 3H_2O$] solution are kept constant.

CHAPTER THREE

3. METHODS AND MATERIALS

3.1 Thin Film Deposition Techniques

A thin film has one of its linear dimensions very small compared to the other two techniques and characterized by a large surface to volume ratio. Thin film devices would typically be about 5 to 50 μm thick in contrast to bulk devices, which are about 50 to 250 μm thick. Thin film properties are strongly dependent on the methods of deposition, the substrate materials, the substrate temperature, the rate of deposition and the back- ground pressure. The application and the properties of the given material determine the most suitable technique for the preparation of thin films of the material [27].

Any thin film deposition process involves the following sequential steps:

i. Transition of the condensed phase (solid or liquid) into the gaseous state (atomic/molecular/ionic) species.
ii. Transport of the vapour from the source to the substrate.
iii. Condensation of the vapour upon arrival on the substrate

Thin film deposition techniques can be broadly categorized into physical deposition and chemical deposition methods depending on how the atoms/molecules/ions clusters of species are created for condensation process. Physical deposition includes physical vapour deposition (PVD) techniques such as thermal evaporation, electron beam evaporation, pulsed ion beam evaporation, RF- sputtering, closed space vapour transport, atomic layer deposition, brush plating, hot wall deposition, pulsed laser deposition and atomic/molecular beam epistaxis. All these physical methods of deposition of thin film were done in a high vacuum system in which a vacuum of 10^{-5}m bar was created using a diffusion pump backed by a rotary pump [28].

Chemical deposition includes chemical bath deposition (CBD), chemical spray pyrolysis (CSP), successive ionic layer adsorption and reaction (SILAR), chemical vapour deposition (CVD), metal organic chemical vapour deposition, plasma enhanced chemical vapour deposition, sol-gel synthesis, solvent evaporation

epistaxis method, electrophoresis, spin coating, dip technique and the solution dispersion method [29].

3.2 Chemical Bath Deposition

There are many dozens of deposition technologies for material formation; however, thin film deposition technologies are either purely physical, such as evaporative methods, or purely chemical, such as gas and liquid phase chemical processes. A considerable number of processes that are based on glow discharges and reactive sputtering combine both physical and chemical reactions; these overlapping processes can be categorized as physical – chemical methods [30].

Chemical bath deposition in present period of time has been extensively used for preparing thin film because of the advantages of this method is relatively inexpensive, easy to handle, occur at easily attainable temperature, capable of yielding good quality thin films, simple and convenient for large scale deposition etc. [31]. Chemical bath deposition (CBD) is a very comfortable method for deposition polycrystalline PbS thin films with a good photoconductive properties [32].

Chemical bath deposition is believed to have originated from the work of **Gerhard Brückman in 1933,** when he produced thin films of lead sulphide from a solution of lead acetate, thiourea and sodium hydroxide. Chemical bath deposition is a thin film deposition technique in which compound semiconductor thin films of typically 0.02 – 1 μm thickness are deposited on the glass substrates immersed in dilute baths containing metal ions and a source of sulfide, telluride or selenide ions. Many II – VI, IV – VI, III – V, IV – IV and V – VI semiconductors are included in the list of materials deposited by this technique. Chemical bath deposition (CBD) which is also known as solution growth, autocatalytic deposition, electrolysis deposition, controlled precipitation, or simply chemical deposition, recently has emerged as a method for the deposition of metal chalcogenides thin films synthesis because it is a relatively simple and inexpensive method for large area deposition and, at the same time, allows depositing thin films at a relatively low temperature. In fact, chalcogenides material has shown to be good candidates for p-type semiconductors and have been demonstrated using chemical bath deposition (CBD). Chemically deposited

semiconductor thin films define the general characteristics of the different stages in the CBD growth process:

- ✓ An induction period during which is the various chemical equilibrium established in the bath and an initial monolayer of the metal chalcogenides is formed on the glass substrate and also called nucleation or incubation period.
- ✓ The initial monolayer of the semiconductor formed on the glass substrate acts as a catalytic surface for the condensation of the metal ions and chalcogenides ions resulting in the film growth called growth phase.
- ✓ Film growth assumes a maximum rate at a certain time depending on the bath parameters and finally reaches a terminal phase at which the film ceases to grow.
- ✓ A decrease in the duration of the induction period with increase in the temperature as well as with the concentration of ions in the bath and
- ✓ An optimum temperature – concentration combination to obtain maximum thin film thickness for a given duration of deposition.

All the above listed stages of deposition process in general consists of a nucleation phase, growth phase, and a terminal phase, each of which depends on the concentration of the ions in the deposition bath, the temperature of the deposition, and dissociation constants of the metal complex ions, etc. In order to investigate the best quality of thin films, the different deposition conditions were carried out during the deposition process [33].

In general, this technique can be used to deposit any compound that satisfies four basic requirements:

- ❖ The material can be prepared by simple precipitation,
- ❖ The compound is highly insoluble in the solution used,
- ❖ The compound is chemically stable in the solution and
- ❖ The reaction should proceed with a free anion that is slowly generated [34].

When an ionic solid (MX) is an aqueous solution, equilibrium is established (if the ions formed are singly charged). When equilibrium is reached, the solution is saturated.

$$MX(s) \leftrightarrow M^{+}(aq) + X^{-}(aq)$$

An expression for this equilibrium constant is given by:

$$K = \frac{[\boldsymbol{M^{+}}][\boldsymbol{X^{-}}]}{[\boldsymbol{MX}]}$$

By convention, the concentration of any solid is unity. The equilibrium constant is given in terms of the equilibrium concentrations of the dissolved ions and is referred to as the solubility product or solubility constant.

$$K_{sp} = [M^{+}][X^{-}]$$

The product of $[M^{+}]\ and\ [X^{-}]$ is called ionic product. When the solution is saturated the ionic product is equal to the solubility product [35].

As a given temperature when ionic product of reactants exceeds the solubility product, 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. These are three main factors which affect the solubility product such as temperature, solvent and particle size. The direction of solubility changes as a function of temperature, since increase in the temperature by a stress, the equilibrium between a precipitate and is ions in solution will shift according to whether the heat of solution is endothermic or exothermic. Using a solvent of lower dielectric constant, the solubility of moderately insoluble substance in water is reduced by the addition of alcohol or some other water miscible solvent. As particle size decreases, solubility appears increase [36].

Another important variation in the deposition of PbS thin films by CBD is the deposition under light. Visible light increases the growth rate of CBD deposited PbS thin film. Using chemical bath deposition methods, a large number of binaries such as CdS, CdSe, Bi_2S_3, Bi_2Se_3, PbS, PbSe, As_2S_3, Sb_2S_3, Ag_2S, CuS, ZnS etc. and ternaries such as CdZnS, CdSSe, $CuInS_2$, $CuInSe_2$, PbHgS, CdPbSe etc. have been

deposited as thin films [37].

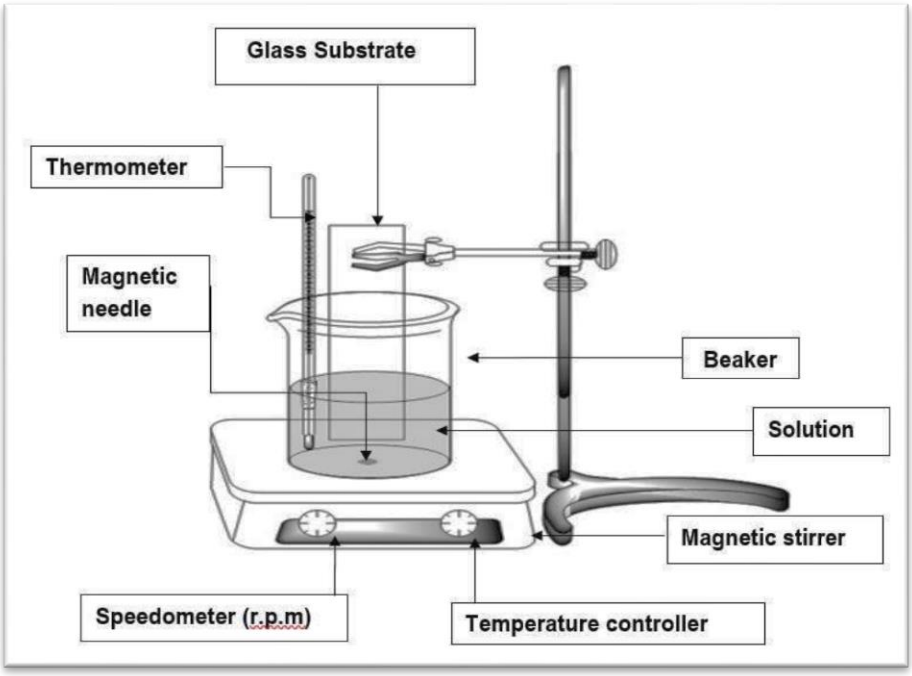


Figure 3.1 Schematic layout of chemical bath deposition method [38].

The main disadvantage of the chemical bath deposition is the wastage of the material due to the deposition on the walls of the container and precipitation into the solution. Preparation of the films with a definite geometric pattern on the substrate is difficult because perfect masking is not possible. The quality of the film deposited depends on the bath parameters like temperature, time of deposition, concentration of the reactants and the chemical bath [10].

3.3 Factors affecting chemical bath deposition (CBD) process

There are several factors which affect thin film deposition process in CBD techniques. Such as bath temperature, nature and concentration of the precursors, nature and concentration of complexing agent, deposition time and nature of the substrate [39]:

(a) Bath Temperature

The dissociation of complex and the anion of the compound (X compound) depend on the temperature. At the higher temperatures, the dissociation is greater and gives higher

concentrations of M and X ions that result in higher rates of deposition [40].

(b) Nature and concentration of the precursors

Nature of the precursors influences the composition of the product. The growth kinetics depends on the salts /compounds used for metal and chalcogenides ion sources. The deposition rate and terminal thickness initially increase with an increase in the chalcogenides ion concentration. At higher concentrations the precipitation becomes very fast, leading to decrease in film thickness on the substrate [34].

(c) Nature and concentration of complexing agent

The increase in anion (X) compound concentration leads to increase in 'X' ion concentration and a film of MX with larger thickness is obtained. Consequently, above certain concentration, when the rate of reaction becomes high, precipitation also becomes important which leads to less amount of MX on the substrates and hence lower thickness is obtained.

(d) Deposition time

In general, the growth of good quality thin films proceeds at a slower rate. At slow deposition rate growing species have enough time to be organized and found a favourable site in contrary to a fast process [26].

(e) The nature of glass Substrate

Film formation takes place only under certain conditions i.e. either under optimum conditions for MX formation or when the substrate has special properties facilitating for the formation of single crystal films. The second condition favours the formation because when the lattice of the deposited material matches well with that of the substrate, the free energy change is smaller, there by facilitating nucleation [34].

3.4 Nucleation and Crystal Growth

Thin film formation from solution can be thought of as a two – step process. The first step is the phase separation, or "birth" of new crystals. The second step is the growth of these crystals to larger sizes. These two processes are known as nucleation and crystal growth respectively [41].

3.4.1 Nucleation

Nucleation is a process by which formation of new phases begins. Any growth starts from a nucleus or crystal seed. It takes place when a state in which atomic particles are cloth enough to each other at a temperature below the melting point so that an ordered arrangement of these atoms is energetically preferred [42]. It can occur either by initial homogeneous nucleation in solution or by heterogeneous nucleation on a substrate, depending on the deposition mechanism. For any precipitate, there is some minimum number of ions or molecules required to produce a stable phase in contact with a solution called nucleus. The formation of nucleation is necessary for a precipitate formation. The concept of nucleation in solution is that the clusters of molecules formed undergo rapid decomposition and particles combine to grow up to a certain thickness of the film [36].

(a) Homogeneous Nucleation

Homogeneous nucleation can occur due to local fluctuations in the solution whether in the concentration, temperature or other variables. Phase transformation occurs when the free energy of the new phase is lower than that of the initial (metastable) phase. The first stage in growth is collision between individual ions or molecules to form embryos (embryos are nuclei that intrinsically unstable against dissolution). Embryos grow by collecting individual species that collide with them [43].

(b) Heterogeneous Nucleation

In heterogeneous nucleation, subcritical embryos (or even individual ions) can absorb on to the substrate. The energy required forming an interface between the embryo and the solid substrate will usually be less than that required for homogeneous nucleation, where no such interface exists. Therefore, heterogeneous nucleation is energetically preferred over homogeneous nucleation and can occur near equilibrium saturation conditions, compared with the high degree of supper saturation often required for homogeneous nucleation [41].

3.4.2 Crystal Growth

As soon as stable nuclei formed, particles larger than the critical size have been formed in a supersaturated or supper cooled system. They also begin to grow in to crystal of

visible size [44]. There are several ways in which they can increase in size. One is continuation process of embryo growth and absorption of ionic species from the solution onto the nucleus. Crystal growth of this type can be considered a self – assembling process. The next growth step will then be absorption of the oppositely changed ion to give an additional semiconductor molecule. This process can continue until either all the ions of anyone type are used up or growth is blocked, e.g., by aggregation or by blocking of the crystal surface by a foreign absorbed species [34].

3.5 Thin Film Characterization Techniques

Many techniques have been used to characterize CBD thin films. These methods include X – ray Diffraction (XRD), UV – Vis spectroscopy, Fourier Transforms Infra – Red spectroscopy (FTIR), Scanning Electron Microscope (SEM), Energy Dispersive X – Ray (EDX), Photoluminescence, Thermal Gravimetric Analysis (TGA), and others. In this study, XRD and UV – Vis Spectroscopy were specifically employed for analysing the structural and optical properties of thin films as part of the characterization process is used in this work.

3.5.1 Structural characterization: X – ray diffraction technique

The analysis of crystal structure is a great importance in the description of materials; such as analysis typically performed by employing X – ray diffraction techniques (Other techniques include electron and neutron diffraction method). X – Rays have wavelengths on the order of a few Angstroms (1n m = 1 0 Angstrom). A crystal may be defined as a solid composed of atoms arranged in a pattern periodic in three dimensions. Using this technique, one can get the information regarding the crystalline nature of a material, lattice parameter, strain energy and dislocation density [45].

Since atoms are arranged periodically in a lattice, x – ray scattered from a crystalline solid can constructively interfere, producing a diffracted beam through these atoms as it illustrated in **1912, *W. L Bragg*** recognized a predictable relationship among several factors. These factors are combined in Bragg's law as:

$$n\lambda = 2d_{hkl}\sin\theta \text{ ------------------------- } 3.1$$

Where, n = an integer 1, 2, 3… etc, λ = wave length of the incident x – radiation, symbolized

by the Greek letter lambda which is equal to 1.5406 Angstroms, d = the distance between similar atomic planes in a mineral (interatomic spacing) which is called d – spacing, θ = the diffraction angle in degree and lattice parameter (a) can be calculated the relation using from equation 3.1 above.

$$d^2 = \frac{a^2}{(h^2+k^2+l^2)} \ , \ or \quad a^2 = d^2(h^2 + k^2 + l^2) ------------ 3.2$$

Where d = planer space, a = lattice parameter, and (h, k, l) is the miller indexes of the plane.

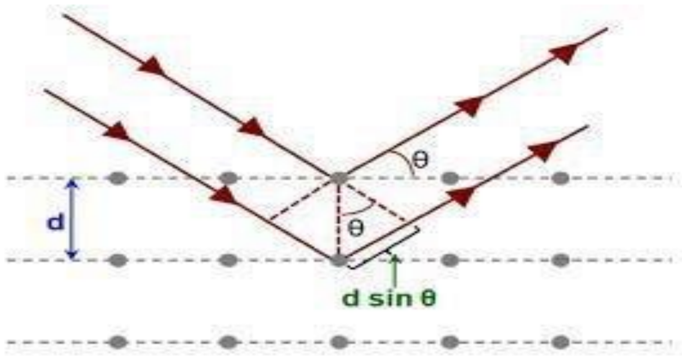


Figure 3.2 X-ray diffraction from plane [45].

The size of the crystallite (D) can be obtained by Debye Scherer formulas [46]:

$$D = \frac{K\lambda}{\beta_{hkl} \cos\theta} \quad ------------------------------ 3.3$$

Where, D is the size of crystallite, "θ" is the diffraction angle, β (FWHM) is the full width at half maximum in radians, (**K = 0.94)** is the constant known as the shape factor, by assuming the crystallites to be cubic in shape and (**λ = 1.5406 Å** or **λ = 0.15406 nm**) is the wave length of the X – ray radiation.

The values of dislocation density (ρ) and micro strain (ε) were calculated using equation bellow.

$$\rho = \frac{\mathbf{1}}{\boldsymbol{D^2}} ---------------------------- 3.4$$

$$\varepsilon = \frac{\beta_{hkl} \cos\theta}{4} ---------------------------- 3.5$$

Where ρ is dislocation density, D is crystalline size; ε is micro strain, β_{hkl} is full width at half

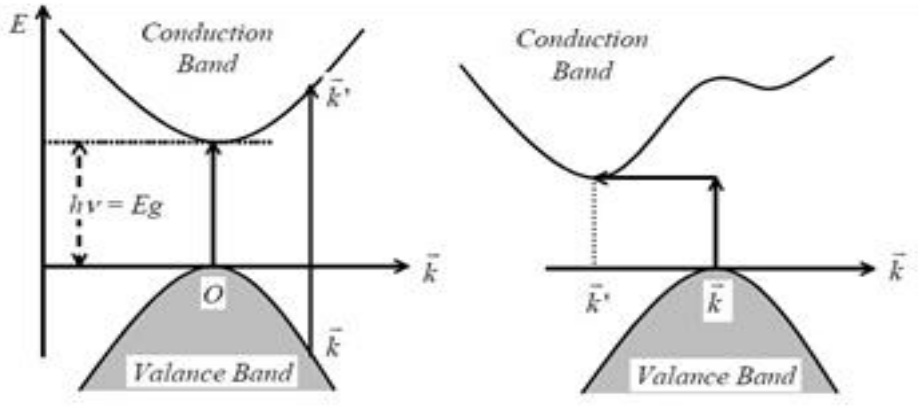
maximum and θ is the Bragg's angle.

3.5.2 Optical characterization: UV – Vis spectroscopy

Optical properties of a material change or affect the characteristics of light passing through it by modifying its propagation vector or intensity. Measurement of the absorption of light is one of the most important techniques for optical measurements in solids. In optical absorption spectroscopy, electromagnetic radiation in the near – ultraviolet, visible or near – infrared regions are used to excite transitions between the electronic states. Optical measurements have many unique and attractive features for studying and characterizing semiconductor properties. UV – Vis spectrometers collect the data over the required range and generate the spectrum of the compound under analysis as a graph representing the transmittance or absorbance as a function of wavelength along the abscissa, given in nanometres, the recommended unit in this region. This region of the spectrum is conventionally divided into three sub – domains termed near UV (200 – 400 nm), visible (400 – 700 nm) and very near infrared (700 – 1100 nm). One of the defining features of a semiconductor is the band gap, which separates the Conduction and valence bands. Upon absorption of light, an electron is promoted from the valence to the conduction band. The wavelength of light absorbed and emitted from this material is determined by the width of the band gap. The UV – Vis absorption spectroscopy is frequently used to characterize semiconductors thin films, to determine the band gap of the nanostructure materials and also to understand the quantum confinement of the nanoparticles [28].

3.5.3 Energy band gap calculation from the absorbance spectra

In the present study, optical characterization was carried out to determine the nature of absorption and energy band gap of PbS thin films. These properties have dependence on grain size and chemical composition of the thin films. During this study the optical absorption measurement was carried out by using an instrumental model PG Ltd T80 UV – Vis spectrophotometer within the wave length range of 200 – 800 nm. The direct inter-band optical transition involves a vertical transition of electrons from the valence band to the conduction band such that there is no change in the momentum of the electrons and energy is conserved.



a) direct band gap b) indirect band gap

Figure 3.3 Direct and indirect electron transitions in semiconductors (a) direct transition with accompanying photon emission; (b) indirect transition via a defect level [45].

Hence the wave vector k for electron remains unchanged in E – K space. The optical transition is denoted by a vertical upward narrow. A clean glass substrate was used for baseline the data were analysed using the following relation for optical absorption in a semiconductor. The energy band gap from the **Stern relation** for near edge absorption which is given as [45];

$$Ahv = k(hv - E_g)^{\frac{n}{2}} \quad \text{3.6}$$

Where **A** is absorbance, k is constant, *v* is the frequency, *h* is the Planck's constant, E_g is the separation between the valence and conduction bands of energy, and n is a constant which is equal to 1 for direct band gap materials and 4 for indirect band gap materials.

The energy band gap can be obtained by extrapolating the linear portion of $(Ahv)^2$ *versus photon energy* (hv) to the energy axis at$(Ahv)^2 = 0$; will give the band gap energy$E_g = hv$. This procedure has been previously described in determining band gap energy [28].

Fundamentally, the spectrophotometer (single beam) consists of the following elements:

- A light source (usually a deuterium lamp for the UV spectral range and a tungsten lamp for the VIS and IR spectral ranges).

- In operation light source is focused on the entrance to a mono chromator, which is used to select a single frequency wavelength from all those provided by the lamp source and scan over a desired frequency range.
- A sample holder, followed by the light detector to measure the intensity of each monochromatic beam after crossing the sample.
- A computer to save the reflectance/absorption spectrum.

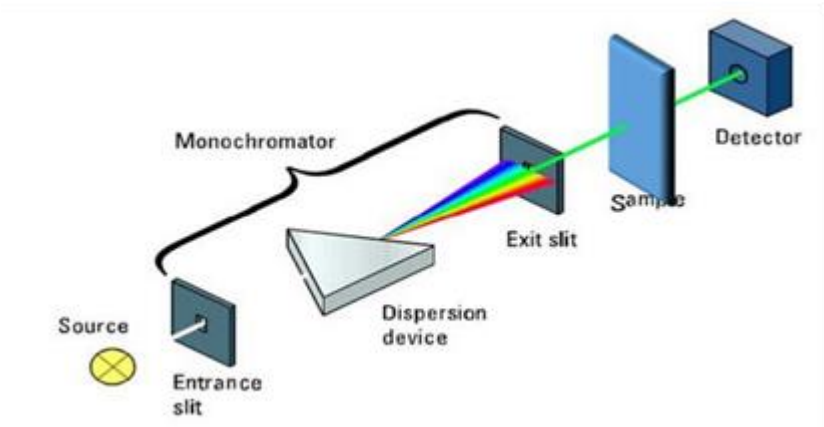


Figure 3.4 Single beam of UV-visible spectrometer [47].

The absorption is seen as tops in the absorption spectrum and drops in the transmission spectrum. This can be used to characterize the band gap energy of the material in **Stern relation** without thickness of thin film on the above equation 3.6.

3.6 Experimental Procedures

In the present study, PbS thin films were prepared using the chemical bath deposition method with varying concentrations of thiourea, following the procedures outlined below.

3.6.1 Materials used

- In the preparation of the PbS thin films, several materials and equipment were used, including:
- Beaker
- Beam balance
- Spoon
- Various flasks of different volumes
- Glass substrates and substrate holder
- Thermometer

- Magnetic stirrer (with stirrer holder/magnetic plate)
- Filter paper
- Heat supply (heater)

These materials were essential for the accurate preparation and deposition of the thin films.

3.6.2 Chemicals and Regents used

In this study different chemicals were used such as:

- Lead acetate (Pb $(CH_3COO)_2 . 3H_2O$) as source of lead ion (379.34 g/mol and 99.5%).
- Thiourea (SC $(NH_2)_2$) as source of sulphur ion (76.12 g/mol and 98%).
- Sodium hydroxide (NaOH) as a complexing agent (40 g/mol and 99%).
- Nitric acid (HNO_3) for cleaning substrate.
- Distilled water for dissolving the solution.

3.6.3 Preparation of precursor's solution

When I have been prepared the solution on the amount in gram to be measured using the relation.

$$m = C * V_L * M_w * P_{pt} \quad ---------- \quad 3.7$$

Where m = amount of substance in gram, C = concentration in molarity, V_L = Volume of solution, M_w = molar weight in (gram/mol) and p_{pt} = percentage purity.

Using the relation provided in equation 3.7, a 0.2 M solution of lead acetate was prepared by dissolving 18.87 g of $Pb(CH_3COO)_2 \cdot 3H_2O$ in 250 mL of distilled water. Similarly, a 0.2 M thiourea solution was prepared by dissolving 3.768 g of $(NH_2)_2CS$ (thiourea) in 250 mL of distilled water. A 0.6 M sodium hydroxide (NaOH) solution was prepared by dissolving 5.88 g of NaOH in 250 mL of distilled water.

3.6.4 Glass substrate cleaning

The cleaning of glass substrates is crucial for the formation of smooth, uniform, and well-adhered thin films. Thorough cleanliness is essential to remove common contaminants such as dust particles, absorbed moisture, and other residues that may be present due to various processes during substrate manufacturing. Glass substrate cleaning involves breaking the bonds between the substrate and these contaminants without causing damage to the substrate

itself. In thin film deposition, a clean substrate is necessary for successful chemical deposition, as a contaminated surface can provide unwanted nucleation sites, leading to uneven film growth, different orientations, and the inclusion of impurities. Cleaned glass substrates were used for the deposition of the thin films.

The following process has been adopted for cleaning the glass substrates.

- They were soaked with nitric acid overnight.
- They clean with ordinary water and soaked with ethanol for 30 minutes.
- The glass substrates were washed wit distilled water and dried in ambient condition

3.6.5 Preparation of solution and deposition of PbS thin films

Microscope glass substrates, cleaned according to the procedure outlined above, were used for the deposition of PbS thin films. Lead acetate and thiourea served as the sources of cations (Pb^{2+}) and anions (S^{2-}), respectively. Sodium hydroxide (NaOH) was used both as a complexing agent and to maintain the alkalinity of the chemical bath. The deposition process involved an aqueous solution containing 0.2 M lead acetate, 0.6 M sodium hydroxide, and varying concentrations of thiourea (8, 9, 10, 11, and 12 mL) for the deposition of PbS thin films.

Freshly prepared lead acetate was added to the chemical bath as the source of lead ions, while thiourea provided the sulfur ions. PbS thin films were formed through a reaction between lead ions from the lead acetate and sulfur ions from the thiourea. The deposition procedure was as follows: 10 mL of lead acetate, 10 mL of sodium hydroxide, 37 mL of distilled water, and various concentrations of thiourea (ranging from 8 to 12 mL) were combined to make a total of 65 mL of solution. The resulting mixture was placed in a heated water bath and stirred with a magnetic stirrer. After mixing, a milky white solution was obtained.

The pre-cleaned substrates were vertically immersed in the chemical bath. The beaker was placed on a hot plate set to 80°C for the deposition process. After 8 to 11 minutes, the solution color gradually changed from white to dark brown, indicating the initiation of the chemical reaction and the formation of the film on the glass substrate. Over time, the solution color transitioned from dark brown to dark grey. After 20 minutes of deposition, the samples were removed from the bath, washed with distilled water, and air-dried.

The resulting thin films were smooth, reflective, homogeneous, highly adherent to the glass substrate, and dark grey in color. The same deposition procedure was followed for all PbS thin films, with thiourea concentrations of 9, 10, 11, and 12 mL, while keeping other parameters constant (i.e., deposition time of 20 minutes and temperature of 80°C). The deposition process for all samples was carried out following the same steps as described above.

3.7 The effects of annealing on structural and optical properties of PbS thin film

Annealing has significant effects on the structural and optical properties of PbS thin films. Structurally, annealing promotes crystallization, increasing the grain size and reducing the number of defects, which leads to improved film uniformity and better adhesion to the substrate. It can also enhance the crystallinity, resulting in more defined and well-aligned crystal structures. Optically, annealing typically reduces scattering defects, improving the transparency and optical clarity of the film. Additionally, it can alter the band gap, often narrowing it, which can influence the film's optical absorption and emission characteristics. Overall, annealing can enhance both the structural integrity and optical performance of PbS thin films. The present study, annealing 200^0c for 1.5 hrs PbS thin films were physically more crystallinity size (less dislocation density) and adherent after annealed.

3.8 Reaction Mechanism

The CBD is based on sequential reaction at the substrate surface. The formation of PbS may involve the following steps. The reaction process for forming lead sulphide thin films is considered as follows [12]:

$$Pb\,(CH_3COO)_2 + 2NaOH \rightarrow Pb(OH)_2 + 2NaCH_3CO_2$$

$$Pb(OH)_2 + 4NaOH \rightarrow Na_4Pb(OH)_6$$

$$Na_4Pb\,(OH)_6 \rightarrow 4Na^+ + HPbO^-_2 + 3OH^- + H_2O$$

In the alkaline medium, the thiourea decomposes and releases S^{2-} ions. Pb^{2+} ions precipitate from the solution leading to the formation of PbS as shown below.

$$SC\,(NH_2)_2 + OH^- \rightarrow CH_2N_2 + H_2O + SH^-$$

$$HPbO_2^- + SH^- \rightarrow PbS + 2OH^-$$

The reaction solution colour changed to brownish black after heating around 8 – 11 min.

3.9 Sample Characterization

Characterizing the deposited thin films is essential for assessing their quality and understanding their properties, such as crystal structure, composition, and optical characteristics. In this study, the characterization of PbS thin films was performed following preparation via the chemical bath deposition (CBD) method, using various analytical techniques. The structural and optical properties were analyzed using X – ray diffraction (XRD) and UV – Vis spectroscopy, respectively.

The crystallographic structure of the PbS thin films was examined using a SHIMADZU XRD-7000 X – ray diffractometer, with Cu Kα (0.15406 nm) radiation. The XRD instrument was operated at 30 mA and 40 kV. Optical properties were studied using a PG Ltd T80 UV-Vis spectrophotometer, covering the wavelength range from 200 to 800 nm.

CHAPTER FOUR

4. Result and Discussion

This chapter presents the final results derived from the experiments conducted in the previous chapter. It includes the structural characterization of the PbS thin films, as analyzed through X-ray diffraction (XRD), along with the optical characterization of their band gap energy, determined using UV-Vis spectroscopy. The chapter concludes with a summary of the findings and recommendations for further research.

4.1 Structural Analysis

XRD measurements were performed to analyse the crystal structure and various microstructural parameters of the PbS thin films, with thiourea concentration varied within the range of interest. The qualitative assessment of the material was based on comparing the experimentally obtained diffraction pattern of the sample with the standard patterns of the target compound. The Joint Committee on Powder Diffraction Standards (JCPDS) provides a comprehensive database of powder diffraction files (PDFs) that contain standard patterns for different elements and compounds, which were used for comparison in this study.

The structural characterization of the PbS thin films was conducted using X-ray diffraction in the 2θ angle range of 10° to 80°, with a step size of 0.02°. The XRD measurements were carried out with a tube current of 30 mA and a functional voltage of 40 kV.

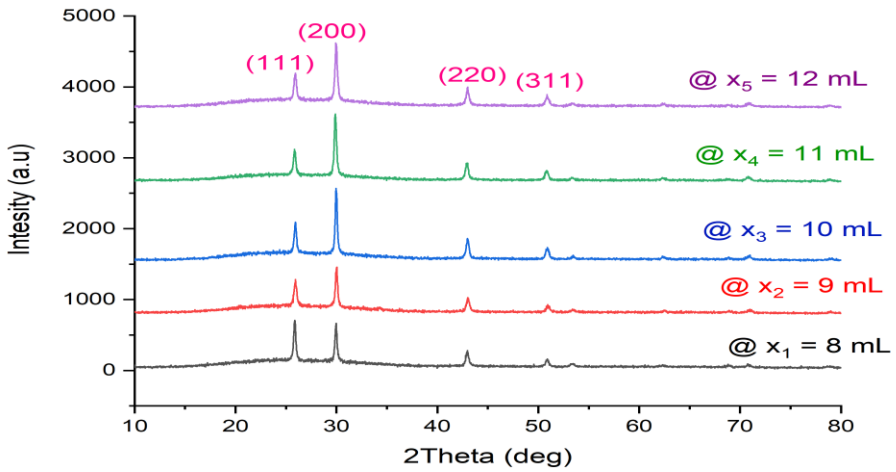


Figure 4.1 XRD patterns of PbS thin films for various concentration of thiourea.

The possible peaks observed in all samples were (111), (200), (220) and (311) around the 2θ values of 25.866^0, 29.9550, 42.964^0 and 50.879^0 respectively. The PbS thin films deposited 8 mL of thiourea concentration has a preferential orientation along (111) while the thin film deposited from 9 – 12 mL at an interval of 1 mL has a preferential orientation along (200) plane. This variation of preferential orientation is due to the change of the total system free energy during the film growth and higher thiourea concentrations typically leads to higher sulfur contents in the solution, which can cause shifts in the preferred orientation of the crystalline planes [48]. Furthermore, any peak referring to impurity phases were not detected. This may confirms the formation of high purity PbS thin films [49]. It can be seen from the figure 4.1 that all diffraction peaks are in good agreement with Joint Committee on Powder Diffraction Standards (JCPDS: 00--005--0592) data for face centered cubic structure. The sharpness of peaks in figure 4.1 revealed that the synthesized PbS thin films were well crystalline. The XRD patterns of prepared PbS thin films revealed that the synthesized thin films have face center cubic structure ($Fm3m$) [50]. The conditions for expressing the **FCC** lattice**:**

i. h, k, l all are even or odd for the presence of reflection,
ii. h, k, l mixed even and odd for the absence of reflections and
iii. $h^2 + k^2 + l^2 = 3, 4, 8, 11, 12, 16, 19, 20, 24, 27, 32$ for the presence of reflections, have been verified for all reflections between 2θ = 10° to 80°.

The lattice parameters of all films were compared with standard and observed (calculated) values using preferential orientation of d – values (inter – planar spacing) for the cubic structure, which is given by equation 3.1 and 3.2 above.

Table 4.1 The comparison of observed and standard XRD parameters for thiourea concentration of PbS thin film.

Thiourea Concentration (mL)	Plane (hkl)	2 Theta (degree)		FWHM (β) in degree		d – space (Å)		Lattice parameter (Å)		
		Standard	Observation	Standard	Observation	Standard	Calculated	Standard	Calculated	Average Lattic (a)
8	111	25.894	25.866	0.2472	0.2461	3.438	3.442	5.9362	5.9616	5.9614
	200	29.972	29.955	0.2367	0.2332	2.979	2.981		5.9612	
9	111	25.954	25.929	0.3121	0.2993	3.43	3.433		5.9456	5.9484
	200	30.025	30.006	0.2565	0.2444	2.974	2.976		5.9512	
10	111	25.954	25.926	0.2539	0.2534	3.43	3.434		5.9483	5.9524
	200	29.997	29.979	0.2365	0.2352	2.977	2.978		5.9565	
11	111	25.886	25.857	0.273	0.2562	3.439	3.443		5.9642	5.9685
	200	29.915	29.896	0.2466	0.2438	2.985	2.986		5.9727	
12	111	25.942	25.915	0.3068	0.2946	3.432	3.436		5.9509	5.9543
	200	29.991	29.973	0.2768	0.2828	2.977	2.979		5.9577	

The calculated average lattice parameter value (a = 5.9569 Å) shows good agreement with the standard value of (a = 5.9362 Å). The experimental analysis of PbS thin films in all samples, with thiourea concentrations ranging from 8 to 12 mL at interval of 1 mL, revealed the effects on the preferential orientation peaks (111) for 8 mL and (200) 9 to 12 mL by increment of 1 mL. The crystalline size (D), dislocation density (ρ), and lattice strain (ε) were calculated using equations 3.3, 3.4, and 3.5, respectively.

Table 4.2 Different crystallographic parameters calculated from XRD patterns in the thiourea concentration.

Thiourea Concen. (mL)	Plane (hkl)	2 Theta (degree)	FWHM (β) in degree	d – space (Å)	Lattice parameter (Å)	Average lattice (Å)	Crystal Size (D) in (nm)	Average size ($D_{av.}$) in (nm)	dis (ρ) (li/m^2) (**ρx10^14**)	Micro strain (**ε x10^-4**)	Average micro strain
8	111	25.866	0.2461	3.442	5.9616		34.59	35.71		10.47	
	200	29.955	0.2332	2.981	5.9612	5.9614	36.83		7.84	9.83	10.15
9	111	25.929	0.2993	3.433	5.9456		28.45	31.80		12.73	
	200	30.006	0.2444	2.976	5.9512	5.9484	35.15		9.89	10.30	11.52
10	111	25.926	0.2534	3.434	5.9483		33.60	35.06		10.77	
	200	29.979	0.2352	2.978	5.9565	5.9524	36.52		8.14	9.91	10.34
11	111	25.857	0.2562	3.443	5.9642		33.23	34.23		10.90	
	200	29.896	0.2438	2.986	5.9727	5.9685	35.23		8.54	10.28	10.59
12	111	25.915	0.2946	3.436	5.9509	5.9543	28.90	29.64		12.53	
	200	29.973	0.2828	2.979	5.9577		30.37		11.39	11.92	11.23

Table 4.2 were observed that the crystalline size to be decrease with increasing thiourea concentration in bath solution. This is because of fast precipitation with in the solution may not set enough time to form a thick film in the substrate and found a favourable site in contrary to a slow process [26].

It was also observed that the sample with 8 mL thiourea concentration exhibited higher crystallinity compared to the reduced dislocation density, good agreement results were reported by Fekadu G. Hone, (2014). Increasing concentration of thiourea affects crystallite size, dislocation density and micro strain of PbS thin films [28]. Before characterize the annealing of PbS thin film with 200^0c for 1.5 hrs affects crystallite size and dislocation density but this is not enough temperature and time.

4.2 Optical Analysis

Band gap energy (Eg) is very important parameters to be considered while studying the optical properties of materials. In this study, the optical band gap energy (E_g) of PbS thin film was determined from the absorption measurements by using UV – Vis spectrophotometer in the wave length range of 200 - 800 nm and its value was estimated by applying **Stern relation** analysis of absorbance. Figure 4.2 indicates the graph of absorbance versus wavelength in various thiourea concentration PbS thin films. According to this figure the optical edge of absorbance plotted in the 200 – 800 nm range from wavelength. In the spectrum of higher absorbance edge the wavelength range from visible 400 – 700 nm region.

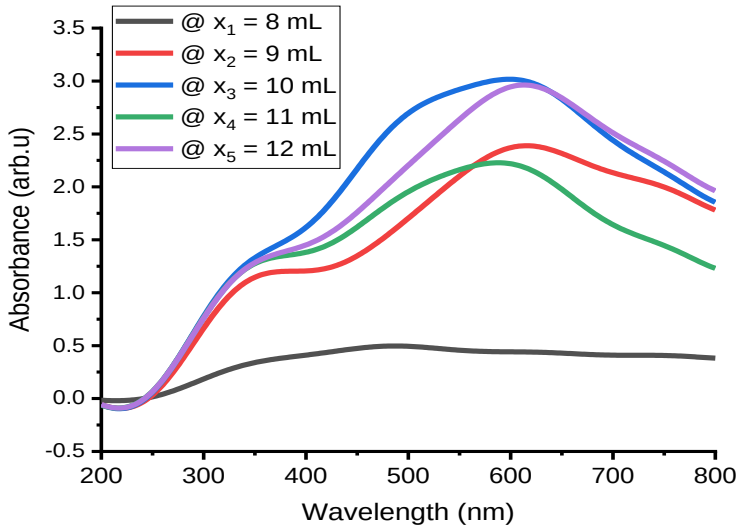
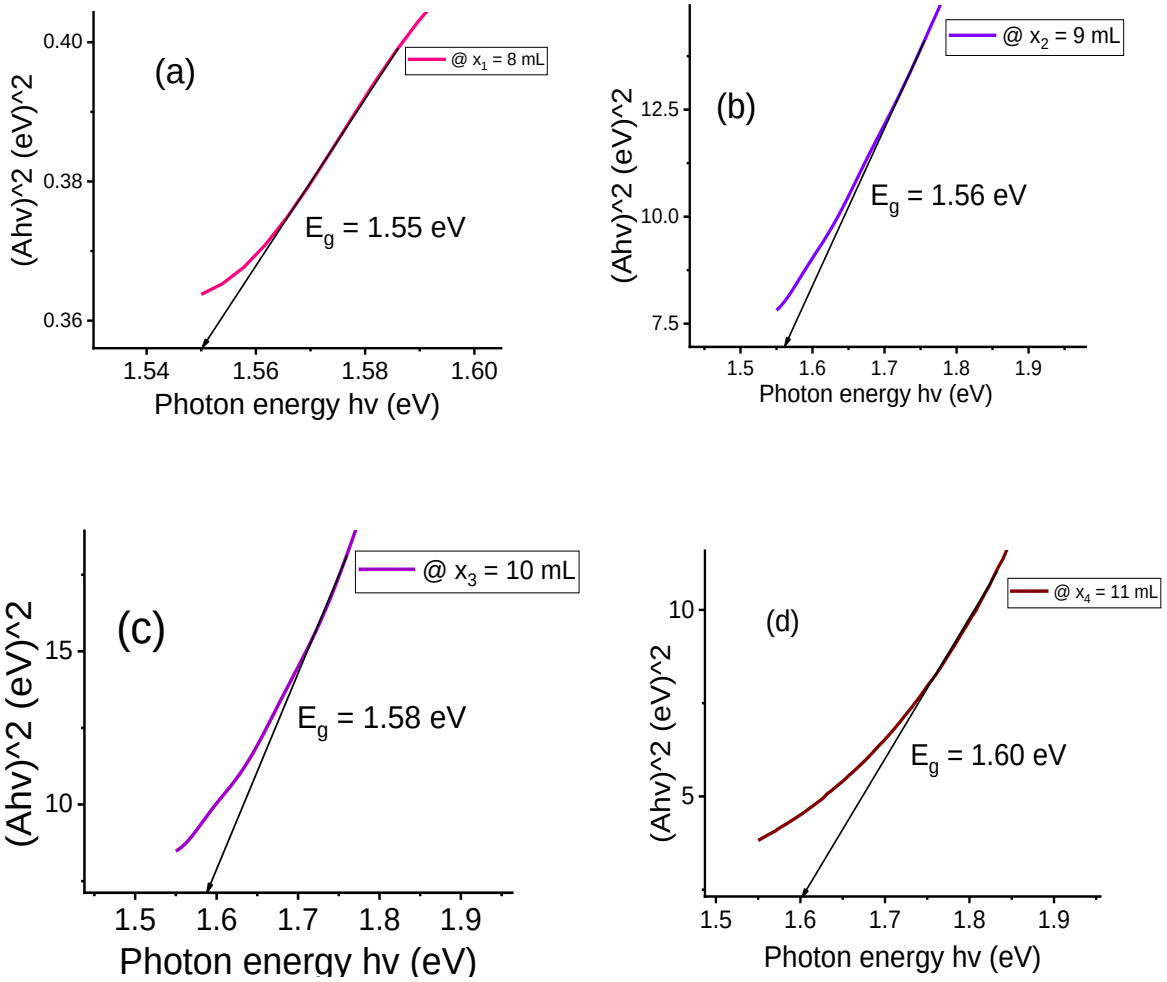


Figure 4.2 Graph of absorbance versus wave length with various thiourea concentrations for PbS thin film.

4.3 Optical band gap determination

The absorbance were examined to determine the optical band gap of the semiconductor by using the classical **Stern relation** and the value is obtained by extrapolating the linear portion of $(Ahv)^2$ $versus$ hv to the energy axis at $(Ahv)^2 = 0$, (see equation 3.6). According to optical absorption measurement, the optical band gap of the present work has been determined at various thiourea concentrations.

As seen from the figure 4.3 the estimated E_g of the films deposited at 8, 9, 10, 11 and 12 mL are 1.55, 1.56, 1.58, 1.60 and 1.61 eV respectively. The band gap energy increases with decreases of crystallite size and linearly increases thiourea concentration. Similar results were reported by Rajathi, S. *et al.* (2015) [24] and Beddek, L. et al (2016) [26]. As thiourea concentration increase the estimated band gap energy is slightly higher when compared to reported bulk value 0.41 eV of deposited PbS thin film due to the quantum size effects of polycrystalline PbS thin films induced [51]. Semiconductor materials with band gap energy lies in the range of 1.55 – 1.61 eV are suitable for solar cells absorber components. This possibility for E_g variation in PbS thin films presents the opportunity for the design of solar cells [52]. So, PbS thin film at this condition may be considered as a profound material for solar cell applications.



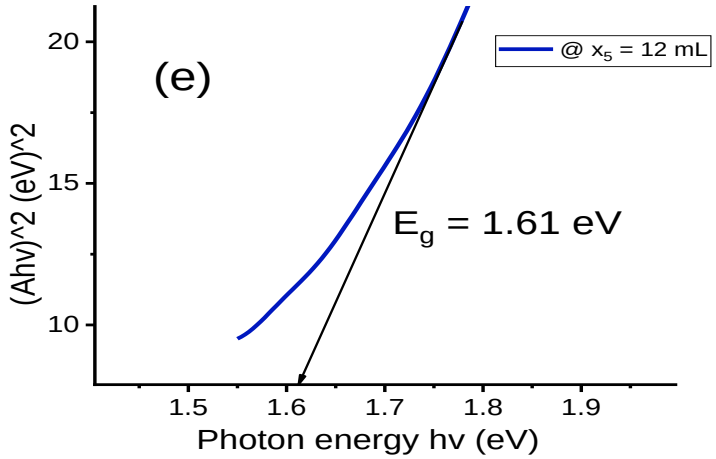


Figure 4.3 The graph of $(Ahv)^2$ plotted as a function of the photon energy (hv) in various thiourea concentration for PbS thin film.

Table 4.3 The parametric factors of structural and optical properties in various thiourea concentration.

Thiourea Concent. (mL)	Crystallinity size (Å)	Disloc. density in line/m^2 (*10^14)	Band gap energy (Ev)
8	35.71	7.84	1.55
9	31.8	9.89	1.56
10	35.06	8.14	1.58
11	34.23	8.54	1.6
12	29.64	11.39	1.61

As the thiourea concentration increases, the band gap energy of the PbS film also increases, while the dislocation density rises and the crystallite size decreases, affecting the overall film structure.

CHAPTER FIVE

5. Conclusion and Recommendation

5.1 Conclusion

Lead sulfide thin films, produced using chemical bath deposition technique are highly valuable for electronic devices and solar cell electrodes. To ensure material quality various studies have been conducted with different parameters. PbS thin films were effectively deposited on glass substrates with 0.2M thiourea concentrations ranging from 8 mL to 12 mL in 1 mL increments, under constant heating temperature 80°C for 20 minutes. The deposited films adhered well to the substrates and appeared dark grey. These films were annealed at 200°C for 1.5 hours and characterized using several techniques.

The effects of thiourea concentration on the structural and optical properties of PbS thin films were analyzed using X – ray diffraction (XRD) and UV – Vis spectrophotometer, respectively. XRD analysis showed a face – centered cubic (FCC) polycrystalline structure thin films from 8 mL of thiourea concentration preferential orientation along (111) and 9 – 12 mL by 1 mL increment for (200) planes. The increasing in thiourea concentration generally results in a more intense peak along the (200) plane compared to the (111) plane, except at 8 mL, due to change of nucleation and growth rates from the thiourea solution. The average crystalline size decreases from 35.71 nm to 29.64 nm with higher thiourea concentration. Optical absorption measurement indicates the film exhibited a direct band gap, which increases from 1.55 eV to 1.61 eV with increasing thiourea concentration. These findings could enhance the properties of PbS thin films and facilitate the development of devices such as solar cells, photographic applications, and diode lasers.

5.2 Recommendation

The research presented in this paper primarily examines the characteristics of PbS thin films produced by the chemical bath deposition (CBD) method, specifically focusing on the impact of thiourea concentration. The investigation concentrated on the structural and optical properties of the films, utilizing X-ray diffraction (XRD) and UV-Vis spectroscopy techniques.

To gain a more comprehensive understanding of the effects of deposition parameters, additional characterization techniques could be employed, such as:

- **Morphological, Electrical, and Photoluminescence Analysis**: To assess the surface morphology, electrical properties, and photoluminescence characteristics of the PbS thin films synthesized by the same CBD method.
- **FTIR Spectroscopy**: To identify functional groups present in the prepared samples through Fourier-transform infrared spectroscopy.
- **Effect of pH Variations**: To explore how lower pH values (in acidic conditions) influence the deposition of PbS thin films and to evaluate the resulting film thickness.

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