STUDIES OF STRUCTURAL AND OPTICAL PROPERTIES OF LEAD SULFIDE THIN FILM AT DIFFERENT DEPOSITION TIME PREPARED BY CBD TECHINIQUE

MSc (SOLID STATE PHYSICS)

BY

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This is to certify that the thesis entitled "**STUDIES OF STRUCTURAL AND OPTICAL PROPERTIES OF PbS THIN FILM AT DIFFERENT DEPOSITION TIME BY CBD TECHNIQUE**" submitted in partial fulfilment of the requirements for the degree of Master's with specialization in solid state physics, the Graduate Program of the Department of physics, and has been carried out by **Yirgalem Fikire Aleker** ID. No. **GPphys K/015/11**, under my supervision. Therefore I recommend that the student has fulfilled the requirements and hence hereby can submit the thesis to the department.

HAGOS TSEGAYE (Ph.D) _____ _____

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We, the undersigned, members of the Board of Examiners of the final open defence by YIRGALEM FIKIRE have read and evaluated his thesis entitled "STUDIES OF STRUCTURAL AND OPTICAL PROPERTIES OF LEAD SULFIDE THIN FILM AT DIFFERENT DEPOSITION TIME PREPARED BY CBD TECHINIQUE" and examined the candidate. This is, therefore, to certify that the thesis has been accepted in partial fulfilment of the requirements for the degree.

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DECLARATION

I hereby declare that this thesis is my own work and that all sources of materials used for this thesis have been duly acknowledged. This thesis has been submitted in partial fulfilments of the requirements for M.Sc. Degree in Solid State Physics at Hawassa University. I earnestly declare that this thesis is not submitted to any other institution anywhere the award of any academic degree, diploma, or certificate.

Name: Yirgalem Fikire Aleker Signature: _____Date:_____

ACRONYMS AND SYMBOLS

A	Absorbance
Å	Angstrom
AFM	Atomic force microscopy
AlAs	Aluminium arsenide
BD	bath deposition
CBD	chemical bath deposition
CD	Chemical deposition
CdS	Cadmium sulphide
CdSe	Cadmium selenide
CVD	chemical vapour deposition
E	Energy
EDX	Energy dispersive X-ray
Eg	energy band gap
eV	electron volt
FCC	face centred cubic
FWHM	full width at half maximum
GaAS	Gallium Arsenic
GaN	Gallium nitride
Ge	Germanium
K	wave vector/constant
M	molar concentration/metal
MACB	Micro assisted chemical bath deposition
min	minuets
ml	mile litters
MOE	minister of education
n	order of diffraction
$N(CH_2CH_2OH)_3$	Triethanolanomine
NaoH	sodium hydroxide
NIR	Near infrared
nm	nano meter
NH3	Ammonia

Θ	theta
^{o}C	Degree centigrade
$Pb(CH_3COO)_2 2H_2O$	lead acetate
$Pb(NO_3)_2$	Lead nitrate
Pb^{2+}	Lead ion
PbS	Lead Sulphide
PbSe	Lead selenide
PbTe	Lead telluride
PLD	Pulsed laser deposition
PV	photovoltaic
S	sulphur
SEM	Scanning electromicroscopy
Si	Silicon
SILAR	successive ionic layer absorption and reaction
UV	Ultra violet
VB	Valance band
VIS	visible spectrum
XPS	X-ray photon spectroscopy
XRD	X-ray diffraction
α	Absorption coefficient
β	Beta
γ	Gamma
δ	dislocation
ε	micro strain
λ	wave length
μm	micrometre
a	lattice parameter
d	inter planer spacing
ν	Photo frequency

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ABSTRACT

In this study, PbS thin films were deposited on glass substrates using the chemical bath deposition (CBD) technique. Lead acetate, thiourea, and sodium hydroxide were used as precursors for the Pb^{2+}, S^{2-} source, and complexing agent, respectively. The deposition was carried out at a bath temperature of 80°C for varying durations of 20, 25, 30, 35, and 40 minutes. Following deposition, the films were annealed at 200°C for 90 minutes. The structural and optical properties of the films were characterized using X-ray diffraction (XRD) and UV-Visible spectroscopy. XRD analysis revealed that the as-deposited PbS films exhibited a nanocrystalline cubic (galena) structure with a face-centered cubic lattice, showing diffraction peaks corresponding to the (111), (200), (220), (222), (311), (400), (420), (331), and (422) planes, with a preferred orientation along the (200) plane. The crystallite size was estimated to increase from 33.27 nm to 37.50 nm as the deposition time increased. Additionally, both dislocation density and lattice strain decreased with increasing deposition time. Optical absorption measurements revealed strong absorption in the wavelength range of 500 nm to 750 nm. The optical band gap was reduced from 1.62 eV to 1.51 eV as the deposition time increased from 20 to 40 minutes in 5-minute intervals

***Key words**: CBD; Band Gap Energy; PbS thin Film and Deposition Time.*

CHAPTER ONE

1. Introduction

The engineering application of solid state physics is concerned with the development of new materials and materials with modified properties with the development of the theory this need no longer be an entirely empirical process. The growth of crystals of specified size and purity of new crystal structure or with a particular surface calls for a combination of theory and engineering know how [1].

The conductivity of semiconductors lies between conductors and insulator. Semiconductors are high sensitivity to temperature, external electric field, magnetic field etc. Because of these high sensitivity of fields, semiconductor have excellent and unique properties. Due to this property they are the building block of electronic and optoelectronic devises[2]. Lead sulphide (PbS) is the most studied material, among the group IV–VI compound semiconductors because of having wonderful applications in the field of optoelectronics[3]. Due to its functional nature, it has been widely used in many fields such as Pb^{2+} ion exchange sensor, photography and as a solar absorber[4]. Its emission and absorption lines are consequently broader, but by varying its crystallite size, tuneable emissions can be obtained within a large spectral region, ranging from the visible to near infrared. This spectral range is of great interest for fabricating light sources or optical amplifiers [5]. PbS exhibits strong quantum size effects below excitonic Bohr radius of 18 nm and hence the energy band gap of its nanocrystals can be tuned to anywhere between 0.41eV (bulk) to 5.2eV. Therefore, it is possible to build optical sensors with adjustable properties[6].

Now a day, semiconductors recently gained great interest among researchers due to their unique physical and chemical properties. These materials have been a new generation of advanced materials due to their novel structural, morphological, optical and electrical properties originating from size quantization. On the growth of nano crystalline PbS thin films has increased due to their future application like luminescent devices, photochemical cells, solar cell etc. [7]. PbS thin films were prepared using different techniques such as electro deposition, successive ionic layer absorption and reaction (SILAR), spray pyrolysis, vacuum Evaporation, chemical bath deposition[8]. Among these methods chemical bath deposition has several advantages compared to other techniques such as uniform film deposition, inexpensive, convenient for large area deposition and does not require sophisticated instrument[9].

This research investigates the structural and optical properties of PbS thin films deposited over varying time intervals using the Chemical Bath Deposition (CBD) technique. The study focuses on films created with lead acetate, thiourea, and NaOH as the precursors and complexing agents. The researcher aims to analyze the effects of different deposition times on the thin films, while keeping other deposition parameters constant, using various characterization instruments.

1.1 Semiconductors

Semiconductors are materials that have an electrical conductivity intermediate between the electrical conductivity of good conductors (such as aluminium and copper) and good insulators (some glasses and plastics)[10]. Semiconductors can conduct electricity under preferable conditions or circumstances. This unique property makes it an excellent material to conduct electricity in a controlled manner as required. The electronic and optical properties of semiconductor materials are strongly affected by impurities, which may be added in precisely controlled amounts. Such impurities are used to vary the conductivities of semiconductors over wide ranges. This process of controlled addition of impurities is called doping [11].

The 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 combination of group III with group V elements and group IV with group VI[12].

1.1.1 Elemental semiconductors

The elemental semiconductors are formed from single chemical elements and important members of this family include silicon and germanium. The crystal structure of Si and Ge is the same as that of diamond. Germanium was widely used in the early days for the development of transistors and diodes. Silicon is now used in majority of transistors, rectifiers and integrated circuits[13].

1.1.2 Compound semiconductors

Compound semiconductors represent the largest group and are formed as a result of the chemical reaction between two or more different elements. For example Gallium Arsenide (GaAs), Indium Arsenide (InAs), Indium Phosphide (InP), and Gallium Nitride (GaN) are common in light – emitting diodes (LEDs)[14].

1.2 Extrinsic and intrinsic semiconductors

For every electron excited from valance band into the conduction band, a vacant site, known as a hole, is created in the valence band. This hole behaves like a positive charge carrier with the same magnitude of charge as the electron, but with opposite sign.

In a pure semiconductor, the number of electrons in the conduction band must be equal to the number of holes in the valence band because each electron gives rise to one hole. In the presence of an electric field, the position of the hole within the crystalline lattice can be thought of as moving as other valence electrons repeatedly fill the vacant site. Under such conditions, electrons and holes move in opposite directions. The electrical conductivity of semiconductors is therefore a direct function of the number of free electrons and holes.

Beside the temperature, the presence of impurities in the crystal lattice also affects the conductivity. Intrinsic semiconductors display electrical properties based on the inherent electronic structure such as silicon (Si), gallium (Ga). On excitation, each electron is promoted into the conduction band creating hole (vacant site) in the valence band[15].

Extrinsic semiconductors have their electrical properties based on impurities, also known as dopants. They have considerably higher conductivity compare to intrinsic semiconductors. The commercially available semiconductors belong to this type. The process of addition of controlled impurities is known as doping which can tailor the electronic and conductivity properties. The addition of impurity atoms into a semiconductor material produces new energy levels within the band gap. When doping is created with such atoms which have one less valence electron than host (doping of Silicon with Boron) impurity atoms act as electron acceptor and create holes (positive charge) in host materials. They are known as p-type and Fermi level shifts close to valence band (VB) as shown below in figure 1.1 (a). However, when a semiconductor is doped with atoms having more valence electrons (doping of Silicon with Phosphorus), materials are termed as n-type semiconductor. The extra non-bonded electron remains bonded to phosphorus atom. When this electron is promoted to conduction band by utilizing thermal energy at room temperature, a positive charge on each phosphorus atom is created. This positive charge remains attach to the phosphorus nuclei and does not act as mobile hole. Under the charge imbalance, Fermi level shifts towards the conduction band (CB) and a new energy level is thus formed as is shown in figure 1.1 (b). Besides, a number of compound semiconductors can act as n-type or p-type materials based on defects within the crystal lattice. These defects arise due to vacant sites in the lattice corresponding

from stoichiometry. For example, in PbS, due to excess of sulphur vacancies it acts as n-type or due to excess of Pb sites it act as p-type semiconductor

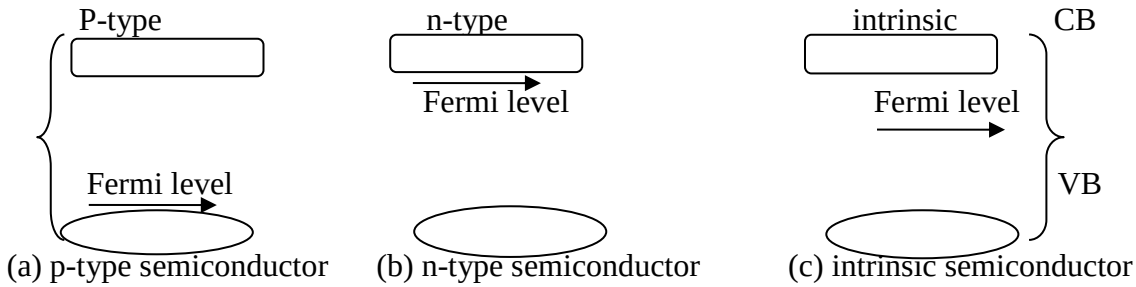


Figure 1.1 A pictorial representation of electronic diagram of Fermi level position on extrinsic (a, b) and intrinsic (c) semiconductors [16].

1.3 Direct and indirect band gap semiconductors

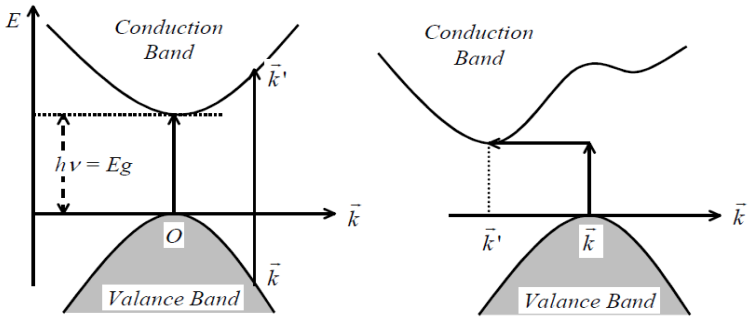
Band-to-band absorption occurs due to the photo excitation of an electron from the valence band to the conduction band. In crystalline solids, the band structures depend on the electron wave vector K. On the basis of transition between band to band, semiconductors can be grouped as direct and indirect band gap semiconductors[17].

1.3.1 Direct band gap

A direct transition from the valence band (VB) to the conduction band (CB). For a direct band gap semiconductors (GaAs, PbS or ZnO)[18]; satisfies the condition of energy and momentum conservations, the K-vector does not change. A direct transition on the E-K diagram is a vertical transition from an initial energy E' and wave vector K in the VB to the final energy E and wave vector K' in the CB where K'=K with the maximum of the valence band and the minimum of the conduction band are at the same momentum (k) value in the Brillouin zone as shown in the figure 1.2(a)

1.3.2 Indirect band gap

For indirect band gap semiconductor like silicon, an electron cannot be directly excited to the conduction band with energy E_g. The absorption coefficient for indirect semiconductors is smaller than that for direct semiconductors; in essence light absorption is a less efficient process for indirect semiconductors. Those semiconductors for which maximum of VB and minimum of CB do not occur at same value of K vector as shown in figure below 1.2(b). This makes indirect band gap materials less suitable for optoelectronic devices.



a, direct band gap b, indirect band gap

Figure.1.2**.** schematic diagram of the difference between (a) Direct transitions with accompanying photon emission; (b) indirect transition via a defect level

By comparison, crystalline silicon (indirect band gap material) requires 20 μm thickness layers. Similarly, in the case of light emission, a direct band gap material is also more likely to emit a photon than an indirect band gap material. Indirect band gap materials are occasionally used for some transistors and rectifiers' they result in low conversion efficiency. Direct band gap materials are used exclusively for semiconductor LEDs and laser diodes.

Table 1.1shows band gaps and other important parameters of selected semiconducting materials

Semiconductors	Group	Band-gap (eV)	Band gap Type	Lattice Parameters (Å)	Crystal Structure
Ge	IV	0.66	Indirect	5.646	Cubic
Si	IV	1.12	Indirect	5.437	Cubic
GaAs	III-V	1.42	Direct	5.653	Cubic
InP	III-V	1.35	Direct	5.869	Cubic
InAs	III-V	0.36	Direct	6.058	Cubic
AlAs	III-V	2.16	Indirect	5.661	Cubic
PbTe	IV-VI	0.29	Direct	6.439	Cubic
PbSe	IV-VI	0.27	Direct	6.12	Cubic
PbS	IV-VI	0.41	Direct	5.93	Cubic

1.4 General Properties of Lead sulphide (PbS)

Nano crystalline semiconducting materials have attracted a great deal of attention because of their size dependent properties and wide range of applications [19]. Lead sulphide (PbS) is one of these interesting compounds that is suitable for the development of an absorber layer in the hetero junction solar cells because of its favourable optical and electrical properties. PbS belongs to the IV-VI group of semiconductor compounds with face centred cubic (FCC) crystal structure. In addition, PbS is a p-type semi-conductor with a direct narrow band gap of 0.41ev at room temperature and a relatively large exaction Bohr radius (18-20nm)

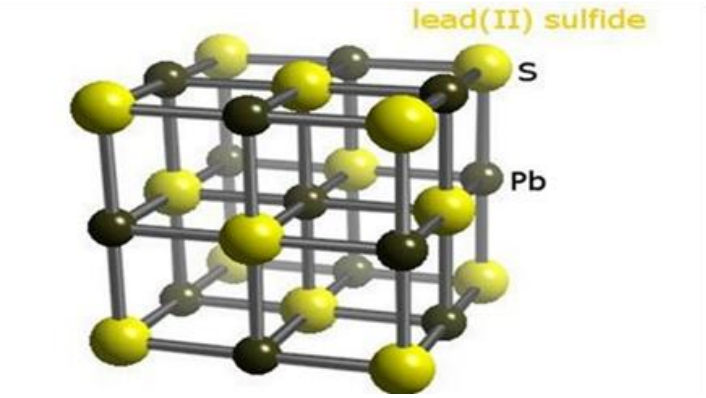


Figure1.3The Cubic Structure of PbS[20].

The rock salt structure in which the lead chalcogenide (PbS, PbSe, and PbTe) crystallize is typical of strongly ionic materials such as NaCl and KBr. This suggests that the chalcogenide atoms acquire two electrons from neighbouring Pb atoms and become doubly negatively charged with closed shell electronic configurations similar to those of halide ions in the alkali halides. Although the bonding in lead salt seems to be predominantly ionic there is evidence that the bonding also has some covalent character. Indeed, in none of compound semiconductors the bonding is purely covalent or purely ionic[21].

$$Pb + S \longrightarrow Pb^{2+} + S^{-2}$$

PbS thin films can be deposited by various methods such as, electro deposition, spray pyrolysis, successive ionic layer absorption and reaction (SILAR) 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; nature of substrate, reaction time, temperature, pH, annealing temperature and the presence of impurities (doping) in the solution [22]. 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 comfortable conditions, scalable and technically straight forward[23].

1.5 Statement of the problem

The thin film compounds of type IV-VI, which include materials formed from elements of groups IV and VI of the periodic table, have been extensively studied, revealing important insights into their general properties, structure, morphology, and optical characteristics, including energy gaps at various temperatures, concentrations, deposition times, and doping levels. Lead sulfide (PbS) thin films, a semiconductor compound from the IV-VI group, have garnered significant interest due to their practical applications. The properties of PbS thin films, particularly those produced through chemical bath deposition (CBD), are highly sensitive to growth conditions such as bath temperature, deposition time, reactant concentrations, and bath pH. These factors present challenges in controlling the films' thickness, size, transmittance, absorbance, and energy band gap. Given the ongoing research in this field, particularly for applications in solid-state micro- and nano-electronic devices, the researcher is motivated to investigate PbS thin films deposited using the CBD technique. This study specifically focuses on using lead acetate, thiourea, and sodium hydroxide as precursors for Pb^{2+}, S^{2-} ions, and complex agents, respectively, aiming to optimize in short deposition time and achieve high-quality PbS thin films.

1.6 Objectives of the research

1.6.1 General objective

General objective of this research is to study the structural and optical properties of PbS thin films at different deposition time using CBD technique.

1.6.2 Specific objectives

- To synthesize PbS thin films by chemical bath deposition method at various deposition time.
- To determine structure of lead sulphide thin film by using X-ray diffraction (XRD) and UV-Vis spectrophotometer.
- To evaluate the effect of deposition time on structural and optical properties of Lead sulphide thin film.

1.7 Significance of the study

The findings of this research could be used in technologies that PbS thin film is an important material due to its properties in optical and crystallographic structure. PbS thin films has increased their future application like Photodetectors, Infrared Sensors, Solar Cells, Optoelectronic Devices, Gas Sensors, Thermoelectric Devices, Telecommunications, Medical Imaging, solar control coating, photography and they have received much attention because of their potential application in opt electric devices. Direct narrow band gap semiconductors are of 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.

1.8 Thesis Structure

The thesis is classified in five chapters. The first chapter deals about general background of semiconductors. It starts with the introduction part and explains general properties of semiconductor materials. Moreover, Basic Properties of IV-VI compound semiconductors and Lead Sulphide (PbS) are also described. The chapter ends by stating objectives of the present work, significance of the present study and describes how the thesis is organized.

The introduction of thin film materials and a brief review of PbS thin films prepared by CBD method is given in the second chapter. The third chapter of this thesis concentrates on the methodology of thin film deposition techniques, factor affecting thin film, characterizing instruments and experimental procedures were included; results and discussion obtained by different characterization techniques of thin films are discussed in detail in the fourth chapter. Finally, the fifth chapter concluding points of my work and gives recommendation.

CHAPTER TWO

2. Literature Review

2.1. Thin films

Thin film is an art of science which plays a dominant role in all persistent fields of science and technology. The term thin film is used for coatings that are used to modify and increase the functionality of a bulk surface or substrate. They are used to protect surfaces from wear, improve lubricate, corrosion and chemical resistance. In many cases thin films do not change the properties of the bulk material. However, they can totally change the optical, electrical transport and thermal properties of a surface or substrate[24]. A thin film is nothing but a low dimensional material created by condensing, one by one, molecular/atomic/ionic species of matter. A thin film is a layer of material ranging from fractions of a monolayer to several micrometres in thickness. Thin films are different from thick films. A thick film is defined as a low dimensional material created by a three dimensional material or assembling large grains/aggregates/clusters of atomic/molecular/ionic species [25].

The basic properties of thin film, such as composition, crystal phase, orientation, thickness and microstructure are controlled by the deposition conditions. Thin films have been extensively studied in relation to their applications for making electronic devices. Thin film devices for practical use were limited to passive devices such as thin film resistors and capacitors[26].

2.2 Review of Lead Sulphide (PbS) Thin Films

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[27].

Abdallah, B., et al. (2018), Lead sulfide thin films were prepared by chemical bath deposition (CBD) on both glass and Si (100) substrates. XRD analysis of the PbS film deposited at 25°C showed that the prepared films have a polycrystalline structure with (200) preferential orientation. Larger grains could be obtained by increasing the deposition time. The prepared films were also chemically characterized using X-ray photoelectron spectroscopy (XPS), which confirmed the presence of lead and sulfur as PbS. While energy dispersive X-ray spectroscopy (EDX) technique was used to verify the stoichiometry of the prepared films. Atomic force microscopy (AFM) was used to study the change in the films' morphology

with the deposition time. The effect of the deposition time, on both optical transmittance in the UV-Vis-NIR region and the structure of the film, was studied. The obtained results demonstrated that the optical band gap decreased when the thickness increased[28].

Hone, Fekadu Gashaw, et al. (2014), Nanocrystalline lead sulphide thin films have been deposited on glass substrates from chemical baths containing lead acetate, sodium hydroxide, ammonia and thiourea at a bath temperature of 90 ^{0}C and a pH of about 12. Three different samples were prepared with deposition times of 30, 45 and 60 minutes respectively. The films were characterized using a variety of techniques. X-ray diffraction analyses revealed that all the films were polycrystalline in nature with the diffraction peaks indexed to the face centred cubic structure. The deposition time strongly influenced the preferred orientations of the crystallites as well as structural parameters such as average crystallite size, strain and dislocation density. SEM micrographs of all the films showed a highly compact surface composed of sharp-edged cubic shaped grains of different sizes. The elemental compositions of the films were confirmed by energy dispersive X-ray spectroscopy. The optical band gap of the films decreased from 1.32 eV to 1.10 eV with increasing deposition time[29].

Obaid, A. S., et al. (2012), Nano crystalline lead sulifed (PbS) thin films have been successfully deposited on glass substrate from lead acetate (Pb^{2+} ions) and thiourea (S^{2-} ions) precursors using microwave assisted chemical bath deposition technique (MACB). The effect of deposition time (30, 60, 90 and 120 min) on the structure and microstructure evolution and the corresponding variation of the optical properties of the as-prepared films were studied using X-ray diffraction (XRD), scanning electron microscopy (SEM), and UV Vis spectrophotometer. XRD analysis shows that all thin films are polycrystalline with crystallites, pure and crystallize within a cubic rock salt (NaCl) type structure. The surface morphology studied using scanning electron microscopy (SEM) showed that the films have uniform surface morphology over the entire substrate and were of good quality. Images revealed that the particle size increased with increasing of the deposition time, thus confirming XRD results. Energy band gap Eg decreased from 2.7 to 1.6 eV as the deposition time was increased due to the increase in the particle size [30].

Kumar, Rajesh, et al. (2014), Nanocrystalline Sb doped PbS thin films have been deposited by chemical bath deposition technique. After deposition, the films have been annealed at 673 K for 1 h in air. The X-ray diffraction (XRD) pattern of the films shows the formation

of well crystallized PbS with face centred cubic structure with the preferential orientation (2 0 0). The values of average crystallite size have been found to be in the range 40–43 nm. AFM surface analysis indicates a uniform and smooth surface with average grain size of 52.3 nm. The optical properties, absorption, and transmission of the films, as a function of doping have been measured. The increase of Sb doping in PbS thin films leads to decrease of band gap Eg from 1.69 eV to 1.59 eV, which satisfied on blue shift of the absorption edge in nanostructured thin films such high values of band gap can be attributed to quantum confinement effect, due to the small grain size of the polycrystalline films. The measured room temperature electrical resistivity of the films is in the range 1.29–3.7 × 10^6 Ω cm[22].

Choudhury 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 diffractograms of samples show preferred orientation along (111) and (200) planes. The band gap of the film determined from UV spectrograph is found in the range of 1.9-2.6eV[31].

Aadim, K., A. Ibrahim, and J. Marie. (2017), Lead sulphide (PbS) thin films has attracted interest due to its potential applications in optoelectronics devices, gas sensors, solar cell technology and transparent conducting electrodes. Thin films were grown on glass substrates by pulsed laser deposition (PLD) technique at room temperature and different annealing temperatures (573, 673 and 773) K. The structural measurements for PbS thin film show face-centred-cubic structure. Atomic force microscopy (AFM) was used to examine PbS surface. The films exhibit more homogeneity. The root mean square, surface roughness and average grain size were increased after annealing. The optical properties of PbS thin films are studied as a function to wavelength in region (375 - 1100) nm. The optical transmittance of PbS thin films shown that the transparency decreases with increase of annealing temperature. The direct energy gap for PbS thin film was decreases with increasing of annealing temperature for all sample due to the growth of the crystallites. The optical constants such as refractive index, extinction coefficient and dielectric constant were also calculated. [32].

Osherov et al. (2010), deposited PbS thin films onto single-crystal GaAs (100) substrate by the method of chemical bath deposition (CBD) with precursors of solution containing thiourea ($SC(NH_2)_2$), lead nitrate $Pb(NO_3)_2$ and sodium hydroxide (NaOH). Infrared transmissions and photoluminescence spectroscopy show a tuneable band gap for bulk and nanostructures as from 0.41-0.48eV when deposited on GaAs coated substrates while blue shifts in both absorbance and emission peaks of the nano-structured layers are obtained due to quantum size effects and the band gap edge respectively[27].

Chaudhary, Minakshi, et al. (2021), the influence of deposition time on structural, morphology and optical properties have been investigated systematically. The XRD analysis revealed that PbS films are polycrystalline with preferred orientation in (200) direction. Enhancement in crystallinity and PbS crystallite size has been observed with an increase in deposition time. The formation of single-phase PbS thin films has been further confirmed by Raman spectroscopy. The surface morphology analysis revealed the formation of prismatic and pebble-like PbS particles and with an increase in deposition time, these PbS particles are separated from each other without secondary growth. The data obtained from the EDX spectra show the formation of high-quality but slightly sulfur-rich PbS thin films over the entire range of deposition time studied[33].

M. M. Abbas 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^oC 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 - 1.55eV 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 and 100^oC respectively. A dense surface composed of multilayer grains of films was obtained with the crystal size around 37.67 nm [34].

Sheeba, N. H., et al. (2021), Polycrystalline nanostructured PbS thin films are deposited onto soda-lime glass substrates by the method of chemical bath deposition (CBD) at different duration of deposition time. The structure and surface morphology of the films are

characterized by X-ray diffraction (XRD) and field effect scanning electron microscopy (FE-SEM). XRD pattern exhibits polycrystalline structure with preferential orientation along (200) direction, parameters such as crystallite size, lattice constant, lattice-strain and dislocation density are calculated. The FE-SEM images show appearance of flower like structure on formation of PbS films which is indicative of suitability in gas sensing applications. Studies on optical properties carried out by UV-Vis spectroscopy measurements show bandgap in the range 1.65eV – 1.41eV. The photoluminescence spectra of the films exhibit two peaks centred at around 613 nm and 738 nm after excitation at 450 nm. Electrical studies from Hall measurements indicate the carrier concentration and mobility of the PbS samples corroborate the variations in the conductivity[35].

Puiso et al.(2002), Lead sulfide thin films were grown on (100)Si and (111)Si crystalline substrates by successive ionic layer adsorption and reaction, (SILAR), technique from solution phase at room temperature and normal pressure. The stress development, crystallinity and crystallite size, morphology and roughness and composition of the films were characterized as a function of the film thickness. The PbS thin films were polycrystalline and cubic. The residual stress in PbS was tensile and changed depending on the growth mode and thickness of the PbS films[36].

Hussain, A. et al.(2012), Nanocrystalline lead sulphide thin films were deposited on clean glass substrates by chemical bath deposition technique using lead acetate and thiourea as Pb^{+2} and S^{-2} ions source respectively. Films of five different molarities (0.05 M–0.150 M) of same pH value 10.5 were prepared at 318 K. Characterization was carried out using X-ray diffraction (XRD), X-ray fluorescence, scanning electron microscopy, optical absorption and electrical conductivity measurements. Average crystallite size calculated from the XRD spectra using Scherrer's formula were between 13 and 18 nm. The optical absorption spectra shifted towards the lower wavelength. The band gap energy of 2.13–2.44 eV was determined from the optical absorption spectra. The electrical conductivity measured using two co-planar Aluminium electrodes was found to increase with increase in temperature showing semiconducting nature of the films. The electrical conductivity at room temperature was found to be of the order of $10^{-4}\ \Omega^{-1}\ cm^{-1}$ [7]

All the above reviewed literature's revealed that almost limitation have been done so far to study of structural & optical properties of lead sulphide thin film only by using lead acetate, thourea and (NaOH) as precursors of Pb^{2+} ,S^{2-} and as complex agent by employing CBD

technique with in short time interval respectively . Currently due to its potential application and functional nature, the study on the structural and optical properties of lead sulphide has motivated the researcher. Hence in the present study lead sulphide thin film is deposited by CBD technique using sodium hydroxide (NaOH) as a complex agent in 20' ,25',30',35'and 40' deposition time ; by fixing other parameters such as temperature, concentration of solutions of lead acetate [$Pb(CH_3COO)_2.3H_2O$] and thiourea [$SC(NH_2)_2$].

CHAPTER THREE

3. Materials and Methods

3.1 Thin Film Deposition Techniques

Thin film deposition is an art of preparing a thin film onto a surface called substrate or onto previously deposited layers. Here the deposition techniques control the thin film thickness. Thin films vary in thickness from a few hundred angstroms to tens of microns. The properties and versatility of the thin films can be obtained by selecting proper technique of film deposition. Thin film deposition methods can be broadly classified as either chemical or physical methods. The difference between the chemical and physical thin film deposition methods depends upon the method of depositing thin film material on the substrate. In chemical deposition technique, fluid precursor is used which chemically react with the substrate. Since the thin film material is conducted through the fluid precursor, chemical deposition is conformal approaching the substrate without preference to a particular direction. A conformal is an uneven interface with the body and has a constant thickness on horizontal and vertical surfaces. In physical deposition technique, mechanical or electromechanical methods are used to deposit the thin films on the substrate. Materials to be deposited on the substrate depend upon the temperature, pressure and other physical conditions. In these physical methods, the thin films formed are directional on nature because particles will follow a straight path form the target to the substrate[37].

3.2. Chemical Bath Deposition (CBD) Technique

Chemical Bath Deposition technique involves controlled precipitation of a compound from the solution on a suitable substrate. This technique offers many advantages over the more established vapour phase routes to semiconducting thin films, such as CVD and spray pyrolysis. The first CBD thin films were prepared in 1884 and this method was limited to PbS and PbSe for a long time. After the deposition of CdS, a wide range of chalcogenide and chalcopyrite materials have been prepared by this method. In CBD a wide range of substrates such as ebonite, iron, steel, porcelain and brass were specifically used apart from glass. The films were uniform, adherent and able to with stand considerable friction. Around 1980, the focus of CBD films slowly turned towards solar energy applications. One of the earlier developments towards this method was in solar absorber coatings. Application in the field of solar control coatings was suggested in 1989 [38].

If you are referring to literature, you can find that PbS thin films have been prepared using Chemical Bath Deposition (CBD) technique has significant advantages over the other methods as follows[39];

I. This technique is the simplest cost effective method.

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

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

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

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

VI. An inexpensive method for large scale industrial applications

VII. The material consumption is low and minimizes the loss.

VIII. The crystallite size of the CBD films is very small.

IX. CBD unit is portable.

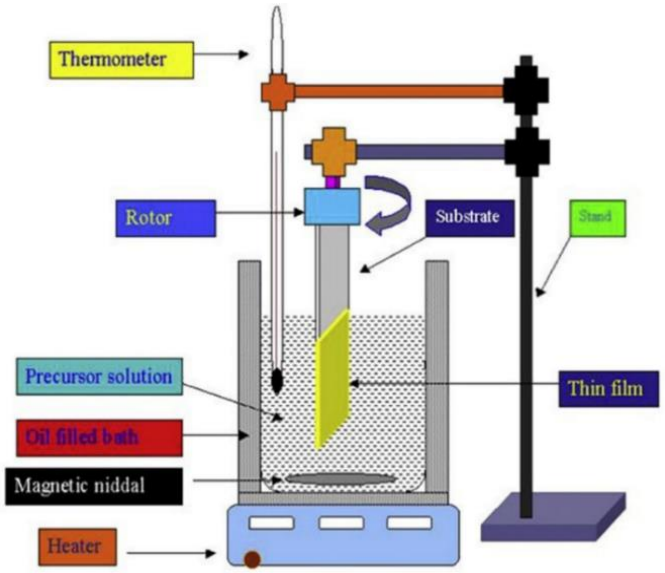


Figure 1.1 Experimental set-up of chemical bath deposition method[40].

3.3 Formation of Precipitate in the Solution

The process of precipitation involves two steps: I) Nucleation II) Growth of particle

I) Nucleation

Nucleation is the process where a new phase begins to form within a material. In the context of thin films, nucleation refers to the formation of new crystalline domains or nuclei.

The minimum number of ions or molecules required to produce a stable second phase in contact with a solution is called a nucleus. The rate at which nuclei form in a solution depends on the degree of super saturation. The rate of nucleation increases exponentially in highly supersaturated solution i.e.

$$\text{Rate of nucleation} = k(Q - S)^x \quad \text{---------- 3.1}$$

Where, Q is the concentration of solute in solution k and x are the constants and x>1.

II) Growth of particle

Once nucleation has occurred, the process of crystal growth begins, characterized by the increase in size of the existing nuclei to form larger crystalline regions. The second step is the growth of the particles already present in solution. In the case of ionic solids, the process involves the combination of cat ion and anion on appropriate sites. If the super saturation is maintained at low level throughout the process, the precipitation occurs, instead of film formation. Due to this, a large number of nucleation centres are formed, upon which growth can occur. As a result, none of the particle grows very large and a colloidal suspension consisting of finely divided solid particle is formed. Under the same circumstances, colloidal particles come together and adhere to one another. The resulting solid is called coagulation. Colloidal particles when coagulated have different properties from a crystalline solid, since the particles are arranged irregularly [41]

3.4 Factors Affecting Thin Film Deposition Process in CBD

The various factors that influence the deposition process in CBD technique. Those are nature of the substrate, bath temperature, deposition time, nature and concentration of complexing agents, nature and concentration of reactants and etc. The effect of deposition conditions on these parameters are discussed below[9].

3.4.1. Nature of the substrate

The produced thin film by CBD is known to be affected by the type of substrate employed. Nucleation of the thin film is dependent on surface defects and lattice mismatch with the

substrate. If the lattice mismatch is high, the number of nucleation site is reduced, and larger isolated particles are deposited. However if the lattice mismatch is small the number of nucleation sites increases and compact films with smaller particle are formed[42].

3.4.2. Temperature

The dissociation of complex and the anion of the 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. The thickness increases or decreases with increase in the bath temperature depending on the condition under which films are prepared. At low pH values, super saturation is high even at low temperature and increase further with increasing in temperature. This results in formation of precipitation and consequently lower thickness is obtained. At high pH values precipitation is limited due to the low super saturation and most of the product is formed on the substrate surface. Further the thermal dissociation of the complex and anion compound is increased at higher temperature so that more M and X are available for MX formation and thus higher thickness is obtained. Bath temperature has an important effect on crystal size. In most cases higher temperatures allow more grain growth whereas, lower temperatures gives very small nuclei in solution that are thermodynamically unstable. However, if the cluster is smaller than the critical nucleus size, then there is the possibility that the nucleus will re-dissolve.

3.4.3. Deposition Time

Deposition time is one of the parameter which affects thin film deposition in CBD method. The deposition time strongly influenced the preferred orientations of the crystallites as well as structural parameters such as average crystallite size, strain and dislocation density for PbS thin films. It can also affect optical band gap thin films. 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 increases with deposition time.

3.4.4 Complexing Agent

Complexing agents, also known as ligands, are typically added to the chemical bath to control the availability of the free cation through thermodynamic equilibrium. The free metal ion concentration is controlled by the formation of complex species according to the general reaction:

$$M(A)^{+2} \leftrightarrow M^{+2} + A \quad \text{---------- 3.2}$$

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:

$$K = \frac{M^{+2}[A]}{[(A^{+2})M]} -------------------- 3.3$$

Where K being the instability constant of the complex ion. The instability constant is different for different complexing agents. As the instability constant increases, more number of ions will be released.

3.4.5 Concentration of cation and anion

The increase in X compound concentration leads to an increase in X ion concentration and a film of MX with larger thickness is obtained. However, above a certain concentration when the rate of reaction becomes high and precipitation also becomes important leading to a lesser amount of MX on the substrate and hence lower the thickness. For high concentrations, the films formed are 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[9].

3.5 Characterizing Instruments

X-ray diffraction (XRD) and UV -visible spectrometer are used to study structural and optical properties of lead sulphide (PbS) thin film respectively.

3.6 Thin Film Characterization Techniques

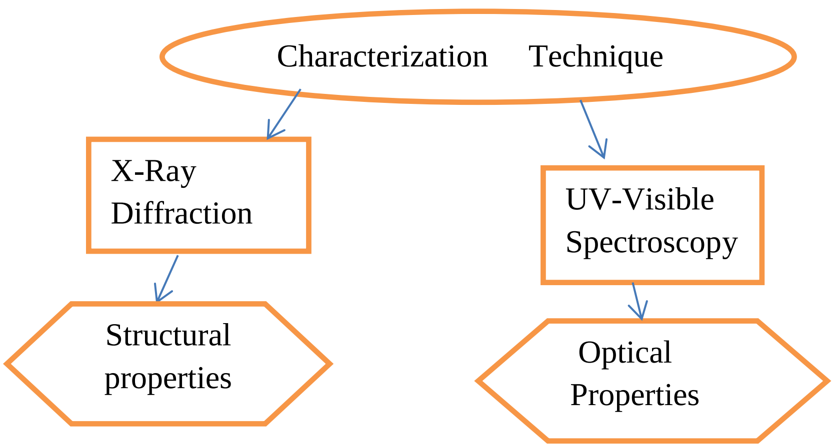


Figure 3.2 Schematic diagram of characterization technique

A wide variety of characterization techniques are used to evaluate the material quality of the semiconductor thin films. Lead sulphide (PbS) thin films have been deposited on glass substrate slide using the chemical bath deposition (CBD) technique. X-ray diffraction (XRD) is used to establish the structure and crystallite size of thin films and the optical properties, such as band gap energy, absorption spectrum of the PbS thin films were determined using UV-Visible spectroscopy.

3.6.1 X-ray diffraction (XRD)

XRD is the most common and first hand instrument used by solid-state scientists. It is a powerful method to investigate the detailed structure, composition and related properties of nano-materials. This information can be derived from peak position, intensity and the peak profile. A great advantage of X-ray powder diffraction is that it requires virtually no sample preparation, in comparison to the techniques. The sample can be either in the form of smear or compact flat pack or a capillary and is exposed to monochromatic beam of X-ray and the diffracted beam intensity is collected in a range of angles (2θ) with respect to the incident beam. The intensity corresponding to a constructive interference of the diffracted beam from a crystallographic plane is observed as peak, corresponding to the Bragg angle; when x-rays are scattered from a crystal lattice, peaks of scattered intensity are observed. Therefore the possible 2θ values where we can have reflections are determined by the unit cell dimensions. However, the intensities of the reflections are determined by the distribution of the electrons in the unit cell. The highest electron density is found around atoms. Therefore, the intensities depend on what kind of atoms we have and where in the unit cell they are located. Planes going through areas with high electron density will reflect strongly, planes with low electron density will give weak intensities[43].

1. The angle of incidence = angle of scattering.
2. The path length difference is equal to an integer number of wavelengths.

$$n\lambda = 2d \sin\theta \quad ---------- \quad 3.4$$

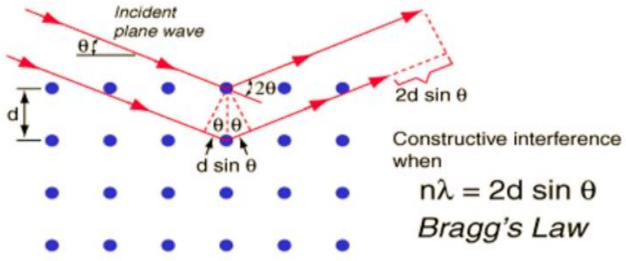


Figure 3.3 X-ray diffraction from plane[44].

And lattice constant a; $a = d\sqrt{h^2 + k^2 + l^2}$ ---------- 3.5

where d is inter planer spacing, n is order of diffraction, λ is wave length of x-ray, θ is Braggs angle and h, k &l are miller index of plan. In all other angles a back ground is obtained. The intensity corresponding to background has several origins. The breadth of the peaks in an X-ray diffract organ provides a way to determine the average crystallite grain size, assuming no lattice strain or defects, through the Debye-Scherer formula[45];

$$D = \frac{K\lambda}{\beta_{2\theta}\cos\theta} \text{ ---------- } 3.6$$

Where D is the size of the crystal, λ is the wavelength of the X-rays, β is the full width at half maximum of the diffraction peak, θ is the Braggs angle of the peak and K is the constant known as the shape factor, taken as 0.94. The origin of strain is related to lattice disorder which in turn depends upon the growing conditions of the films. The lattice strain (ε) is calculated using the relation[46]

$$\varepsilon = \frac{\beta\cos\theta}{4} \text{ ---------- } 3.7$$

The dislocation density (δ), is a linear defect within a crystal lattice that represents a departure from perfect crystal order. It involves the misalignment of atoms along a line within the crystal and calculated using Williamson's and Smallman's formula[47].

$$\delta = \frac{n}{D^2} \text{ ---------- } 3.8$$

where δ is the measure of the amounts of defects in a crystal[48] and n is a factor which equals a unity for a minimum dislocation density and D is the crystalline size . Strain and dislocation density were calculated from the most intense peak of the X-ray diffraction pattern for each PbS thin films deposited at different lead deposition time. Since dislocation density and strain are the manifestation of dislocation network in the films, the decrease in dislocation density indicates the formation of high quality films[49].

3.6.2 UV-VIS Spectrophotometer

In order to determine the optical properties such as optical absorption spectrum and energy band gap optical spectrophotometer is used. The instrument consists of light source with monochromatic sample reference part and the detecting system. A light of selected

wavelength is passed through the sample. There is a provision to select a range of wavelengths in the light coming from the lamp using the monochromatic. Then a particular wavelength based on the requirements was selected and passed through the rotating mirror, which directs the light beam alternatively through the sample and reference[50]. The two beams that strike the detector provide a measure of the amount of light absorbed or transmitted by the sample. When light passes through or is reacted from a sample, the amount of light absorbed is the difference between the incident radiation (Io) and the transmitted radiation (I). One can determine the absorbance of the sample by measuring the intensity of light reaching the detector after passing through the sample and comparing to the reference sample. The transmitted intensity is given by Beer's law equation[51];

$$I = I_0 exp^{-\alpha t} \quad ---------- 3.9$$

Where Io is the intensity of the incident ray at a given wavelength, I is the transmitted light intensity, α is the absorption coefficient and t the thickness of the sample.

Band gap energy of the thin films can be derived from mathematical treatment of data obtained from optical absorbance using Stern relationship at near-edge absorption calculated [52]. For a given thin film, we can plot $(hvA)^2$against photon energy hν.

$$AhV = k[(hV - Eg)]^{n/2} \quad ----------3.10$$

Where A is absorbance, the value of n is either 1 for direct allowed transition or 3 for direct forbidden transition and also n is either 4 for indirect allowed transition or 6 for indirect forbidden transition; k is constant; planks constant (h), frequency (ν) and band gap energy (Eg). The optical bandgap Eg is determined by extrapolating the linear portion to the x-axis where $(hvA)^2 = 0$ .The intercept on the photon energy axis will give the bandgap energy of the thin film.

3.7 Experimental Procedures

3.7.1. Material used to produce lead sulphide thin film

Thin films were deposited in laboratory of Hawassa university physics department. Equipment used is glass substrate, beaker, water distiller, flask, magnetic stirrer, magnetic stirrer rod, glove, different measuring cylinder and electronic balance.

Lead acetate ($Pb(CH_3COO)_2.3H_2O$), thiourea ((NH2)2CS, FINKEM), sodium hydroxide (NaOH, AVICHEM) and distilled water are chemicals used for deposition of PbS thin film on CBD method.

3.7.2 Reagents/ Chemicals used for synthesis PbS Thin Film.

Lead sulphide thin films were deposited on glass substrate by the chemical bath deposition method.

The chemicals used for the film preparation, as well as their source and percentage purity are explained as follows;

- 10ml of 0.2M lead acetate [$Pb(CH_3COO)_2.3H_2O$], (percentage purity =99.5 %)
- 10ml of 0.2M thiourea [$SC(NH_2)_2$], (percentage purity =99 %)
- 10ml of 0.6M sodium hydroxide (NaOH),and (percentage purity =98 %)
- 35ml of distilled water (H_20)

  Total of 65ml at 80^0c temperature for each sample.

- Thiourea and Leads acetate are used as source of sulphide ion (S^{2-}) and lead ion (Pb^{2+}) respectively ; NaOH used as complexing agent.

3.7.3. Reagents solution preparation.

A separate preparation of appropriate solutions of the starting reagent is very important and were prepared using distilled water and carefully measured.

• Preparation of 0.2M lead acetate.

Mass = concentration x volume x molar weight x percentage purity.

0.2x0.25x379.34x0.995=18.872gram

To prepare 0.2M of lead acetate dissolving by 18.872 g of ($Pb(CH_3COO)_2.3H_2O$) in distil water. The solution was then topped up to the 250ml mark with distilled water and thoroughly shaken to dissolve the salt completely.

- **Preparation of 0.2M thiourea.**

Mass = concentration x volume x molar weight x percentage purity.

0.2x0.25x76.12x0.99=3.7679gram

Thiourea was prepared by dissolving 3.7679 g of $(NH_2)_2$ CS in the distil water. The solution was then topped up to the 250ml mark with distilled water and thoroughly shaken to dissolve completely. The resulting solution had a concentration of 0.2M of $(NH_2)_2$ CS.

- **Preparation of 0.6M sodium hydroxide**

Mass = concentration x volume x molar weight x percentage purity.

0.6x0.25x40x0.98=5.88gram

By dissolving 5.88 g of NaOH in distil water. The solution was then topped up to the 250ml mark with distilled water and thoroughly shaken to dissolve the salt completely. The resulting solution had a concentration of 0.6M NaOH.

3.7.3. Substrate Cleaning

Substrate cleaning plays an important role in formation of smooth, uniform and well adherent thin film. Microscope glass slides were used as substrates for the deposition of PbS thin films. The microscope glass slides were degreased in diluted nitric acid overnight for 12:00 hours and then washed with ordinary water by soapsuds for 5 minutes. Finally the substrates cleaned with distilled water and dried under ambient conditions before being used for the deposition. Since extreme cleanliness is required as in order to remove the common contaminates such as dust particles, absorbed water contents, other deposits and also cleanliness of the substrate is required for the chemical deposition as the contaminated surface provides nucleation sites facilitating growth resulting into non-uniform films with different orientation and impurities.

3.7.4. Synthesize of PbS Thin Films

Nearly on microscope glass substrates which are cleaned as the procedure described above were used for the deposition of PbS thin films. The chemicals used were lead acetate Trihydrate, ($Pb(CH_3COO)_2 \cdot 3H_2O$), as the source of lead ions and thiourea ($CS(NH_2)_2$) which provided sulphur ions. Sodium hydroxide, (NaOH) were used as a complexing agent of the chemical bath. All the chemicals used were of analytical grade. That means 10ml of 0.2M Lead acetate and 10ml of 0.2M thiourea are used as a source of cations (Pb^{2+}) and anions (S^{-2}), respectively in each of 250ml flask and 10ml of 0.6M Sodium hydroxide (NaOH) used as a complexing agent to facilitate reaction of the chemical bath with 35ml of distilled water having total volume of 65ml.

$Pb(CH_3COO)_2 + 2NaOH \rightarrow Pb(OH)_2 + 2CH3COONa$

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

$Na_4Pb(OH)_6 \rightarrow 4Na^+ + HPbO_2^- + 3OH^- + H_2O$

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

$HPbO^-_2 + SH^- \rightarrow PbS + 2OH^-$

The film growth is achieved through the complex-decomposition process according to the above reactions [53]

The mixture for the bath was prepared by mixing an appropriate amount in a 100 ml beaker. The cleaned substrates were immersed vertically into the Mather solution with the help of a substrate holder. The reaction mixture was continuously stirred with a magnetic stirrer and maintained at a temperature of 80 ^{0}C for deposition. For the first 3 min of reaction time, the solution remained transparent turned to milky colour, indicating the occurrence of decomposition reactions. After 5 min, the solution turned dark brown, indicating the formation of PbS and deposit onto the sides of the beaker and the substrate confirming the formation of PbS. Five samples were prepared with deposition times of 20, 25, 30, 35 and 40 minutes. After completion of each deposition time, samples were removed from the solution, rinsed ultrasonically with distilled water and dried under ambient conditions. Mirror-like brownish thin film surfaces were obtained. Finally all samples were taken to annealed at a temperature of 200^{0}c for 1:30 hours before characterizing the thin film ; since annealing thin films offers several advantages that are crucial for optimizing thin film performance in various applications like improved crystallinity, reduced defects, enhanced electrical and optical properties of thin film[32, 54]. All deposited PbS thin films were mirror-like with a brown colour, homogeneous, well adherence, and specula reflecting.

Figure 3.4. Experimentally produced thin film and optical characterization device in physics laboratory at Hawassa University.

CHAPTER FOUR

4. RESULT AND DISCUSSION

4.1. Structural analysis

The crystallographic structure and microstructural parameters of PbS thin films were analysed with a Shimadzu corporation powder X-ray diffractometer with a Cu-kα radiation (λα = 1.5406 Å) source over the diffraction angle 2θ between 10^{O} and 80^{O}. The machine was operated at 30 mA and 40 KV.

The X-ray diffraction patterns of five samples with different deposition time prepared at bath temperature 80^{o}c are shown in Figure 4.1. The observed d-spacing and the respective prominent peak correspond to reflection (111), (200), (220), (311), (222), (400), (331), (420) and (422) planes, are in good agreement with the standard PDF'S Card No: 00- 005–0592 for pure PbS. Therefore, it has been suggested that the deposited PbS thin films are nanocrystal in nature with cubic structure and the most intense peak at (200) comparison with the other for all deposition time. This indicates that the orientation of the crystal growth is preferably along (200) direction. Thin films often exhibit preferred orientation, where certain crystal planes are more aligned than others. This alignment affects the relative intensity of different diffraction peaks and the same result has been reported by Sheeba, N. H., et al. [35] and Puiso et al [36]. It is also noticeable from the XRD pattern that the peaks of deposited films indexed as all (hkl) are even or odd and sequential (i.e. a pair of peaks are followed a single peak, which is again followed a pair of peaks and continuous periodical). This confirms typical characteristics of FCC structure[55]. No impurity peaks were detected in the XRD diffraction; suggesting high purity of the prepared PbS film. The sharpness of the peaks in the X-ray diffraction pattern reveals the good crystallinity of the films and also confirms the stoichiometric nature of the PbS films the same result was reported by Fekadu Gashaw, et al.[29, 56].

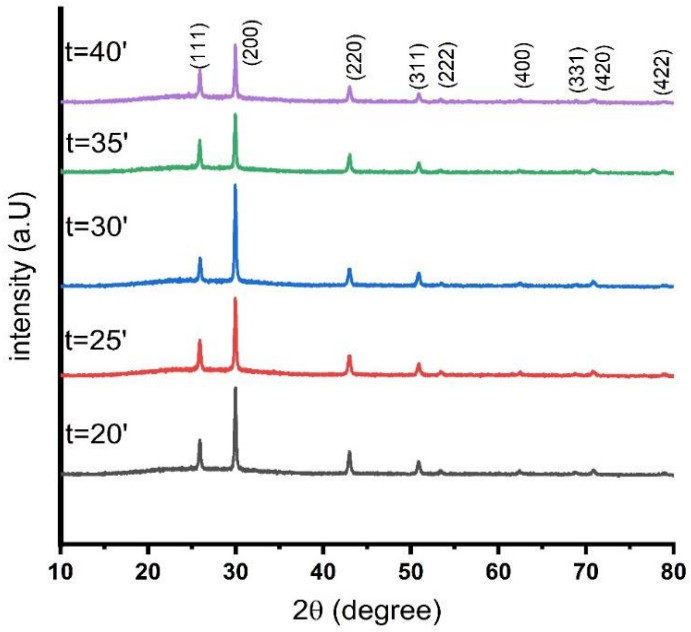


Figure 4.1 Merged XRD patterns of PbS thin films prepared at different deposition time.

The lattice constant (a) of the sample was calculated using the relation (a); $a = d\sqrt{h^2 + k^2 + l^2}$ (see equation 3.5).The calculated average value of the lattice constant were ($a = 5.95A^O$) of the films show a slight deviation from its standard value ($a = 5.93A^0$). The deviation of the calculated lattice constant from the bulk sample value mentioned above, shows that the crystallites may be under some strain; thin films often experience mechanical strain due to lattice mismatches between the film and the substrate[42]. The Crystallographic lattice parameter result were tabulated as table 4.1

Table 4.1 Crystallographic parameters of PbS thin films obtained from XRD analysis

Time (min)	Bragg angle 2Θ in (degree)		FWHM (degree)		d-spacing in (A^O)		Lattice parameter in (A^O)	
	calculated	Observed	calculated	Observed	calculated	Observed	calculated	Standard
20	29.969	29.9873	0.2581	0.2064	2.979	2.977	5.95	5.93
25	29.972	29.9909	0.2747	0.2159	2.978	2.977	5.95	5.93
30	29.967	29.9867	0.2587	0.2128	2.979	2.977	5.95	5.93
35	29.959	29.9793	0.2761	0.2304	2.980	2.978	5.96	5.93
40	29.972	29.9919	0.2290	0.2007	2.978	2.977	5.95	5.93
				Average	2.979	2.977	5.95	5.93

The crystallite size (D) was calculated from the most intense peaks which is (200) plane on X- ray diffraction pattern, because it provides a clearer, more accurate signal, making it more suitable for precise measurements of peak width, crystal size, and dislocation density. This peak typically represents a dominant crystallographic plane and minimizes issues related to peak overlap and background noise for XRD calculations using the Scherer (1918), formula as $D = \frac{k\lambda}{\beta\cos\theta}$ (see equation 3.6). The crystallite size of the films increased with deposition time from 33.273nm for a deposition time of 20 minutes, to 37.504nm for a deposition time of 40 minutes the same result is reported by M. M. Abbas et al.[34].

The micro strain value (ε) of the deposited PbS thin films were evaluated by using the mathematical relation as equation $\varepsilon = \frac{\beta\cos\theta}{4}$ (see equation 3.7) Where θ and β are as defined in equation 3.3 and the dislocation density (δ) which is a measure of the defects in the film, and this was calculated by using Williamson and Stallman's formula $\delta = n/D^2$ (see

equation 3.8), Where n is a factor, which equals one for a minimum dislocation density and D is the crystalline size. Strain and dislocation density were calculated from the most intense peak of the X-ray diffraction pattern for each PbS thin films deposited at different deposition time. The results are tabulated in Table 4.2.

Table 4.2 The relations of FWHM, crystallite size, dislocation density, micro strain and band gap energy of PbS thin film

Time	Miler indices	FWHM	Crystallite size	Dislocation density	Micro strain	Band gap energy
T	Plane	β	D	$\delta \times 10^{14}$	$\varepsilon \times 10^{-4}$	Eg
Mi	(h k l)	Degree	(nm)	(lines/m^2)	($line^{-2}m^{-2}$)	eV
20	2 0 0	0.2581	33.273	9.03	10.88	1.62
25	2 0 0	0.2747	31.264	10.23	11.58	1.61
30	2 0 0	0.2587	33.201	9.07	10.90	1.55
35	2 0 0	0.2761	31.105	10.34	11.64	1.54
40	2 0 0	0.2290	37.504	7.11	9.65	1.51

From table4.2, it can be observed that the dislocation density, strain and band gap energy decreases with increasing crystallite size and Vis versa. Since dislocation density and strain are the manifestation of dislocation network in the films, the decrease in dislocation density indicates the formation of high quality thin films. As the dislocation density is the measure of the defects in the crystalline structure, the smaller value of δ obtained for the film deposited at 40 minutes, suggests the film has a comparatively higher degree of crystallinity the same result was reported by Fekadu Gashaw, et al. [29].

4.2 Optical analysis

4.2. 1.Absorbance

The study of optical absorption is important means of determining the band structures, and band gap energy (Eg) of thin film. PbS thin film were investigated by measuring the absorbance of the thin film using T80 UV/VIS spectrometer in the wavelength range of 200nm__800nm.The absorption spectra of PbS thin films the spectrum typically shows

peaks or edges where the absorbance increases, indicating electronic transitions were takes place within the film. Due to its narrow band gap, PbS exhibits strong absorption in the infrared region of the electromagnetic spectrum[57]. This makes it suitable for applications such as infrared sensors and imaging devices. The fundamental absorption edge of the PbS films, which corresponds to electron excitation from the valance band to conduction band, can be used to determine the nature and value of the optical band gap energy of the thin film[32]. From the figure 4.2 below indicates that PbS thin film have high absorbance in the visible region of wave length 500nm-750nm; that visible spectrum of light is made strong absorption in the visible and sub-bandgap regime of the NIR range of the spectrum their electronic structure and band gap are well-matched to the energies of photons at wavelength range 500nm to 750nm with red (bathochromic)-shift that the edge moves to longer wavelengths (lower photon energy). Here, the wavelengths of absorption increase. This could happen due to a decrease in the bandgap energy of a thin film [33].

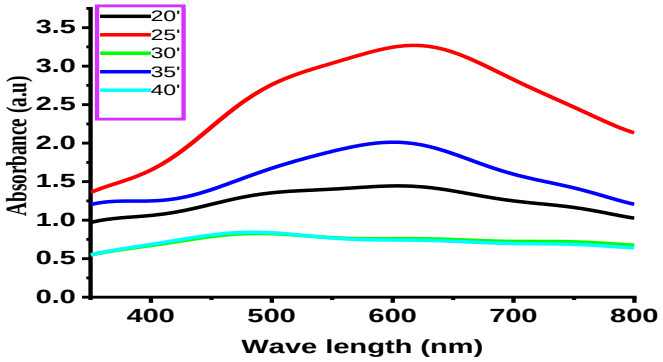


Figure4.2 Absorbance vs wavelength plot of the PbS thin films at different deposition time.

4.2.2 Determination of the Optical Band gap energy

The energy band gap and transition type was derived from mathematical treatment of data obtained from optical absorbance versus wavelength with the Stern (1963), relationship of near-edge absorption $AhV = k[(hV - Eg)]^{n/2}$ (see equation 3.10), Where V is the frequency, h is the Planck's constant, k is a constant while n carries the value of either 1 for direct transition or 4 for indirect transition. PbS is a direct band gap material[18], thus n is taken as 1. The energy band gap is obtained by extrapolating the linear portion of $(Ahv)^2$ versus hv to the energy axis at $(Ahv)^2 = 0$. The linear nature of the plot of $(Ahv)^2$ versus hv shown in fig. 4.3(a- e) verifies the presence of a direct transition.

The plot of variation of the energy band gap (eV) with deposition time (min) and it revealed that the band gap energy of the thin film at 20', 25', 30', 35' and 40' are 1.62eV, 1.61eV, 1.55eV, 1.54eV and 1.51eV respectively .This optical band gap shows a decreasing trend, as deposition time increases but it is higher than the bandgap of bulk value attributed to quantum size effects,[29, 30, 58].

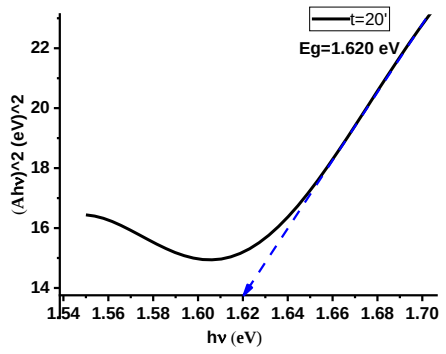


Figure 4.3 (a)

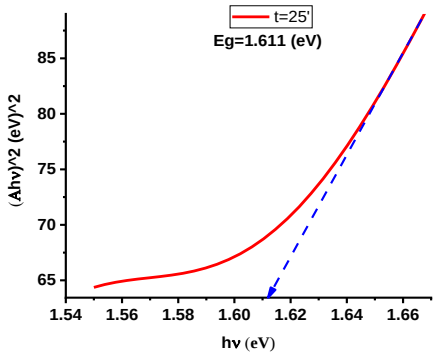


Figure 4.3 (b)

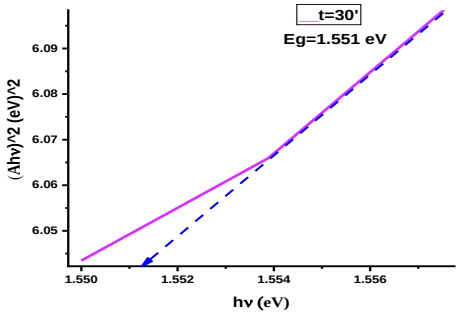


Figure 4.3 (c)

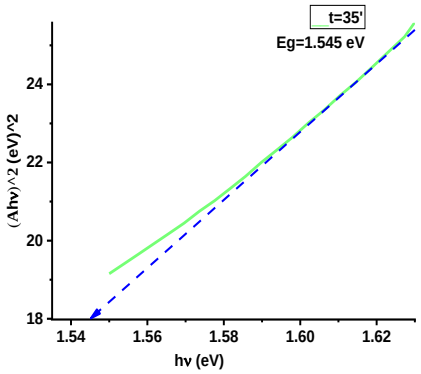


Figure 4.3 (d)

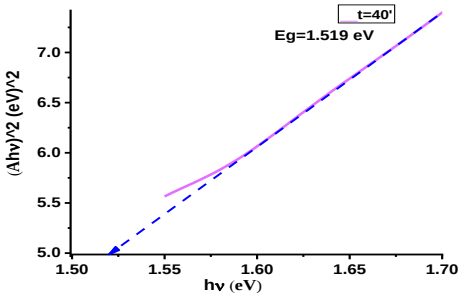


Figure 4.3 (e)

Figure 4.3(a-e) the band gap energy for PbS thin film as different deposition time.

CHAPTER FIVE

5. CONCLUSION AND RECOMMENDATION

5. 1 CONCLUSION

In this study, PbS thin films were successfully deposited on glass substrates using the chemical bath deposition (CBD) method. The process involved lead acetate, thiourea and sodium hydroxide, as precursors and complexing agent, with the bath maintained at a temperature of 80°C for varying deposition times (20, 25, 30, 35, and 40 minutes). Following deposition, the films were annealed at 200°C for 90 minutes. The influence of deposition time on the structural and optical properties of the films was thoroughly investigated. X-ray diffraction (XRD) analysis revealed that the PbS films exhibited a face-centred cubic (FCC) crystal structure, with diffraction peaks corresponding to the (111), (200), (220), (311), (222), (400), (331), (420), and (422) planes. The films showed a preferred orientation along the (200) plane, and as deposition time increased, the crystallite size also increased from 33.27 nm to 37.50 nm, indicating more ordered atomic arrangement. UV-Vis spectroscopy results demonstrated strong absorbance in the visible region (500 nm to 750 nm), with the optical band gap decreasing from 1.62 eV to 1.51 eV as deposition time increased. The higher optical band gap of the films compared to the bulk material can be attributed to quantum size effects, which become more pronounced when the film thickness approaches or is smaller than the exciton Bohr radius.

5.2 Recommendation

Although the deposition process was successful, there are still areas that warrant further investigation:

1. **Electrical Characterization**: A detailed study of the conductivity and resistivity of PbS thin films is needed to better understand their electrical properties.
2. **Morphological Characterization**: Additional research on the morphological properties of the PbS thin films, such as surface texture and grain structure, would provide a more comprehensive understanding of the material's behaviour and performance.

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Appendix

Data file for PbS, observed on XRD PDF'S

Name and formula

Reference code: 00-005-0592

Mineral name: Galena, syn

Compound name: Lead Sulfide

PDF index name: Lead Sulfide

Empirical formula: PbS

Chemical formula: PbS

Crystallographic parameters

Crystal system: Cubic

Space group: Fm-3m

Lattice Parameter value (angstrom/degree)

a= 5.93

b =5.93

c =5.93

Alpha =90.0000

Beta =90.0000

Gamma =90.0000

Observed density (g/cm^3): 7.60

Calculated density (g/cm^3): 7.52

Observed Volume of cell (10^6 pm^3): 208.52

Calculated Volume of cell (10^6 pm^3): 210.64

Photos of how to prepare and one simple applications of PbS thin film