INFLUNCE OF DEPOSITION TIME ON THE STRUCTURAL AND OPTICAL PROPERTIES OF CdS THIN FILMS SYNTHESIZED BY CHEMICAL BATH DEPOSITION (CBD)

MSc THESIS

BY

NEGASH HERAMO

ADVISOR; Dr. ABEBE GETACHAW

NOVEMBER, 2024

HAWASSA, ETHIOPIA

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A THESIS SUBMITTED TO THE DEPARTMENT OT PHYSICS COLLEGE OF NATURAL AND COMPUTATIONAL SCIENCE, SCHOOL OF GRADUATE STUDIES HAWASSA UNIVERSITY, IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF MASTER OF SCIENCE IN PHYSICS (SOLID STATE PHYSICS)

PRINCIPAL ADVISOR: Dr. ABEBE GETACHEW

NOVEMBER, 2024

HAWASSA, ETHIOPIA

DECLARATION

I hereby declare that this M.Sc. thesis report is my original work and has not been done for the degree in any university, and all source of material used for this work have been duly acknowledged.

Name:_____

Signature_____

Date_____

HAWASS UNIVERSITY

SCHOOL OF GRADUATE STUDIES

ADVISORS' APPROVAL SHEET I

This is to certify that the thesis entitled **"Influence of deposition time on structural and optical properties of CdS thin films synthesized by chemical bath deposition (CBD)"** submitted in partial fulfillment of the requirement 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 **Negash Heramo** Id. No. **GPPhys K/011/11**, under our supervision. Therefore, we recommend that the student has fulfilled the requirements and hence hereby can submit the thesis to the department for defense.

Name of Major Advisor	Signature	Date
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Name of Co-Advisor	Signature	Date
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We undersigned, members of the Broad of Examiners of the final open defense by **Negash Heramo** have read and evaluated his/her thesis entitled **"Influence of deposition time on structural and optical properties of CdS thin films synthesized by chemical bath deposition (CBD)"** and examined the candidate. This is, therefore, to certify that thesis has been accepted in partial fulfillment of the requirements for the degree.

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

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ABSTRACT

CdS thin films were deposited on the glass substrates by using chemical bath deposition method (CBD) at temperature of 80^0C. The effect of deposition time on the structural and optical properties of CdS thin film was studied. The bath containing 3CdSO4.8H2O, CS(NH2)2, distilled water and ammonia(25%) as starting materials. Five samples were deposited for different deposition time (30, 40, 50, 60 and 70) min. The structural and optical properties of CdS thin films were investigated using X-ray powder diffraction (XRD), and ultraviolent visible (UV-vis) spectroscopy respectively. It was confirmed from X-ray diffraction analysis that all the structures are with (111) plane as a preferred orientation, confirms CdS thin films are cubic structure formed and peaks (101) plane showed the formation of hexagonal structure. Hence, the CdS thin films have the mixed structure phase. The crystal structural parameters such as crystal size, micro strain, dislocation density were calculated and the results confirmed that the deposition time had visible influence on the structural parameters. CdS thin films calculated a crystallite size in the range of (10.47-13.34nm) with the deposition time of (30-70min). The UV-Visible spectroscopy study showed that the optical band gap energy for CdS thin films were find to be in the range of (1.89-1.64ev).

CHAPTER ONE

INTRODUCTION

1.1 Semiconductor

Semiconductors are the materials which have a conductivity between conductors (generally metals) and non-conductors or insulators (such ceramics). The valence band of a semiconductor is full similarly to that of an insulator, but the band gap is much smaller (about 1ev compared to about 5ev). In fact the band gap in several semiconductors is so small that electrons are easily able to be thermal excited in to the conduction band [1]. This means that the electrical conductivity of many semiconductors is strongly reliant on temperature. Even though conductivity is not dependent only on the number of free electrons, materials with less than one electron per million will not easily be able to conduct electricity. To have practical uses for semiconductor, the conductivity must be able greatly increase and raising the temperature is not a very reliable to achieve this goal. However it is accompanied by doping (adding a very small amount of other atoms in with semiconductor), which increases conductivity by adding either electron or holes to a semiconductor [2].

Semiconductors are the basic building block of modern electronics ,including transistors ,solar cells light emitting diodes (LEDs)[2],and digital analog integrated circuits. The modern understanding of the properties of a semiconductor lies on quantum physics to explain the movement of electrons and holes inside a crystal structure and also in a lattice. An increased knowledge of semiconductor materials and fabrication processes has made possible continuing increases in the complexity and speed of microprocessors. Semiconductor devices can display arrange of useful properties such as passing current more easily in one direction than the other, showing variable resistance ,and sensitivity to light or heat. Because the electrical properties of semiconductor material can be modified by controlled addition of impurities or by the application of electrical fields or light, devices made from semiconductors can be used for application, switching and energy conversion. Current conduction in a semiconductor occurs through the movement of free electrons and holes, collectively known as charge carriers. Electron-hole pairs generated in CdS are well separated with electrons being highly localized

copper impurities behaves as acceptor in CdS, change the resistivity ,band gap energy ,photoelectrical properties and types of semi-conductivity (n-type to p-type). Many methods used such as wet chemical method[3, 4],chemical synthesis method .Chemical route method[5] ,chemical precipitated method[6] ,microwave assisted method[7] ,wet chemical route method[8] are used for the synthesis of chemical bath deposition(CBD)[9] CdS thin films .

1.1.1. Compound semiconductor

Compound semiconductors represent the largest group and are formed as a result of the chemical reaction between two or more different elements. Examples are gallium arsenide (GaAs), indium phosphide (InP). Compounds formed from the elements of group III to V of the periodic table (such as GaAs) have properties similarities to their group IV counterparts. In going from the group III elements to the group III -V compounds, the bonding becomes partly ionic due to transfer of electronic charge from the group III atom to the group V atom. The iconicity causes significant changes in semiconductor properties. It increased the Coulomb interaction between the ions and also the energy of the fundamental gap in the electronic band structure. Iconicity becomes even large and more important in the group II to VI compounds such as zinc sulphide (ZnS). As a result, most of the group II-VI compounds semiconductors have band gaps larger than 1ev. Exceptions are the compounds containing the heavy element mercury (Hg). Mercury telluride (HgTe) is actually a zero band gap semiconductor (or a semimetal) similar to gray tin. While the large band gap group II-VI compounds semiconductors have potential applications for displays and lasers, the smaller band gap group II-VI semiconductors are important materials for the fabrication of infrared detectors [10].

1.2. Statement of the Problem

CdS thin film has a great importance in technological application due to its remarkable physical and chemical properties. Currently, intensive research work is conducted to obtain better performing CdS based thin film materials. From intensive literature survey, it is identified that by the variation of deposition time on the CdS thin film, and producing CdS in thin films scale level, important modification in structure, as well as optical properties can be obtained. In this connection, CdS thin films were synthesized by chemical bath deposition method. Comparison

investigations on the structural and optical properties of the synthesized samples were investigated using different characterization techniques.

1.3. Objectives of Research

1.3.1 General Objective

General objective of this research is to study the effect of time variation on the structural and optical properties of CdS thin films synthesized by chemical bath deposition method.

1.3.2 Specific Objectives

The specific objective of this research is

- To synthesis CdS thin films using chemical deposition method
- To investigate the effect of deposition time on structural properties of CdS thin films.
- To investigates the effects of deposition time on the optical properties of CdS thin films

1.4. Significance of The study

In this research, CdS thin films were prepared by chemical bath deposition method. The main contribution of this study was to give a clear picture on structural and optical properties of CdS thin films at different deposition time. Thus, this finding was hopefully providing useful information about the synthesized materials. It can also contribute to future work in the same field of study.

1.5 Thesis Structure

The thesis is structured in to five chapters. The first chapter deals with some introduction about Semiconductor materials, their classification, Objectives of the work, justification of the study and significance of the study. The second chapter deals properties of CdS thin films, application of CdS, thin film and review of literature CdS thin film. In the third Chapter methodology and characterization techniques of thin films are discussed. And also Chemical bath deposition techniques are briefly explained which is followed by discussing important conditions for films. Experimental procedures are discussed in this chapter and explain the details of preparation mother solution. The fourth chapter deals with results and discussion. The final chapter deals conclusion and recommendation

CHAPTER TWO

2. REVIEW OF LITERATURE

2.1 Thin Film Materials

Although the study of thin film phenomena dates back well over a century, it is really only over the last four decades that they have been used to a significant extent in practical situations. The requirement of micro-miniaturization made the use of thin and thick films virtually imperative. The development of computer technology led to a requirement for very high-density storage techniques, which has stimulated most of the research on the magnetic properties of thin films. Many thin film devices have been developed, often finding themselves looking for an application or, more importantly, a market. In general, these devices have resulted from research into the physical properties of thin films [24]. Additionally, fundamental research has led to a dramatic improvement in understanding thin films and surfaces.

Thin films are particles (crystalline or amorphous) of organic or inorganic materials, with sizes in the range of 1–100 nm. Thin films are regarded as two-dimensional materials fabricated through the condensation of atoms, molecules, or ions [29]. This unique fabrication process makes them exhibit properties arising from changes in their physical dimensions, geometry, and microstructure [28]. These properties, combined with their large surface-to-volume ratio, make thin films highly useful across various applications, including nonlinear optics, luminescence, electronics, catalysis, solar energy conversion, and optoelectronics.

The solar energy sector exemplifies the application of thin films, with various types of thin-film solar cells, including crystalline silicon, amorphous silicon, gallium arsenide, polycrystalline copper indium gallium diselenide (CIGS), and polycrystalline cadmium telluride (CdTe)[11]. Cadmium sulfide (CdS), in particular, has been widely used as a window layer in photovoltaic devices [12, 13]. CdS is a group II-VI semiconductor, and its nanoparticles exhibit unique size-dependent chemical and physical properties [15], such as intrinsic n-type conductivity caused by sulfur vacancies due to excess cadmium atoms [23]. These properties enhance the electronic, electrical, and optical characteristics of devices and make CdS an essential material for hetero-junction solar cells and photoconductive devices [14, 15].

Semiconductor materials exhibit a range of unique properties owing to their electronic structure. They can be fabricated in bulk, wafer, or thin-film forms. A semiconductor is said to be in thin film form only when it is built up as a thin layer on a solid support (substrate) through controlled condensation of atomic, molecular, or ionic species [27]. Thin-film semiconductors possess high optical absorption coefficients, allowing light to be absorbed by layers as thin as a few micrometers, and their electrical properties can be controlled over a broad range. These characteristics have led to their use in various optoelectronic devices, such as optical coatings, solar cell windows, electro-optic modulators, photoconductors, and field-effect transistors [2, 21, 22].

A variety of thin-film deposition techniques are available for producing high-quality thin films of CdS. These include spray pyrolysis, evaporation, sputtering, chemical vapor deposition (CVD), chemical bath deposition (CBD), and electro-deposition [28]. Each method produces films with different crystal structures, grain sizes, and structural defects. Among these, chemical bath deposition is particularly economical, simple, and time-efficient, with minimal chemical wastage. This method was employed in the present work to synthesize CdS thin films and study their structural, morphological, and optical properties.

The intense interest in thin-film technology arises from its potential for reducing costs, minimizing material consumption, and enabling innovative applications [30]. CdS, as one of the most interesting II-VI semiconductors, continues to gain attention for its optical, electrical, and optoelectronic properties. Thin-film technologies play a pivotal role in advancing renewable energy solutions and addressing environmental challenges. Moreover, nanotechnology applications of thin films extend to fields like biology and medicine, including protein purification, drug delivery [16], medical imaging [17], fluorescent biological labeling [18], pathogen detection [19], and separation and purification of biological molecules [20].

In recent years, semiconductors, especially those in the II-VI class, have gained importance due to their optoelectronic properties and potential applications [31]. CdS remains a critical material for advancing technologies in solar energy and other areas, providing a promising future for thin-film-based devices

2.2. Structures Of CdS Materials

Hexagonal CdS: Cadmium sulfide(CdS) is a semiconductor material that exhibits unique structural properties, making it significant in various applications, such photovoltaic, photodetectors, and optoelectronic devices[32].

The primary crystal structure of CdS is the wurtzite structure, which crystallizes in the hexagonal $P6_3mc$ space group. In this configuration, cadmium ion (Cd^{2+}) are tetrahedrally coordinated to sulfer ion (S^{2-}), forming corner-sharing CdS4 tetrahedra. This arrangement results in a stable and robust lattice structure that contributes to the material that contributes to the material's electronic and optical properties, including a direct band gap of approximately 2,42eV at room temperature, which is essential for light absorption and emission process in semiconductor applications.

Cubic CdS: Cadmium sulfide (CdS) primarily crystallizes in the zincblend structure, which is atype of cubic lattice. In this structure, CdS forms a face centered cubic(FCC) arrangement were Cadmium ions (Cd2+) and sulfur ions (S2-) occupy tetrahedral sites. Each unit cell of the sincblend structure contains four formula units of CdS, with two interpenetrating FCC sub lattices: one for Cd and other for S. The lattice parameter for CdS in this Cubic form is approximately 0.582nm, which has been confirmed through X-ray diffraction studies. This cubic arrangement contributes to the semiconductor properties of CdS making it suitable for various electronic applications such as solar cells and photo detectors. The electronic properties of zincblende structure are characterized by a direct band gap typically around 2.42eV at room temperature. The direct band gap allows for efficient absorption and emission of light which is crucial for electronic devices. The ban structure calculations indicate that conduction band minimum and valance band maximum occur at the same momentum value enhancing its applicability. This form of CdS has a cubic crystal structure and is often used in thin-film applications, such as in the production of thin film transistors or solar cells[32].

Amorphous CdS: This type of CdS has a disordered, non-crystalline structure. It is used in a variety of applications, including as a buffer layer in thin-film solar cells and as a pigment in paints and plastics[33].

2.2.1. Applications Of CdS materials

Thin-film CdS is commonly used in a variety of electronic and optoelectronic devices, such as solar cells, photo-detectors, and sensors. It is high optical absorption and high electrical conductivity makes it ideal material for such applications. Nano crystalline CdS has unique properties due to its small size, such as quantum confinement effects, which make it suitable for applications in nanotechnology, including in fabrication of quantum dots, nanowires, and other nanostructures. It also used in production of high efficiency solar cells, catalysis, and light emitting diodes.

Bulk CdS is often used traditional electronic applications, such as in optical filters, lenses, and windows due to its strong absorption of ultraviolet and visible light. It is also used in production of cadmium sulfide- based paint and pigments, and as well as plastics[34].

2.2.2. Review On CdS Thin Films

In this section , some works done by different researchers the influence of deposition time on structural and potical properties of CdS thin films using Chemical bath deposition ,Inert Gas Condensation Techniques , Scanning Ion Layer and Reaction ,Electron Beam Evaporation method have been reviewed.

A.I. Oliva et al(2001)[35], reported that the band gap formation during the first stage of growth of CdS thin films deposited on the glass substrates by close spaced sublimation techniques was studied. To obtain the first stages of were growth; they used deposition time between 4 and 40min for CSS films. Morphological, structural, optical and stoichiometrical results were obtained on each CdS films group. Higher values of the band gap energy (3.2ev) were obtained for the thinnest films (2-3nm); other films showed similar band gap energy values those reported for polycrystalline CdS thin films (2.4ev). Energy vs α^2 curve, presented strong differences between the deposition times. The behavior of the optical window effects, the surface roughness, the structural results and the films thickness related to the deposition techniques are discussed.

P.K. Ghosh et al. (sep 11, 2007),[38] reported that CdS nanoparticles have been prepared by using different techniques such as CBD, pyrolysis of organometallic reagents and controlling precipitation of nano-crystals in inverted micelles. The properties of CdS thin films depended on

the XRD parameters, the reduction of size with which the bulk properties change remarkably and provide the possibility of observing novel behaviors such size dependent, structural, electrical and optical properties. X-ray diffraction of CdS powder (target material) and thin films were studied. The several peaks on the XRD planes (100), (002), (102), (103), (112) and (203) are peaks of hexagonal phase have been obtained. And XRD patterns changes with the reduction of number of peaks on the planes (111), (220) and (311) are Cubic phase thin films formed. According to these hexagonal and cubic phase difference, it is clear that as the deposition time decreases the intensity of XRD peaks for thin films decreased and the crystallinity decreased with decrease of deposition time.

Khallaf et al. (9 January 2008),[36]reported that, a comprehensive study of the influence of Cd sources on electrical/optical as well as thickness, structure, surface morphology and stoichiometry of chemical bath deposited CdS films is presented. Film thickness was found to decrease in the order $CdSO_4$, $Cd(CH_3COO)_2$, $CdCl_2$, CdI_2. However, the band gap was found to decrease in order to $CdSO_4$, $Cd(CH_3COO)_2$/CdI_2. All films were found to be cubic, regardless of the Cd salt. The grain size decrease in order to above order. According to this report the RBS data showed that the usage of $Cdcl_2$ and CdI_2 results in highly stoichiometric films(S:Cd ratio=1:1). More Cd was detected when $CdSO_4$ and $Cd(CH_3COO)_2$ were used. Using $CdSO_4$ as Cd source of leads to the highest growth rate, band gap, carrier concentration, and mobility.

M.A. Islam et al.(2013),[37] reported that CdS thin films were grown from three different processes; CSVT, CBD and sputtering technique on ITO coated glasses. The structural and optical properties of as-deposited and thermally annealed films were observed through XRD, SEM, EDX and UV-Vis spectrometry, respectively. The crystallite grain size, lattice constant, microstrain and dislocation densities of the films are found quite different in these processes as observed from XRD analysis. However, the highest crystallinity was observed for sputtered CdS thin films and the lowest crystallinity is observed for CBD-CdS thin films. Interestingly, crystallinity of both films is increased by thermal annealing, while CSVT-CdS has lost its crystalline form with annealing. From SEM images, no significant grain changes are observed for thermally annealed CdS thin films but some cracked lines are visible in CBD and CSVT-CdS thin films. Moreover, quite smooth surfaces are observed for sputtered CdS thin films and no changes are observed for annealed films too. The absorbance in the visible wavelength decreases

for annealed CdS thin films indicating that films are becoming denser followed by thermal annealing. The bandgap found for as-grown CSVT-CdS is 2.44 eV, for CBD-CdS is 2.38 eV and for sputtered-CdS is 2.42 eV, respectively. The higher disorder of phonon states in the films are observed for CBD grown CdS and the highest width of localized states in the optical band is observed for CSVT grown CdS thin films.

F.Lisco et al. (2015),[2] reported that the deposited and compared the properties of CdS thin films deposited by pulsed DC magnetron sputtering and chemical bath deposition. The DC magnetron sputtering process produced CdS thin films with the preferred hexagonal (001) oriented crystalline structure. TEM analysis shows evidence of columnar grain growth. Conversely, the CBD deposited films were polycrystalline with a cubic structure, showing small grainy crystallites throughout the thickness uniformity while the pulsed DC magnetron sputtered films were highly uniform.

O. K. Echendu et al (2016)[39] reported that the effects of deposition time and post-deposition annealing on the physical and chemical properties of electrodeposited CdS thin films have been presented. The electrodeposition of these films was carried out using two electrode systems for process simplification and cost reduction[40]. Deposition time was seen to have significant influence on the structural, optical, morphological and chemical composition properties of the deposited CdS films under the conditions described. As the deposition time increased, thickness of the films increased. Increase in deposition time resulted in appearance of more and intense CdS XRD peaks. This also resulted in increased absorbance and reduced transmittance. The optical constants also varied significantly with deposition time/film thickness especially for the as-deposited films, while annealing tends to narrow the spread in these parameters. The morphology of the films showed that there is better coverage of the glass/FTO substrates as deposition time increased and the CdS grains became more compacted. Also, the Cd/S ratio in the as-deposited films gradually increased as deposition time increased while it remained fairly constant after annealing[41]. Post-deposition annealing is generally observed to result in improvement of the physical and chemical properties of the films for all the deposition times/ thicknesses considered[42].

All the above researchers using different synthesizing method, deposition time, complexing agent, compound as a source of cadmium and sulfur than this work. In this work CdS thin films synthesized by CBD method using cadmium sulfate as of source cadmium and thiourea as a source of sulfur, and 25% ammonia(NH_3) as complexing agent, at bath temperature of 80^0C for deposition time of (30min, 40min, 50min, 60min and 70min).

CHAPTER THREE

3. METHODOLOGY

3.1 Thin Films Deposition Techniques

A variety of thin film deposition techniques are suitable for producing semiconductor thin films. Thin films prepared by these methods can differ significantly from each other in terms of their crystal structure, grain size and structural defects [43].

3.1.1 Physical Deposition Techniques

I. Physical Sputtering

Sputtering and sputter deposition are widely used techniques for the erosion off surfaces and the deposition of films. Sputter deposition on semiconductor wafers, on magnetic media and head surfaces, for coating tools and cutting surfaces for wear resistance (this includes ,by the way, such tool as shaving razors), for reflective coatings on window glass ,for coating insides of plastic bags and surfaces of automobile parts, and a number of other wide ranging applications[43]

II. Thermal Evaporation Technique

One of the oldest techniques used for depositing thin films is thermal evaporation or vacuum evaporation and it is widely used in the laboratory and in industry for depositing metal and metal alloys[44]. Thermal evaporation deals with the evaporation of the source materials in a vacuum chamber and condensing the evaporated particles on a substrate. This process is conventionally called vacuum deposition. A thermal evaporator uses an electric resistance heater to melt the material and raise its vapor pressure to the useful range. On heating the material in vacuum, sublimation take place; the atoms are transported and are deposited on the cleaned substrates. During thermal evaporation, the substrate, crucible and source materials are placed inside the vacuum chamber at room temperature and also at different substrate temperature temperatures to deposit thin films. High-purity films can be deposited from high purity source material. The

possible problems that can be encountered in this technique are the source material to be vaporized and its purity[45].

3.1.2 Chemical Deposition Techniques

I. Chemical Vapor Deposition

Chemical vapor deposition (CVD) is the process of chemically reacting, a volatile compound of a material to be deposited, with other gases, to produce a nonvolatile solid that deposits atomistic ally on a suitably placed substrate. Among the reasons for the growing adoption of CVD methods is the ability to produce a large variety of films and coatings of metals, semiconductors, and compounds in either crystalline or vitreous form, possessing high purity and desirable properties [46]. Furthermore, the capability of controllably creating films of widely varying stoichiometry makes CVD unique among deposition techniques. Other advantages include relatively low cost of the equipment and operating expenses, suitability for both batch and semi continuous operation, However, CVD has a number of disadvantages. One of the primary disadvantages lies in the properties of the precursors. Ideally, the precursors need to be volatile at near-room temperatures. This is non-trivial for a number of elements in the periodic table, although the use of metal-organic precursors has eased this situation. CBD precursors can also be highly toxic (Ni $(CO)_4$), explosive (B_2H_6), or corrosive ($SiCl_4$). The byproducts of CVD reactions can also be hazardous (CO, H_2, or HF). Some of these precursors, especially the metal-organic precursors, can also be quite costly. The other major disadvantage is the fact that the films are usually deposited at elevated temperatures. This puts some restrictions on the kind of substrates that can be coated. More importantly, it leads to stresses in films deposited on materials with different thermal expansion coefficients, which can cause mechanical instabilities in the deposited films. Additionally, it requires expensive high temperature reaction furnace and/or vacuum environment, and expensive high vapor pressure compounds.

II. Successive Ionic Layer Adsorption and Reaction (SILAR)

SILAR is aqueous solution technique based on sequential reactions at the substrate solution interface for the deposition of thin films. The SILAR was developed by Nicolau for the deposition of zinc and cadmium chalcogenides thin films[47]. The adsorption is a surface

phenomenon between ions and surface of substrate and is possible due to attraction force between ions in the solution and surface of the substrate. These forces may be cohesive forces or Van der Waals forces or chemical attractive forces. Atoms or molecules of substrate surface possess unbalanced or residual force and hold the substrate particles. Rinsing follows each reaction, which enables heterogeneous reaction between the solid phase and the solvated ions in the solution. In spite of its simplicity, SILAR has a number of advantages. It is relatively inexpensive, simple and convenient for large area deposition. In principle, it is possible to deposit metal chalcogenide thin films using this method on to variety of substrates. The starting materials are commonly available and cheap. As it is a chemical method, a large number of varieties of substrates can be coated. Thus, any insoluble surface to which the solution has free access will be a suitable substrate for the deposition.

III. Chemical Bath Deposition Method

Chemical bath deposition (CBD) has been used as synthesis method for over 130 years[48] and in the recent two decades it has been widely applied successfully, reproducibly, and at low cost, to the synthesis of thin films and other morphologies for solar cells. Many different types of chalcogenide (CdS, CdSe, ZnS, PbS), chalcopyrite ($CuInS_2$, $CuInSe_2$), and oxide (ZnO, TiO_2) materials have been successfully deposited by CBD. The deposition process in CBD uses a controlled chemical reaction or reactions which result in the deposition of a thin film by precipitation. A ligand or complexing agent acting as a catalyst is usually employed in a bath to control the reaction in a suitable medium as indicated by the pH of deposition solution to obtain crystal growth. Otherwise, spontaneous reaction and sedimentation of materials will be obtained. When a solution of a suitable complexing agent of a metal is mixed with a solution bearing the metal ions, fairly stable complex ions of the metal are formed. Complex ions are formed when a cation or an anion is joined to one or more ligands by dative bonds. Those appropriate complexing agent can be chosen so that the concentration of the metal ions is controlled by the concentrations of the complexing agent as well as the solution temperature. This ensures that the cations can be released very slowly from their original compounds in a controlled fashion. The advantages of CBD technique are several and it is becoming an alternative deposition technique for thin films of compound materials like chalcogenides, oxides and halides. A major success can be found in the recent period with the deposition of semiconducting cadmium sulphide or zinc

sulfide buffer or window layers in efficient copper indium diselenide or cadmium telluride thin film solar cells. However, CBD has some drawbacks: Firstly, in the classical beaker configuration, the material yield during film formation is very low, about a few percent, leading to an unnecessary waste production and increased treatment costs. The reason is that the volume to surface ratio is very high and that only a small part of the solution is contributing to the film formation, the remaining leading to the formation of colloids in the bulk of the solutions. Secondly, the formation of particles leads not only to the generation of significant amount of waste but also to the creation of defects in the deposited film [58].

Chemical Bath Deposition (CBD), a solution growth process, allows low temperature deposition, chemical interaction with the substrate, and ionic precursor interaction. Chemical bath deposition which is also sometimes referred to as solution growth or dip coating is a very attractive method used to produce thin films for polycrystalline solar cells such as CdS, CdTe and CuInSe. This work was based on this method. Although several deposition techniques for growing high quality CdS thin films exist, chemical bath deposition is more commonly used compared to the other deposition method because: (i) it is a low cost deposition technique (ii) the apparatus mostly used are common and less expensive (iii) it gives room for large area deposition (iv) it allows for more flexibility in device designs and (v) it is easier to tune the properties through appropriate manipulation of the deposition variables such as Time, pH, etc.

3.3. The Factors affecting the deposition of CdS thin films

3.3.1 Effect of bath temperature

The rate of chemical reaction in the bath can also be influenced by the bath temperature. As temperature increases dissociation of the complex increases hence the kinetic energy of the molecules also increases leading to greater interaction between ions and subsequent deposition at volume nucleation centers of the substrate.

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 redissolve. Studied the effect of temperature on the

tructural and optical properties of CdS thin films. Their result revealed that the crystallinity of films was improved by temperature. In most cases chemical bath deposition can be used to carefully control the crystallinity of the thin film semiconductors by adjusting the deposition temperature. The lifetime of the nucleus will then depend on its size and also on the temperature; lower temperatures will slow the redissolution step. Thus lower temperature increases the chance that a subcritical nucleus will eventually grow to a stable size rather than redissolve. In CdS thin film the band gap increases with increasing temperature, in contrast to the normal semiconductor band gap dependence on temperature[49].

3.3.2 Effect of PH

In most examples of CBD from alkaline solution, the deposition rate increases with increase in pH. This is due to both the greater rate of decomposition of the chalcogenide precursor at higher pH (this decomposition usually involves hydroxide ions) and, in many cases, the greater probability of solid hydroxide formation (as long as this is not excessive). The hydrated metal hydroxyl complex is a soluble species. However, if the pH is sufficiently high, the metal hydroxide, which is relatively insoluble for most metals (apart from the alkali group metals) will precipitate[50].

3.3.3 Effect of complexing agent

In CBD technique usually a complexing agent is added to control the hydrolysis of the metal ion. The process depends on the slow release of chalcogenide ions into an alkaline/acidic solution in which the free metal ion is buffered at a low concentration. In general complexing agents usually form complexes with metal ions used to increase the bath stability, control deposition rate and good quality films, it also greatly influence the structural and electro- optical properties of the thin film[51].

3.3.4 Precursor concentration

Surface modifier concentration also plays an important role in the size and morphology of nanoparticles. Ionic surface modifiers adsorb on to the surface and generate a uniform charge on the particle surface. It is therefore, possible to generate smaller size of particles by reducing the agglomeration tendency of the particles. They adsorb on to the surface play a dual role (namely,

in size control and through surface modification enhance the driving force for formations) in the particle synthesis. The density increases with increase in concentration up to a certain limit and then become constant. In general, a narrow particle size distribution is obtained for ionic surface modifiers[52].

3.4. Thin film Characterization techniques

3.4.1. Structural and Optical properties

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

i. X-ray diffraction (XRD) technique

X-ray diffraction is a tool for the investigation of the crystal structure and phase of material. This technique had its beginnings in von Laue's discovery in 1912 that crystals diffract x-rays, the manner of the diffraction revealing the structure of the crystal[53]. The phenomenon of X-ray diffraction consists of reflection of X-rays from the different crystallographic planes of material and Bragg's law governs it,

$$2d\sin\Theta = n\lambda \qquad (3.1)$$

Where,

d – Inter planer spacing,

ϴ- Bragg's angle or diffraction angle,

λ- Wavelength of x-ray used, and

n - Order of diffraction.

The possible d-spacing defined by the indices h, k, l are determined by the shape of the unit cell. Rewriting Bragg‘s law we get:

$\text{Sin}\theta(hkl) = \frac{\lambda}{2d(hkl)}$……..... (3.1)

The crystalline of the films increased as deposition time increases in each sample, the width of the prominent peaks of the high deposition time film is smaller than that of the low deposition time film which implies that reduction in strain within the film, and improvement of in crystalline. Crystalline size (D) was calculated using Scherer’s formula

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

where λ is wavelength of x-ray, β is FWHM (full width half maximum), θ is the diffraction angle and K is 0.9 which varies with (hkl) and crystallite shape. Therefore, we can calculate the diameter of CdS crystals size (D) and the micro strain (ε) which contribute to the line broadening in the XRD pattern, improvement in the degree of the crystalline of the films. The micro strains (ε), dislocation density (δ) have been calculated using the following relations and their values are given in below table 4.1. The lattice constant (a) was calculated with:

$a_{(hkl)} = d_{(hkl)} \text{ X } \sqrt{h^2 + k^2 + l^2}$…...…….. (3.3)

$\varepsilon = \frac{\beta css\theta}{4}$……..……..…..… (3.4).

Dislocation density (δ) = $\frac{\mathbf{1}}{\boldsymbol{D^2}}$ …… (3.5).

ii. Ultraviolet-Visible Spectroscopy

Ultraviolet-Visible (UV-Vis) spectroscopy is useful characterization of technique to investigate the absorption, transmission and reflection of a variety of compounds and materials. When samples are characterized by UV-Vis spectroscopy, molecules of a given compound absorb energy and this energy can bring out translational, rotational or vibration motion or ionization of the molecules depending upon the frequency of the electromagnetic radiation. Excited molecules are unable and quickly drop down to ground state again off the received energy in the form of electromagnetic radiation. The

wavelength and intensity of the electromagnetic radiation absorbed or emitted can be recorded to get a spectrum.

In this study, UV-Vis spectroscopy were employed to determine the band gap, i.e. the energy difference between the top of the valance band to the bottom of the conduction band of both CdS thin film materials[54]. The absorbance of sample is determined by measuring the intensity of light reaching the detector without the sample (the blank) and comparing it with the intensity of light reaching the detector after passing through the samples. From the absorption spectra, the optical band gaps of the films were estimated by using stern relation.

$(Ahv) = K (hv-E_g)^{n/2}$ …… (3.6)

Where K is constant,Eg is the optical energy gap, *A* is absorbance, ν is the frequency of radiation, h is the Planck's constant and n carries the value of either 1 or 4. The value n is 1 for the direct transition and 4 for indirect transition; respectively is a pure number. Since most compound semiconductors including CdS have a direct band gap, the value of n was taken to be 1 the energy band gap can be obtained by extra-plotting the linear portion of $(Ahv)^2$ verses hv to the energy axis at $(Ahv)^2=0$.

3.4.2. Experimental procedures

1. Material used

The equipment's were used in the deposition of CdS thin film are Beam balance, Petri dish, Beakers of different sizes, Test tubes, Thermometer, Glass substrates, magnetic stirrer, and chemicals were aqueous solutions of 0.1M of Cadmium sulfate, 0.2M of Thiourea, 25% of Ammonia Sample of used chemicals.

- **Preparation aqueous solutions of cadmium sulfate and thiourea**
  - **I. Preparing aqueous solution of 0.1M $3CdSO_4 .8H_2O$**

To prepare the aqueous solution of cadmium sulfate firstly determine the molar mass of $3CdSO_4.8H_2O$

- Molar mass of $CdSO_4$ = 208.47gm/mole

- Molar mass of $3CdSO_4$ = 3x208.47gm/mole
  =625.41gm/mole
- Molar mass of $8H_2O$ = 8x18.02gm/mole
  =144.16gm/mole
- Total molar mass of $3CdSO_4.8H_2O$ = 625.41gm/mole + 144.16gm/mole
  =769.57gm/mole

  To calculate the mass needed in100ml volume

  Mass = molarity x molar mass x volume x purity

  = 0.1mole/lit x 769.57gm/mole x 0.1lit x 0.99

  7.618gm.

Weigh 7.618gm of $3CdSO_4.8H_2O$ dissolved with small amount of distilled water in separated beaker and transfer the solution in to 100ml volumetric flask (bottle) then add distilled water up to 100ml mark to ensure the correct concentration. The result made aqueous solution of cadmium sulfate.

II. Preparing aqueous solution of $CS(NH_2)_2$

Determine the molar mass of thiourea to preparing aqueous solution of it

- Molar mass of $CS(NH_2)_2$ = molar mass of Carbon + molar mass of Sulfur + 2 x molar
  Mass of nitrogen + 4 x molar mass of hydrogen
  =12.01gm/mole + 32.07gm/mole + 2 x 14.01gm/mole
  + 4 x 1.01gm/mole = 76.14gm/mole

  To calculate the mass of thiourea needed for 100ml volume

  Mass = molarity x molar mass of thiourea x volume x purity

  = 0.2mole/lit. x 76.14gm/mole x 0.1lit. x 0.99

  = 1.507gm

Weigh 1.507gm of CS(NH2)2 dissolved with small amount of distilled water in separated beaker and transfer the solution in to 100ml bottle, then add distilled water up to 100ml mark. Then the result is formed aqueous solution of thiourea.

2. Substrate cleaning procedure

Glass substrates were properly cleaned prior to deposition. The cleaning procedure consisted take the glass substrate from the store and put in concentrated nitric acid for a long time, then took from the nitric acid and put in ethanolamine next took the substrate from the ethanolamine and washed with distilled water in the given sequence. The substrates used for the deposition of CdS thin films were commercial microscope glass slides clean and transparent with the size of 75 x 25 x 1.35 mm. Before deposition, the substrates were degreased in HNO3 solution for 24 h, cleaned by commercial detergent and finally rinsed with distilled water and dried in air. This process was carried to ensure clean surface, essential for formation of nucleation centers, required for thin film deposition. After proper cleaned, substrates sticks on the place were prepared and dried by air before deposition.

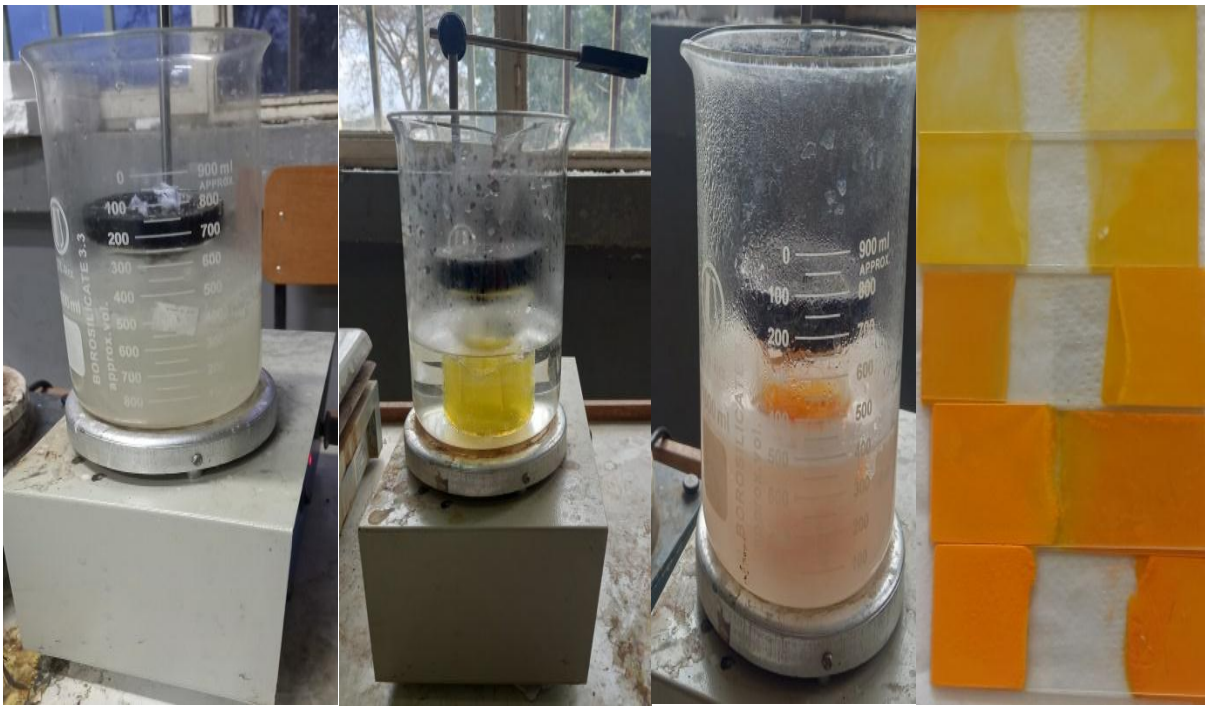
3. Sample preparation

Preparation of CdS and formation of thin film

The CdS thin films were deposited using mixture of aqueous solutions of CdSO4 and thiourea (CS $(NH_2)_2$. Ammonia (NH_3) was used as both the complexing agent and pH adjuster. CBD enables decomposition of CdSO4 in an alkaline solution containing thiourea and a suitable complexing agent. The deposition process is based on the slow release of Cd^{2+} and S^{2-} ions in the solution, which then condenses on the glass substrate. The deposition of CdS occurs when the ionic product of Cd^{2+} and S^{2-} exceeds the solubility product of CdS. Control of Cd^{2+} and S^{2-} ions in the solution ultimately controls the rate of precipitation and hence the rate of film growth. All chemicals used in the present investigations were Analytical Reagent (AR) grade.

A 10 ml of cadmium sulfate solution was dropped in to a 100 ml glass beaker. Addition of 10ml of 25% NH_4 solutions were dropped slowly, led to the dissolution of turbidity. Initially the solution was milky. Under continuous stirring 10ml of thiourea in to solutions were dropped slowly and turbid due to the formation of thiourea suspension made the solution yellow. Pre-cleaned glass substrates were inserted into the reaction mixture standing parallel with the walls of the beaker. The deposition bath and the solution were stirred well with the help of magnetic

stirrer to maintain the homogeneous mixture which was kept for 30 to 70minutes at 80°C temperature at 10min difference.



(a) (b) (c) (d)

Figure 3. 1:Expermental set up of (a) color of solution before heating (b) color of deposition before 30min (c) color of deposition at 30min (d) CdS thin films at the deposition time from (30 to 60)min

CHAPTER FOUR

4. RESULT AND DISCUSSION

4.1 Structural Characterization

X-ray diffraction patterns of the CdS thin films at various deposition times are shown in Figure 4.1. The crystallographic studies of the CdS thin films were conducted using an X-ray diffractometer with a Cu Kα line (λ = 1.54056 Å) in the 2θ range of 20° to 80°. The peak at 26.57° corresponding to the (111) plane exhibits the highest intensity, while the peaks at 31.61°, 44.11°, and 52.09° correspond to the (200), (220), and (311) planes, respectively, confirming the formation of cubic CdS thin films. However, the peak associated with the (101) plane at 29.60° indicates the presence of a hexagonal phase at the deposition time of (40min, 50min and 60min). The intensity of the peaks increases with deposition time, suggesting that the deposition time significantly impacts the crystallization of the film. The crystal size of the CdS thin films increased from 11.34 nm to 13.16 nm with deposition times ranging from 40 to 60 minutes; however, degradation of the crystal structure was observed at 70 minutes. Depending on the synthesis technique, CdS can exhibit either a more stable hexagonal (Greenockite) structure (JCPDS #00-041-1040) or a cubic sphalerite (Hawleyite) structure (JCPDS #00-010-0454). During deposition times between 40 and 60 minutes, the mixed crystal structure of CdS is formed and also additional peaks are observed at 2θ = 32.24° and 38.96° indicate the presence of other compound structures. These peaks correspond to the (111) and (200) planes, confirming the formation of a CdO cubic structure (JCPDS #00-005-0640).

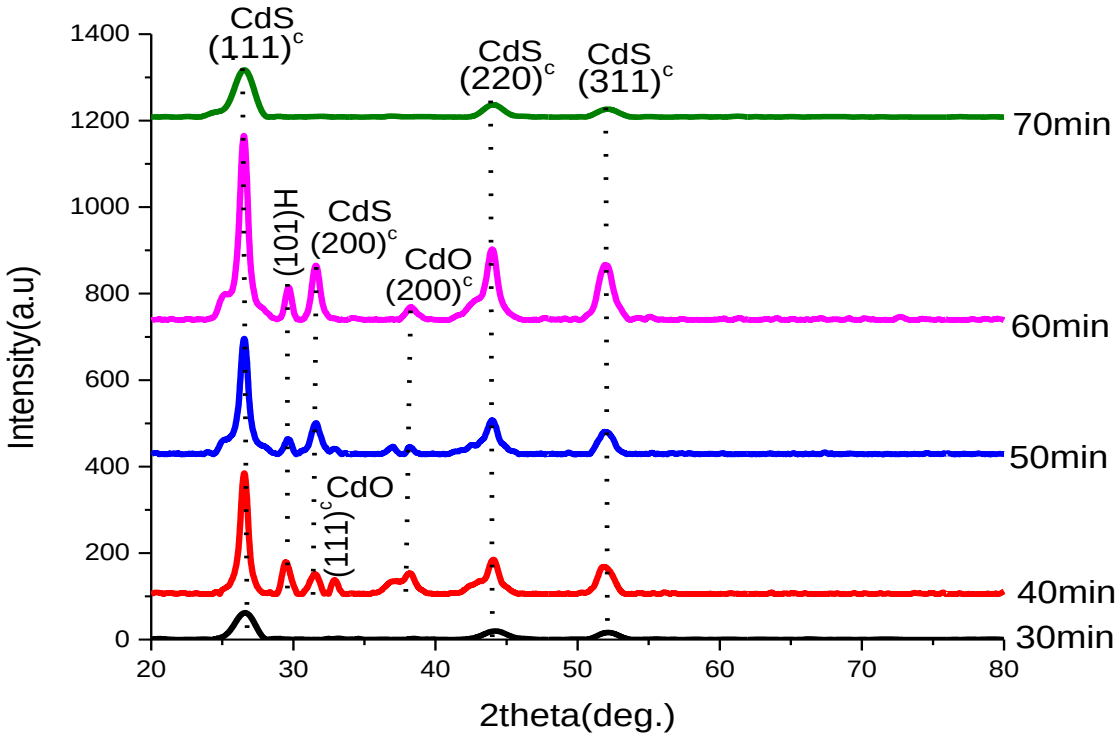


Figure 4. 1: XRD structure of CdS thin films at various deposition times

Table 4.1.The value of 2θ FWHM, crystal size, dislocation density, and strain

Deposition time	2θ(111) Value	FWHM (β^0)	Crystal size (nm)	Dislocation density(□) x 10^{15} line/m^2	Micro-strain(□) x10^{-3}line
30min	26.77	0.72	11.34	7.776	3.0574
40min	26.54	0.7	11.66	7.355	2.9728
50min	26.53	0.624	12.75	6.151	2.6502
60min	26.51	0.62	13.16	5.774	2.6331
70min	26.43	0.76	10.74	8.669	3.2260

The table shows that as deposition time increases from 30 to 60 minutes, the crystal size increases, reaching a maximum at 60 minutes. This is accompanied by a decrease in dislocation density and micro-strain, indicating better crystallinity. However, at 70 minutes, the crystal size

decreases, and both dislocation density and micro-strain increase, suggesting a deterioration in the crystal structure.

These results indicate that optimal crystallization and structural integrity of CdS thin films are achieved at a deposition time of 60 minutes, while longer deposition times may lead to degradation in the film's crystalline quality.

4.2. Ultraviolet visible Spectroscopy Study

In this study, we conducted a UV-vis spectroscopy analysis to investigate the optical properties of CdS thin films synthesized by the chemical bath deposition method at a bath temperature of 80°C for each sample [55]. The band gap energy of these materials was estimated using the Stern relation (Equation 3.6) by plotting hν versus $(Ah\nu)^2$. The band gap represents the amount of energy required to promote a valence electron from the valence band to the conduction band, allowing the electron to move freely within the crystal lattice and serve as a charge carrier for conducting electric current. To estimate this band gap energy, the straight line of the obtained curve in Figures 4.2-4.6 was extrapolated to the intersection point with the hν axis.

The energy band gap values of the CdS thin films for the five samples were found to decrease with increasing deposition time (1.89 eV, 1.84 eV, 1.68 eV, and 1.65 eV for deposition times from 30 minutes to 60 minutes), but increased at 70 minutes. The variations in the energy band gap of the synthesized samples are attributed to slight differences in particle size. It has been reported that the band gap energy of CdS thin films correlates with their crystal sizes (table4.1); as the crystal size increases, the value of the band gap energy decreases.

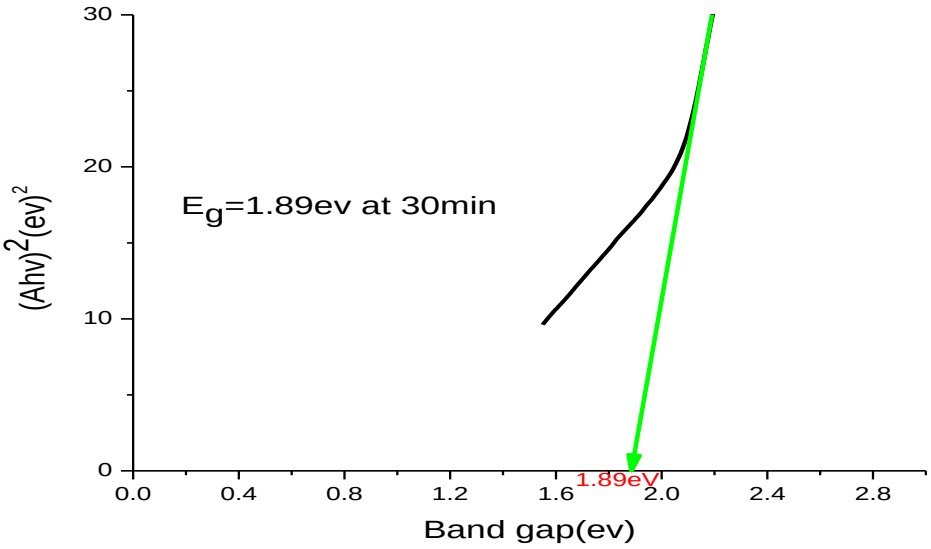


Figure 4.2.Band gap energy in 30min

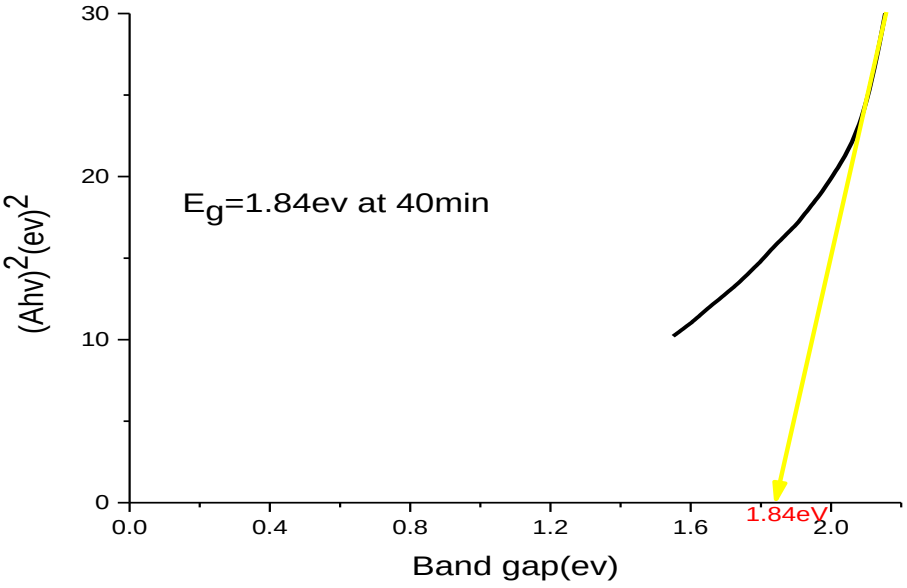


Figure4.3. Band gap energy in 40min

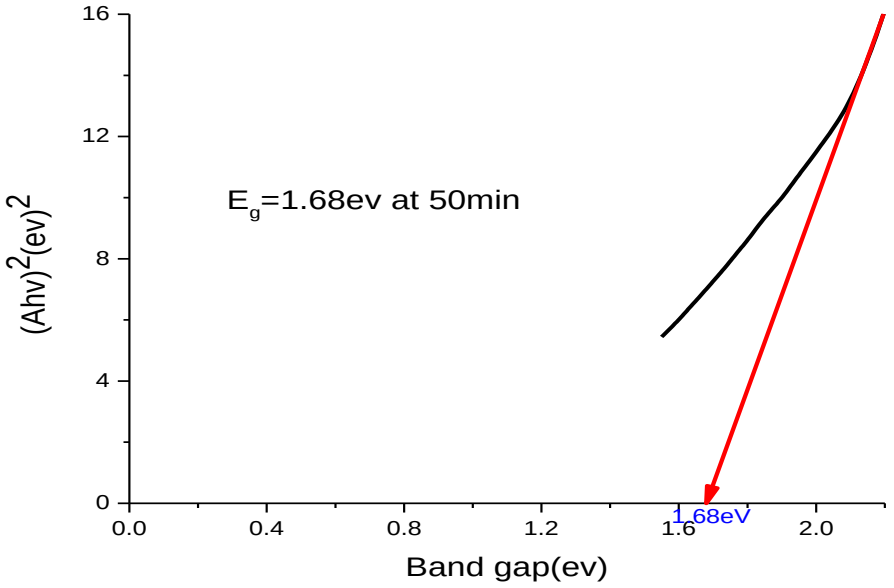


Figure 4.4.Band gap energy in 50min

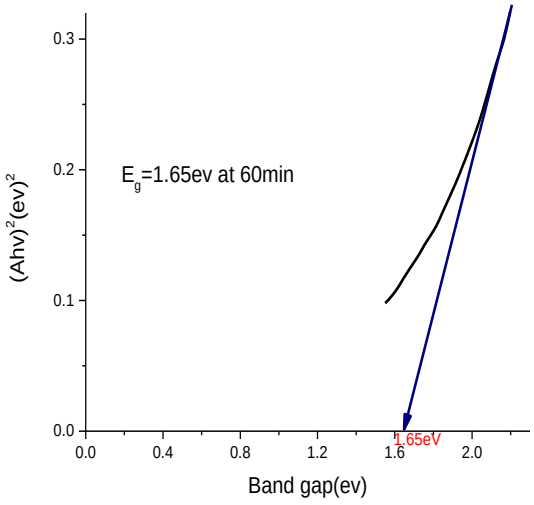


Figure 4.5.Band gap energy in 60min

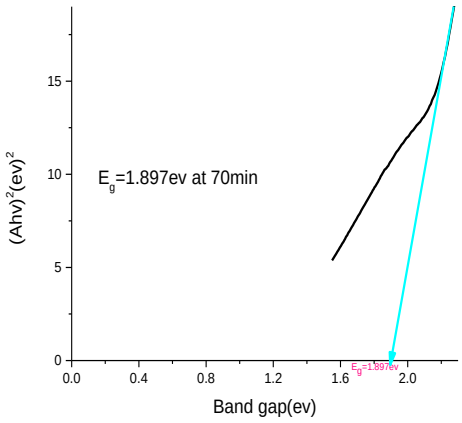


Figure 4.6 Band gap energy in 70min

CHAPTER FIVE

5.1. Conclusion

Chemical bath deposition (CBD) which is designed in the present work is an accurate method that can be used to prepare stoichiometric cadmium sulfide (CdS) thin films. The structural study of the deposited thin films shows that they have cubic structure at 30min of deposition time and mixed phases (hexagonal and cubic) at 40, 50, and 60min. At 70min the structure has pure cubic phase. The crystal size of CdS thin films increased with increasing deposition time (30-60min). Annealing process made these films more crystalline structure formed. The thin film's energy gap decreased from 1.89 -1.65ev for the deposition time of 30-60min in 10min difference one to another sample. At the deposition time 70min the band gap became highest value of all (1.897ev). At the deposition time from 40 to 60min another peak is emerged which corresponds to CdO.

5.2. Future work

This study has helped establish a basic scientific understanding of the structural and optical properties CdS thin films, and important results are reported. However, x-ray photon spectroscopy (XPS) for the composition/elemental analysis of thin films, magnetic properties, the electrical conductivity and dielectric properties of CdS thin films were not addressed in this study. Therefore, in the further studies could have to consider them for additional understanding and giving concrete conclusion on the synthesized CdS thin films.

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