EFFECT OF CADMIUM ION CONCENTRATION ON THE STRUCTURAL AND OPTICAL PROPRTIES OF CdS THIN FILMS BY CHEMICAL BATH DEPOSITION METHOD

BY

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This Thesis is submitted to the School of Graduate studies in Partial Fulfillment of the Requirement for the Degree of Master of Science in Physics (MSC Solid State Physics)

DEPARTMENTS OF PHYSICS

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DECLARATION

I declare that this MSc thesis has not been submitted to any other institution for the award of an academic degree, diploma or certificate. In the preparation, sample collection, data analysis, and compilation of this work, I have followed all ethical and technical principles of the thesis. This work was submitted in partial fulfillment of the requirement for the MSc degree physics with Solid State Physics at Hawassa University. The experimental work is my own work and the collaborative contributions have been clearly identified and acknowledged.

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ABSTRACT

Cadmium Sulfide (CdS) thin films were successfully deposited on glass substrates at four different concentration of cadmium ion (Cd^{2+}) by chemical bath deposition technique at a bath temperature of 80^0c for 50 minutes. The reagents used for the deposition were cadmium sulphate ($CdSO_4$) for Cd^{2+} source, thiourea ($CS(NH_2)_2$) for S^{2-} source and ammonia (NH_3) as complexing agent. The synthesized thin films were characterized by XRD and UV-Vis Spectrophotometer. The XRD analysis of CdS thin films revealed that cubic crystal structure with preferred orientation along the (111) plane and the crystalline size increases in the range of 8.78nm to 18.98nm with increasing cadmium ion (Cd^{2+}) concentration in the solution. Moreover, after the increase of Cd^{2+}ion concentration one peak of CdO with cubic structure appeared. Also the dislocation density (δ) and strain (ε) were calculated. From VU-Vis Spectrophotometer study, the optical band gap values of CdS thin films decreased in the range of 2.0eV to 1.85eV with increasing the cadmium ion (Cd^{2+}) concentration.

Key words: Cadmium Sulfide (CdS), thin films, chemical bath deposition, cadmium ion (Cd^{2+}ion) concentration.

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ABRREVATION AND SYMBOLS

A	Absorbance
CBD	Chemical bath deposition
CD	Conduction Band
CdS	Cadmium sulfide
CVD	Chemical vapor deposition
D	Crystalline size/ Grain size
E_g	Band gap energy
h	Plank‘s constant
K	Shape factor
M	Mole
PV	Photovoltaic
UV	Ultraviolet
VIS	Visible spectrum
XRD	X-ray Diffraction
β	Full width at half maximum
ε	Strain
λ	Wavelength
δ	Dislocation density

CHAPTER ONE

1. GENERAL INTRODUCTION

Materials are probably more deep-seated in our culture than most of us realize. Transportation, housing, clothing, communication, recreation, and food production virtually every segment of our everyday lives is influenced to one degree or another by materials. Historically, the development and advancement of societies have been intimately tied to the members‘ ability to produce and manipulate materials to fill their needs[1]. Modern electronic materials and devices arguably are built upon nearly the entire periodic table (excluding only the actinides and a few other unusual or unstable elements). These diverse materials are required to meet the intense challenges which electronic device applications present[2]. Materials science is well known for being one of the most interdisciplinary sciences. It is the interdisciplinary aspect of materials science that has led to many exciting discoveries, new materials and new applications[3].

Semiconducting materials play an important role in our modern day electronics. In the early days of radio and television, transmitting and receiving equipment relied on vacuum tubes, but these have been almost completely replaced in the last four decades by semiconducting materials, including transistors, diodes, integrated circuits and other solid-state devices[4]. Such devices have found wide applications due to their numerous advantages such as compact sizes, reliability, power efficiency, and low cost. As discrete components, they have found use in power devices, optical sensors, and light emitters, including solid-state lasers. More importantly, they can be easily incorporated into easily manufacturable microelectronic circuits. They are, and will continue to be one key element for almost all electronic systems in the foreseeable future.

Compound semiconductors have been a subject of semiconductor research for nearly as long as elemental semiconductors such as silicon and germanium. Compound semiconductors, whose merit of superior transport was recognized as early as 1952 by Welker, have continued to be of interest although their success has been narrower in scope. The areas of significant applications include light sources (light emitting diodes and light amplification by stimulated emission of radiation), microwave sources (Gunn diodes, Impatt diodes, etc.), microwave detectors (metal semiconductor diodes, etc.), and infrared detectors. All of these applications have been areas of the semiconductor endeavor to which compound semiconductors are uniquely suited. Compound semiconductors have

also made significant contributions to the generation of electricity from solar radiation. Today's most efficient technology for the generation of electricity from solar radiation is the use of multi junction solar cells made of II-VI compound semiconductors. Efficiencies up to 39 % have already been reported under concentrated sunlight. These solar cells have initially been developed for powering satellites in space and are now starting to explore the terrestrial energy market through the use of photovoltaic concentrator systems. This opens a huge potential market for the application of compound semiconductor materials due to the large areas that are necessary to harvest sufficient amounts of energy from the sun. Concentrator systems using II-VI solar cells have shown to be ecological and could play an important role for the sustainable energy generation of the future[5].

A thin film solar cell is also presented as a particular thin film technology. Just as rapid advancesin vacuum technology were necessary to launch the modern era of thin film technology, it wasthe phenomenal growth of surface science and applications, together with the continued development and increasing availability of high resolution transmission electron microscopy, that allowed the emerging field of thin films to slowly evolve from a highly advanced empirical art, driven by a very real set of economic and social benefits, toward an identifiable field of science[6]. Historically, thin films have been used for more than a half century in making electronic devices, optical coatings, instrument hard coatings, and decorative parts. Thin film materials and devices are also available for minimization of toxic materials since the quantity used is limited only to the surface and/or thin film layer. Thin film processing also saves on energy consumption in production and is considered an environmentally benign material technology for the next century[7].

Cadmium sulfide is an inorganic compound, yellow solid and semiconductor of electricity. It is a direct and wide band gap semiconductor (gap 2.4eV). Naturally exist in two crystal forms : hexagonal (wurtzite)and cubic (zincblende) ,insoluble in water , soluble in acid(slightly soluble in ammonium hydroxide) ,Melting point is 1,750^{o}C, Boiling point 980^{o}C, Molar mass 144.47g/mol, refractive index (n_D) is 2.582 and density 4.826g/cm3[8, 9]. It is sensitive to visible and near infrared light. High electrical resistivity when deposited by Chemical bath method. Conductivity of CdS films are n-type[10]. The conductivity of CdS increases when irradiated with light (leading to uses as a photo-resistor) when combined with a p-type semiconductor it forms the core component of a photovoltaic (solar) cell and a CdS/Cu2S solar cell was one of the first efficient cells to be reported

(1954)[7] that fulfills the requirement of having both high optical transmittance and high optical absorbance within the visible spectrum of radiation[11].

Extensive research has been devoted to grow various kinds of binary and ternary semiconductor thin films[12]. This is due to their potential applications in the area of solar cells, optoelectronic devices, photoconductors, sensors, thin films polarizes, thermoelectric cooling materials and infrared detector devices. One of such binary semiconductor thin film is cadmium sulfide (CdS).

1.1. STATEMENT OF THE PROBLEM

Deposition of CdS thin films by CBD technique is the need for inexpensive and abundant semiconducting materials that can be used in many applications such as for the buffer layer in thin-film solar cells, photocells and other photoconductive devices, thin film transistors and diodes, piezoelectric ultrasonic transducers and amplifiers, piezoelectric acoustic resonators and electron beam-pumped lasers.

There are few reports on the effect of Cadmium ion concentration on the deposition rate, dominant mechanism and characteristics of cadmium sulfide (CdS) thin films. Thus, this motivated us to study the effect of Cadmium ion (Cd^{2+} ion) concentration on the structural and optical properties of cadmium sulfide (CdS) thin films deposited by using CBD method.

1.2. OBJECTIVE OF THE STUDY

1.2.1. General objective of research

The aim of this research is to study the effect of Cadmium ion (Cd^{2+} ion) concentration on the structural and optical properties of CdS thin films prepared by chemical bath deposition method.

1.2.2. Specific objectives of research

- To synthesize CdS thin films using chemical bath deposition technique at various cadmium ion concentrations.
- To characterize the structure of CdS thin films using the powder x-ray diffraction analysis.
- To determine the crystal size, strain, and dislocation density of CdS thin films.
- To investigate the optical band gap using UV-Vi Spectroscopy.

1.3. SIGNIFICANCE OF THE STUDY

This study will fill the gap of knowledge related to the effect of cadmium ion concentration of CdS thin films prepared by CBD. This knowledge can be used to give input and display appropriate deposition condition of CdS thin films at various cadmium ion concentration. They also incite researchers to use CdS thin films for man applications.

1.4. STRUCTURE OF THE THESIS

The thesis is organized in to five chapters. The first chapter gives an introduction to the importance of semiconductor research over the years and some properties of CdS. It also talks about the statement of the study and objectives of the research. The second chapter deals with thin film materials, the various thin film deposition techniques and theory of semiconductor discussed in detail. This chapter also reviews literature on the deposition of CdS thin films by chemical bath deposition technique. The CBD techniques, characterization techniques and experimental details are discussed in chapter three. Chapter four deals with the results in graphical representation coupled in depth discussion, while the fifth chapter deals with conclusion and future work. Lastly, reference cites are presented in this thesis.

CHAPETER TWO

2. LITERATURE REVIEW

2.1. THIN FILM MATERIALS

A thin film is defined as a low-dimensional material created by condensing, one-by-one; atomic/molecular/ionic species of matter[7]. Thin film is a layer of material ranging from fractions of a nanometer to several micrometers. The act of applying or depositing a thin film onto a surface or substrate is termed thin film deposition. “Thin” is a relative term, but most of the deposition techniques control the layer thickness within a few tens of nanometers[13]. They define a thin film as a material created abs initio by the random nucleation and growth processes of individually condensing/reacting atomic/ionic/molecular species on a substrate[3].

The film technology developed primarily for the silicon integrated circuit industry is finding its way into several other areas of application. It has become a general technology for designing and constructing complex structures, layer-by-layer. The technology of thin film deposition has advanced dramatically during the past 30 years. This advancement was driven primarily by the need for new products and devices in the electronics and optical industries[14]. Thin film studies have directly or indirectly advanced many new areas of research in solid state physics and chemistry which are based on phenomena uniquely characteristic of the thickness, geometry and structure of the film.

Thin films are generally used to improve the surface properties of solids. Transmission, reflection, absorption, hardness, abrasion resistance, corrosion, permeation and electrical behavior are only some of the properties of a bulk material surface that can be improved by using a thin film. Nanotechnology also is based on thin film technology. Thin films are used if no low- priced bulk material that corresponds to the required specifications of the material exists. Examples from optics are: changes of reflection or fitting of the transmission of glass bodies; micro, nano and opto-electronics are based on thin film technology. Thin film technologies are divided into PVD (physical vapor deposition) and CVD (chemical vapor deposition) processes[15].

2.2. THIN FILM DEPOSITION TECHNIQUES

The technology of thin film deposition has advanced dramatically during the past 30 years. This advancement was driven primarily by the need for new products and devices in the electronics and optical industries. The rapid progress in solid-state electronic devices would not have been possible without the development of new thin film deposition processes, improved film characteristics and superior film qualities. Thin film deposition technology is still undergoing rapid changes which will lead to even more complex and advanced electronic devices in the future. Basically, thin-film deposition technologies are either purely physical, such as evaporative methods, or purely chemical, such as gas- and liquid-phase chemical processes[14].

Any thin-film deposition technique involves three main steps:

1. Production of the appropriate atomic, molecular, or ionic species.
2. Transport of these species to the substrate through a medium.
3. Condensation on the substrate, either directly or via a chemical and/or electrochemical reaction, to form a solid deposit.

2.2.1. Physical deposition techniques

Physical vapor deposition is a technique whereby physical processes, such as evaporation, sublimation or ionic impingement on a target, facilitate the transfer of atoms from a solid or molten source onto a substrate. Evaporation and sputtering are the two most widely used PVD methods for depositing films[16]. Physical vapor deposition refers to vacuum deposition methods that produce the source gas by evaporation, sputtering, or a related non chemical method. Broadly, these methods transfer kinetic energy to atoms in a solid or liquid sufficient to overcome their binding energy. Evaporation refers to heating a material until the source atoms vaporize. Sputtering is a process of physical impacts transferring kinetic energy to atoms in a target[17].

Physical sputtering is well understood and a wide variety of high deposition rate systems are available. Much of the current work in PVD technology areas is either in the area of applications, such as interconnection-wiring on semiconductors, or in the realm of materials, such as the development of high dielectric or piezoelectric films. Several recent developments have helped extend PVD technology; including collimated sputtering, re-flow or high temperature sputtering and ionized magnetron sputter deposition or I-PVD[14].

2.2.2. Chemical deposition techniques

Chemical vapor deposition is a versatile deposition technique that provides a means of growing thin films of elemental and compound semiconductors, metal alloys and amorphous or crystalline compounds of deterrent stoichiometric.

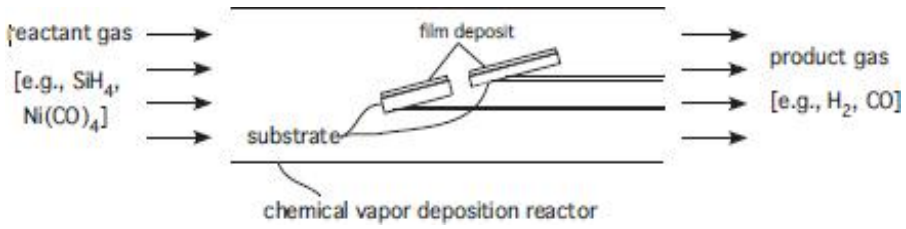


Figure 2.1: Thin film deposition methods

The basic principle underlying this method is a chemical reaction between volatile compounds of the material from which the film is to be made with other suitable gases so as to facilitate the atomic deposition of a nonvolatile solid film on a substrate[16].

Chemical vapor deposition (CVD) is a class of methods in which a solid is grown by reaction of gaseous source materials and yielding a product effluent gas. CVD can also be conducted in an atomic layer deposition (ALD) mode in which single layers of atoms are produced one at a time and has a number of advantages over physical vapor deposition. For example, the reaction can often be arranged to be selective more easily, depositing material only in certain regions of the substrate rather than covering it with a blanket layer. Therefore CVD is generally more conformal than physical vapor deposition, meaning that it covers a rough surface relatively uniformly, tracking the morphology rather than resulting in thin, low quality coatings on vertical walls of the substrate, as is the case for physical vapor deposition methods. Other advantages include that CVD uses source materials that flow into the process chamber from external reservoirs that can be refilled without contamination of the growth environment, it does not require very high vacuum levels, it can generally process substrates in larger batches than evaporation, and is more forgiving in terms of its tolerance for precision in the process conditions[17].

2.3. THEORY OF SEMICONDUCTOR

2.3.1. Semiconductors

Semiconductors have electrical properties that are intermediate between the electrical conductors (viz. metals and metal alloys) and insulators (viz. ceramics and polymers. Materials that are utilized in high-technology (or high-tech) applications are sometimes termed advanced materials. Advanced materials include semiconductors, biomaterials, and what we may term materials ofthe future[1]. Semiconductors are identified as a unique material group on the basis of their common macroscopic properties, as is done for metals, dielectrics and magnetic materials. The name semiconductor' stems from the fact that such materials have moderately good conductivity, higher than that of insulators, and lower than that of metals. At absolute zero temperature, semiconductor conductivity almost vanishes, in contrast to the conductivity of metals, which rises modestly with falling temperature[18].

Semiconductors have been the subject of very extensive research over recent decades, not simple because of their intrinsic interest but also because of ever more numerous and powerful applications: rectifiers, transistors, photoelectric cells, magnetometers, solar cells, reprography, lasers, and so forth. A main feature of many of these applications is the possibility of miniaturization of the devices. The definition of semiconductor as "insulators with narrow forbidden gap" should be complemented by a description of the essential physical properties of materials, namely:

1) Their resistivity decreases as the temperature rises, at least for a certain temperature range, unlike metals.
2) Semiconductors are sensitive to visible light but transparent in the infrared.
3) They often give rise to rectifying or non-ohmic contacts.
4) They exhibit a strong thermoelectric effect, i.e. an electric field induced by a temperature gradient.
5) Their resistivity lies b/n 10^{-5} and 10^{6} ohm-cm[19].

2.3.2. Classification of semiconductors

There are several ways of classifying semiconductors and one important division is into elemental semiconductor materials and compound semiconductor materials. The elemental semiconductor materials made up of elements found in group IV of the periodic table and the compound semiconductor materials composed of elements from different groups such as II-VI, III- V, and IV-IV[20].

Semiconductors can also be classified as intrinsic- and extrinsic semiconductors. An ideal intrinsic semiconductor is a pure semiconductor with no impurity atoms and no lattice defects in the crystal (e.g., puresilicon). An extrinsic semiconductor is defined as a semiconductor in which controlled amounts of specific impurities, either donors or acceptors, have been added so that thermal-equilibrium electron and hole concentrations are different from the intrinsic carrier concentration[21].

Compound Semiconductors

The progress made in physics and technology of semiconductors depends mainly on three families of materials: the group-IV elemental, III–V, and II–VI compound semiconductors. Almost all II–VI compound semiconductors crystallize either in the zincblende or wurtzite structure. At present, the II–VI compound semiconductors are widely used as photo detectors, x-ray sensors and scintillators, phosphors in lighting, displays, etc. New applications are continuously being proposed. Thus, it seems to timely bring together the most up-to-date information on the material and semiconducting properties of II–VI compound semiconductors[22]. This group includes compounds like ZnS, ZnSe**,** ZnTe, CdTe, HgSe and HgTe, which crystallize into the zincblende structure, and compounds like CdS, CdSe and MgTe which have the wurtzite structure. The cubic phase of ZnS is the mineral zincblende**,** and the hexagonal phase is the mineral wurtzite[18].

By selecting appropriate compound semiconductor materials, it becomes possible to realize various devices which cannot be achieved using the main elemental semiconductor materials. Itis therefore important to understand the physical properties of compound semiconductor[23]. Compound semiconductors have covalent tetrahedral bonds because of sp^3 hybrid orbital's like elemental semiconductors. They also possess ionic bonds because compounds are formed from different elements which have different valence (except II-VI semiconductors) and electro negativity. The

difference in electro negativity of the constituent elements is an indication of the ionicity strength[8]. When the ionicity is strong, constituent elements are strongly attracted.

Table2.1: Binary and Ternary compound of semiconductor

Periodic table Group	Binary compounds	Ternary compound
II-VI	CdS, CdSe, CdTe, ZnS, ZnSe, ZnTe	Hg1-xCdxTe, Cd1-x ZnxTe, ZnS1-x Sex, Cd1-x ZnxS, Cd1-x ZnxSe
III-V	GaP, GaAs, GaSb, InP, InAs, InSb	
IV-VI	PbS, PbSe, PbTe	Pbl-xSnxTe, Pb1-xSnxSe, PbS1-xSex
IV-IV	SiC, Si1-xGex	
V-VI	Bi2Te3	

As with group IV materials, the energy gaps of compound semiconductors decrease as we go down the periodic table due to increase in electron screening for heavier elements. If we compare the energy gaps of a set of semiconductors composed of elements from the same row of the periodic table but with increasingly ionic bonding, energy gaps increase as the degree of ionic character becomes stronger. As the degree of ionic bond character increases the magnitude of the periodic potential and hence the energy gap also increases. Increasing energy gap results in lower carrier concentrations at a given temperature. For solar cell application II-VI are superior tosilicon by having direct band gap which enable them to absorb light within a very thin layer. Similarly, II-VI photo-detectors have a high potential to convert the energy of most of the incident photons in to electron hole pairs; in other words they have high quantum efficiency. The other, very exciting area of applications for II-VI's are green, blue or higher energy lasers which can be used for full color displays and white light emitting devices, optical communications, laser printers, numerous sensor a optical processing, their use as detectors in the X-ray and ɤ-ray energy regions and as refractory materials[24, 25].

2.3.3. General properties of Cadmium Sulfide (CdS) thin films

Cadmium sulfide (CdS) is a well-known II-VI group semiconductor and favorable material for electronic and optoelectronic applications. CdS thin film has attracted much interest because ofits high photoconductivity in the visible region, high absorption coefficient, high electron affinity, easy ohmic contact and low resistivity. Since it has direct and wide band gap energy 2.42eV at room temperature, it`s thin film is widely used in many devices such as transistors, photo sensors, gas sensors, light emitting diodes, and logic circuits. It is a naturally n-type semiconductor[26]. CdS can exist in three different crystal structures: hexagonal (wurtzite), cubic (zincblende), and both tetrahedral coordinated and cubic (rock salt), which is six fold coordinated. Except in a few cases, the rock salt modification of CdS has been observed only at very high pressures. The CdS should be as transparent as possible to the incoming radiation. The transmission is a function of thickness, band gap, and film structure[27].

Group II–VI semiconductor (CdS, ZnS) thin films have attracted considerable attention from the research community because of their wide use in the fabrication of solar cells and other opto-electronic devices. CdS is one of the very important widegap semiconductors, because of their wide applications in opto-electronics, such as non-linear optics, visible-light emitting diodes and lasers. Due to its low band gap, CdS window layer absorbs the blue portion of the solar spectrum, which causes decrease in the efficiency of solar cells[28]. The thin film CdS based solar cell has been considered to be a promising alternative to themore widely used silicon devices for several years. Due to the high cost of such a material, studies have been developed towards polycrystalline compound semiconductors and particularly thin polycrystalline films. CdS thin films are regarded as one of the most promising materials for hetero-junction thin film solar cells[29].

2.3.4. Band theory of solids

The band theory of solids is a model for studying the electronic properties of periodic structures, or crystals. The band theory led to a classification of all crystals into metals and semiconductors (insulators) according to the degree of filling of energy bands in the ground state. A substance is metallic, i.e. a conductor of electricity in its ground state (at T = 0°K) if it has an energy band which is only partially filled with electrons, since the electrons can be accelerated only under condition that the nearest higher levels are empty. Absence of such bands forms the criterion fora semiconductor, i.e. material which does not conduct electricity in its ground state[30].

A fundamental understanding of electron behavior in crystalline solids is available using the band theory of solids. This theory explains a number of fundamental attributes of electrons in solids including[31]:

i) Concentrations of charge carriers in semiconductors;

ii) Electrical conductivity in metals and semiconductors;

iii) Optical properties such as absorption and photoluminescence;

iv) Properties associated with junctions and surfaces of semiconductors and metals.

2.3.5. Energy band gap

The energy band gap is the difference in energy between the lowest point of the conduction band and highest point of the valance band. The lowest point in the conduction band is called the conduction edge; the highest point in the valance band is called valance edge. As temperature is increased, electrons are thermally excited from the valance band to the conduction band. Both the electrons in the conduction band and vacant orbital and holes left behind in the valance band contribute to the electrical conductivity. The conduction band is vacant at absolute zero temperature and is separated by an energy gap E_g from the filled valance band as shown in figure 2.2 below.

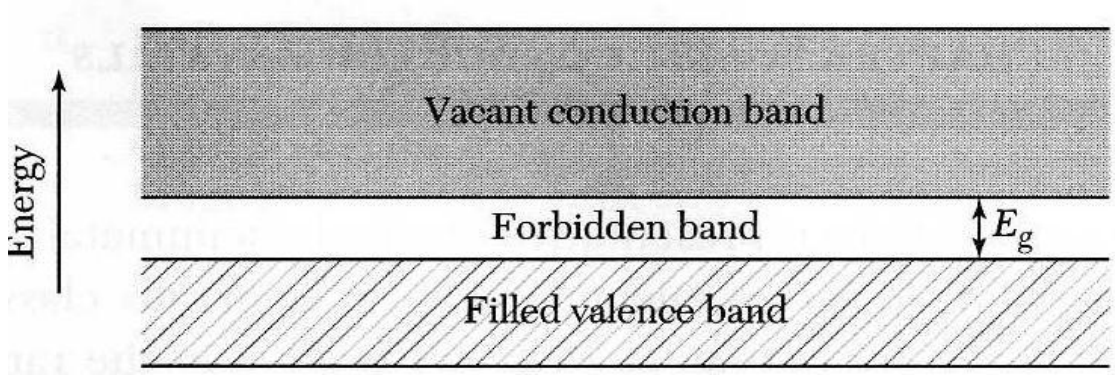


Figure 2.2: Band schemes for intrinsic conductivity in a semiconductor:

The intrinsic conductivity and intrinsic carrier concentrations are largely controlled by $E_g / K_B T$, the ratio of band gap to the temperature. When this ratio is large, the concentration of intrinsic carriers will be low[32].

2.3.6. Direct and indirect band semiconductors

In a direct band gap semiconductor, an electron can be promoted from the conduction band to the valence band without changing the momentum of the electron. An example of a direct band gap

semiconductor is GaAs. When the excited electron falls back into the valence band, electrons and holes combine to produce light. This is known as radiative recombination. Thus, direct band gap materials such as GaAs and solid solutions of these (e.g., GaAs-AlAs, etc.) are used to make light-emitting diodes (LEDs) of different colors. The band gap of semiconductors can be tuned using solid solutions. The change in band gap produces a change in the wavelength (i.e., the frequency of the color (v) is related to the band gap Eg as $Eg = hv$, where h is Planck's constant). Many lasers and LEDs have been developed using these materials. LEDs that emit light in the infrared range are used in optical-fiber communication systems to convert light waves into electrical pulses. Different colored lasers, such as the blue laser using GaN, have been developed using direct band gap materials[33].

In an indirect band gap semiconductor (e.g., Si, Ge, and GaP), the electrons cannot be promoted to the valence band without a change in momentum. As a result, in materials that have an indirect band gap (e.g., silicon), we cannot get light emission. Instead, electrons and holes combine to produce heat that is dissipated within the material. This is known as non radiative recombination. Note that both direct and indirect band gap materials can be doped to form *n*- or *p*-type semiconductors[33].

Electrons in the conduction band rapidly relax to the minimum band energy. Holes equally rapidly move to the maximum energy of the valence band. Therefore, electrons and holes do not have the same momentum in an indirect semiconductor while in a direct-gap semiconductors have the same momentum. Optical absorption/emission involves absorption/creation of a photon with a consequent change in energy of an electron, usually resulting in the transfer of that electron to/from the conduction band from/to the valence band. However, because photons have almost no momentum, only vertical transitions on an E (k) band diagram are allowed in purely optical processes. The only alternative to this is the rare case when a phonon is present together with a photon[2].

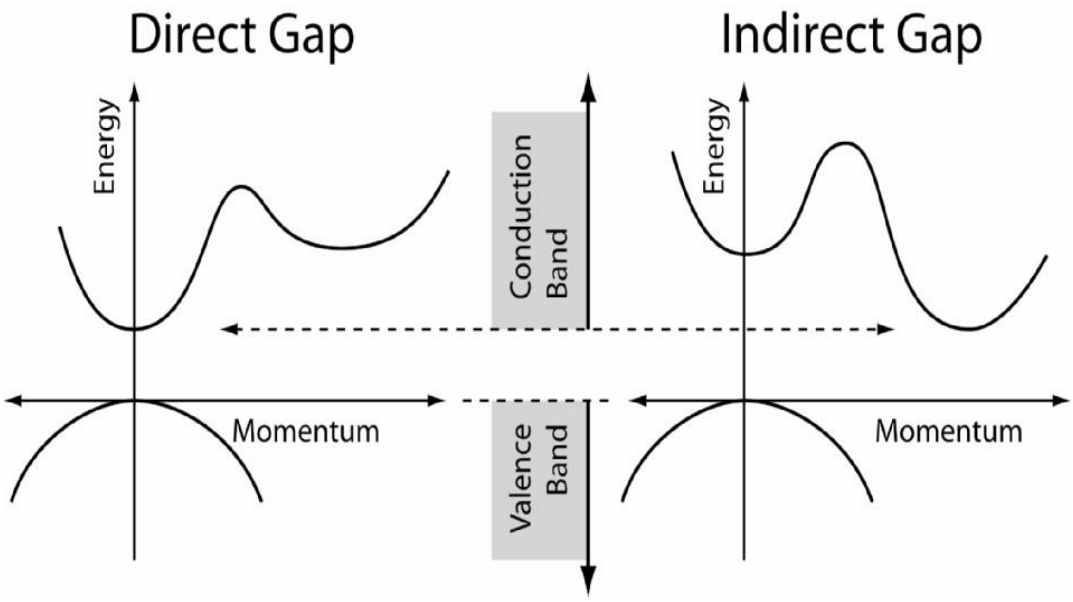


Figure 2.3: A schematic of the difference between a direct gap and an indirect gap semiconductor.

2.4. REVIEW OF CADMIUM SULFIDE THIN FILMS DEPOSITED BY CHEMICAL BATH DEPOSITION

Chemically deposited CdS films were developed during 1960s, the photo detector applications of CdS were confined to screen-printed and sintered layers[34]. In the late 1970s and early 1980s the motivation in the work on chemically deposited thin films has been their prospective solar energy applications. CdS thin films have been prepared by chemical deposition from an aqueous acidic and alkaline and non- aqueous baths by many researchers[35].

Ganesh R. et al. (2014) reported the effects of cations (Cd^{2+}) ion CdS hin films by CBD. Chemical baths used for the deposition of CdS thin films consist of cadmium Sulphate, thiourea and ammonium hydroxides. The effects of cation (Cd^{2+} ions) on structural and optical properties were studied. Structural analysis is done using X-ray Diffraction (XRD) and Scanning Electronic Microscope (SEM) revealed that the films are polycrystalline in nature. The crystalline size lies from 8.9nm to 185nm. Also the dislocation density (d) and strain (ξ) were calculated. All the films have high optical transmittance (>70%) in the visible region. The optical band gap values are decreased in the range of 2.55eV to 2.12eV with increase in cation (Cd^{2+} ions) density in the solution[36].

Pushpalatha H.L. et al. (2014) explained structural and optical properties of CdS thin film obtained by chemical bath deposition and effect of annealing. Chemical baths used for the deposition of CdS thin films consist of Cadmium Sulphate, thiourea and ammonium hydroxides. The bath-temperature was at 80°C and pH at 11. The film was annealed in air at 300°C for one hour. The deposited and annealed films were characterized by XRD, UV-visible spectroscopic meter, EDAX and photo-luminescence study. The film- thickness of 391.1 nm was revealed by Ellipsometry. Coexistence of hexagonal and cubic structure of the deposited film was confirmed by XRD. On annealing, the film was confirmed to be purely hexagonal. The band gaps of 2.35eV of the as deposited film and 2.29eV of the annealed film were derived from the optical transmittance data of UV-Vis spectrum. Photo-luminescence (PL) spectrum of the CdS thin film exhibits green and red emission peaks with different intensity on annealing. EDAX spectrum confirms the transformation of CdS thin film from off stoichiometric to near stoichiometric state on annealing[37].

Hani H. et al.(2012) were synthesized the effect of cadmium ion concentration on the structural and optical properties of the CdS films has been considered in this work. Chemical baths used for the deposition of CdS thin films consist of Cadmium nitrate, thiourea, and ammonium hydroxides. Structure of these films was characterized by X-ray diffraction, where shown of CdS films deposit have polycrystalline structure cubic(zinc blend) and hexagonal (diamond) and the grain size increases with increasing cadmium ion concentration in solution. The optical properties shown that CdS thin films have highly transmittance invisible region of spectrum and reach to more than 85% with wide band gap decreases from 2.45 to2.35eV with increasing of cadmium ion concentration in the solution[38].

Selna M.H Al-Jawad et al.(2009) Studied Investigation of optical properties of Cadmium Sulfide (CdS) thin films by chemical bath deposition. Chemical baths used for the deposition of CdS thin films consist of Cadmium Sulphate, thiourea and ammonia._The films grown from the bath are uniform and adherent, have a high transmittance in the visible region. The CdS films properties studied include optical transmission, optical constant, dielectric constant, optical conductivity, and band gaps. The films in this study produced fairly high transmission (>86% between 500 and 900). Band gaps of (2.4eV) for direct transition were obtained. Such films could be used as photocells and other photoconductive devices, thin film transistors and diodes, piezoelectric ultrasonic transducers and amplifiers, piezoelectric acoustic resonators and electron beam-pumped lasers[39].

Kakhaki Z.M. et al. (2022) reported a comparative study of the photo detection properties of CdS thin films deposited via the CBD method at different cadmium chloride concentration of Cd ion with 0.008 M, 0.02M & 0.08M. The structural properties, surface morphology, compositional properties, film thickness and optical properties of CdS thin films were studied by XRD, FE-SEM, TEM, EDXS CSM, UV-Vis Spectroscopy, and PL, respectively. The increase in cadmium salt concentration dominated the cluster deposition mechanism of the chemical bath deposition (CBD) method, leading to the cubic crystal phase and the thicker CdS thin films. Also, with the increase in cadmium salt concentration, the photosensitivity decreased. Besides, the optical sensor characteristics of these samples were analyzed by the I Vs V curves at a bias voltage of 5V. The results showed more than 200 times the photosensitivity of sample 0.008M Cd^{2+} ion compared to sample 0.08M Cd^{2+} ion concentration[40].

Saiful I. et al.(2020) explained a systematic study on chemical deposited Cadmium Sulfide (CdS) thin film on glass substrates. The samples were prepared using a simple aqueous solution containing cadmium sulfate ($CdSO_4.8H_2O$), thiourea [$SC(NH_2)_2$], ammonium sulfate [$(NH_4)_2SO_4$] as a source of cadmium, sulfur, and a complexing agent, respectively. The deposition films were characterized to study the surface morphology, crystallographic structure, chemical composition, optical and electrical properties. Through this study, the structure was determined to cubic with (111) preferential orientation and the crystallinity of the films was improved with the increase of film thickness. The transmission spectra were recorded in the range of wavelength 300-600 nm. The optical band gap of the optimized CdS films was varied from 2.43 to 2.74eV. All the films exhibit n-type of conductivity which was found in the order of 10^{-4} to 10^{-5} (1/Ω-cm), suggesting that it would be suitable for the buffer layer in thin-film solar cells[41].

Fang R.D. et al.(2013) explained effect of Cd^{2+} Concentration on the Structure and Properties of CBD-CdS. The CdS films were deposited on soda lime glass (SLG) substrate by Chemistry Bath Deposition (CBD). The influence of cadmium concentration on structure and properties of CdS films had been investigated. The phase compositions of the films were characterized by X-ray diffraction (XRD). The microstructure of the films was observed by Scanning Electron Microscope (SEM). The transmittance of the films was measured by Ultraviolet-visible Spectrophotometer. The results show that the cadmium concentration has great influence on Crystallite structure and grain size of the films. Under the condition of Cd^{2+} concentration of 0.006mol/L, the crystalline degree of the film is

higher and the crystal growth is more remarkable, which help to make great progress on transmittance and optical band gap of the films[42].

Demir R. et al. (2015) reported Cadmium sulfide thin films prepared on glass substrates at 82 °C for 1 hour by chemical bath deposition. After deposition, the films are annealed at 480 °C for 1 hour in air atmosphere. Both as-grown and annealed films are characterized by X-ray diffraction, scanning electron microscopy, energy dispersive spectroscopy, optical absorption spectroscopy and current voltage characteristics and their structural, morphological, compositional, optical and electrical properties are investigated. The X-ray diffraction patterns of deposited films show the formation of polycrystalline of CdS with both cubic and hexagonal structure. Moreover, after the thermal treatment of 480 °C, they mostly turn into polycrystalline CdO with cubic structure. The grain size of the deposited film decreases approximately from 10−20 nm to 2-3.5−5.5 nm by annealing. The band gap energy of the films is determined for the direct transitions of 2.15eV and increased to 2.25eV by the thermal treatment. After thermal process, the electrical conductivity of the films calculated from the current–voltage characteristic in the dark increases from 5.482×10–10 (Ω cm)–1 to 5.304 × 10–8 (Ω cm)–1. The observed conduction mechanism in both as-grown and annealed films is ohmic[43].

Most of the above reviewed literatures have been done to synthesis CdS thin films by CBD techniques. They were applied different deposition conditions to synthesis the films. In the present study we synthesized CdS thin films with exceptional amount of molar concentration of cadmium ion (Cd^{2+}ion) in the range from 0.005M to 0.2M by CBD techniques. We used ammonia as a complexing agent in alkaline medium. The deposition time and bath temperature kept constant at 50 minutes and 80 ^{0}C. The films were annealed at a temperature of 300^{0}c for 90 minutes.

CHAPTER THREE

3. METHODOLOGY

3.1. CHEMICAL BATH DEPOSITION METHOD

Chemical bath deposition refers to the deposition of films on a solid substrate from a reaction occurring in a solution (almost always aqueous). CBD can be carried out in both acidic and alkaline solutions; most CBD reactions have been carried out in alkaline solutions[27]. Chemical bath deposition (CBD), also known as chemical solution deposition and can be easily implemented by immersing a substrate into a beaker, filled with an aqueous solution of chemical precursors, sitting on top of a hot plate. Usually carried out as a batch process, CBD has received a great deal of attention, due to its low temperature and low cost nature[44].

Chemical Bath Deposited films are now being developed to be utilized in converting solar radiations into electricity. The effectiveness of a thin film surface in narrowing the photon energy distribution has been extensively established in a technique has been severally used for deposition of thin films of different materials. It is a relatively inexpensive, simple thin film process that is able to produce a stoichiometrically accurate crystalline phases. The properties of the deposited material can be varied and controlled by proper optimization of the chemical baths and deposition conditions. The possible areas of application of the films are based on the optical and solid-state properties of the films[45].

It is the simplest and most economical method for the large-area productions in obtaining semiconductor thin films and it is well known that semiconductor thin films may be exist in either cubic or hexagonal phase or as a mixture of both phases depending on many factors including deposition technique. Therefore, it is very important to vary morphological, optical and electrical properties of semiconductor thin films by adjusting the grain size for technological applications using low cost and an easy method[46].

Chemical bath deposition technique (CBD) has been widely used to deposit films of many different semiconductors. It has proven over the years to be the simplest method available for the typical components of a CBD system are a container for the solution bath, the solution itself made up of common chemical reactive salts, the substrate where the deposition of the film is going to take place, a device to control the stirring process and temperature, sometimes a water bath is included to ensure an homogeneous temperature, an schematic diagram of the CBD system is shown in figure 3.1.

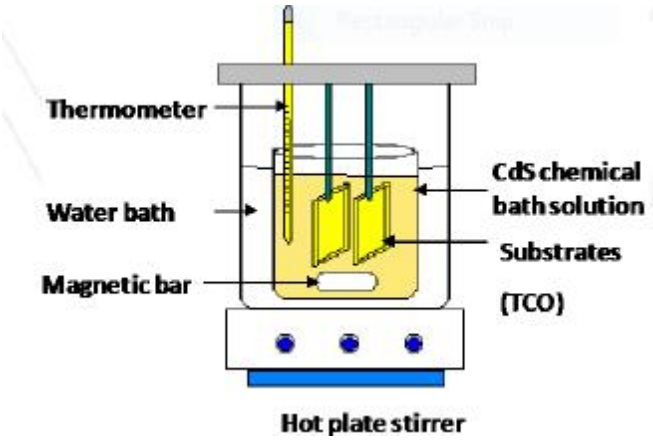


Figure 3.1: Schematic diagram of a chemical bath deposition

3.1.1. Basics/ principle of chemical bath deposition technique

CBD technique is a convenient and non-sophisticated method for deposition of thin films. This method uses a controlled chemical reaction to deposit a thin film on a substrate. The basicprinciple behind the CBD process is based on the solubility product of the compound.

$$M_a + X_b = aM^{n+}bX^{m-} \quad \text{3.1.}$$

At equilibrium, the concentration of ions in the solution is defined by the solubility product (SP) equation (equation 3.1).

$$K_{sp} = [M^{n+}]^a[X^{m-}]^b \quad \text{3.2.}$$

Where K_{sp} is the solubility constant and $[M^{n+}]^{a}$ $[X^{m-}]^{b}$ is the ionic product (IP). The film formation occurs when the ionic product (IP) of the metal and Chalcogenide ions exceed the solubility constant (Ksp) of the corresponding Chalcogenide (IP >Ksp), aM^{n+} ions and bX^{m-} ions are formed from the solid as:

$$M_aX_b(s) = aM^{n+}(aq) + bX^{m-}(aq) \quad \text{3.3.}$$

The more soluble the salt, the greater the ionic product and the greater is K*sp*. However, K*sp* also depends on the number of ions involved. The concentration of metal ion in solution can be controlled by controlling the concentration of the complexing agent[47].

3.1.2. Thin film deposition mechanism in chemical bath deposition process

There are four ways by which the growth of the films in the CBD technique can proceed and have been briefly described below.

1) Ion by ion mechanism
2) Hydroxide cluster mechanism
3) Complex decomposition mechanism
4) Cluster mechanism

3.1.2.1. Simple ion- by-ion mechanism

The ion-by-ion mechanism is the simplest mechanism, and occurs by sequential ionic reactions. The principle of this mechanism is explained with the example of CdS, and is given by

$$Cd^{2+} + S^{2-} \rightarrow CdS$$

If the ion product $[Cd^{2+}]$ $[S^{2-}]$ transcends the solubility product, *Ksp*, of CdS, then CdS turns into a solid phase.

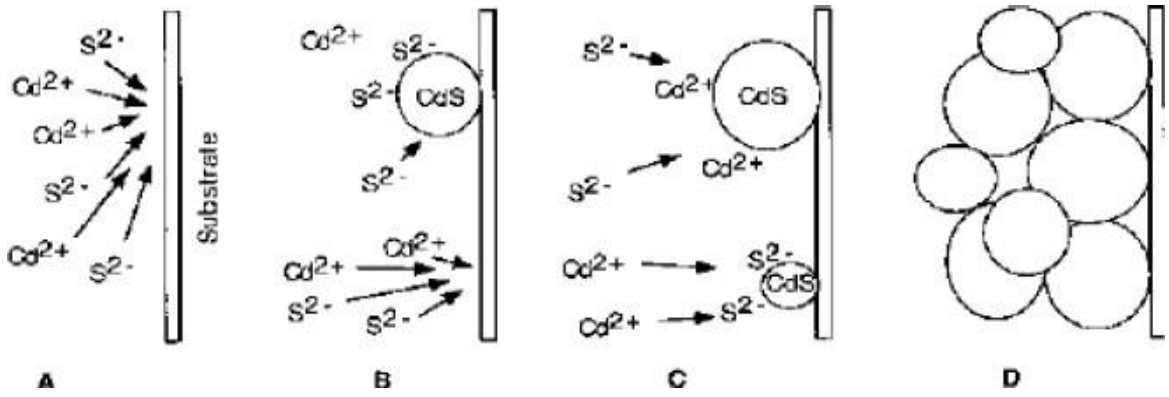


Figure 3.2: Schematic diagram indicating various steps in the ion-by-ion mechanism.

A: diffusion of ions to the substrate, B: nucleation of the ions to form the compound nuclei, C: growth of CdS nuclei by adsorption of Cd and S ions from solution and nucleation of new CdS crystals, D: continued growth of CdS crystals.

3.1.2.2. Simple cluster (Hydroxide) mechanism

Usually during the CBD process, complexation of the Cd was necessary to fortify Cd $(OH)_2$ precipitation, which would impede the growth of CdS thin films. The CdS is then formed by reaction of slowly generated S^{2-} ion with the Cd $(OH)_2$:

$$Cd^{2+} + 2OH^- \rightarrow Cd(OH)_2$$

$$Cd(OH)_2 + S^{2-} \rightarrow CdS + 2OH$$

In this case, sulfide formation will occur preferentially at the surface of the hydroxide rather than nucleate separately in the solution. This reaction occurs both at the surface-adsorbed colloids and at those dispersed in the solution. The reaction continues till all of the hydroxides get converted into sulfides. Finally, these sulfide particles adhere to each other and grow to form the continuous sulfide film on the substrate[48].

3.1.2.3. Complex- decomposition ion- by- ion mechanism

This mechanism has been proposed in the cases of strong complexation between the chalcogen compound and the metal ion (e.g., as occurs between thiosulphate and Hg, Ag, and Cu). The weak secondary bond is thought to break easily than the very strong metal chalcogen bond. Hence, the chemically complex species that contains both metal and sulfur will decompose to form the binary sulfide.

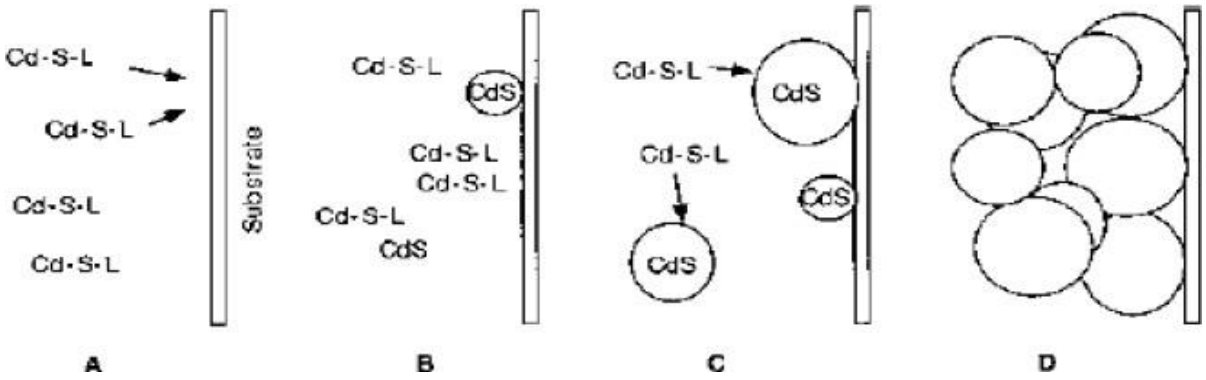


Figure 3.3: The complex (Cd-S-L, where L is a ligand or part of the S-forming species) decomposes to CdS on the substrate and also homogeneously in the solution(A, B). The CdS nuclei formed grow by adsorption and decomposition of more complex species (C) until a film of aggregated crystals is formed (D) in the same manner as for the previous two mechanisms.

3.1.2.4. Cluster mechanism

In this mechanism, the free anion does not react directly, in fact a solid phase is formed and it forms an intermediate complex with the anion forming reagent. For the example of CdS, this would be given as:

$$Cd(OH)_2 + (NH_2)_2 CS \leftrightarrow Cd(OH)_2 SC(NH_2)_2$$

Where $Cd(OH)_2$ is one molecule in the solid-phase cluster. This complex or a similar one containing also ammine ligands, then decomposes to CdS:

$$Cd(OH)_2 . SC(NH_2)_2 \rightarrow CdS + CN_2H_2 + 2H_2O$$

i.e., the S-C bond of the thiourea breaks, leaving the S bound to Cd[48].

3.1.3. Factors influencing the deposition process in chemical bath deposition method

There are several factors which affect thin film deposition process in CBD techniques. The various preparative parameters such as concentration of metal and chalgonide ions, pH of the deposition solution, deposition time, temperature and nature and spacing of the substrates[49]. The effect of various deposition conditions on these parameters are discussed below.

3.1.3.1. Concentration of the reactants

Increasing the concentration of reactants increases the rate of reaction. The deposition rate and terminal thickness initially increases with an increase in the ionic concentration of the reactants. However, at high concentration precipitation occurs very fast, leading to decrease in film thickness on the substrate[27]. It is clear that if the reaction is too fast, it will terminate with most of the product precipitating homogeneously in solution rather than depositing on the substrate (which requires time to occur).These results in a very thin film, if any film at all. Similarly, for the less extreme case of a CBD reaction that terminates, not within a second, but still in a short time, the final film thickness will be small.

3.1.3.2. Complaxing 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 complexing agents can also exert profound morphological effects on the growing crystal[50]. In a general reaction the metal ion concentration decreases with increasing concentration of the complexing ions. Consequently the rate

of reaction and hence precipitation are reduced leading to a larger terminal thickness of the film. Even more important, if the complexing agent to metal ion ratio increases above a certain value, the mechanism of deposition may changes (commonly from a hydroxide cluster mechanism to ion-by-ion deposition).The free metal ion concentration is controlled by the formation of complex species according to the general reaction:

$$M(A)^{+2} = M^{2+} + A \quad \text{.....3.4}$$

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

$$K = \frac{[M^{+2}][A]}{[M(A)^{+2}]} \quad \text{.....3.5}$$

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. 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[27].

3.1.3.3. pH of the bath Solution

The reaction rate as well as rate of deposition depends on the super saturation condition and rate of the formation of MX (where M and X is the number of metals and OH^- / ions respectively). If the concentration of ion in the solution is higher, the M ion concentration will lower and the reaction rate will be slow according Hankar (2006). At a certain pH, the concentration of M ion decreases to a level such that the ionic product of M and X becomes less than the solubility ofMX and a film will not be formed. For the growth of good quality thin films, the hydroxide ions in precursor solution are necessary. The thin film formation depends on the pH of the reaction mixture and pH depends on ions. The decrease in pH results in porous, non-reflecting, powdery and weakly adhered thin films on the substrates. At higher pH metal ion concentration will be lower and the reaction rate will be slow. With an increase in pH as the metal ion concentration decreases, the rate of film formation decreases[51]. 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).

3.1.3.4. Effect of reaction temperature

The rate of chemical reaction in the bath can also be influenced by the bath temperature. As temperature increases, dissociation of the metal complex to release free metallic ions and hydrolysis of the chalcogenide source increases. The kinetic energy of the molecules also increases leading to greater interaction between ions. These effects will result in increase or decrease of terminal thickness, depending on the extent of super saturation of the solution. In most cases chemical bath deposition can be used to carefully control the crystallinity of the thin film semiconductors by adjusting the deposition temperature.

3.1.3.5. Effect of deposition time

Deposition time is one of the parameter which affects thin film deposition in CBD method. In most cases it has a great influence on structural, morphological and optical properties of thin films. 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 thin films.

3.1.3.6. Effect of preparation of the substrate(s)

Glass is one of the most commonly used substrates in CBD, however, metals make good substrates in general, either because chalcogenides tend to adsorb strongly on many metals, or the non-noble metals are covered with a (hydroxylated in the deposition solution) oxide layer. If the metal in the deposition solution has a sufficiently negative potential, an internal electrochemical reduction may occur[27]. Apart from adhesion, the crystallographic properties of chemically deposited films are sometimes dependent on the nature of the substrate. One example is epitaxial deposition on a crystallographically ordered substrate. Substrate should be cleaned properly with a standard procedure before being immersed in the reactant mixture. Moreover, shape and electrical conductivity of the substrates are usually not important very irregularly shaped substrates can be used. However, the nature of the substrate is usually important in order to obtain an adherent film[52]. A large variety of CBD thin films have been also deposited on different polymer surfaces. Deposition sometimes is satisfactory on the clean polymer with various activation treatments, such as treatment with permanganate, have been used to improve the adhesion and homogeneity[53].

The separation of substrate during deposition has significant effect on film thickness, it observed that the film thicknesses reach an asymptotic maximum with increase in substrate separation[54].

3.2. THIN FILM CHARACTERIZATION TECHNIQUES

The complete characterization of any material consists of phase analysis, compositional characterization, structural elucidation, micro-structural analysis and surface characterization, which have strong bearing on the properties of materials. This has led to the emergence of variety of advanced techniques in the field of materials science[55]. In this section different analytical instrumental techniques used to characterize our thin films are described with relevant principles of their operation and working.

3.2.1. X-Ray Diffraction

X-ray diffraction (XRD) is a powerful technique for determination of crystal structure and lattice parameters[56]. X-rays were discovered in 1895 by the German physicist Roentgen and were so named because their nature was unknown at the time. These rays were invisible, but they travelled in straight lines and affected photographic film in the same way as light. The analysis of crystal structure is of great importance in the description of materials; such an analysis is typically performed by employing x-ray diffraction techniques[57].

X-Ray diffraction method can be used to measure the thickness of thin film (coatings). The X- Ray diffraction method is a non destructive and fairly fast method for the determination of thickness of the thin film. The diffraction technique can be used to determine the thickness of polycrystalline thin film deposition on polycrystalline or amorphous substrate[58].

X-ray Diffraction technique is a powerful method to characterize films and thus to determine the epitaxial relationships between the films and substrates. Diffraction, the constructive interfere of the X-ray beam, occurs only when the X-ray wavelength and the distance between the atomic planes in a crystal satisfy Bragg‘s Law:

$$n\lambda = 2d_{khl}\sin\theta \quad \ldots\ldots 3.6$$

Where, n is an integer (1, 2, 3, etc), and λ is the wavelength in unit of, A^0 dependent on the X-ray source and d_{hkl} is the distance between atomic layers in, A^0 and θ is the diffraction angle in degrees or radians[59].

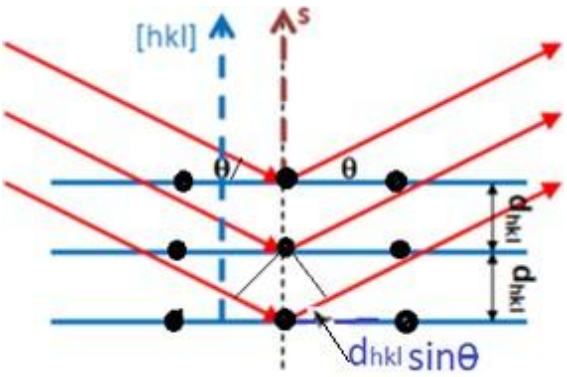


Figure 3.4: Schematic representation of Bragg's law; the black sphere represents atoms or molecules on a lattice site.

The possible 2θ values where we can have reflections are determined by the unit cell dimensions, even though, the intensities of the reflections are determined by the distribution of the electrons in the unit cell. Therefore, Planes going through areas with high electron density will reflect strongly, planes with low electron density will give weak intensities.

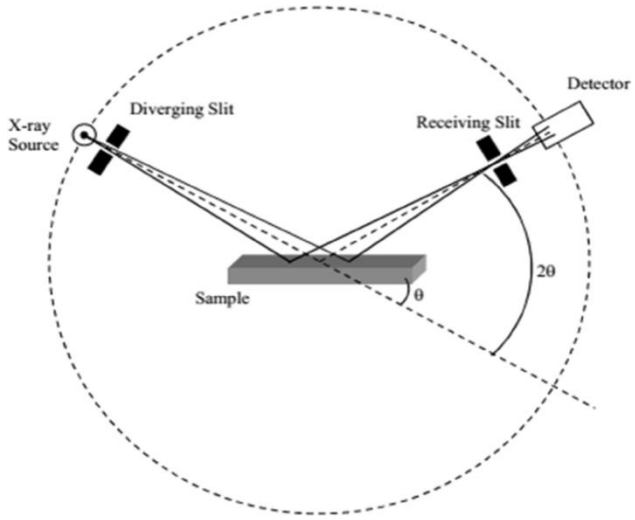


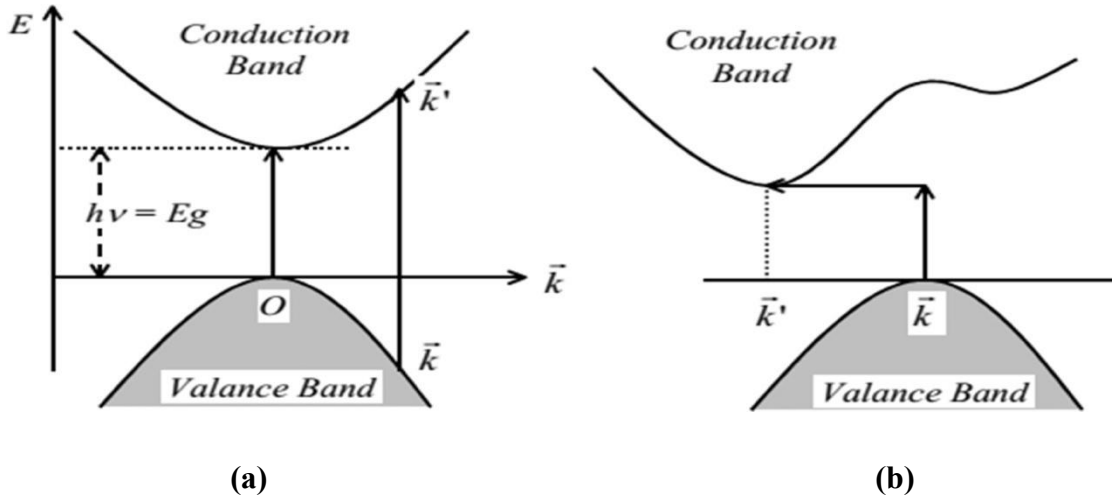
Figure 3.5: Schematics of X-ray diffractometer

3.2.2. Optical characterization by UV-Vis spectrophotometer

An UV/Vis Spectrophotometer measures the intensity of light passing through a sample (*I*), and compares it to the intensity of light before it passes through the sample (I_0) expressed in absorbance (A)

or transmittance (T). It uses light over the ultraviolet range (185 - 400 nm) and visible range (400 - 700 nm) of electromagnetic radiation spectrum. Spectrophotometry is a measurement of how much a chemical substance absorbs or transmits and a spectrophotometer is an instrument that measures the amount of the intensity of light absorbed after it passes through sample solution. With the spectrophotometer, the concentrations of a substance (the amount of a known chemical substance) can also be determined by measuring the intensity of light detected[60].

Optical properties of semiconductors typically consist of their refractive index n and extinction coefficient K or absorption coefficient α (or equivalently the real and imaginary parts of the relative permittivity) and their dispersion relations, that is their dependence on the wavelength, λ, of the electromagnetic radiation or photon energy hν. The conservation of energy and momentum must be satisfied in optical absorption process. Basically there are two types of optical transitions that can occur at the fundamental edge of the crystalline semiconductor, direct and indirect. Both involve the interaction of an electromagnetic wave with an electron in the valence band, which is rose across the fundamental gap to the conduction band. The optical transition is denoted by a vertical upward arrow transitions[61]. Direct inter band optical transition involves a verticaltransition of electrons from the valence band to the conduction band such that there is no change in the momentum of the electrons and energy is conserved as shown in Fig. 3.6 (a). Hence the wave vector k for electron remains unchanged in E-K space[62].



(a) **(b)**

Figure 3.6: E-K diagrams showing (a) direct and (b) indirect inter-band.

Indirect transitions the electron cannot directly jump into the conduction band, but once the electron at the valence band edge E_v absorbs energy (photon, phonon, or electric field) and reaches the energy

level of the conduction band edge E_C across the energy band E_g, it can indirectly jump into the conduction band with the aid of phonon energy because phonon usually exists anyway[63]. Phonons are quantum of lattice vibration having a small amount of energy and a large amount of momentum, and one or more phonons can take part in the transition process if they have the required amount of momentum and energy. The energy band gap and transition type can be determine from mathematical treatment of data obtained from optical absorbance versus wavelength, with the Stern (1963), relationship of near edge absorption whichis given as.

$$A = K\left[\frac{hv - (E_g)}{hv}\right]^{\frac{n}{2}} \qquad \text{3.7}$$

Where A is absorbance, hν is the incident photon energy, E_g is separation between valence and conduction bands, K is a constant, and n carries the values 1, 4 ,3 and 6 for allowed direct, allowed indirect, forbidden direct indirect and forbidden transitions, respectively. The energy band gap can be obtained by extrapolating the linear portion of $(Ahv)^2$ versus hν to the energyaxis at $(Ahv)^2 = 0$[8].

3.3. EXPERIMENTAL PROCEDURES

3.3.1. Material used

The materials used to deposited CdS were Beam Balance where was used to measure the mass of chemical, Thermometer to measure bath temperature, Substrates (glass) to deposit a film on it, Magnetic stirrer for stirring chemical solution, Water beaker used to keep a water bate and reaction solution and Heater (magnet + motor) used to heater reaction bath.

3.3.2. Reagent/Chemical used

In order to deposit the cadmium sulfide (CdS) thin film, the following reagents such as cadmium Sulphate ($CdSO_4$), thiourea (($CS(NH_2)_2$) and ammonia (NH_3) were used. The cadmium Sulfate ($CdSO_4$) was the source of cation (Cd^{+2}), thiourea ($CS(NH_2)_2$) was the source of anion (S^{2-}) and ammonia (NH_3) as complex agent.

3.3.3. Reagent preparation

i) Preparation of 0.05M ,0.1M, 0.15M, and 0.2M of cadmium Sulphate

(1.9045, 3.809, 5.713, and 7.618) gram of Cadmium Sulphate was measured by beam balance respectively. Then put in to the four 50ml of volumetric flask and diluted to the mark with distilled water and careful shaken to dissolve salt completely. Finally the resulting solution had a concentration of 0.05M, 0.1M, 0.15M, and 0.2M respectively. The appropriate concentration of reagents preparation was prepared by dissolving intended mass of the reagents. The mass of the reagents was obtained by:

$$m_R = C \times V \times M.W \times PPT \quad \ldots\ldots 3.8$$

Where: m_R −mass of a given reagent (in gram), C- concentration (in mol.), V- Volume (in litter), M.W- molecular weight (in g/M.L) and PPT- percentage purity (in %).

ii) Preparation of 0.2m thiourea ($CS(NH_2)_2$)

0.75 gram of thiourea ($CS(NH_2)_2$) was measured and put in to the 50 ml volumetric flask and diluted to the mark with distilled water and careful shaken to dissolve salt completely. Lastly the resulting solution had a concentration of 0.2 M.

3.3.4. Substrate cleaning procedure

One of the advantages of CBD thin films is the range of substrates that can be used on which films deposit. The main criteria for substrate selection are that the growing film will attach to substrate and that the substrate will not dissolve in the chemical bath. Glass substrates are commonly used: microscope slides for small scale project and glass sheets for large scale project. Glass generally has been immersed in a vertical position in the bath solution, although with large coating areas, two sheets have been supported with a set distance between them and the CBD solution filled in the gap. In the preparation of substrate are critical aspects that can contribute to film adherence. In these work glass substrates were used. Glass substrates have been cleaned with detergent, immersed with nitric acid for 12 hour, then washed with distilled water and dried on air at least for 30 minute.

3.3.5. Solution preparation and deposition of Cadmium Sulfide thin films

Before the preparation of the solutions, the precursor solutions must be prepared appropriately. In this work there were four different deposition conditions, with different concentration of cadmium Sulphate ($CdSO_4$) and the same concentration of thiourea ($(CS(NH_2)_2$) and ammonia (NH_3) were used for the deposition CdS thin film**.**

In the first deposition condition, 10 ml of 0.05M cadmium Sulfate and 10 ml of distilled water was added in a 100 ml beaker and stirred with magnetic bar stirrer for few minutes until a homogeneous solution was obtained, then 10 ml Ammonia was added slowly in that beaker. The solution shown color change immediately from milky to clear, then 10ml distilled water was added. Finally 10 ml thiourea and 10 ml distilled water were added. After the solutions were prepared, heat supplied and substrates were inserted in solution and kept the temperature at 80^0c for 50 minutes to complete the deposition of the film. As shown in figure 3.7 the solution color before 50 minutes like yellow lemon and at 50 minutes yellow. The substrates were removed from the bath after 50 minute and washed in distilled water and dried in air. The other films were synthesized with the same deposition condition but different cadmium ion concentration.

(a) : **(b):** **(c):** **(d):**

Figure 3.7: Experimental set up of (a) color of solution before heating (b) color of deposition before 50 minute (c) color of deposition at 50 minute (d) CdS thin films from 0.05M to 0.2M Cadmium ion.

3.4. REACTION MECHANISM OF CADMIUM SULFIDE THIN FILM DEPOSITION

In the growth of the CdS thin film from chemical bath, ammonia as the complex agent to bind the Cd^{2+} ions. Formation of complex ion is essential to control rate of the reaction and to avoid the immediate precipitation of the compound in the solution. The metal complexes hydrolyses slowly to generate the Cd^{2+} ion the solution.Thiourea furnishes the necessary S^{2-} ions by hydrolysis[64]. A reaction mechanism for the formation of CdS is suggested below[65].

1) Cadmium salt reacts with ammonia to from the complex compound.

   $CdSO_4 + 4(NH_3) \rightarrow (Cd(NH_3)_4SO_4)$

2) Diffusion of the thiourea on CdS catalytic surface in an alkaline medium.

   $CS(NH_2)_2 + 2OH^- \rightarrow S^{2-} + CN_2H_2 + 2H_2O$

3) Formation of bivalent Sulfide ions.

   $HS^- + OH^- \rightarrow S^{--} + H_2O$

4) Formation of CdS

   $Cd(NH_3)_4^{++} + S^{--} \rightarrow CdS + 2NH_3$

CHAPTER FOUR

4. RESULT AND DISCSSION

4.1. STRUCTURAL CHARACTERIZATION ANALYSIS BY XRD

The X-ray diffraction (XRD) is one of the most powerful techniques for the characterization of the structural properties of semiconductor thin films. The structural analysis of the Cd^{2+}ion concentration of CdS thin film was carried by X-Ray Diffraction (XRD) with (λ = 1.5406A^0) radiation in the range of 2θ= 20^0 - 80^0 as shown in figure 4.1 below. The average crystalline size (D) was obtained from the X-ray diffraction pattern, using the Scherrer formula which is given by:

$$D = \frac{K\lambda}{\beta COS\theta} \text{ ....} \mathbf{5.1}.$$

Where, θ is the diffraction angle, β is the full width at half maximum in radians, K is the constant known as the shape factor, taken as 0.94.[66].

The dislocation density (δ) estimated using the equation

$$\boldsymbol{\delta = \frac{1}{D^2}} \text{ ....} \mathbf{5.2}$$

The strain (ε) of the films can be determined by using the following formulae:

$$\boldsymbol{\varepsilon = \frac{\beta \cos\theta}{4}} \text{ .... } \mathbf{5.3}$$

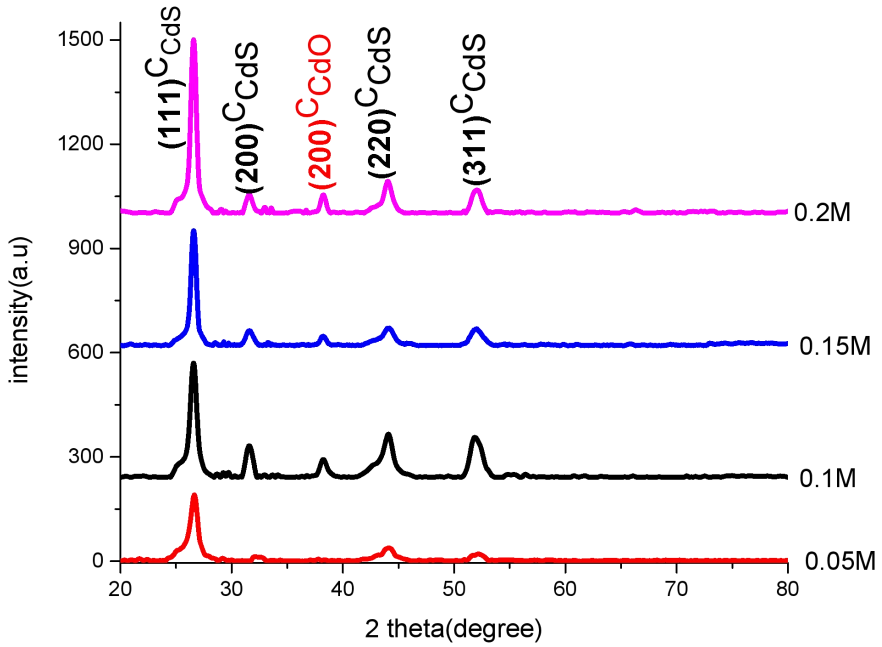


Figure 4.1: XRD patterns of CdS thin films at different concentration of Cadmium ion.

In fig 4.1 XRD results showed that annealed film of 0.05M Cd^{2+}ion concentration have clearly cubic structure with four peaks at angle of 26.6^0,31.57^0,$44.13^0$and 52.33^0 corresponding to the $(111)^C$, $(200)^C$, $(220)^C$ and $(311)^C$ planes for the CdS phase respectively.

When the Cd^{2+}ion concentration increases the XRD results indicates five peaks. Moreover it shows four strong reflection peaks the same as the previous one around to an angle of 2θ values of 26.6^0, 31.57^0, $44.13^0$and 52.33^0 corresponding to the $(111)^C$, $(200)^C$, $(220)^C$ and $(311)^C$ planes for the CdS phase respectively and another one additional less intensity diffraction peaks at an angle of 38.44^0corresponding to the planes of $(200)^C$ crystalline belongs to the cubic phase of CdO. This may be due to thermal treatment (annealing effect) and another reason may be due to excess cadmium elements in the chemical bathes at 0.1M – 0.2M of Cd^{2+}ion concentration. The diffracted planes are well matched with JCPDS card number: 010-0454 CdS of space group F-43m. It is also notice that the preferred orientation of the crystal was along the (111) plane. By comparing with the standard of cubic CdS structure, the main diffraction peaks are indexed with the lattice planes of (111), (200), (220) and (311). The peaks are in good agreement with the standard (JCPDS card no 0018113) of cubic structure at 2θ 26.57^0, 30.78^0, 44.09^0, and 52.22^0[67].

Table4.1: comparison of crystalline size, dislocation density and Strain of cubic phase (111) of CdS thin films with increased in concentration of Cd^{2+}ion.

Cd^{2+}ion concentration	2Theta of (111) (degree)	Full Width At Half Maximum(β) (degree)	Crystalline size(D) (nm)	Dislocation density(δ) (x 10^{+15}) (lines/m^2)	Strain (ε)
0.05M	26.63	0.93	8.78	12.97	0.226
0.1M	26.59	0.65	12.56	6.33	0.158
0.15M	26.61	0.46	17.75	3.21	0.112
0.2M	26.60	0.43	18.98	2.77	0.104

From the table the crystalline size of CdS thin films increase in the range from 8.78nm to 18.98nm with increasing the concentration of solution in the range from 0.05M to 0.2M XRD. Moreover, it clearly indicates that the diffraction peak intensity increases as the Cd^{2+}ion concentration of the bath solution increases. This is an indication of the crystallinity improvement with increasing Cd^{2+}ion concentration. The strain and dislocation density decreases with increasing Cd^{2+}ion concentration. Similar structures and values were reported by Ganesh R. et al (2014) and Demir R. et al. (2015).

4.2. OPTICAL PROPERTY ANALYISIS BY UV-Vis SPECTROSCOPY

i) Absorption

The absorption spectra of CdS thin films at various Cd^{2+}ion concentrations are portrayed in Fig. 4.2. Absorbance peak intensity of the films increases by increasing the Cd^{2+}ion concentration in the solution. This is due to the increases of the crystalline size. The same results were reported by Ganesh R. et al (2014) and Hani H. et al (2012). The next figures show optical absorption of the CdS thin film for the concentration of Cd^{2+} ion with 0.05M, 0.1M, 0.15M, and 0.2M respectively.

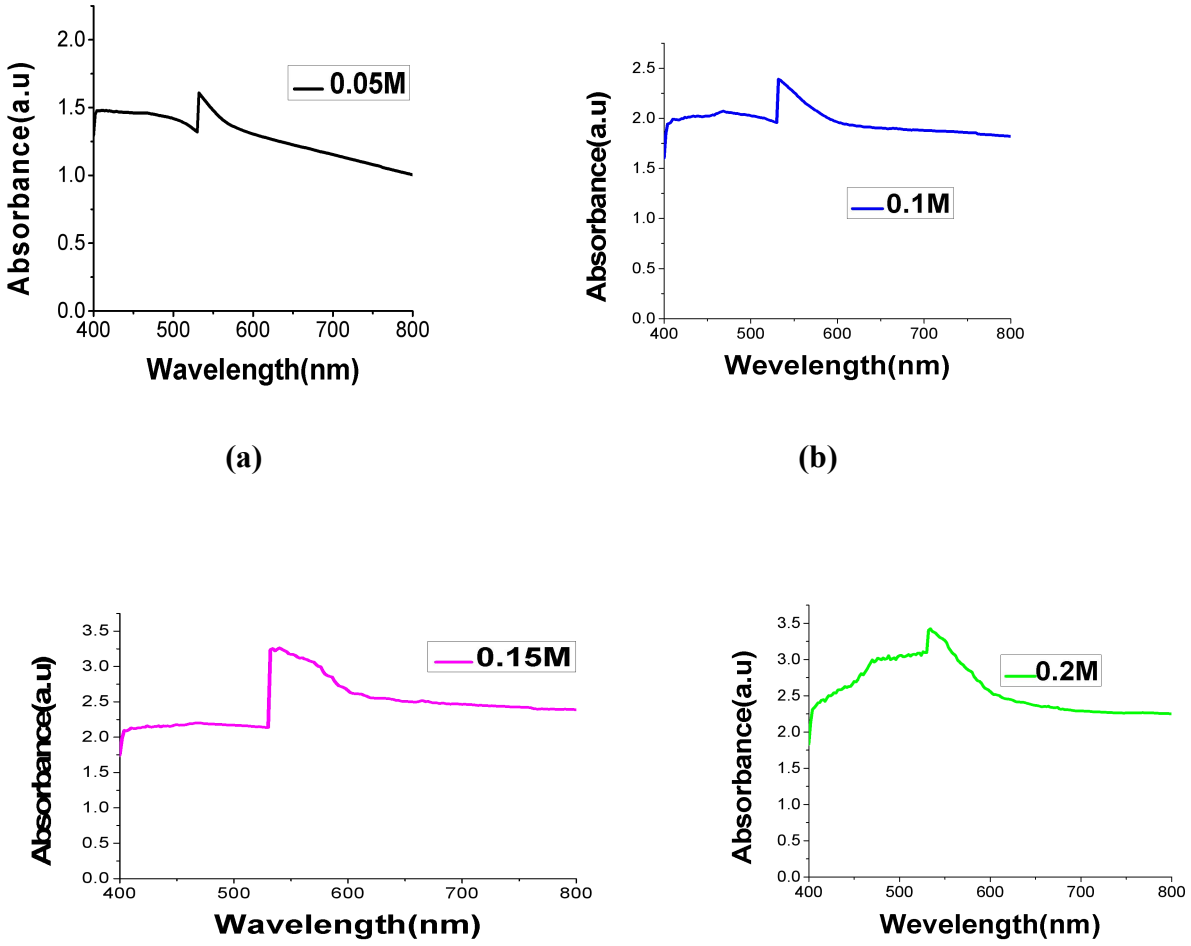


Figure 4.2: Optical absorption spectra of CdS thin films at (a) 0.05M (b) 0.1M (c) 0.15M and (d) 0.2M of Cd^{2+} ion concentration.

ii) Optical energy band gap

From UV-VIS optical studies of the CdS thin films, the band gap of the films was determined by plotting a graph between $(Ahv)^2$ and (hv). The band gap energy (E_g) was estimated by a linear interpolation of each curve to energy axis. The next figures shows optical energy band gaps of the CdS thin film for the concentration of Cd^{2+} ion with (0.05M, 0.1M, 0.15M, and 0.2M).

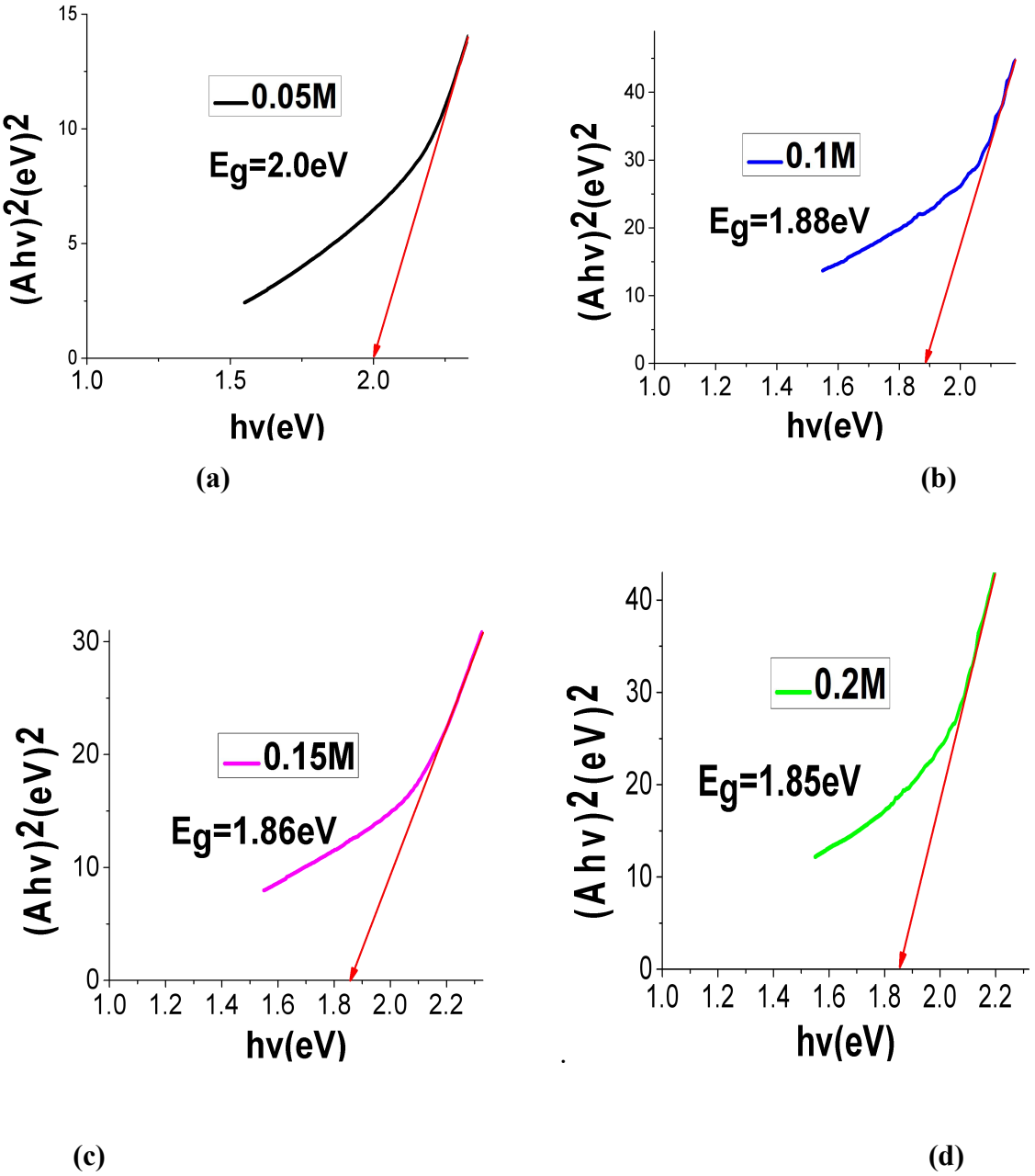


Figure 4.3: The band gap of CdS thin films at (a) 0.05M (b) 0.1M (0.15M) and (d) 0.2M of Cd^{2+}ion concentration.

The energy band gap value of the CdS film was determined from the above Figures. It was found that the band gap decreased from 2.0eV to 1.85eV with increasing the cadmium ion concentration. This decrease in the band gap is due to the improvement in the film crystallinity, i.e. the crystalline size. High concentrations lead to the films become more crystalline and the crystalline size increase. These values are in good agreement with the values reported by Ganesh R.et al.(2014), Hani H. et al.(2012) and Kakhaki Z.M. et al.(2022).

Table4.2: Summery of energy band gap of CdS thin films with increasing Cd^{2+}ion concentration

Cd^{2+}ion concentration (M)	0.05	0.1	0.15	0.2
Energy band gap (eV)	2.0	1.88	1.86	1.85

CHAPTER FIVE

5. CONCLUSION AND FUTURE WORK

5.1. CONCLUSTION

The depositions of CdS thin films were successfully prepared with different cation (Cd^{2+}ion) concentration in an alkaline medium by chemical bath deposition. From XRD results, the crystal size increases in the range from 8.78nm to 18.98nm and crystallinity improved with the increases of cadmium (Cd^{2+}) ion concentration. When the Cd^{2+}ion concentration increases the XRD results indicates five peaks with four strong reflection peaks around 2θ at the value of 26.6^0, 31.57^0, 44.13^0 and 52.33^0 corresponding to the (111) ^{C}, (200) ^{C}, (220) ^{C} and (311) ^{C} planes for the CdS phase and another one additional less intensity diffraction peaks at an angle of 38.44^0 corresponding to the planes of (200) ^{C} crystalline belongs to the cubic phase of CdO. This may be due to annealing effect and another reason may be due to excess cadmium elements in the chemical bathes at 0.1M – 0.2M of Cd^{2+}ion concentration. of CdS thin films. The strain and dislocation density decreases with increasing Cd^{2+}ion concentration. From UV-Vis Spectrophotometer study, the band gaps are decreases from 2.0eV to 1.85eV with increases in Cd^{2+}ion concentration from 0.05M to 0.20M of bath solution. Absorbance peak intensity of the films increases by increasing the Cd^{2+}ion concentration in the solution. This is due to the increases of the crystalline size. These result shows CdS thin films will serve well in a specific application.

5.2. FUTURE WORK

Even though the deposition carried out was successful, a few questions still remain unanswered and further investigation should be carried out in the following areas:

- An investigation into the morphology of the Cd^{2+}ion concentration of CdS thin film by carrying out Scanning electron microscopy (SEM) or Transmission electron microscopy (TEM).
- An investigation into the composition of the the Cd^{2+}ion concentration of CdS thin film by carrying out Energy dispersive analysis of X-ray (EDAX).

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