THE EFFECT OF DEPOSITION TEMPRATURE ON THE CADMIUM DOPED COPPER OXIDE THIN FILMS DEPOSITED BY CHEMICAL BATH DEPOSITION METHOD

MSC THESIS

BY

SIMACHEW SHITAHUN

HAWASSA UNIVERSITY, HAWASSA ETHIOPIA

NOVEMBER, 2024

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DECLARATION

I hereby declare that this MSc Thesis is my original work and has not been presented for a Degree in any other university, and that all sources of material used for the Thesis have been Duly acknowledged.

Name: Simachew Shitahun

Signature: _____

This MSc thesis has been submitted for the examination with my approval as thesis advisor.

Name:-_____

Signature:_____

Hawassa, Ethiopia
November, 2024

ADVISORS'S APPROVAL SHEET-1

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This is to certify that the thesis titled "**the effect of Deposition Temperature on the Cadmium Doped Copper Oxide Thin Films Deposited By Chemical Bath Deposition Method**" submitted in partial fulfillment of the requirements for the degree of Masters in Physics, Hawassa University, and is record of original research carried out by **Simachew Shitahun ID. No GGPhy/012/10** under my supervision and not part of the thesis has been submitted for another degree or diploma. The assistance and the help received during the course of this investigation have been duly acknowledge d. Therefore I recommended that it may be accepted as fulfilling the thesis requirement.

Dr. Tizazu Abza

_____	_____	_____
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November, 2024

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We, the undersigned, members of the board of examiners of the final open defense by **Simachew Shitahun Sewagnegn** have read and evaluated his thesis entitled "**the effect of Deposition Temperature on the Cadmium Doped Copper Oxide Thin Films Deposited By Chemical Bath Deposition Method**" and examined the candidate. This is therefore, to certify that the thesis has been accepted in partial fulfillment of the requirement for the degree of Masters in Physics.

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

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Abstract

The cadmium doped copper oxide thin films were deposited on the glass substrate for 30minutes by using chemical bath deposition. The bath contained the solution of cadmium chloride and copper acetate as a source of cadmium and copper ion respectively. Hydrazine and ammonia used as complexing agent at deposited temperature of 40°C, 60°C, 70°C and 80°C. The films were characteri zed using XRD and UV- VIS characterization techniques. According to X-ray diffraction analysis the prepared thin films revealed that monoclinic CuO and cubic Cu_2O phases coexist in all samples. Th ere also was very weak peak of cubic face centered CdO only at lower deposition temperature 40^0C; however it was inhibited at deposition temperature 60^0C, 70^0C and 80^0C. The crystallinity of Cu_2O and CuO phases were increased as deposition temperature increased except a slight decreased from 60^0C to 70^0C for Cu_2O and from 70°C to 80°C for CuO. However, dislocation and lattice strain decr eased with increasing temperature, except a slight increased from 60^0C to 70^0C for Cu_2O and from 7 0°C to 80°C for CuO. The optical study of the films showed that absorbance was higher at shortest wave length. The band gaps of the films were decreased from 1.95 eV to 1.90 eV for deposition temp erature increased from 40^0C - 80^0C.

Key words: Cd:CuO, Thin films, CBD, deposition temperature, XRD and UV-VIS

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ABRIVATION AND ACRONYM

A	Absorbance
A°	Angstrom
β	Half-maximum line breath
CBD	chemical bath deposition
CdO	cadmium oxide
CIGS	copper indium gallium selenides
CIS	copper indium selenides
CuO	copper oxide
D	Average crystallite size
Eg	Band gap energy
FWHM	full width at half maximum
Ge	Germanium
Hν	Photon energy
IP	ionic product
IR	infrared radiation
JCPDS	Joint Committee on Powder Diffraction Standards
K_{sp}	solubility constant
λ(nm)	Wave length in nm
PV cell	photovoltaic cell
Si	Silicon
SP	solubility product
TCO	transparent conducting oxide
T/TD	Deposition temperature
UV-VIS	Ultraviolet visible spectrum
XRD	x-ray diffraction

CHAPTER ONE

1. GENERAL INTRODUCTION

Transition metal chalcogenides: oxides, sulfides, selenides and telluride, are important technological materials. Their potentials are increasingly being recognized, with current and potential applications of transition metal chalcogenide including: solar energy conversion, solar control coatings, microelectronic devices, catalysts, sensors, optical filters and laser sources. More recently, ternary copper chalcogenides, such as copper indium selenides (CIS) or copper indium gallium selenides (CIGS) are being used in solar cell technology. These ternary copper chalcogenides have the potential for widespread use in a range of areas, particularly solar energy conversion, and electronic sensor applications [1-4].

A variety of methods have traditionally been used to prepare high quality transition metal chalcogenides. Each technique has its limitations. For example, solid state reactions require the use of high temperatures to ensure the transition of solid reactants into the molten state. Spray pyrolysis, chemical vapour deposition and vacuum evaporation reactions also require high temperatures to enable the successful formation of the required chalcogenides. Chemical solution methods such as hydrothermal, solvothermal, and chemical bath deposition (CBD) generally require lower temperatures for successful generation of quality films [5].

In CBD, the chalcogenide film forms when the substrate is immersed into a dilute, generally alkaline, solution containing metal ions and an appropriate source of chalcogenide ions. Complexation of the metal ions enables the rate of the reaction to be controlled. The chalcogen anion is usually generated by the decomposition or hydrolysis of an organic or inorganic precursor.

Despite the advances that have been made using CBD, the full development of the technology has been hampered by poor understanding of the relationships between process chemistry and film structure, factors that are dependent on the properties of the bath and deposition precursors. The process is sensitive to precursor concentrations and to the substrate used [7-9].

The optimal deposition parameters are generally different for each compound deposited. Although there have been numerous papers published reporting the preparation of chalcogenides thin films using CBD, Kaur et al. point out that the process has remained recipe oriented with little understanding of the kinetics of the process [10]. There is, therefore, the researcher needed careful investigation of

the CBD process and identification of the conditions that favour high quality coherent deposits.

1.2. Semiconductor materials

Semiconductor materials are defined as materials in solid form whose conductivity has a value between conductors and insulators. Semiconductor materials play an important role in the advances i n the modern electronics industry in the twenty- first century and in the industrial applications of ma ny electronic devices. These materials include many materials such as silicon, gallium arsenide, ger manium, cadmium sulfide, which are widely used today. From the first silicon integrated circuits pr oduced in semiconductor technology, high tech microprocessors, solar cells, and many other electro nic devices have developed rapidly to the present day [11].

Especially with the development of science, interest in the research and production of both efficient and lower cost semiconductor thin film materials is increasing day by day. The use of thin films for t he efficient use of solar cells in the production of n type semiconductor materials is one of the most i mportant sources of energy and new generation energy. To understand the nature of these crucial en gineering materials, the difference and theory between conductors, insulators, and semiconductors m ust be fully understood. In addition, basic concepts such as band theory, doping processes, and p-n c onnection theory of solids are theoretical bases that will give a general idea of understanding semico nductors. Furthermore, the electrical characteristics of these materials are extremely sensitive to the presences of minute concentrations of impurity atoms, for which the concentrations may be controll ed very small partial regions. Semiconductors have made possible the advent of integrated circuitry t hat has totally revolutionized the electronics and computer industries [12].

Two general classifications of semiconductors are, the elemental semiconductor materials found in g roup IV of the periodic table. Examples are Silicon=Si, Germanium=Ge, and Compound Semicondu ctors materials most of them found special combination of group III & group V or group II & group VI elements [13].

1.3. Compound Semiconductors

Compound semiconductors are materials which consist of various elements with wide ranging physi cal properties. They have been a subject of semiconductor research for nearly as long as elemental s emiconductors [14]. With the increasing demand place done voice and data communications, transm itting, receiving, and processing information at high frequencies and high speeds using both microw ave and optical means has become another area where compound semiconductor have also become i

ncreasingly important. Thus ternary copper chalcogenides have the potential for widespread use in a range of areas, particularly solar energy conversion, and electronic sensor applications. In recent ye ars copper oxide has attracted increasingly interests for both fundamental and practical reasons. The copper oxides of transition metals are an important class of compound semiconductors, which have applications in magnetic storage media, solar energy transformation, electronics and catalysis[15]. Among the oxides of transition metals, copper oxide is of special interest because of their efficiency as thin film fluids in heat transfer application. For example it has been reported that 4 % a ddition of CuO improves the thermal conductivity of water by 20%[16]. CuO is a semiconducting c ompound with a narrow band gap and used for photoconductive and photo thermal applications [17] . Copper oxide is a widely used compound semiconductor material

Table 1.1 Common binary and ternary semiconductors [18]

Periodic table group	Binary compounds	Ternary compounds
II-VI	CdS, CdSe, CdTe, ZnS, ZnSe, ZnTe	$Hg_{1-x}CdxTe$, $Cd_{1-x}ZnxTe$, $ZnS_{1-x}Se_x$, $Cd_{1-x}Zn_xS$,$Cd_{1-x}Zn_xSe$
III-V	GaP, GaAs, GaSb, InP, InAs, InSb	
IV-VI	PbS, PbSe, PbTe	$Pb_{1-x}Sn_xTe$, $Pb_{1-x}Sn_xSe$, $PbS_{1-x}Se_x$
IV-IV	SiC, Si1-xGex	

A lot of studies have revealed much about their general nature, features of their chemical stability an d their energy gaps. Before a long period of time, there were different researchers who have been studied the ternary metal chalcogenides semiconductor by using different methods. S ome of them were attended on the chemical bath deposition due to its effectiveness.

1.4. Classification of Semiconductors

In general, depending on the level of doping, semiconductors can be classified into two main groups such as intrinsic semiconductors and extrinsic semiconductors.

1.4.1. Intrinsic Semiconductors

Absolutely pure semiconductors without any impurities inside the crystal lattice are called intrinsic.

The fundamental characteristic of a pure semiconductor is the absolute equality of the number of fre e electrons and free holes at any temperature. These carriers are thermally or optically (absorption of a photon the fundamental process in a PV cell) generated [16].

For an intrinsic semiconductor, the concentration of electrons in the conduction band is equal to the concentration of holes in the valence band. The electron and hole in the intrinsic semico nductor are usually referred to as the intrinsic electron concentration and intrinsic whole concentrati on [19, 20]

1.4.2. Extrinsic semiconductors

By themselves, intrinsic semiconductors are not of particular use. They are neither good conductors nor insulators, and their conduction is largely dependent on temperature. We can alter the properties of the material by introducing foreign substances or impurities into the crystal. These impurities are also known as dopants. A crystal with an added dopant is referred to as an extrinsic semiconductor o r doped material. The amount of impurity added is generally small, perhaps in the neighborhood of o ne part per million [17]. A semiconductor formed from an intrinsic semiconductor by adding impurit y atoms to the crystal in a process known as doping [18].

The doping of impurities into the semiconductor lattice allows modulating its electrical properties: t hese doped semiconductors generally called extrinsic semiconductors. Extrinsic semiconductors wit h a larger electron concentration than holes concentration are known as n type semiconductors, wher eas those with a larger holes concentration than electron concentration are known as p type semicon ductors [20]. Depending on the impurity, there are two types of extrinsic semiconductors, which are called p type and n- type semiconductors.

1.4.2.1. N-type semiconductors and P-type semiconductors

Semiconductor material doped with some pentavalent impurity atoms like Sb, As, P, Bi are known as n-type semiconductors. Semiconductor materials doped with some trivalent impurity atoms such as Al, Ga, B called p-type semiconductor [22, 23]. Doping changes the distribution of electrons within the solid, and hence changes the Fermi level [24]

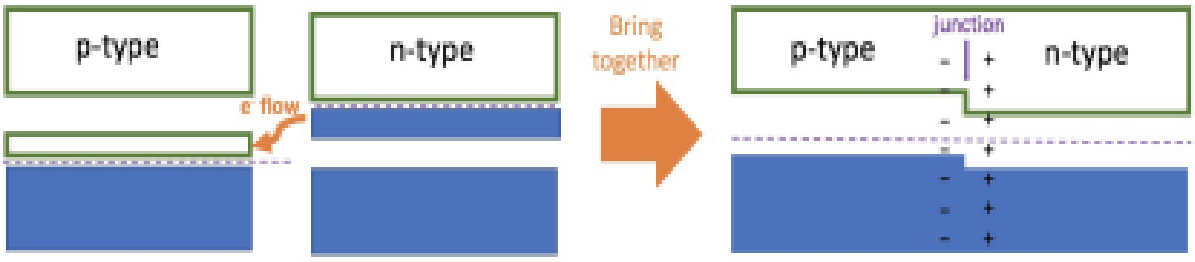

Figure 1.1. When p-type and n-type semiconductors are brought together, electrons move from the n side to the p side. Charge builds up in the interface forming a p-n junction[25].

And also from the figure1.2: below, the researcher reviewed all have a band which is the conduction band at the top and valance band at the bottom. The band gap is the gap between the highest energy electron states in the valance band to the lowest state in the conduction band. In insulators, the valen ce band is separated from the conduction band by a large gap; in good conductors such as metals the valence band overlaps the conduction band, Whereas in semiconductors there is a small gap betwee n the valence and conduction bands, small enough allowing thermal excitation of electrons from the valence to conduction band. These bands represent the outermost energy levels that electrons can oc cupy. Generally speaking electrons in the valence bands are still tightly bound to the atom and cannot move around to other atoms in the crystal. However, electrons in the conduction band have enough energy that they can freely move throughout the crystal material thus acting as mobile charge carriers which can conduct current.

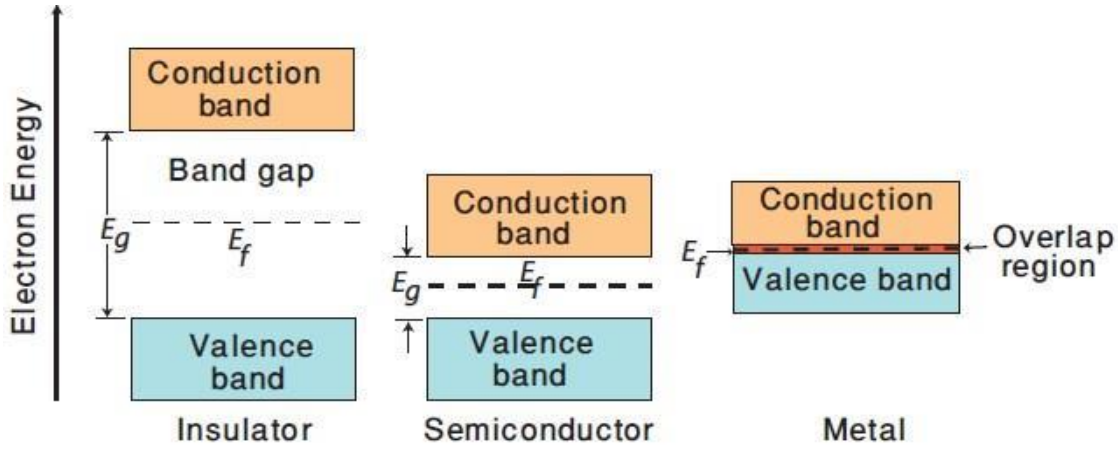

Figure 1.2. Energy band structure of insulator, semiconductors and conductors [26]

1.5. The General Properties of Copper Oxide

Copper oxide (CuO) is one of potential p-type semiconductors and monoclinic in structure that gains considerable attentions due to its excellent optical, electrical, physical, and magnetic properties. Cu O with narrow band gap of 1.2 eV is extensively used in various applications such as catalysis [27], solar energy conversion [28], gas sensor [29] and field emission [30]. Properties can be improved by synthesis in CuO that shown excellent performance counterpart. Among various metal, copper (Cu) and copper oxide (CuO) have attracted considerable attention because copper is one of the most imp ortant in modern technologies and is readily available [31].

Considerable interest has been focused on copper due to their optical, catalytic, mechanical and elec trical properties [30]. It has been applied to the catalyst, superconducting materials, thermoelectric materials, sensing materials, glass, ceramics and other fields. In addition, copper oxide has been use d as rocket propellant combustion catalyst and also more use such as: Ceramic resistors, gas. The int erest in semiconductor copper oxide is justified by the fact that their fundamental physical and chemical properties can be very different from those of the semiconducting materials play an import ant role in our modern day electronics. In the early days of radio and television, transmitting and rec eiving equipment relied on vacuum tubes, but these have been almost completely replaced in the last fifth decades by semiconducting materials, including transistors, diodes, integrated circuits and othe r solid-state devices [30]. Such devices have found wide applications due to their numerous advantages such as compact sizes, reliability, power efficiency, and low cost. The oxide of copper like CuO (cupric oxide) is a monoclinic structure whereas Cu_2O (cuprous) is a cubic crystal structure.

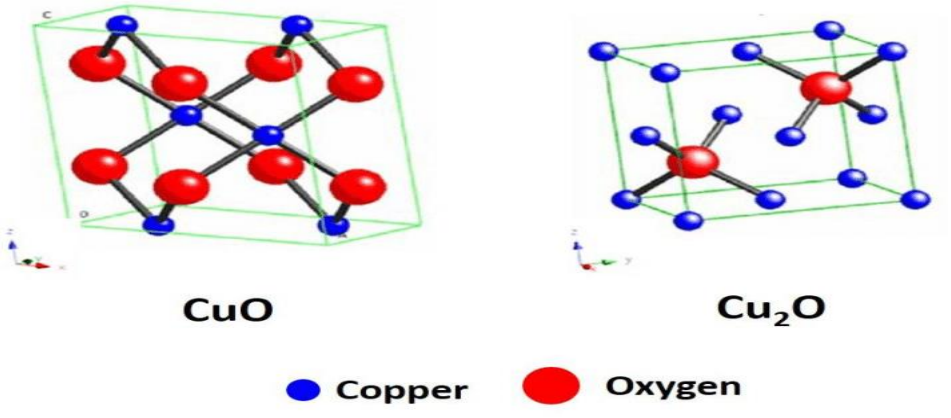

Figure 1.3: Chemical structure of CuO and Cu2O

1.6. The General Properties of cadmium oxide

Transparent conducting oxides (TCOs), in recent years, have attracted the attention of many researchers due to their unique physical properties and wide range of applications in industry. Cadm ium oxide (CdO) is a type of transparent conducting oxide (TCO) material that possesses both high electrical conductivity and high optical transparency in the visible region of electromagnetic spectru m. CdO is an n-type semiconductor with a wide direct optical band gap of ~ 2.2 eV [32] that exhibit s rock salt structure (FCC). Thin films of CdO find wide applications in solar cells, smart windows, optical communications, flat panel displays, phototransistors, as well as other types of applications like IR heat mirror, gas sensors, low-emissive windows, thin films resistors, etc. [33–36].

1.7. Statement of the problem

Copper oxide (CuO) is one of the important semiconductors, advantageous materials and has been studied for photovoltaic applications, could be obtained by the oxidation of copper and has a monoclinic crystal structure as a characteristic. Copper oxide (CuO), a semiconductor has several unique features such as low cost, non toxicity, perfect detector for big number of gases as active sub stance in the gas sensors [37]. Abundant availability in the form of copper and needs to be prepared as copper oxide thin films. Copper oxide has dark brown color and many applications about optical-thermal collectors of solar due to high efficiency [38], good level of stability of CuO and high absor bency in visible wavelengths. CuO is attractive as a selective solar absorber since it has high solar absorbency and a low thermal remittance. Furthermore, it is a promising semiconductor for solar cel l fabrication due to its suitable optical properties [38].

Thin films of copper oxides have been prepared by various techniques such as thermal oxidation, ele ctro deposition, chemical conversion, chemical brightening, spraying, chemical vapor deposition, so l gel method, plasma evaporation, reactive sputtering, molecular beam epitaxy, SILAR method, and chemical bath deposition method for CuO thin films on glass substrates. The properties of CuO can be tuned by doping diffrent elements and deposition parameters like temperature. There were few re ports on cadmium doped copper oxide thin films by chemical bath deposition and the effect of depos ition temperature on its properties. Therefore the researcher was studied cadmium copper oxide thin film using CBD method at different deposition temperature and used different thin film characterizat ion technique like X-ray diffraction (XRD) and Ultraviolet visible spectrum (UV-VIS).

1.8. Objectives of the research

1.8.1. General objective of the research

❖ The general objective of this research is to study the effect of deposition temperature on cadmium copper oxide thin films synthesized by CBD method.

1.8.2. Specific objective of the research

➢ To synthesis Cadmium copper oxide thin film at various temperatures by chemical bath deposition method.

➢ To investigate the effect of deposition temperature on the structural and optical properties of Cadmium Copper oxide thin films by using XRD and UV-Vis.

1.9. Thesis structure

The thesis was structured into five chapters.

The first chapter deals with some introduction about Semiconductor materials, their property and ap plication both copper oxide and cadmium oxide thin films were explained. Objectives of the research and statement of the problem were included in this chapter. The second chapter was dealt with thin film materials and review of literature on cadmium copper oxide thin films. The third Chapter was dealt with methodology and characterization techniques of thin films and the basic principle of the Chemical bath deposition techniques for thin films. Experimental procedures were d iscussed in this chapter and explained in details the preparation of solution. The fourth chapter dealt with results and discussion. Details of cadmium copper oxide thin films deposition, characterization and data analysis were presented. Under this chapter all the thin film characterizations such as XRD and UV/VIS spectrophotometer were presented in graphical format and discussed. Finally in chapter five conclusion and recommendations of this work was presented.

CHAPTER TWO

REVIEW LITERATURE

2.1. Thin films

Thin-film measurements range from a single atom to several micrometers.

Thin films are everywhere in the modern world, with many of the technologies we depend upon in daily life being, in turn, dependent upon thin film technology. These may range in dimension from an atomic or molecular monolayer perhaps only a few angstroms thick to either mono or multilayer coatings with a thickness of several microns [39]. Such materials may have a huge range of extremel y useful properties; they may be, for example, anti-reflective, impervious to oxygen and/or other gas es, optically transparently electrically conductive, catalytic, and self-cleaning. Everyday examples featuring thin film technology include, but are not limited to, mobile phones, touch screens, laptops, and tablets. Other important applications of thin films include band pass filters as used in ga s analysis, mirrors used in astronomy protective (e.g., biomedical anticorrosive, and antimicrobial) c oatings, architectural glass coatings (e.g., to reflect heat while transmitting visible light), photovoltai c electricity generation, and a great many others[40].

2.2. Properties of Thin Films and their Application

There are several properties that are crucial for modern thin film applications. The manufacturing pr ocess must observe certain conditions and take certain precautions, so it's not harming the thin film applications afterwards. When depositing thin films onto a substrate, essential considerations includ e characterization techniques and long term performance of the enhanced properties. Substrate and fi lm type (i.e., metallic films, insulators, and semiconductors), purity and scaling alter electrical prope rties, such as reducing conductivity. Finally, the connect on between deposition parameters and microstructure growths influences a thin film's optical properties [39].

2.3. Review Of Copper Oxide Thin Films

Çetinkaya, S. (2024)[41] Reported on Cobalt (Co) doped Copper Oxide (CuO) thin films at differen t concentrations deposited on glass substrates, using Chemical Bath Deposition method. Copper (II) Acetate Monohydrate (Cu(CH3COO)2.H2O) (≥98%) (0.1 M) and Cobalt(II) Chloride Hexahydrate

(CoCl2.6H2O) (≥98%) metal salts was used as starting solutions for Cu and Co, respectively. The fil ms were characterized by X Ray Diffraction (XRD), all films had the preferential orientation($\bar{1}$11)a nd (111), at 2Θ changed from 35.7^0 to 35.7^0 for ($\bar{1}$11) and 39.0^0 to $38,9^0$ for (111) indices, with inter planar spacing(d) varied from 2.5(Å) to 2.52(Å) for ($\bar{1}$11) and 2.31(Å) to 2.32(Å) for (111), crystal size (D)16.0nm to 18.60 nm, micro strain ($\varepsilon\ 10^{-4}$)= 23.28(10^{15} cm^{-2}) to 23.09(10^{15} cm-^{2}) and dislocat ion density of the films (ρ) 4.22 to 4.14 for both indices respectively when concentration was increas ed. All diffraction peaks were matched with monoclinic CuO (ICCD: 801916) phase and no foreign peaks and/or a secondary phase were observed. The films also were characterized by Ultra Violet-Vi sible Spectroscopy and showed that band gap values changed with Co doping from 1.55eV to 1.44 e V. It was also observed that the conductivity increased with increasing temperature

Saadaldin et al (2015) [42] Reported that thin films of copper oxide were prepared by chemical bath deposition (CBD) method on substrates of glasses by Alternate immersions method (AI) at roo m temperature for 20 second using heated liquid of sodium hydroxide up to 70^0C and copper thiosul fate complex. They annealed at different temperatures (200-300-400) in the air; the crystalline struct ure of prepared samples was studied by using XRD technologies. The crystalline structure the films was related to temperature of annealing of copper oxide (Tenorite) and cubic of Cu_2O (Cuprite). The optical studies showed that the prohibited range between (1.3-2.4)eV was related to annealing temp erature (monoclinic) and the prepared samples at 400^0C were investigated by using Spectrophotomet er, absorbance curve showed high absorbance of the prepared film at short wavelengths, while less a bsorbance was at large wavelengths. Therefore, they were concluding application of solar cells is ve ry promising as a suitable material for conversion of photovoltaic energy with high absorbency solar and low thermal issue.

Aswad (2021) [43] reported thin films of copper oxide (CuO) prepared using a chemical bath deposi tion (CBD) method on glass substrate. Aqueous copper sulfate (CuSo4.5H2O) used to obtain the required thin films and in concentration 0.1M. The films prepared during different deposition times (1, 4 and 8) days at room temperature. The XRD studies showed that the thin film prepared at deposit ion time (8 days) has polycrystalline structure (monoclinic structure). The diffraction pattern showe d three strongest peaks at 2Θ values of 25.8^o , 43.9^o , and 61.1^o at planes (110), (202) and (301) respectively They generally observed from the results of X-ray diffraction that the peaks were not high and not sharp; the reason was that the manufactured films prepared at low temperature (room temperature)

Mondal, S. (2022) [44] Reported about CuO thin films synthesised by chemical bath deposition

(CBD) technique. XRD patterns of CuO thin films of diffraction peaks were observed at ~32.58°, ~36.06°, ~39.04°, 49.16°, ~54.14°, ~58.52°, can be associated with monoclinic copper oxide [JCPDS file no. 481548]. The corresponding diffraction planes were (110), (−111/002), (111/200 different), (−202), (020) and (202), respectively. The average values of crystallite size increase to~20.4 nm for CuO1 to ~26.3 nm for CuO_3 sample. Optical characterization was done by UV-Vis spectroscopy for 45 min deposited film at a sensibly low temperature of 120°C. The strain was found to decrease to $5.72x10^{-3}$ for CuO1 and $2.48x10^{-3}$ for CuO_3 samples. Band gap decreased with the deposition time that is due to increase in crystalline size or deposition time, which may be due to overlapping of CuO layer upon each other.

Singh et al (2011) [45] Reported about copper oxide (CuO) thin films prepared by chemical bath deposition technique (CBD). The films were investigated with respect to annealing temperature. According to XRD analysis, all the prepared thin films were polycrystalline with monoclinic structures and almost oriented at the planes (002) and (111). The observed band gap value of copper oxide thin films ranged from 1.65 eV to 1.59 eV. CuO film exhibits high absorption in the visible spectrum. This activity is particularly intriguing in terms of the use of CuO as an absorber layer in solar cells. These findings showed that CuO films prepared by the CBD method can be used to fabricate optoelectronic devices.

Sadiq et al., (2022) [46] reported that the annealing at temperatures of 400 and 500^{o}C in the air for 2 hours led to the formation of rod-like structures of cupric oxide thin films prepared by the chemical bath deposition technique. The preparation method was 1.70g of copper (II) chloride(CuCl2.2 H2O) is dissolved in 100 ml of de-ionized water to obtain a concentration of 0.1 M for 1 hour at room temperature. Then they added ammonia (NH3). The x-ray analysis showed that the thin films of copper oxide have a monoclinic crystallinity preferred in the (002), and (111 directions) with corresponding angles 32.52^0 and 35.58^0 respectively and the crystallinity increases after annealing. Furthermore, the band gap values after annealing are reduced from 2.1 to 1.61 and 1.63 eV as determined by optical analysis utilizing UV–VIS spectroscopy. Annealing at 400°C and 500 °C reduces the optical band gap, which may be attributed to the increased crystallinity resulting from the reduced number of structural defects and enhancement of CuO phase at the expense of Cu_2O phase.

Alkhayatt et al., (2020) [47] Reported that chemical bath deposition method (CBD) was used for deposited CuO thin films. It was prepared as: 0.1 M (Molarity) of copper chloride solution

was prepared by dissolve 1.7048g of copper (II) chloride dehydrate (CuCl2.2H2O) in 100 ml of deionized water (DI water) at room temperature and added ammonia solution.

X-ray diffraction studies showed the annealed films exhibited low crystallinity of polycrystalline nature in the monoclinic phase and was observed a fixed or very little increment of peaks intensity and the crystallinity of the deposited films as increased of annealing temperature to (150, 200 and 25 0)^{o}C with preferred orientation along (002) and (111) planes with diffraction peaks at 2Θ= 35.2° an d 38.5° respectively. The crystallite size was decreased, whereas the dislocation density and the nu mber of crystallites increased with increment of annealing temperature The optical energy gap for the film was increased to (2.03, 2.06 and 2.09) eV with the increment of annealing temperatures and concluded that the low annealing temperatures used in this work was not suitable temperatures for the growth of CuO films and it can be above 300^{o} C to enhance the film crystallinity and formation of CuO phase.

Johan et al(2011) [48] Reported the study of annealing effects on the properties of copper oxide thin film prepared by chemical deposition. The films were annealed in air at different temperature range of 200 – 400^{o}C. The XRD results reveal that, the as prepared films annealed at 200^{o}C were cuprite structure with Cu_2O composition. Films annealed at 300^{o}C consists of mixed phase of CuO and Cu_2O, whereas film annealed at 400^{o}C completely converts in to CuO phase.

Ezenwa (2012) [49] Reported CuO thin films were deposited on glass substrates using chemical bath deposition technique. The films' growth was based on the decomposition of cupric su lphate in the presence of sodium hydroxide with EDTA disodium salt (CH2N(CH2COOH)CH2CO ONa)22H2O) acting as complexing agent. The deposition process lasted 24 hours at deposition temperature 300K. Optical investigation was also performed with varying EDTA. The films were fo und to have strong absorption of approximately 0.87 at wavelength range of 300 - 320nm. The optic al absorbance generally reduced with increase in wavelength. The optical band gap of the deposited film was found to be 1.7eV.

Guneri (2019)[50] Reported about the effect of annealing Au doped on CuO films prepared by che mical bath deposition method and was studied their structural and optical properties. The solution co ntaining Cu was prepared with a mixed solvent comprised of ethylene glycol (10 ml), ethanol (10 ml) and DI water (10 ml). 0.07 gr of Cu were added to the pre-mixed solvents and was carried at 80 °C for 5hr with doping ratio was 200 µl Au - 500 µl Au. Annealing process was at an oxygen environment at 500°C for 1 h. The CuO peaks were detected using X-ray diffraction and all of the films were polycrystalline in the monoclinic structure with preferential orientation (002) plane and

that was detected in the annealed films but there was no Au peak in this film. Crystal size (D) increased from 145.8nm to 157.6nm but dislocation density δ (nm^{-2}) decreased from 4.7 to 4.0. The optical properties of the films were determined using the optic spectrometer. All films obtained have a higher absorption in the IR region and the energy band gap was varied between 1.86-2.09 eV for the films.

The properties of CuO can be tuned by doping different elements like cadmium and deposition para meters like temperature. But there were few reports on cadmium doped copper oxide thin films by c hemical bath deposition and the effect of deposition temperature on its properties. Therefore the curr ent researcher was studied cadmium copper oxide thin film using CBD method at different deposition temperature and used different thin film characterization technique like X-ray diffraction (XRD) and Ultraviolet visible spectrum (UV-VIS).

2.4. Review of cadmium copper oxide thin films

Al-jawad and Alogili (2009) [51] Reported the annealing effect for film deposited under optimum c onditions with a temperature of 353K° and pH= 9, M=0.2, and deposition time of 30min, the anneali ng is performed in air at temperature of 573K for 15 min. Using XRD pattern films onto glass substr ate, they observed the change of film after annealing. They observed that peaks at 2θ=33°, 38°, and 55° corresponding to diffraction from C(111) , C(200) , and C(220) planes respectively , implying diffraction from cubic phase of polycrystalline CdO.

Dhawale et al., 2008 [52] Reported about the deposited of a whitish CdO film on the glass slide after 45 h and observed whitish when rinsed with distilled water. It was post-treated at 200°C for 1 h which gave a whitish colour after the annealing and investigated it was post-treated at 400°C for 1 h, forming a brownish colour after the annealing. They also investigated the CdO films that were an nealed in oxygen air tight container at 473 and 673K for 1 h which generally facilitates decrease in d islocations. The change in colour from whitish to brown films during annealing confirmed the forma tion of CdO. Recently, the synthesized of copper thin film by different methods have been reported. Thus to synthesize cadmium copper oxide thin film by chemical bath deposion methods, the researc her was used a chemicals of Copper acetate, cadmium chloride and study it deeply.

CHAPTER THREE

METHODOLOGY

3.1. Thin film Deposition

Thin film deposition is the technology of applying a very thin film of material between a few nanometers to about 100 micrometers, or the thickness of a few atoms onto a "substrate" surface to be coated, or on to a previously deposited coating to form layers. Thin film deposition manufacturing processes are at the heart of today's semiconductor industry, solar panels, disk drives, and optical devices industries [53]. Thin films are everywhere in the modern world, with many of the technologies we depend upon in daily life being, in turn, dependent upon thin film technology. A variety of methods have traditionally been used to prepare high quality transition metal chalcogenides. Each technique has its limitations. For example, solid state reactions require the use of high temperatures to ensure the transition of solid reactants. Spray pyrolysis, chemical vapour deposition and vacuum evaporation reactions also require high temperatures to enable the successful formation of the required chalcogenide. Chemical solution methods such as hydrothermal, solvothermal, and chemical bath deposition (CBD) generally require lower temperatures for successful generation of quality films [54]. One of the earliest reports of the use of CBD was in the preparation of lead sulfide and lead selenide thin films for use as photoconductive detectors [55].

Since then, CBD has become an attractive method due to its suitability for large scale deposition. It is characterized by simple formulation, easy of set up and low temperature requirements. The process generally operates under ambient conditions and has the potential to replace expensive energy and equipment intensive techniques. In CBD, the chalcogenides film forms when the substrate is immersed into a dilute, generally alkaline, solution containing metal ions and an appropriate source of chalcogenides ions. Complexation of the metal ions enables the rate of the reaction to be controlled. The optimal deposition parameters are generally different for each compound deposited. There is, therefore, the need for careful investigation of the CBD process and identification of the conditions that favour high quality coherent deposits. Thin film deposition techniques can be broadly classified in to two categories: namely physical vapor deposition techniques and chemical deposition techniques [56]

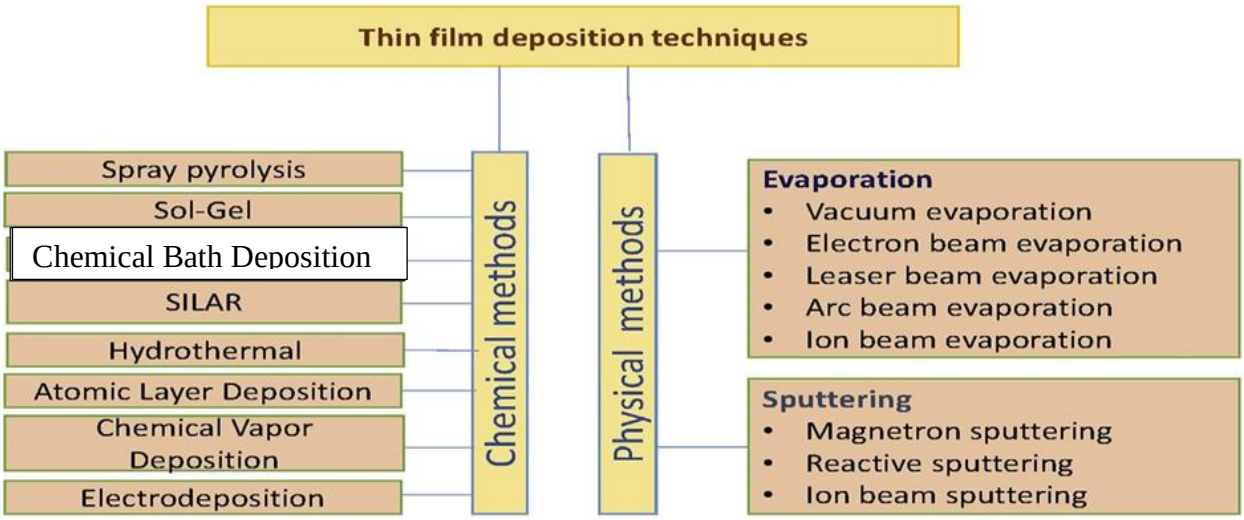

Figure 3.1. The schematic of brief classification of thin film deposition techniques [57]

Among these methods mentioned above, the chemical methods are economical and easier than that of the other such that CBD is the simplest cost effective method for large scale industrial application s, material consumption is low and minimizes the loss.

3.2. Chemical bath deposition method (CBD)

Chemical bath deposition (CBD) is one of the solution phase methods useful for the preparation of compound semiconductors from aqueous solutions. It is widely used for the deposition of various metal chalcogenide thin films. It produces good deposits on suitable substrates by the controlled pre cipitation of the compounds from the solution. Chemical film fabrication method involves chemical reaction and the precursors are mostly undergoing reaction at the substrate surface [58]. In CBD met hod, deposition of metal chalcogenide thin film occurs due to substrate maintained in contact with di lute chemical bath containing metal and chalcogen ions. Chemical bath deposition is a technique in which thin semiconductor films are deposited on substrates immersed in dilute solutions containing metal ions and a source of hydroxide, sulfide or selenide ions[59]. CBD is popular, well established and low temperature chemical method widely used for thin film deposition. The semiconducting thi n films synthesized by CBD method have potential to compete with film by other sophisticated techniques. The CBD works on the principle of super saturation.

The several advantages of CBD are

- CBD can provide simultaneous deposition of several films by suitable modification in chemical bath.
- It is found to be beneficial for deposition of compound semiconductors.

- CBD avoids the corrosion and oxidation of the substrates.
- CBD method provides better orientation of crystallites due to higher reaction time

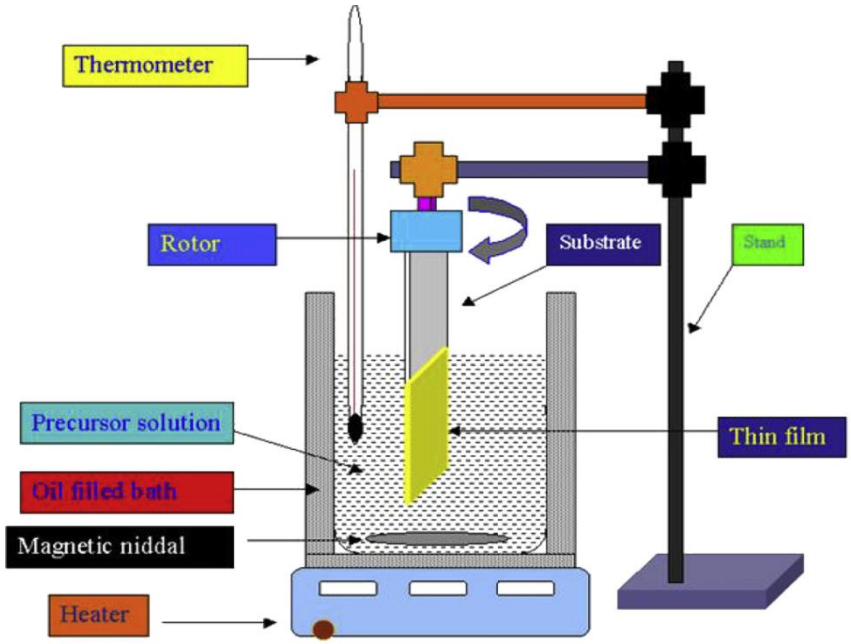

Figure 3.2 Experimental set-up of chemical bath deposition [60]

3.3. Basic principles of chemical bath deposition

The basic principles behind the CBD process are similar to those for all precipitation reactions, and are based on the relative solubility of the product.

The equilibrium concentration of ions in solution is defined by the solubility product (SP) expressio n in (equation 3.2):

$$K_{sp} = [M^{n+}]^a[X^{M-}]^b \quad \text{.....(3.1)}$$

Where K_{sp} is the solubility constant and $[M^{n+}]^a[X^{M-}]^b$ is the ionic product (IP).

aM^{n+} ions and bX^m- ions are formed from the solid as in equation (3.2).

$$M_aX_b(S) \rightleftharpoons aM^{n+}(aq) + bX^{m-}(aq) \text{..... (3.2)}$$

The preparation of metal oxide by introducing O^{2-} ions into an aqueous solution of a metal salt to effect chemical precipitation is well established. O^{2-} ions can be generated by hydrolysis of H_2O gas in aqueous solutions [61]. The equations for this hydrolysis are presented in equations (3.3) and (3.5):

$$H_2O + OH^- \rightleftharpoons HO^- + H_2O \text{.....(3.3)}$$

$$OH^- + HO^- \rightleftharpoons O^{2-} + H_2O \text{.....(3.4)}$$

The oxide ions formed in equation 3.3 react with the metal ions in solution to produce the metal

oxide. Precipitation occurs when IP > K_{sp}.

In CBD, this process is modified such that precipitation is controlled to eliminate or reduce spontane ous precipitation. As the complex dissociates, the following equation applies (assuming a metal ion with a charge of 2^+):

$$M(A)^{2+} \rightleftharpoons M^{+} + A \quad \text{..... (3.5)}$$

At any given temperature, the concentration of free metal ions is given by equation (3.6)

$$K_i = \frac{[M^{2+}][A]}{[M(A)^{2+}]} \quad \text{..... (3.6)}$$

In this equation, Ki is the stability constant of the complex ion. A complex with a small K value is most stable, and will therefore have a lower concentration of metal ions in solution than one with a h igher constant. By controlling the concentration and temperature of complexing reagent, the concent ration of metal ions in solution can also be controlled. If these ions can be generated at a surface, then it leads to CBD of a film.

3.4. Nucleation and Film Growth

Nucleation and film growth are key processes in materials science, particularly in the formation of thin films and coatings. Nucleation is the initial step in the phase transition where small clusters (nuclei) of a new phase begin to form within an existing phase. The nucleation process plays an imp ortant role in determining the crystalline and microstructure of the resultant film. For the deposition of thin films with thickness in the nanometer region, the initial nucleation process is more important. Once nucleation occurs, film growth can take place [62].

3.5. Thin Film Deposition Mechanism in Chemical Bath Deposition

There are four main mechanisms for the compound formation, whose operation depends on the spec ific process and reaction parameters. The thin films CBD deposition occurs via following four possi ble mechanisms [63].

3.5.1. Simple ion-by-ion mechanism

In most of the CBD's, the ion-by-ion conceptually simplest mechanism, often assumed to be the ope rative one in general. It occurs by sequential ionic reactions. The general reaction for the mechanism

$$M^{n+} + X^{m-} \rightarrow M_m X_n \text{ (Adsorbed on the substrate)} \quad \text{..... (3.7)}$$

The formation of solid M_mX_n is based on the principle that when the ion product, $[M^+][X^-]$, exceeds the solubility product, Ksp, of M_mX_n, then M_mX_n can form as a solid phase, although a large r ionic product may be required if super saturation occurs. Solid nuclei will redissolve before growin g to a stable size.

3.5.2. Simple cluster (hydroxide) mechanism

In most of the CBDs, the preparative conditions are so chosen that the formation of metal hydroxide should be avoided. However, in reality, CBDs are quite often carried out under conditions where a metal hydroxide is formed. This might seem to imply that a precipitate of metal hydroxide [M(OH)n] is formed at the start of the CBD. In fact, the metal hydroxide formed is either as a colloid rather than a precipitate or as an adsorbed species on the substrate. In this case metal chalcogenide (M_mX_n) is formed by reaction of X^{m-} ion with the $M(OH)_n$.

$M^{n+} + nOH^- \rightarrow M(OH)_n$……(3.8)

Followed by,

$M(OH)n + X^{m-} \rightarrow M_m X_n + nOH^-$ ……..……. (3.9)

3.5.3. Complex-decomposition ion-by-ion mechanism

In this mechanism, complexation of free metal cations (M^{n+}) by thiourea gives M-thiourea complex ion. This is illustrated by the example of CdS deposition.

This would lead to CdS formation in solution. If Cd^{2+} is absorbed on the substrate then above reactio n occurs and CdS is formed on substrate

$Cd^{2+} + (NH_2)_2 CS = [(NH_2)_2 CS - Cd]^{2+}$ ……. (3.11)

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

$[(NH_2)_2 CS - Cd]_2 + 2OH \rightarrow CdS + CN_2H_2 + 2H_2O$ …… (3.12)

3.5.4. Complex-decomposition cluster mechanism

The complex-decomposition cluster mechanism is based on the formation of solid phase instead of reacting directly with a free anion; it forms an intermediate complex with the anion-forming reagent. Continuing with CdS deposited from a thiourea bath by considering example given as

$Cd(OH)_2 + (NH_2)_2CS \rightarrow Cd(OH)_2.SC(NH_2)_2$……(3.13)

$Cd(OH)_2$ is one molecule in the solid phase cluster. This complex or a similar one if contains ammine ligands then decomposes to CdS. $Cd(OH)_2. SC(NH_2)2 \rightarrow CdS + CN_2H_2 + 2H_2O$…..(3.14)

The S–C bond of the thiourea breaks, leaving the S bond to Cd. It is suggested that Cd $(OH)_2$ forms initially on the substrate and catalyzes the thiourea decomposition. The catalytic effect of the solid surface could be to decompose thiourea to sulfide ion.

3.6. Factors Affects the deposition process

The influences of the deposition process in CBD technique are nature of reactant, concentration of reactant, concentration of complexing agent, temperature, PH value, duration of the reaction, nature and spacing of the substrates etc. [64].

3.6.1. Nature of reactant

Nature of reactants influences the composition of the products. The growth kinetics also depends on the nature of reactants. Concentration of reactant: the deposition rate and terminal thickness initially increases with an increase in the ionic concentration of the reactants. However, at high concentratio n the precipitation becomes very fast, leading to decrease in film thickness on the substrate [65]

3.6.2. Nature of complexion agent

Nature of complexing agents may the final products. Concentration of complexing agent: a few have successfully deposited various types of thin films using chemical bath deposition method in the pres ence of complexing agent. These complexing agents including, Cadmium Acetate, Cadmium chlorid e, ammonia, tartaric acid, triethanolamine, ethylenediamine tetra acetic acid, sodium tartrate, ammo nium sulphate, diethanolamine and hexamine[66].

3.6.3. Effect of 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 mole cules also increases leading to greater interaction between ions and subsequent deposition at volume nucleation centers of the substrate. This will result in increase or decrease of terminal thickness, depending on the extent of super saturation of the solution of the bath. Stirring basically brings fresh parts of the solvent into contact with the solute and particles are forced to connect and the presence of temperature assists the entire process for effective desired results. In most cases higher t emperatures allow more grain growth whereas, lower temperatures gives very small nuclei in solutio n that are thermodynamically unstable. The effect of deposition temperature on the structural, morph ological and optical band gap of chemically deposited PbSe thin films were studied by F. G. Hone

and F. K.[64]. Films deposited at higher temperatures exhibited sharp and intense diffraction peaks, indicating an improvement in crystallinety. The deposition temperature also had a strong influence o n the preferred orientation of the crystallites as well as other structural parameters such as micro stra in and dislocation density. In most cases chemical bath deposition can be used to carefully control th e 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[64].

Thus our study was focused on cadmium CuO thin films would be deposited if the ionic product (IP) of Cu^{2+}, (Cd^{2+}) and (OH^{-}) exceeds the solubility product (SP) of $Cd(OH)_2$ and $Cu(OH)_2$. The growt h kinetics of CuO films with the deposition time of 30 minutes at four different temperatures.

we can observe that the terminal thickness increases with increasing bath temperature, where the heating of the solution helps the decomposition of the reactants and produces the ions which are ver y necessary for film formation. In addition to that, it provides kinetic energy to the ions, resulting in increased number of collisions and hence combination to form $Cu(OH)_2$ and $Cd(OH)_2$ leading to increase in terminal thickness with increasing bath temperature

3.6.4. Nature of substrates

Surface of the substrate plays a major role in the adhesion of the deposited film. Hence cleaning of the substrate surface is a prerequisite for film deposition by CBD. Higher deposition rates and terminal thickness are observed for those substrates whose lattices and lattice parameters match well with those of the deposited material. It was observed that film thickness reach an asymptotic maxim um spacing of substrates: with increase in substrate separation [67, 68].

3.6.5. Reaction PH.

Agent, the bath solution PH value and the When the PH value of the reaction bath increases, the metal complex usually becomes more stable, reducing the availability of free metal ions. This will decrease the reaction rate resulting in higher terminal thickness.

3.7. Thin film characterization technique

The application of thin films is becoming increasingly interdisciplinary in nature, leading to new demands for film characterization and properties measurements for both individual films and m ultilayer films [69]. Measurements and characterization of the film thickness, micro-structure and co

mposition can be carried out using various techniques. They include X ray diffraction (XRD) and U V Vis spectrophotometer which are briefly described below.

3.7.1. X-ray Diffraction (XRD)

X-ray diffraction (XRD) is a powerful technique for characterizing crystalline materials. It provides information on structures, phases, preferred crystal orientations and other structural parameters, such as average grain size, crystallinity, strain, and crystal defects. The peak intensities are determined b y the distribution of atoms within the lattice[70].

The Bragg diffraction condition for X-rays is given by,

$$2d(hkl) \sin \theta = n\lambda, \quad \ldots\ldots (3.15)$$

Where d(hkl) is the interplanar spacing of the (hkl) planes, θ is the X-ray incident angle, λ is the wavelength of the X-ray and n is a positive integer which represents the order of reflection. This is known as Bragg law. From the width of the diffraction line, it is possible to estimate the average gra in size in the film. The X-ay line broadening is commonly used to determine the crystallite size, whi ch is given by,

$$Dg = 0.9\lambda/\beta\cos\theta \ldots\ldots (3.16)$$

Where Dg is the average grain size and β is the full width at half maximum (FWHM) of the peak in radian, which indicates diffraction line. The dimensionless shape factor has a typical value of about 0.9 [71].

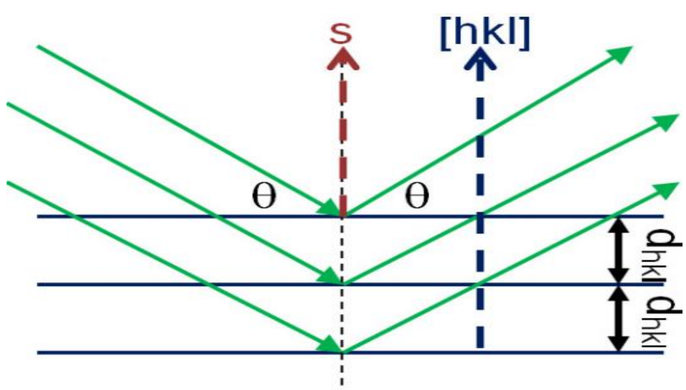

Figure 3.3: Illustrations of Braggs Law[72]

Thus the present study focused on XRD to describe the crystal structure, orientation of the films, crystal size, the diffraction angles and full width at maxima(FWHM) interplanar spacing, disl ocation and microstrain of the films of cadmium doped copper oxide thin films.

3.7.2. Optical characterization visible spectroscopy (UV-VIS)

Ultraviolet-visible (UV-Vis) spectroscopy is absorption spectroscopy in the ultraviolet-visible spectral region. It is often reported as absorbance vs. wavelength of the incident light. Materials absorb light and get excited from the ground state. The energy of the light is used to excite the material so that the wavelength of the absorbed light depends on the energy difference between the g round states and the excited states. A UV/Vis spectrophotometer is used to collect the UV-Vis absorption spectrum. Its value depends on both the wavelength of the incident light and the nature of the species. One common application of UV-Vis absorption spectrum is to be used to calculate the band gap of a semiconductor. Electrons in semiconductor materials get excited from a lower energy state (valence band) to a higher energy state (conduction band) upon absorbing suitable energy from the incident light. The energy difference between the conduction band and the valence band is called band gap. The value of the optical band gap of a semiconductor can be determined using a stern relationship at near-edge of absorption [65].

$$A = \frac{(K((h\nu - Eg))n/2}{h\nu} \quad \text{..... (3.17)}$$

Where A is absorbance, v is frequency of the radiation, h is planks constant, k is constant and n carries the value either 1 or 4. The value n is one for direct transitions, 4 is for indirect transitions respectively. Since most compound semiconductors including CuO thin films have direct band gap, with n value was taken to be one. Thus the band gap edge of cadmium copper oxide thin films were obtained by plotting the square of the product of absorbance and photon energy $(ahv)^2$ against photo n energy (hv). According to equation (3.17), there will be a clear linear region in the plot. Make extrapolation along the linear region. The value of Eg equals to the intercept of the extrapolation to zero absorption [73].

3.8. Materials and Experimental Details

Cadmium copper oxide (Cd:CuO) thin film was prepared using chemical bath deposition method by the following procedure.

3.8.1. Materials used

To synthesize cadmium copper oxide thin films the researcher used the following materials: Electrical beam balance used to measure the mass of the solid compounds in gram. glass substrates used to deposit the films, beakers in different sizes used to measure chemicals, water bath filled by 3 00ml of water, temperature reading instrument used to measure the value of temperature, magnetic

stirrer road used to mix the solutions, water distilled apparatus used to preparing distilled water, heat supplier used to supply heat, Petridis used to hold the deposited thin films. Alcohol used to clean the equipment. Funnel used to filter or transfer liquid in volumetric flask, Cylinder used to measure the volume of solution and water in (ml).

3.8.2. Chemicals Used

The chemical used for the preparation cadmium copper oxide thin films were cadmium chloride($CdCl_2.2\frac{1}{2}H_2O$)) purity of 99% and its molar weight 228.35, copper acetate monohydrate$(CH_3COO)_2Cu.H_2O$ purity of 98% and molar weight 199.65 ,ammonia(NH3) and Hydrazine.

3.8.3. The reagents solution preparation

A Separate preparation of appropriate solution of the starting reagents is very important. All these solutions were prepared using distilled water.

3.8.3.1. Preparation of 0.4 M Copper Acetate Solutions

Ordinarily copper acetate monohydrate $(CH_3COO)_2Cu.H_2O$ purity of 98% and molar weight 199.65 is in powder form. Therefore to prepare copper acetate purity of 98% and molar weight 199.65 solut ions, first convert it in to mass using the mathematical formula:

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

7.826g of copper acetate monohydrate $(CH_3COO)_2Cu.H_2O$ was weighed in the electrical beam balance using beaker. The salt was dissolved by small amount of distilled water in the beaker and then transferred in to 100ml volumetric flask. The solution was then poured in to the volumetric flask of 100ml mark with distilled water and thoroughly shaken to dissolve the salt completely. The resulting solution had a concentration of 0.4 M. The required mass to prepare a certain molar of a sp ecified volume solution is obtained by the formula

Mass = concentration x volume x molar weight x percentage purity

i.e. Mass = C x V x MW x PP……(3.17)

Where, C-concentration, V- volume, MW-molar weight, PP-percentage purity.

Then to prepare 0.4 M Copper acetate solution in a 100 ml the mass to be dissolved is obtained as: Mass = 0.4 M x 0.1 L x 199.65 g / ML x 98% =7.826g Where L is liter, g is gram.

3.8.3.2. Preparation of 0.01M of Cadmium Chloride Solution

Ordinarily Cadmium chloride ($CdCl_2.2\frac{1}{2}H_2O$) purity of 99% and its molar weight 228.35 is in solid form. Therefore to prepare cadmium chloride ($CdCl_2.2\frac{1}{2}H_2O$) purity of 99% and its molar w

eight 228.35 solutions, first convert it in to mass using the mathematical formula:

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

0.226g of Cadmium chloride ($CdCl_2.2\frac{1}{2}H_2O$) purity of 99% and its molar weight 228.35 was weighed in the electrical beam balance using beaker. The salt was dissolved by small amount of distilled water in the beaker and then transferred in to 100ml volumetric flask. The solution was then poured in to the volumetric flask of 100ml mark with distilled water and thoroughly shaken to dissolve the salt completely. The resulting solution had a concentration of 0.01M. The required mass to prepare a certain molar of a specified volume solution is obtained by the formula:

Mass = concentration x volume x molar weight x percentage purity

i.e. Mass = C x V x MW x PP……..(3.18)

Where, C-concentration, V- volume, MW-molar weight, PP-percentage purity.

Then to prepare 0.01M Cadmium chloride ($CdCl_2.2\frac{1}{2}H_2O$) purity of 99% and its molar weight 228.35 solution in a 100ml, the mass to be dissolved is obtained as: Mass = 0.01 M x 0.1 L x228.35 g / ML x 99% =0.226 g Where L is liter, g is gram.

3.8.4. Substrate Cleaning

The substrate cleaning is very important thing in the chemical bath deposition of thin films. Commercially available glass slides were washed using soap solution and subsequently kept in nitric acid for 24hr and then cleaned with distilled water followed by rinsing in alcohol. Finally, the substrates were cleaned with deionized water and dry well.

3.9. Synthesis of cadmium copper oxide thin films

Thin films of cadmium copper oxide have been prepared by chemical bath deposition method. All the chemicals used for the preparation were analytical reagents and all the solutions were prepared i n deionized water. The cadmium copper oxide thin films were prepared from the reaction mixture, c ontaining 5ml of 0.4 M solution of copper acetate, 1.5ml of 0.01 M solution of cadmium chloride, 5 ml ammonia, 3ml hydrazine and 55.5 ml distilled water. All are mixed in the beaker and stirred usin g a magnetic stirrer. The preparation was carried out at a temperature of 40^0C, 60^0C, 70^0C and 80^0C by keeping the chemical bath in a thermo stated water bath for all with constant time 30 minutes. Th e initial colour of the solution was mauve then change brown and the solution colour continue with the red colour until deposition completed at constant of 30 minutes for each, as shown in Figure 3.5. The red colour indicates the formation of cadmium copper oxide thin films.

Figure 3.4: Steps of Cadmium copper oxide color change during deposition process.

After the deposition, the substrates were removed from the chemical bath solution. The Cadmium co pper oxide thin films are formed on the substrates. The color changes from deep brown to red for all temperatures.

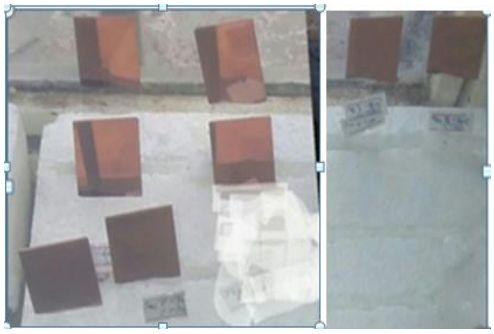

Figure 3.5: The resulting cadmium copper oxide of films at 40ºC, 60ºC, 70ºC, and 80ºC for each 30 minutes before annealing the films.

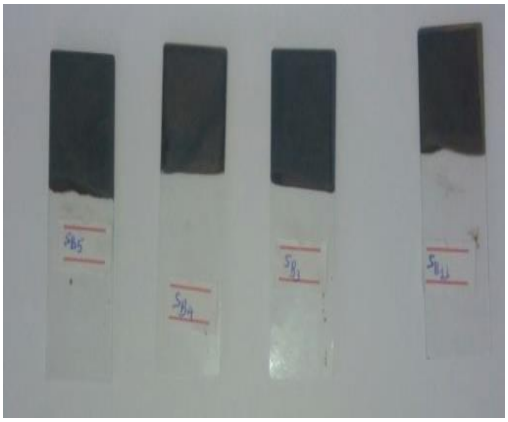

Figure 3. 6: The resulting films of cadmium copper oxide at at 40ºC, 60ºC, 70ºC, and 80ºC from left to right respectively after annealing the films at 300^0C for 1:30 hr

Table 3.1:Experimental data for Cadmium copper oxide thin films by CBD method.

Reaction bath	Copper acetate	Cadmium chloride	Ammonia	Hydrazine	Temperature	Deposition time(min)	Total H_2O volume in ml
Cd:CuO	0.4M 5ml	0.01M 1.5ml	5ml	3ml	40^0C	30 min	55.5 ml
Cd:CuO	0.4M 5ml	0.01M 1.5ml	5ml	3ml	60^0C	30 min	55.5 ml
Cd:CuO	0.4M 5ml	0.01M 1.5ml	5ml	3ml	70^0C	30 min	55.5 ml
Cd:CuO	0.4M 5ml	0.01M 1.5ml	5ml	3ml	80^0C	30 min	55.5 ml

CHAPTER FOUR

RESULT AND DISCUSSION

4.1. Structural Analysis

The crystal structure of Cd-doped CuO film was characterized by using Shimadzu XRD-7000 x ray diffractometer with Cu Ka1 line (k = 1.54056Å) in 2θ range from 10 to 80 in degree. The XRD patt erns of cadmium copper oxide thin film is as shown in Figure 4.1. At deposition temperature 400C three intense peak at 2θ value of 36.360 indexed to (111) plane of cuprite (cubic) (Pn-3m) symme try of Cu2O structure (JCPDS reference code 0050667), 38.670 indexed to (200) plane of tenorite (monoclinic) (C2/c) symmetry CuO structure (JCPDS reference code 0481548) and a weak peak at 42.20 indexed to (110) plane of face centered cubic(Fm-3m) CdO structure (JCPDS reference co de 005 0640) are observed respectively.

As shown figure 4.1: at deposition temperature 60^0C, 70^0C and 80^0C there is one other peaks at 2θ value 35.5^0 that was indexed by (002) plane of tenorite (monoclinic) (C2/c) symmetry CuO structure (JCPDS reference code 0481548). The intensity of the peaks increased as deposition temperature in creases implying improvement in the crystallinity of the films. Thus XRD data analysis of the films revealed the coexistence of the Cu_2O and CuO phase at all temperature consistent with the previous researcher listed in review literature Saadaldin et al (2015) [42] and Johan et al(2011) [48]. As show n in the figure 4.2 below from the emerged graph, The XRD results also reveal that, the deposition t emperature of 40^oC favored the decomposition of CuO, Cu_2O and CdO and at high temperature the deposition of the CdO phase is inhibited.

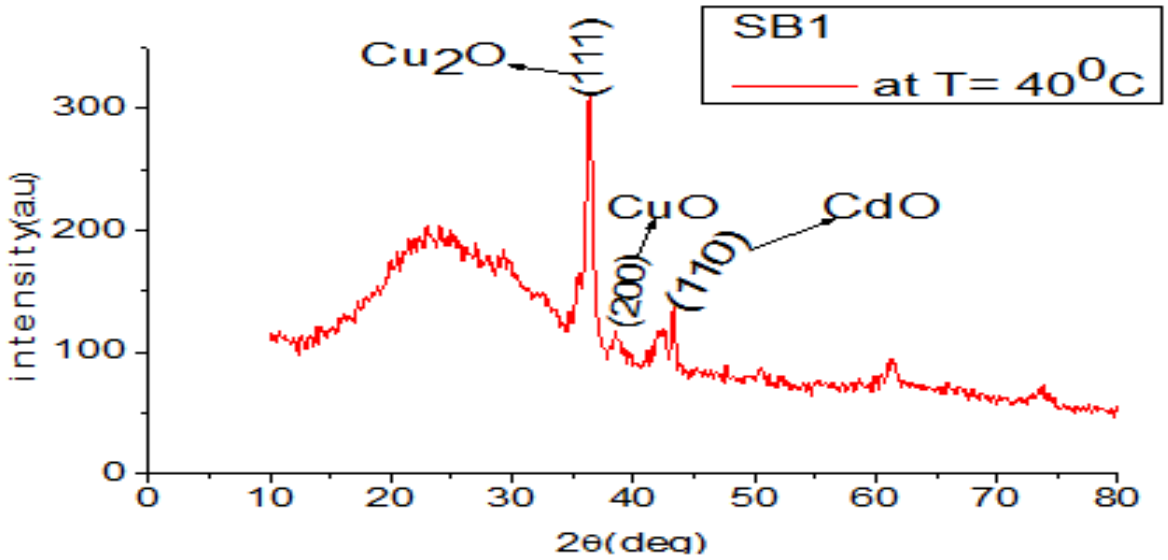

Figure:A

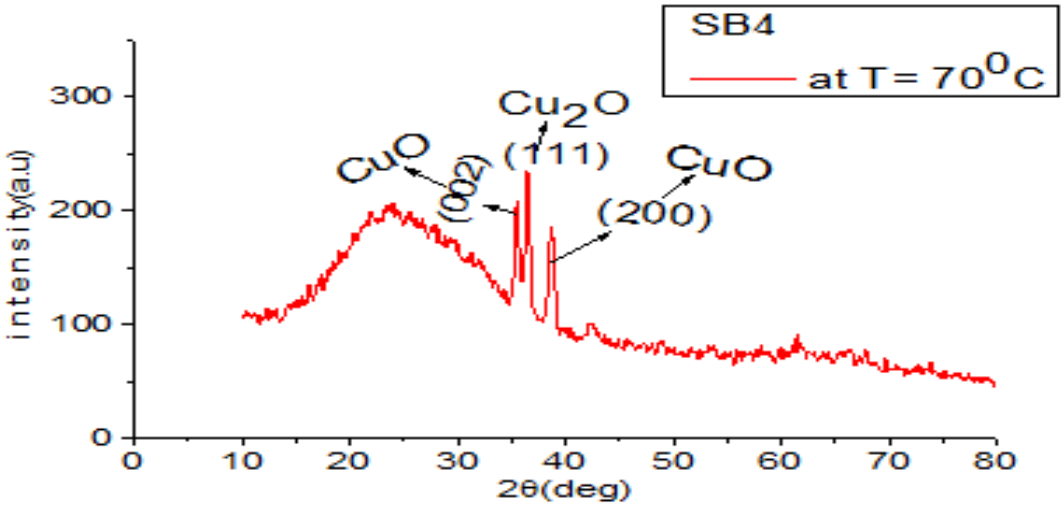

Figure:B

Figure 4.1: A and B shows X-ray diffraction of the cadmium CuO thin composite films at (T=40ºC and 70ºC) respectively.

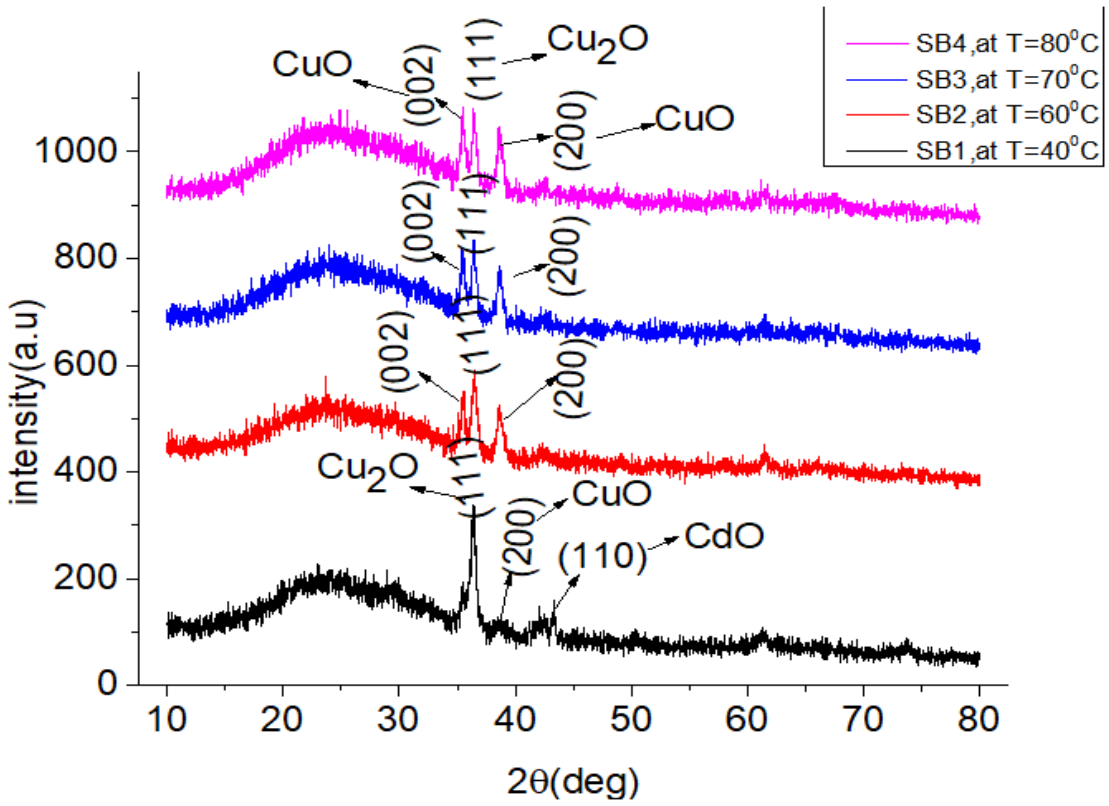

Figure 4. 2: The X- ray diffraction of the cadmium CuO thin film at (at T=40ºC, 60ºC, 70ºC, and 80ºC)

We have also observed that the intensity of Cu_2O (cuprite) decreased throughout each temperature i ncreased and the intensity of CuO (tenorite) increased for each temperature increased, implied that after high deposition temperature Cu_2O would have to convert in to CuO having the same idea with that of the previous researchers Sadiq et al., (2022) [46] and Johan et al(2011) [48].

The crystallite size of the films were calculated the Scherrer's formula [73]

$$D = \frac{\kappa \lambda}{\beta \cos\theta} \quad \text{.....4.1}$$

Where λ the wavelength of CuKá radiation (1.5406 Å), k is shape factor (0.9) which is called Scherrer constant , θ is the Bragg's diffraction angle and β is the broadening of the diffraction line (FWHM). The interplanar spacing (d) can be calculated using Bragg's equation:

$$d = \frac{\lambda}{2\sin\theta} \quad \text{.....4.12}$$

To have further more information on the amount of defects in the synthesized Cu_2Othin films, the dislocation density (δ) was calculated from Williamson Smallman's formula as given below

$$\delta = \frac{n}{D2} \quad \text{.....4.13}$$

Where ‘n’ is a factor, which is equal to unity gives the minimum dislocation density and ‘D’ is the average crystallite size.

In addition, the strain of the thin film (ε) was determined by using the XRD with the following relations

$\varepsilon = \beta\cos\theta/4$……4.14

where, ε is micro strain, β full width at half maximum and θ is diffraction angle

Table 4. 1: Summary of the XRD analyses for Cu2O(coprite) structure.

Samples for Cu_2O	(hkl)	2Θ(deg)	FWHM(rad)	interplanar sapcing(d) nm	crystal size(D (nm)	dislocation density(δ)lines/nm^2	micro strain(ε)	Intensity(a.u)
SB1 at T=40^{0}C	(111)	36.36	0.0132	0.24571	11.0	0.0082	0.0031	184.0
SB3 at T=60^{0}C	(111)	36.49	0.0085	0.24494	17.3	0.0033	0.0020	110.7
SB4 at T=70^{0}C	(111)	36.44	0.0091	0.24520	16.1	0.0038	0.0021	115.3
SB5 at T=80^{0}C	(111)	36.48	0.0069	0.24491	21.2	0.0022	0.0016	93.3

As it can be shown in Table 4.1 Cu_2O phase structural analysis is done, only for (111) plane. It was observed that the crystal size of Cu_2O structure increases with the increase in deposition temperature, except a slight decrease from 60°C to 70°C. However, dislocation and the lattice strain decreased with increased temperature which was clearly seen in the Table 4.1. This indicates that higher temperature favors the growth of Cu_2O phase crystalline involved in the diffraction process which was consistent with the previous researcher in literature review Sadiq et al., (2022) [46]. The diffraction peaks in the (111) plane of Cu2O has high intensities (184.0) at deposition temperature 400C as shown in table 4.1: and has decreased to value 93.3 at deposition temperature 80ºC, however the FWHM decreased from 0.0132 rad to 0.0069 rad.

Table 4. 2 : Summary of the XRD analyses for CuO (tenorite) phase.

Samples for CuO	(hkl)	2Θ(deg)	FWHM(rad)	interplanar sapcing(d)nm	crystal size(D (nm)	dislocation density(δ)nm^{-2}	micro strain(ε)	Intensity(a.u)
SB1 at T=40^{0}C	(200)	38.65	0.0172	0.23164	8.6	0.01365	0.0040	17.0
SB3 at T=60^{0}C	(200)	38.68	0.0117	0.23140	12.6	0.00630	0.0028	77.2
SB4 at T=70^{0}C	(200)	38.67	0.0098	0.23153	15.0	0.00443	0.0023	80.5
SB5 at T=80^{0}C	(200)	38.66	0.0114	0.23150	13.0	0.00596	0.0027	93.6

As it can be shown in Table 4.2 CuO phase structural analysis is done only for (200) plane, It was observed that the crystal size of monoclinic CuO structure increased with the increasing in deposition temperature, except a slight decrease from 70°C to 80°C. However, dislocation and the lattice strain decreased with increasing temperature which was clearly seen in the Table 4.2. The result is consistent with Mondal & Mondal (2022) reported [44] and contradict with the reported by Alkhayatt et al., (2020) [47]. This may be due to different complexant agents used and deposition temperature. The diffraction peaks in the (200) plane of CuO has lower intensities (17.0) at deposition temperature 40^{0}C as shown in table 4.2: and has increased to value 93.6 at deposition temperature 80^{0}C. We observed, in the case of CuO intensity of the diffraction peak rapidly increased as deposition temperature increased means that after higher temperature, would have attributed to the increased crystallinity resulting from the reduced number of structural defects and enhancement of CuO phase which was confirmed with Sadiq et al., (2022) [46]. Thus table 4.1 and table 4.2: generally showed that how deposition temperature affects thin film's structural parameters of Cu2O and CuO. Increasing the temperature of the deposition favors the growth of both monoclinic CuO and cubic Cu2O.

4.2. Studies of Optical Properties of Cd doped CuO Thin Films

The optical properties of the Cd doped copper oxide thin films were determined from the absorption measurements in the wavelength range of 200 - 800 nm. Figure 4.3: shows UV Vis absorbance of Cd doped copper oxide thin films grown from a chemical bath deposition of by temperature of 400C

(SB1) and 600C (SB3), 700C (SB4) and 800C (SB5). All thin films have high absorbance in the visi ble region.

Absorbance curve showed high absorbance of the prepared film at short wavelengths, while less abs orbance was at large wavelengths as shown figure 4.3: this was also confirmed with the previous reported study Saadaldin et al (2015) [42] and Ezenwa (2012) [49].

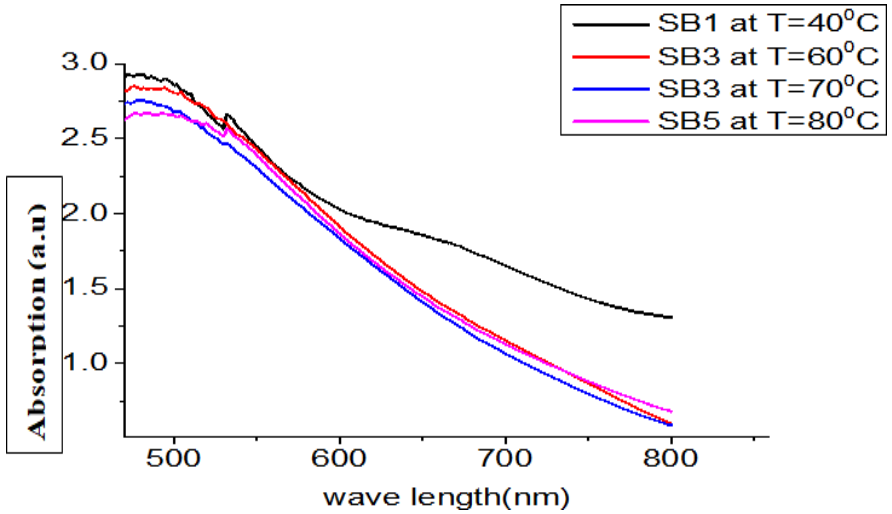

Figure 4.3: The absorbance versus wave length of the cadmium CuO thin film at (at T=40ºC, 60ºC, 70ºC, and80ºC)

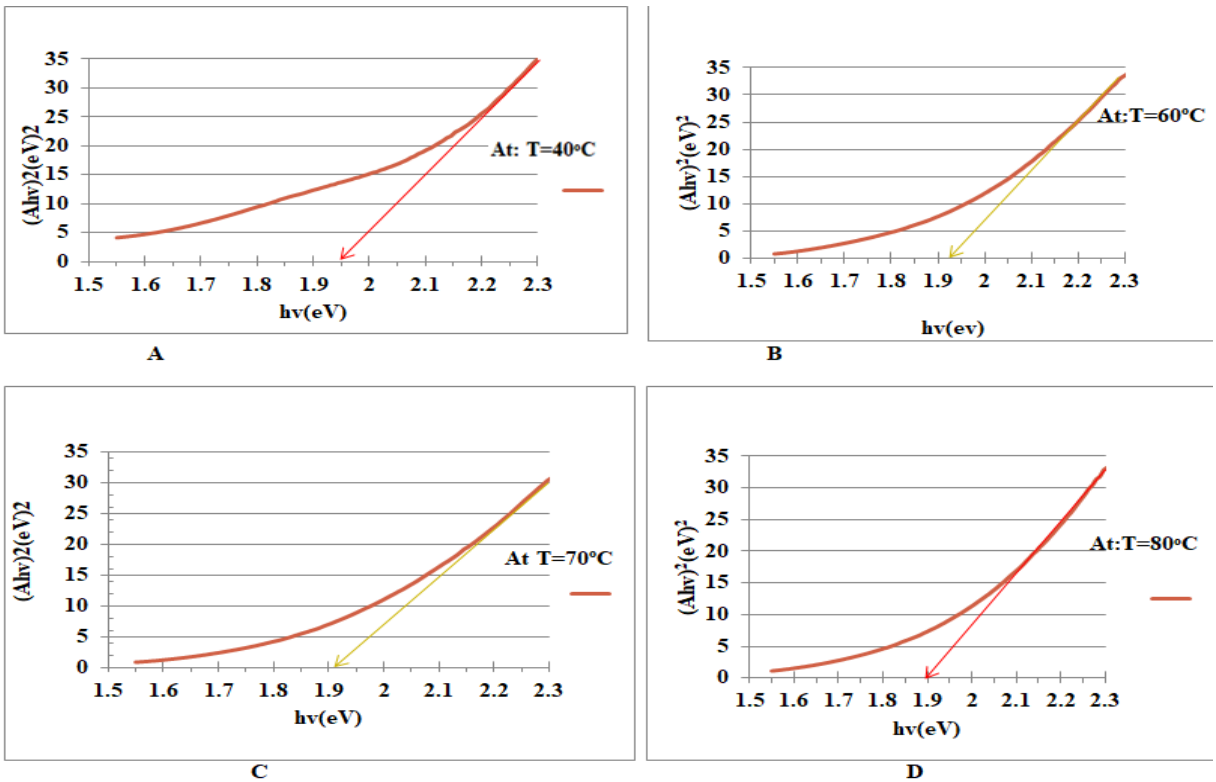

Figure 4.4(A – D): shows:(ahv)2(eV)2 versus hv(eV) cadmium copper oxide thin films at deposition temperature 40ºC, 60ºC, 70ºC and 80ºC respectively.

From figure 4.4(A, B, C and D, the optical band gap of Cd doped CuO thin films were determined using a stern relationship at near-edge of absorption [66].

$$A = \frac{(K((h\nu - Eg))n/2}{h\nu} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (4.15)$$

Where A is absorbance, v is frequency of the radiation, h is planks constant, k is constant and n carries the value either 1 or 4. The value n is one for direct transitions, 4 is for indirect transitions respectively. Since most of compound semiconductors including copper oxide have a direct band gap, the value of n was taken to be 1.Thus the band gaps (Eg) Cd doped copper oxide thin films were obtained by plotting the square of the product of absorbance $(Ahv)^2$ and photon energy hv. To obtain the band gap from the plot, a line was drawn as tangent at the point of inflection in the graph as shown in the Figure 4.4(A-D) and the band gap of Cd doped copper oxide were found at the intersection of the tangent and x-axis to be 1.95 eV, 1.93 eV, 1.92 eV and 1.90eV at a temperature of 40^0C, 60^0C,70^0C and 80^0C respectively. Generally the research revealed that the band gap of cadmium doped on copper oxide was found to decrease with increasing bath temperature, which is consistent with the previous researchers Sadiq et al., (2022) [46]

CHAPTER FIVE

5. CONCLUSION AND RECOMMENDATIO

5.1. Conclusion

The cadmium doped copper oxide thin films were prepared successfully on glass substrates by simple and cost effective chemical bath deposition method using Copper acetate and cadmium chloride as a source to obtain the desired films at constant deposition time of 30 minutes and at bath temperature of 40^0C, 60^0C, 70^0C, and 80^0C. The structural and optical properties of the films were studied using XRD and UV-VIS characterization techniques. From the XRD data analysis of the films, at lower deposition temperature (40ºC) was favored for the decomposition of CdO, Cu_2O and CuO films. However as deposition temperature increased Cadmium oxide was inhibited and we had observed that the coexistence of Cu_2O and CuO phase at all temperatures as well as the crystallinity of all films were increased as deposition temperature increased except a slight decreased from 60^0C to 70^0C for Cu_2O and from 70°C to 80°C for CuO. However, dislocation and the lattice strain decreased with increasing temperature, except a slight increased from 60^0C to 70^0C for Cu_2O and 70°C to 80°C for CuO. The structural study generally indicated that the best crystallinity with the cubic structure for Cu_2O and monoclinic structure for CuO. Also the intensity of (111) plane of cuprite (Cu_2O) was rapidly decreased from values 184 to 93.3 except a slight increased from 60^0C to 70^0C, however the (200) plane of tenorite (CuO) rapidly increased from values 14 to 93.6 without interruption.

The optical study of the films we also had seen that absorbance was higher at shortest wavelength; however the absorbance continuously decreased at longest wave length. The study also investigated that optical band gap decreased from 1.95 eV to 1.90 eV as temperature increased from 40ºC to 80^0C.

5.2. Recommendation

Characterizations of the thin films were limited due to shortage of laboratory instruments in this work. For this reason some samples were selected for characterization techniques that the properties of cadmium doped copper oxide thin films such as morphological and com positional are not studied. Further studies are needed in:

- To investigate the morphological properties of the thin film using Scanning Electron Microscope(SEM) characterization technique.
- To study the influence of temperature on elemental analysis of cadmium copper oxide thin films using EDX measurement**.**

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