INVESTIGATION OF STRUCTURAL AND OPTICAL PROPERTIES OF MANGANESE DOPED COPPER OXIDE THIN FILM SYNTHESIZED BY CHEMICAL BATH DEPOSITION METHOD

M.Sc THESIS

BY

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HAWASSA UNIVERSITY HAWASSA, ETHIOPIA

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A THESIS SUBMITTED TO THE DEPARTMENT OF PHYSICS , COLLEGE OF NATURAL AND COMPUTATIONAL SCIENCES,SCHOOL OF GRADUATE STUDIES

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Acronyms And Symbols

A	Absorbance
Å	Angstrom
AC	Alternative current
C	Concentration
C	Molar concentration of the sample
CB	Conduction Band
CBD	Chemical Bath Deposition
CSP	Chemical spray pyrolysis
Cu_2O	Copper dioxide
CuMnO	Copper manganese oxide
d	Path length
D	Crystallite size
d	Spacing between atomic planes in the crystalline phase
Dc	Direct current
DW	Deionized water
Eg	Optical band gap
FWHM	Full wave half maxima
h	Planck constant
I	Intensity after passing the substrate
IC	Integrated circuit
Io	Incident intensity
IR	Infrared
k	Shape factor Constant
L	Liter
LED	Light emitting diode
LEDs	Light emitting diodes
M	Molar concentration
Min	Minute
ml	Milliliter
mm	Millimeter
Mn	Manganese

Mw	Molar weight
n	Order of the diffraction
Pp.	Percentage purity
SILAR	Successive ionic layer absorption and reaction
UV	Ultraviolet
UV-VIS	Ultra violet- visible spectroscopy
V	Volume
VB	Valence band
VIS	Visible Spectrum
XPS	X-ray photoelectron spectroscopy
Xrd	X ray diffraction
ε	Extinction coefficient
θ	Diffraction angle
λ	Wavelength
v	photon frequency

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Abstract

This study investigates the synthesis and characterization of manganese-doped copper oxide (CuMnO) thin films deposited onto glass substrates using the chemical bath deposition (CBD) method. The objective were to understand how varying manganese concentrations affect the structural and optical properties of the films. The process involved preparing solutions with varying manganese sulfate concentrations (1.5 ml, 3 ml, 4.5 ml, and 6 ml) and maintaining constant conditions for copper acetate, ammonia and hydrazine. The films were deposited at 50°C for 30 minutes, followed by annealing at a temperature of 300°C for 1 hours and 30 minutes. Structural analysis using X-ray diffraction (XRD) revealed that the films possessed a monoclinic copper manganese oxide and cubic Cu_2O structure .The crystallite size initially increased with manganese concentration, reaching a maximum at 4.5 ml, before slightly decreasing. The dislocation density and strain showed corresponding trends, indicating improved crystal quality up to a certain concentration. Optical properties were assessed using UV-Vis spectroscopy. The band gap of the films increased from 1.7 eV to 1.9 eV as the manganese concentration rose from 1.5 ml to 6 ml. This shift in the band gap reflects the impact of manganese doping on the electronic structure of the films, potentially enhancing their suitability for optoelectronic applications. Overall, the results demonstrate that manganese doping effectively tunes the structural and optical characteristics of CuMnO thin films, offering insights into their potential use in various technological applications, including sensors and photovoltaic devices.

Key words: Chemical bath deposition, manganese doped copper oxide thin films, XRD, UV-Visible spectroscopy

CHAPTER ONE

1.GENERAL INTRODUCTION

The knowledge of physical properties of different materials for their possible applications in the daily life has always been a prime field of interest of the human civilization .The scientists of the present day technologically advanced society are still struggling hard for the fabrication of chief and efficient materials for a variety of technological applications. Condensed Matter Physics is enormously grown since the discovery of a p-n junction; one of the greatest achievements where in replacement of many circuit elements takes place by a single semiconductor chip, called integrated circuit(IC)[1]. Materials are exceptionally diverse. Metals, polymers, ceramics, semiconductors, and composite materials constitute the main classes of materials. Based on their specific properties they constitute the foundation of technology, whether the technology pertains to structural, electronic, optical, thermal, electrochemical, environmental, biomedical, or other applications [2] . The recent trend of research in the physical properties of matter has progressed so much during the last ten decades that today physics is divided into a large number of groups of special branches, which are often very different from each other. In the current years thin film technology is an important special branch of research area of Physics in which the characteristics of different materials such as metals, semiconductors, and insulators are investigated in the form of thin film. This new special branch of physics has become known as thin solid films which have been developed very rapidly since 1940[3]. The annual consumption of energy in the world increased more than tenfold over the 20^{th} century and is expected to increase further as the world population increases and the countries get more industrialized [4]. Thin films could be used to produce solar panels which in turn could be used to produce clean and quiet electricity. Such alternative source of cheap electricity will reduce electricity bills, guard against rising energy costs, protect the environment, add comfort, security and value to homes; and provide uninterrupted power supply. Because, there are no moving parts, there is little or no breakdown in the provision of such systems. The systems have long life times. The solar panels themselves (the “engine of the system”) are guaranteed for 20 – 30 years. There is virtually no maintenance on the panel. Distribution can be decentralized. It can be used to supply direct current (DC) or also alternative current (AC) by using an

inverter. The main component of a solar panel is the solar cell which is made from thin films. Hence the main thrust of our work is to grow thin films of competitive standard[5] .

1.1 Semi-Conductor Materials

Semiconductor materials are crystalline or amorphous solids with distinct electrical characteristics with higher resistance than typical resistance materials, but lower than insulators. They are a group of materials either organic or in organic compounds having electrical conductivity between metals and insulators. The conductivity of these materials may be varied by changes the temperature, addition of impurity content, and optical excitation. The changes in electrical properties display a range of useful in nature, and then they are commercially choices for electronic device. Electronic devices such as diodes, transistors are used in many applications for example in amplification, switching, and convertor of energy[6] **.**

1.2 Classification of Semiconductor

Generally there are two categories of semiconductors. These are: elemental and compound semiconductors. Elemental semiconductors are found in group IV of the periodic table (Eg Silicon and Germanium; while compound semiconductors are formed from combination of different group elements of the periodic table. A compound formed from elements in group III and V, as well as certain combinations from II and VI, and from IV, makes up the compound semiconductors. These combinations are as follows: III-V, II-VI, IV-VI and I-III-VI_2 group elements. In ancient time elemental semiconductor (Germanium, Silicon) were used more in development of diodes and transistors. Now days they are used in majority of amplifiers, rectifiers, transistors, switching, and energy conversions etc. Compound semiconductors also can be grown to provide for choosing material properties for specific device applications [7]. The binary or two element group III-V compounds such as GaAs, GaP and GaSe, are commonly known in light emitting diodes (LEDS). Compound semiconductors offer high performance, high frequency, higher power than elemental semiconductor and designed due to mixing of materials[8]. Some elements in the periodic table that can form elemental and compound semiconductor materials are as shown below in table1.1.

Table1.1 some elements in the periodic table that can form elemental and compound semiconductor materials

Group	II	III	IV	V	VI
Element		B	C	N	O
		Al	Si	P	S
	Zn	Ga	Ge	As	Se

The iconicity causes significant changes in the semiconductor properties. It increases the Coulomb interaction between the ions and also the energy of the fundamental gap in the electronic band structure. The energy band gap of semiconductor is the most distinct property of semiconductors that separate them from insulators and metals. It determines wavelengths of light that can be absorbed or emitted by the semiconductors. The iconicity becomes even larger and more important in the II-VI compounds. As a result, most of the II-VI compound semiconductors have band gaps larger than 1 eV. The exceptions are compounds containing the heavy element mercury (Hg). Mercury telluride (HgTe) is actually a zero band gap semiconductor (or a semimetal) similar to gray tin. While the large band gap II-VI compound semiconductors have potential applications for displays and lasers, the smaller band gap II-VI semiconductors are important materials for the fabrication of infrared detectors [9].

1.2.1 Compound Semi-Conductors

Compound semiconductors are formed from a certain combination of elements in columns: II, III, IV, IV, V, and VI groups of periodic table. The two-element (binary) III-V compounds such as GaP, GaAs, and InP are common in light-emitting diodes (LEDs). Compounds formed from elements of the groups III and V of the periodic table (such as GaAs) has properties very similar to their group IV counter-parts. In going from the group IV elements to the III-V compounds, the bonding becomes partly ionic due to transfer of electronic charge from the group-III atom to the group V atom[10].

1.2 .2 Intrinsic and Extrinsic semiconductors

Semiconductor may be classified as under: Intrinsic Semiconductors and extrinsic semiconductor.

1.2.2.1 Intrinsic Semiconductors

An intrinsic semiconductor is one which is made of the semiconductor material in its extremely pure form. Examples of such semiconductors are: pure germanium and silicon which have forbidden energy gaps of 0.72 eV and 1.1 eV respectively. The energy gap is so small that even at ordinary room temperature; there are many electrons which possess sufficient energy to jump across the small energy gap between the valence and the conduction bands. Alternatively, an intrinsic semiconductor may be defined as one in which the number of conduction electrons is equal to the number of holes[11].

1.2.2.2 Extrinsic semiconductors

Those intrinsic semiconductors to which some suitable impurity or doping agent or doping has been added in extremely small amounts are called extrinsic or impurity semiconductors[11]. Depending on the type of doping material used, extrinsic semiconductors can be sub-divided into two classes:

(i) N-type semiconductors and

(ii) P-type semiconductors

i) N-type Extrinsic Semiconductor

This type of semiconductor is obtained when a pentavalent material like antimonty (Sb) is added to pure germanium crystal. each antimony atom forms covalent bonds with the surrounding four germanium atoms with the help of four of its five electrons. The fifth electron is superfluous and is loosely bound to the antimony atom. Hence, it can be easily excited from the valence band to the conduction band by the application of electric field or increase in thermal energy. It is seen from the above description that in N-type semiconductors, electrons are the majority carriers while holes constitute the minority carriers

ii) P-type Extrinsic Semiconductor:

This type of semiconductor is obtained when traces of a trivalent like boron (B) are added to a pure germanium crystal. In this case, the three valence electrons of boron atom form covalent bonds with four surrounding germanium atoms but one bond is left incomplete and gives rise to a hole. Thus, boron which is called an acceptor impurity causes as many positive holes in a germanium crystal as there are boron atoms thereby

producing a P-type (P for positive) extrinsic semiconductor. In this type of semiconductor, conduction is by the movement of holes in the valence band.

1.3 The Important Properties of Semiconductors

Semiconductors are substances with properties somewhere between conductors and insulators [1 2] .Electrical properties can be indicated by resistivity. Therefore these important properties of semiconductors are:-

- ✓ The resistivity of semiconductor is less than an insulator but higher than a conductor.
- ✓ Semiconductor shows a negative temperature coefficient of resistance in simple words the resistance of semiconductors decreases as the temperature increases and vice-versa.
- ✓ At zero kelvin semiconductors behave as insulators.as the temperature is increased it works a conductors .
- ✓ The conductivity of the semiconductor increases when impurities are added

1.4 The Application of Semiconductor*s*

Semiconductors are used in essential components of electronic devises enabling advances in communication computing, health care, military systems transportation, clean energy and countless other application. Compound semiconductors thin films have attracted considerable attention from the research community because of their wide use in the fabrication of solar cells and other optoelectronic devices [1 3] . Semiconductors are used in almost every sector of electronics, consumer electronics, mobile phone, laptops, game consoles, microwaves and refrigerator all operate with the use of semiconductor components such as integrated chips, diodes and transistor and in our daily life there are some related applications of semiconductors[14]. These are:-

- ✓ Semiconductors are used in solar technology
- ✓ Used in 3D printing machine
- ✓ Temperature sensors which used in air conditioners are made with semiconductors devices.
- ✓ Semiconductors play a central role in the operation of bank ATMs, trains, the internet, communications and other parts of the social infrastructure:-such as the medical network used for the care of elderly, among other things. Used in self-driving cars.

- ✓ Semiconductor devices are used in computer, calculator solar plates and other electronics devices.
- ✓ Semiconductor devices are used in microchips which are used in our electronics devices such as the computer mobile etc.

1.5 Copper Oxide

Copper oxide is a p-type transitional basic inorganic semiconductor material with a direct energy gap of about 2 eV and closes enough to the optimum energy gap in the radioactive spectrum [15].Copper oxides are usually present in two stable forms, copper oxide (Cu_2O) and copper oxide (CuO)[16]. Copper oxide thin films have wide range of applications including energy harvesting and storage as solar cells , photo electro-chemical cells , photo-catalysts , and lithium ion batteries .These also find applications in the domain of catalysts , field-emission devices , gas sensors, photovoltaic devices ,and super conductors [17].Thus developing a good quality CuO thin film is highly important to fabricate electronic and photovoltaic devices with superior performance by utilizing such films. In this context, several techniques have already been employed to grow CuO films with superior quality . Further, the chemical as well as physical properties of CuO depend significantly on thickness and morphology of the film , and therefore, the precise control and thickness optimization along with its morphology is immensely crucial for utilizing such films in Nano-electronics, optoelectronics and bio-sensing applications . And it can also be used as a solar absorbent due to its high absorption coefficient and low thermal emission[18] .

The Chemical structure of Copper oxide as shown below in figure 1

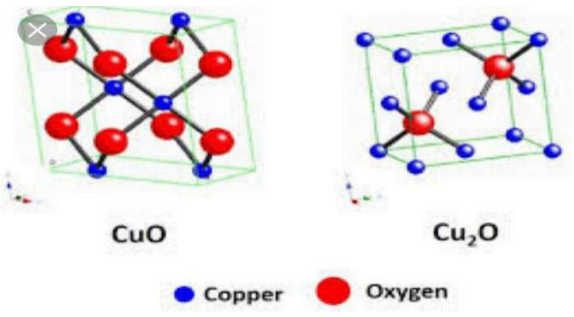


Figure 1. 1 Chemical structure of Copper oxide

The oxides of copper like CuO (cupric oxide) is a black solid that is insoluble in water and it has a monoclinic crystal structure and Cu_2O (cuprous) is a red solid and it has cubic crystal structure. It is a strong oxidizing agent and will react with most metals

to form cupric salts. It used as pigment paints and other products.it also used as a catalyst in some chemical processes .The properties of copper oxide are:-

- ✓ CuO is antiferromagnetic non-lustrous element.
- ✓ It does not react with water/steam because it is very low on the reactivity scale
- ✓ Like manganese copper are not magnetic but can be transformed in to magnet.

1.6 Statement of the Problem

. There are several techniques used to synthesize copper manganese oxide (CuMnO) thin films including thermal oxidation, atomic layer precipitation, sol-gel method , laser pulse deposition, permeable coating method, activated microwave atomization, magnetic spray ,chemical vapor deposition, vacuum evaporation, electronic beam evaporation , oxidation of copper sheets , electro deposition , ultrasonic spray pyrolysis and reactive sputtering[19]. All these method require comparatively high processing temperature, sophisticated instruments & procedure and extended deposition period. So that the simple and inexpensive fabrication routes for the synthesis of copper manganese oxide thin film are sought by researchers, however such route is limited. Considering this fact, the researcher tried to develop a simple and fast chemical bath deposition (CBD) routes for the synthesis of copper manganese oxide thin films. In most CBD reports the deposition period is an hour or hours and the commonly used complexing agent is ammonia. The researcher uses a combination of ammonia and hydrazine as a complexing agents and copper acetate as a source of copper ion and manganese sulphate as a source of manganese ion. As far as the researcher is aware that there is no report on such combination of precursors. We have able to synthesis copper manganese oxide thin films in a short period of time (30minute) at $50C^0$ using the afore mentioned combination. The thin films were characterized by XRD and UV-VIS.

1.7 Objectives of the study

1.7.1. General objective of the research

The general objective of this research is to investigate the structural and optical properties of manganese doped copper oxide thin film using CBD method for different manganese precursors concentration.

1.7.2. Specific objectives of the research

The specific objectives of this research are

- ✓ To synthesis manganese doped copper oxide thin films at different manganese precursors concentration by chemical bath deposition method.
- ✓ To analyze the structural properties of manganese doped Copper oxide thin films .
- ✓ To determine the optical properties of manganese doped Copper oxide thin films .

1.8 Thesis structure

This thesis was arranged into five chapters. The first chapter deals about general introduction, semiconductors, copper oxide, statement of the problem, objective and thesis structure. The second chapter deals about thin film materials and review of Copper oxide manganese copper oxide thin films synthesized by CBD method. The third chapter deals about methodology, deposition technique and application of thin films, chemical bath deposition and its uses, factor affecting the size and distribution of thin films, characterization techniques and experimental procedures. The fourth chapter deals about result and discussion. And finally conclusion and recommendation of the research are discussed in chapter five

CHAPTER TWO

2. REVIEW OF LITERATURE

This chapter introduces the general aspects of thin films, review of copper oxide and manganese copper oxide thin films at different manganese concentration on the structural and optical property of manganese copper oxide thin films by using CBD and different selected deposition techniques

2.1 Thin film materials

Thin film is defined as a material created by the random nucleation and growth processes of individually condensing (reacting atomic, ionic) molecular species on a substrate. It is defined as a solid layer having thickness varying from a few angstroms to about 10 micrometer. Further it may broadly be classified in three subdivisions according to its thickness as,

I) Ultra-thin (50-100 Å)

II) Thin (100- 1000 Å)

III) Comparatively thick one (greater than 1000 Å)

However, this thickness limit is an arbitrary one. An ideal film can mathematically be defined as 'Homogenous' solid material contained between two parallel planes and extended infinitely in two directions (but say X and Y) restricted along the third direction (Z), perpendicular to the XY plane. Thickness plays an important role in thin films. It is an important parameter, which affects the optical, electrical, structural etc properties of metals considerably. Reproducible characteristics can be obtained by choosing specific thickness and proper combination of deposition parameters for a particular material. they are also classified as crystalline or non - crystalline materials developed two dimensionally on a substrate's surface by physical or chemical methods [20]. The beginning of "Thin Film Science" can possibly be traced to the observations of Grove, who noted that metal films were formed by sputtering of cathodes with high energy positive ions. Since then it has come a long way and today it is no long era subject of some casual academic interest but has become a full-fledged discipline. The phenomenal rise in thin film research is no doubt due to their extensive applications in the diverse fields of electronics, optics, space science, aircrafts, defense and other branches of science and technology. These investigations have led a numerous inventions in the forms of active devices and passive components, microminiaturized power supplies, sensor elements, storage of solar energy and its

conversion to other forms, magnetic memories, superconducting films, interference filters, reflecting and antireflection coatings and many others. A thin film is a two dimensional material created to the ability by the process of condensation and growth of atoms, molecules or ions. Their properties are usually different from those of corresponding bulk materials due to their physical dimension, geometry and microstructures. They are largely affected by the high surface-to volume ratio and that influence number of phenomena such as gas adsorption, diffusion and catalytic activity[21] .The controlled synthesis of the thin film is a traditional well-established material technology. However; the study of thin film phenomena dates back well over a century, it is really only over the last four decades that they have been used to a significant extent in practical situations. The requirement of micro miniaturization made the use of thin and thick films virtually imperative. The development of computer technology led to a requirement for very high density storage techniques and it is this which has stimulated most of the research on the magnetic properties of thin films. Many thin film devices have been developed which have found themselves looking for an application or, perhaps more importantly market. In general these devices have resulted from research into the physical properties of thin film . The thin film technology is still being developed on a daily basis since it is a key in the twenty first (21^{st}) century development of new materials such as nanometer materials or man-made super lattices. In the recent years, thin films are being freely studied for their potential applications in Photovoltaic (PV) technology. The PV technology engages solar cells and modules which turns sunlight directly into electricity[22]. General the application of a thin films are used to in our homes to perform different activity a simple example is the house hold mirror typically has a thin metal coating on back of a sheet of glass to form a reflective interface[23, 24]. Thin films of semiconducting Nano crystals are emerging as an important class of materials for electronic and optoelectronic devices such as field emission transistor, Photo detector, Thermal images, Light emitting diodes and Solar cells.

2.2 Review of Copper oxide thin films synthesized by CBD method

Das, A. et al. (2016) synthesized CuO thin films using the chemical bath deposition (CBD) method. The CuO seeds were first prepared using RF sputtering, and CuO thin films were then synthesized by CBD with varying molar concentrations of solutes. The

films were annealed at 400°C for one hour. Both the as-grown and annealed films exhibited a monoclinic structure with particle sizes ranging from 22 to 100 nm[25].

Ho, S. M. et al. (2016) reported that copper oxide films have a direct band gap ranging from 1.2 to 2.6 eV, making them suitable for various applications, including solar cells, sensors, and optoelectronics. The study aimed to investigate the properties of copper oxide thin films produced through different deposition methods, and the results on structure, optical, morphological, and electrical properties were discussed. The findings showed that different experimental conditions lead to varied properties of copper oxide thin films[26].

Ahirrao, P. B. et al. (2011) studied the photoluminescence properties of CuO thin films deposited on glass substrates. Structural analysis showed that the Cu_2O films primarily exhibited (111) and (200) crystalline orientations. Photoluminescence studies at room temperature revealed a green band at 503 nm and 540 nm, as well as a strong red emission at 627 nm. Uniform and crack-free CuO films, synthesized using CBD with $Cu(NO_3)_2$ and ammonia, displayed p-type conduction and photosensitivity, making them suitable for use as absorber materials in hetero structure solar cells [27].

Oral, A. Y. et al. (2004) prepared copper(II) oxide thin films using a sol-gel-like method on glass substrates. The precursor solution was made by dissolving copper acetate in isopropyl alcohol, with stabilizers and additives enhancing solubility and adhesion between the films and the glass substrates. After heat treatment at 600°C for 30 minutes, the films crystallized into a CuO tenorite structure. The films were uniform and brownish-black in color, and their microstructures were influenced by the precursor solution chemistry. The optical band gaps ranged from 1.6 to 1.75 eV [28].

Saadaldin, N. et al. (2015) synthesized copper oxide thin films using the chemical bath deposition (CBD) method and the alternate immersion (AI) technique at room temperature. Sodium hydroxide was heated to 70°C, and the films were annealed at temperatures between 200°C and 400°C. XRD and SEM analysis showed that the crystalline structure of the films varied with annealing temperature, transitioning from cubic Cu_2O to monoclinic CuO. Optical studies revealed that the band gap values, ranging from 1.3 to 2.4 eV, were affected by the annealing temperature, indicating that the films could be suitable for solar cell applications[29].

2.3 Review of Copper manganese oxide thin films synthesized by CBD method

Bayón, R. et al. (2008) prepared copper–manganese oxide thin films using the dip-coating method, annealing them at temperatures between 400°C and 500°C for 15 to 90 minutes. The study examined the effects of annealing time and temperature on the composition and optical properties of the films. X-ray photoelectron spectroscopy (XPS) revealed that an initial mixture of copper and manganese oxides transformed into $Cu_{1.5}Mn_{1.5}O_4$ through a solid-state redox reaction, which occurred above 450°C and required at least 60 minutes. The formation of $Cu_{1.5}Mn_{1.5}O_4$ significantly increased solar absorbance from 0.6 to 0.9, with XPS confirming the presence of Mn^{3+} and Mn^{4+} in octahedral sites and Cu^{+} and Cu^{2+} in tetrahedral sites, contributing to the films' high conductivity [30]..

Hussin, H. A. et al. (2020) synthesized nanostructured CuO thin films doped with manganese using the chemical spray pyrolysis (CSP) technique, with doping levels of 2% and 4%. XRD analysis confirmed that the films were polycrystalline, with a preferred orientation along the (002) plane. Atomic force microscopy (AFM) was used to study film morphology, while spectrophotometry revealed that the band gaps of CuO and Mn-doped CuO nanostructures ranged from 1.72 to 1.92 eV [31]..

Ganesan, K. et al. (2019) reported the deposition of Mn-doped Cu_2O thin films on fluorine-doped tin oxide (FTO) glass substrates using electro-deposition, with $CuSO_4$ and $MnSO_4$ as sources. The study explored how Mn doping affected the films' structural, morphological, optical, and magnetic properties. XRD patterns revealed a cubic crystal structure with a predominant (111) orientation, and crystallite size increased from 29.03 nm to 39.40 nm with higher Mn concentrations. AFM analysis showed that surface roughness increased with Mn doping. Optical studies indicated increased absorbance and band gaps with higher Mn concentrations, and magnetic measurements revealed a transition from diamagnetic to ferromagnetic behavior as Mn doping increased [32].

Gao, W. et al. (2010) deposited un-doped and Mn-doped CuO nanostructures on glass substrates using the SILAR method. The study used scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), XRD, and UV–Vis spectrophotometry to investigate the morphological, compositional, structural, and optical properties of the films. The results indicated that Mn doping influenced the shapes of the nanostructures,

with XRD revealing a monoclinic structure in all films. UV–Vis analysis showed that the optical band gap increased with higher Mn doping concentrations [33].

Review of literature shows that there are very few reports on chemical bath deposited copper oxide thin films. However, there are very few reports on the manganese doped copper oxide thin films. This motivates the researcher to investigate the effect of manganese doping on structural and optical properties of copper oxide synthesized by chemical bath deposition method. The films were characterized by X-ray diffraction and UV-VIS spectroscopy to study structural and optical properties.

CHAPTER THREE

3. RESEARCH METHODOLOGY

3.1 Thin Film Deposition Technique

. Thin film deposition refers to the process of applying a thin layer of material onto a substrate or onto previously deposited layers. The term "thin" is relative, but most deposition techniques are capable of controlling the thickness of the layer to within a few tens of nanometers[34]. Thin films have various applications, including the production of optics (such as reflective and anti-reflective coatings or self-cleaning glass), electronics (where layers of insulators, semiconductors, and conductors form integrated circuits), and packaging (such as aluminum-coated films). Additionally, similar processes are used where thickness control is not a priority, for example, in the purification of copper through electroplating or the deposition of silicon and enriched uranium using a chemical vapor deposition (CVD)-like process following gas-phase treatment[35]. Deposition techniques can be broadly classified into two categories: chemical processes and physical processes.

3.2 Classification of Thin-Film Deposition Techniques

The technique classifies as physical and chemical Process. Physical method covers the deposition techniques which depend on the evaporation or ejection of the material from a source, i.e. evaporation or sputtering, whereas chemical methods depend on physical properties. Structure property relationships are the key features of such devices and basis of thin film technologies. Underlying the performance and economics of thin film components are the manufacturing techniques on a specific chemical reaction. Thus chemical reactions may depend on thermal effects, as in vapor phase deposition and thermal growth. However, in all these cases a definite chemical reaction is required to obtain the final film[19] .

The Classification of thin film deposition technique as shown below in figure 3.1

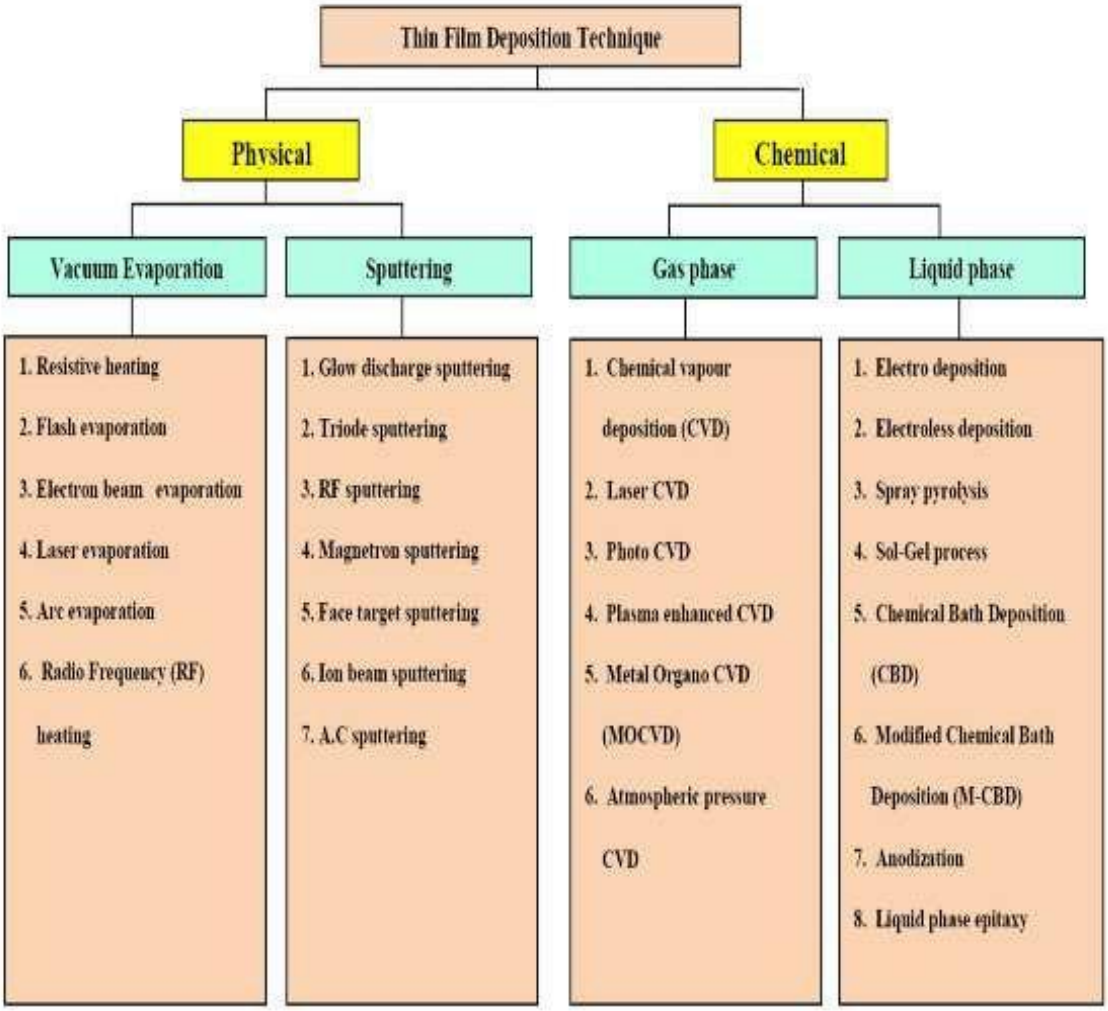


Figure 3.1 The Classification of thin film deposition technique [36]

3.2.1. Physical Methods

physical or thermodynamic means to produce a thin film of solid. The production of thin films via physical methods gives good quality and functionalizes properties, it is highly expensive and perhaps requires a large amount of material target [37].

3.2.1.1. Vacuum Evaporation

The evaporation of a material requires that it be heated to a sufficiently high temperature to produce the desired vapor pressure. The vapor atoms traverse the medium and are made to condense on a substrate surface to form a thin film. The rate of condensation/deposition of the vapor atoms depends on the vapor source-substrate geometry and the condensation coefficient on the surface under given physical conditions. The vapor atoms are scattered by collisions with residual gas atoms in the vacuum system [38].

3.2.1.2. Sputtering

If a surface of target material is bombarded with energetic particles, it is possible to cause ejection of the surface atom, the process is known as sputtering. The ejected atoms can be condensed onto the substrate surface to form a thin solid film [39].

3.2.2 Chemical Methods

Although the production of thin films via physical methods as previously described gives good quality and functionalizes properties, it is highly expensive and perhaps requires a large amount of material target. Since the need to produce good-quality thin films with low economical cost is necessary, chemical deposition techniques are widely used globally. These techniques are cheap producing good-quality films. Most of them do not require expensive equipment. The chemical deposition is strongly dependent on the chemistry of solutions, pH value, viscosity, and so on [40].

3.2.2.1 Gasses Phase

Methods of film formation by purely chemical processes in the gas or vapor phases. It is a materials synthesis process whereby constituents of the vapor phase react chemically near or on a substrate surface to form a solid product[40] .

3.2.2.2. Liquid Phase

The growth of inorganic thin films from liquid phases by chemical reactions is accomplished primarily by electrochemical processes , and by chemical deposition processes[40] .

3.3 Chemical Bath Deposition

Chemical bath deposition (CBD) is the analog in liquid phase of the well-known chemical vapor deposition technique in the vapor phase. In CBD, deposition of thin films takes place from aqueous solutions at low temperatures by a chemical reaction between dissolved precursors, with the help of a complex agent. Chemical bath deposition technique involves controlled precipitation of a compound from the solution on a suitable substrate . Among all techniques used to grow group II-VI semiconductors, CBD has the advantage of being a simple, low temperature, and inexpensive large-area deposition technique. CBD is presently attracting considerable attention as it does not require sophisticated instrumentation like vacuum system and other expensive equipment's. The starting chemicals are commonly available and inexpensive. Using CBD, a large number of substrates can be coated in a single run. Unlike electroplating, electrical conductivity of the substrate is not necessary requirement. Any insoluble

surface to which the solution has a free access will be a suitable substrate for deposition, which makes CBD suitable for coating surfaces of any morphology and geometry. The low temperature deposition avoids oxidation and corrosion of metallic substrates. Chemical deposition results in pin hole free, uniform and highly stoichiometric films since the basic building blocks are ions instead of atoms. The preparative parameters are easily controllable and better orientations and improved grain structure can be obtained[41] . In the CBD process, the heat necessary to activate chemical reaction is transferred from the bath to the sample surface, inducing a heterogeneous growth on the surface and homogeneous formation in the bath volume[42] . It is possible to control the film thickness and chemical composition by varying the deposition parameters such as temperature, precursor concentration, complex agents used and the pH of the solution . Films produced by CBD are often used in semiconductor, photovoltaic cells, and supper capacitor, and there is increasing interest in using Chemical Bath Deposition to create nanomaterial's[43].

The Experimental set up of CBD method as shown below in figure 3.2

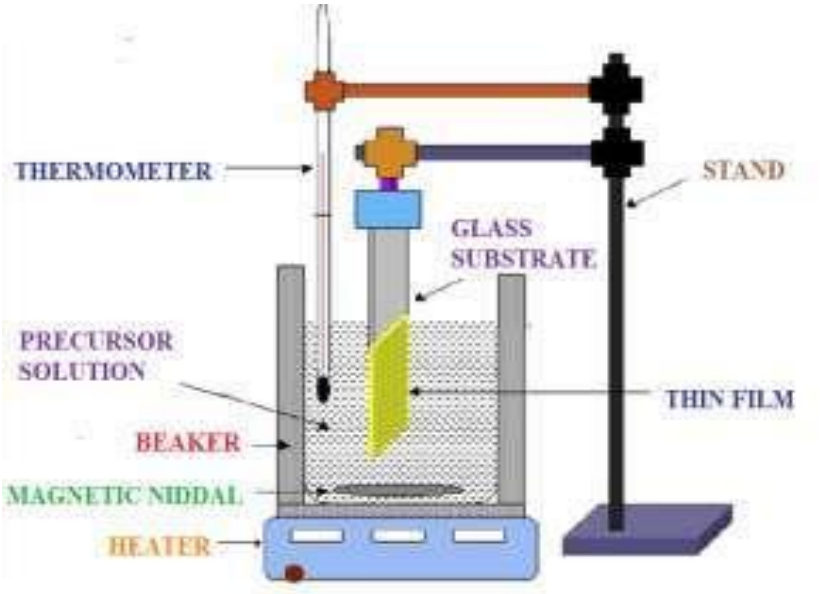


Figure 3.2 The experimental set up of CBD method

3.3.1 Principles of Chemical Bath Deposition Technique

In principle, CBD can be used to deposit any compound that satisfies four basic requirements .

1.The compound can be made by simple precipitation. This generally, although not exclusively, refers to the formation of a stoichiometric compound formed by ionic reaction.

2. The compound should be relatively (and preferably highly) insoluble in the solution used (except in a very few cases, this has been water).

3. The compounds should be chemically stable in the solution.

4. If the reaction proceeds via the free anion, then this anion should be relatively slowly generated (to prevent sudden precipitation). If the reaction is of the complex-decomposition type, then decomposition of the metal complex should similarly occur relatively slowly [44].

3.5 Mechanism of Film Growth in Chemical Bath Deposition

The mechanism of film formation by CBD method can be divided into four fundamentally different types[45] [46].

i. simple ion-by-ion,

ii. Simple cluster,

iii. Complex decomposition ion-by-ion,

iv. Complex decomposition cluster mechanism

3.5.1. Simple Ion-by-Ion Mechanism

Ion by ion growth is defined as the formation of chalcogenide nuclei on the surface of the substrate followed by subsequent growth on those nuclei [41]. In simple ion by-ion mechanism, first ions diffuse over the substrate which serve as a catalyst and facilitate the nucleation. The nucleation grows as a result of absorption of ions in the solution and nucleation of new crystals occurs. At further stage the crystals bonds with one another by the Vander Walls forces forming a film . The general reaction for the mechanism .

$M^{n+} + X^{m-} \rightarrow MmXn$..……………………..…...................………………………3.1

3.5.2. Simple Cluster (Hydroxide) Mechanism

Cluster by cluster growth results from the formation of colloids in solution, which then adsorb onto the substrate and coagulate to form a film [41]. In simple cluster mechanism, hydroxide colloidal particles diffuse to substrate and adhere to it. These hydroxide colloidal particles adsorbed to substrate react with free ions in the solution resulting in displacement of hydroxide by the free ions. Such displacement reaction can occur both on the substrate and in the solution and continues until most of the hydroxide converts into sulfide. The primary particles occurring by reaction adhere to each other to make up an aggregated film on the substrate and other non-adsorbed particles also aggregate and precipitate out of the solution[47]. 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 (or hydrated oxide) 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 but not in the bulk of the solution. In this case metal chalcogenide (MmXn) is formed by reaction of Xm ion with the M(OH)n [48].

$M^{n+}+nOH^{-} \rightarrow M(OH)n$…….....3.2

Followed by

$M(OH)n+X^{m-} \rightarrow MmXn + nOH^{-}$ …….……...……...…….....3.3

3.5.3. Complex Decomposition Ion-By-Ion

Complex Decomposition Ion-by-Ion Mechanism This mechanism involves the complexation of free metal ions ($Mn+$) with a chalcogenide source (for, e.g., thiourea), which gives M-thiourea
complex ion [42].

$M^{n+}+CS(NH2)2 \rightarrow [(NH2)2CS\text{-}M]^{n+}$……..……...…….....3.4

This complexed ion undergoes the process of hydrolysis by the S–C bond breaking to form M–S.

$[(NH2)2CS\text{-}M]^{n+} + 2OH \rightarrow M\text{-}S + CN2H2 + nH2O$……..……...….....3.5

3.5.4. Complex Decomposition Cluster Mechanism

This mechanism is based on the formation of solid phase via formation of an intermediate complex instead of reacting directly with a free anion.

$M(OH)n + CS(NH2)2 \rightarrow M(OH)n.CS(NH2)2$……..……...…….....…3.6

$M(OH)n.CS(NH2)2 \rightarrow M\text{-}S + CN2H2 + nH2O$ ……..……..….....3.7

The formation of M(OH)n on the substrate catalyzes the decomposition of thiourea to sulfide ions, but it is not necessary that it will catalyze the whole complex decomposition mechanism [42].

3.6. Factors Influencing the Deposition Process

The formation of thin film by chemical bath deposition is influenced by the factors such as

- Bath temperature
- Nature and concentration of the precursors
- Nature and concentration of complexing agent
- pH of the solution

• Deposition time

• Nature of the substrate

3.6.1. Bath Temperature

As the temperature increases, dissociation of the complex increases. The kinetic energy of the molecule also increases leading to greater interaction between the ions. This results in more increase or decrease in the film thickness depending on the extent of super saturation of the solution [49].

3.6.2. Nature and concentration of the precursors

Nature of the precursors influences the composition of the product. The growth kinetics also depends on the nature of the precursors. The deposition rate and terminal thickness initially increase with an increase in the ionic concentration of precursors. However, at higher concentrations the precipitation becomes very fast leading to decrease in film thickness [2]. In a reaction, metal ion concentration decreases with the increase of complexing ion concentration. As a consequence, the rate of reaction and hence the precipitation are reduced

leading to a large terminal thickness of the film .

3.6.3. Nature and concentration of complexing agent

Thin film deposition is an adsorption phenomenon that results in the formation of material on the template (glass). Thin film formation occurs by combination of ions released from complexed metal source and chalcogen source. The nature of complexed metal ion is metastable and is related to dissociation constant of metal-complex. The complexing agent was used to limit the hydrolysis of the metal ion and impart some stability to the bath, which, otherwise undergo rapid hydrolysis and precipitation[50] .

3.6.4. PH of the Solution

The solubility of metal hydroxide depends on the pH of the solution. that the presence of hydroxide ions in solution is necessary for the growth of a good-quality film [51]. The reaction the supers is anion ion concentration). If the concentration of OH ion in the solution is higher, the M ion concentration will be lower and the reaction rate will be slow. With an increase in the pH as the M ion concentration decreases, the rate of deposition of MX is decreased and increases the terminal thickness. At a certain pH, the concentration of M ions decreases to a level such that the ionic product of M and X becomes less than the solubility product of MX and a film is formed.

3.6.5. Deposition Time

The growth of good quality thin films proceeds at a slower rate a gradual increase in the thickness of the films as deposition time increased, an indication of homogeneous precipitation process taking place with time. The thickness of thin solid films in which the film formation and kinetics takes place ion by ion condensation has a linear relationship with deposition time[51] .

3.6.6. 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. Also rough surfaces are better to obtain an adherent film, probably due to the greater actual surface area of contact per pores of the substrate. Higher deposition rates and terminal thickness are observed for those substrates whose lattices and lattice parameters match well with those of the deposited film A low lattice mismatch between the film and substrate improves the film quality and large mismatch usually leads to structural defects and larger strain on the films surface [52].

3.6.7. Effect of Stirring

Stirring affects CBD grown films mainly by preventing deposition of loosely adhering, large aggregates. These loose deposits are readily removed by the stirring action. This is important, since they block the substrate, preventing normal adherent film growth[53] .

3.6.8. Effect of Doping

Doping is adding small amounts of impurities to the semiconductor material. Impurities that are added intentionally to control the carrier concentrations are called dopants. It is possible to alter the structural, electrical, optical and magnetic properties of material though doping with various elements. Adding donor or acceptor impurity atoms to a semiconductor will change the distribution of electrons and holes in the material. This result in the change of Fermi energy level since it depends on the distribution of electrons and holes . Doping is fundamental in the fabrication of various semiconductor devices[54].

3.7 Uses of Chemical Bath Deposition Method

Chemical Bath Deposition is useful in industrial applications because it is extremely cheap, simple, and reliable compared to other methods of thin-film deposition, requiring only aqueous solution at (relatively) low temperatures and minimal infrastructure. The CBD process can easily be scaled up to large-area batch processing or continuous deposition. Chemical Bath Deposition forms small crystals, which are less

useful for semiconductors than the larger crystals created by other methods of thin-film deposition but are more useful for Nano materials. However, films formed by CBD often have better photovoltaic properties (band electron gap) than films of the same substance formed by other methods .Photovoltaic cells are the most common use of films deposited by Chemical Bath Deposition because many films have better photovoltaic properties when deposited via CBD than when deposited by other methods . This is because thin films formed by Chemical Bath Deposition exhibit greater size quantization, and therefore smaller crystals and a greater optical band gap, than thin films formed by other methods . CBD is also used to deposit buffer layers in photovoltaic cells because CBD does not damage the substrate. Chemical bath deposition films can be made to absorb certain wavelength and reflect or transmit others as desired. This is because films formed by chemical bath deposition have an electrical –band gap which can be precisely controlled. This selective transmission can be used for ant-reflection and anti-dazzling coatings, solar thermal applications, optical-filters polarizers, total reflectors, etc. [5 5] . The films deposited by CBD have possible application in anti-reflection, ant-dazzling, thermal control widow coatings, optical-filters, total reflectors, poultry protection and warming coatings, light-emitting-diodes, solar cell fabrication and visitors.

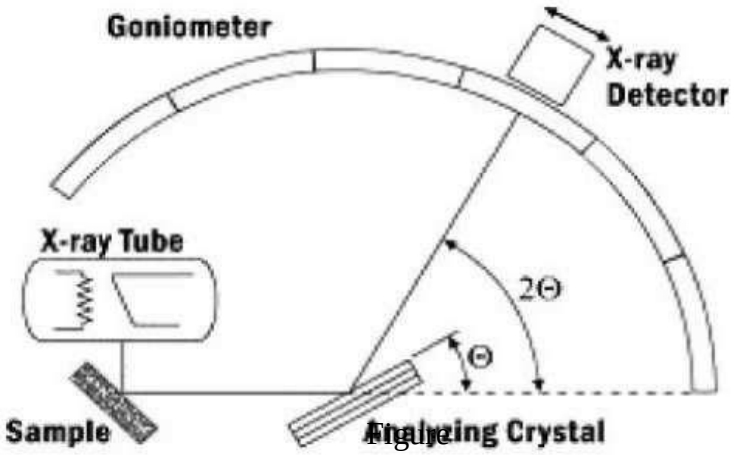
3.8 Characterization techniques

3.8.1 X –ray diffraction

XRD is considered to be a very important experimental technique that has long been used to address all issues related to crystal structure of solid, including lattice constant and geometry, identification of unknown material, orientation of single crystal, defects and stress etc **[56].** Scattering occurs when a wave propagates in a medium. As a special case, when a wave is incident on a medium with a periodic structure, which has spatial modulations with the size comparable to the wavelength of the wave, diffraction effects can be observed. So the diffraction from waves with different wavelength reveals the structure of a medium at different length scales. X-rays are a form of electromagnetic radiation with wavelengths in the range of 100 to 0.1 ºA. This range spans the inter-atomic distances in condensed matter. In addition, the soft and hard x-rays can detect distances outside this range. So the diffraction of x-ray is a powerful technique for characterizing the structure of various kinds of objects [57].X-ray diffraction is now a common technique for the study of crystal structures and atomic spacing. X-ray diffraction is based on

constructive interference of monochromatic X-rays and a crystalline sample. These X-rays are generated by a cathode ray tube, filtered to produce monochromatic radiation, collimated to concentrate, and directed toward the sample. This law relates the wavelength of electromagnetic radiation to the diffraction angle and the lattice spacing in a crystalline sample. These diffracted X-rays are then detected, processed, and counted. By scanning the sample through arrange of 2θ angles, all possible diffraction directions of the lattice should be attained due to the random orientation of the powdered material. Conversion of the diffraction peaks to d-spacings allows identification of the compound because each compound has a set of unique d spacing.

Typically, this is achieved by comparison of d spacing's with standard reference patterns [58].



Figure

3.3 Schematic diagram of a diffractometer system

Diffraction can occur only when the Bragg's law equation is satisfied [59]. When a collimated beam of X-rays strikes pair of parallel lattice planes in a crystal, each atom acts as a scattering center and emits a secondary wave. All of the secondary waves interfere with each other to produce the diffracted beam. Regard crystal as parallel planes of atoms separated by distance *d*. Assume specular reflection of X-rays from any given plane. Peaks in the intensity of scattered radiation will occur when rays from successive planes interfere constructively. The interaction of the incident rays with the sample produces constructive interference (and a diffracted ray) when conditions satisfy Bragg's law: When Bragg's Law is satisfied, "reflected" beams are in phase and interfere constructively . When two parallel X-rays from a coherent source scatter from two adjacent planes their path difference must be an integer number of wavelengths for constructive interference to occur.

Bragg's Law:

$$n\lambda = 2d \sin\theta \quad \ldots\ldots 3.6$$

Where d is the spacing between atomic planes in the crystalline phase, θ is the diffraction angle; λ is the wavelength of X-rays and n is the order of the diffraction .

The X-ray diffraction from plane as shown below in figure 3.4

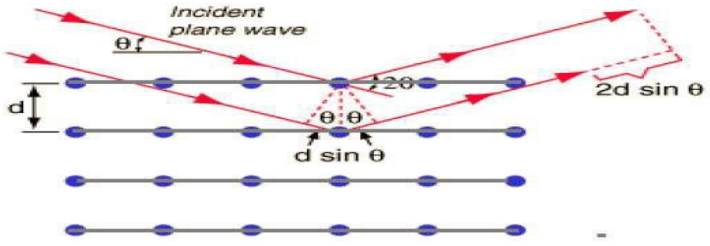


Figure 3.4 X-ray diffraction from plane

According to the Debye Scherrer equation, the average size of the nano crystals can be determine as: $D=\frac{K\lambda}{\beta Cos\theta}$ 3.7

Where D is the average crystallite size of the nano crystals, λ is the wavelength of the X-ray radiation used, β is the full width of half-maximum intensity of the peak, θ is the angle at which the diffraction peak occurs, and k is a constant(0.94) and unit less.

3.8.2. UV-Visible Spectroscopy

Study the interaction of Ultra violet (UV)-Visible radiation with molecules. To determine the optical properties such as optical absorbance and energy band gap [6 0] . The instrument operates by passing a beam of light through a sample and measuring wavelength of light reaching a detector. The wavelength gives valuable information about the chemical structure and the intensity is related to the number of molecules, means quantity or concentration.

The Schematic diagram of UV-Vis spectroscopy as shown below in figure 3.5

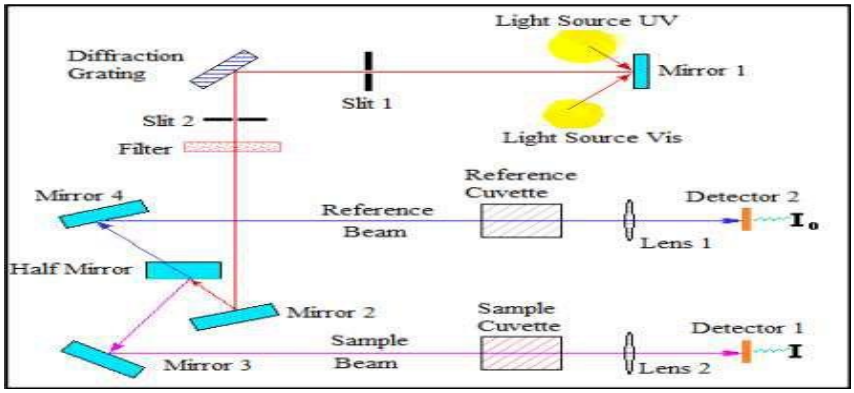


Figure3.5 : Schematic diagram of UV-Vis spectroscopy

The light source is a monochromatic; the light is split into two equal intensity beams by a half mirrored device before it reaches the sample. One beam, the sample beam, passes through a small transparent container (cuvette) containing a solution of the compound being studied in a transparent solvent. The other beam, the reference, passes through an identical cuvette containing only the solvent. The containers for the sample and reference solution must be transparent to the radiation which will pass through them. Quartz or fused silica cuvettes are required for spectroscopy in the UV-Visible region. The light sensitive detector follows the sample chamber and measures the intensity of light transmitted from the cuvettes and passes the information to a meter that records and displays the value to the operator on an LCD screen[61] . Polychromatic light from the source is focused on the entrance slit of a monochromatic, which selectively transmits a narrow band of light. This light then passes through the sample area to the detector. The absorbance of a sample is determined by measuring the intensity of light reaching the detector without the sample (the blank) and comparing it with the intensity of light reaching the detector after passing through the sample[62]

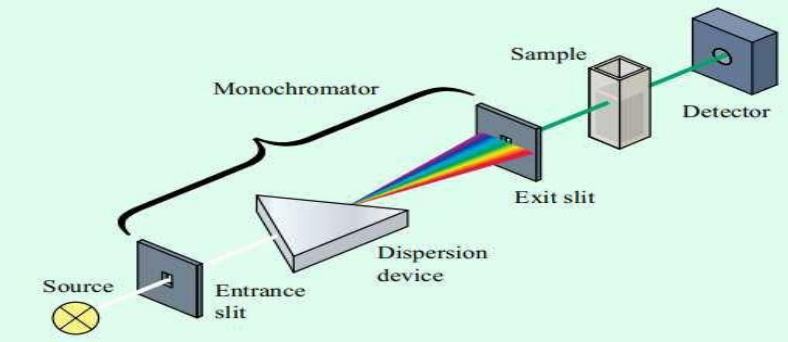


Figure 3.6. Shows a schematic of a conventional single-beam spectroscopy

If I and Io are the intensities of light rays before and after passing through the sample, then the ratio (I/Io) is called as transmittance and from that, the absorbance is given by the Beer- Lambert law as: $A = \text{Log}(I/I_0)$……...3.8

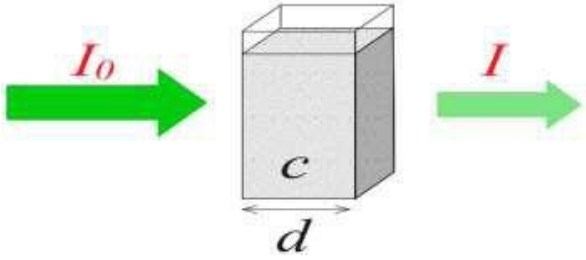


Figure 3.7 The attenuation of the light intensity is proportional to the concentration of the sample solution as well as the length of the cuvette [62] .

The Beer-Lambert law states that the absorbance of a solution is directly proportional to the concentration of the absorbing species in the solution and the path length. Thus, for a fixed path length, UV-VIS spectroscopy can be used to determine the concentration of the absorber in a solution. It is necessary to know how rapidly the absorbance changes with concentration[63]. Both factors can be summarized by expressing the absorbance *A* as a function of the concentration and of the cuvette length. In particular, the absorbance *A* is equal to the product of the extinction coefficient ε, the concentration *c* and the path length d[63] .$\mathbf{A = \varepsilon cd}$…….…….....…..3.9

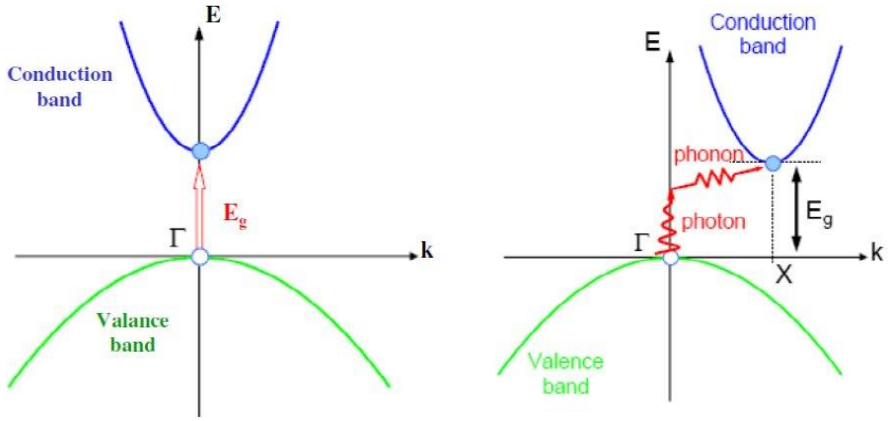
3.8.3 Energy band gap calculation from the absorbance spectra

On the basis of their optical properties there are two types of optical transition that can occur at the fundamental edge of crystalline semiconductors: direct and indirect transitions. Both involve the interaction of an electromagnetic wave with an electron in the valance band, which is raised across the band gap to the conduction band [63]. However, indirect transitions also involve simultaneous interaction with lattice vibrations see (Figure 3.8b). Thus the wave vector of the electron can change in the optical transition, the momentum change being taken or given up by the phonons. 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 direct inter-band optical transition involves a vertical transition of electrons from the valence band to the conduction band such that there is no change in the momentum of the electrons and energy is conserved as shown in (Figure 3.8a). Hence the wave vector k for electron remains unchanged in E-K space. The optical transition is denoted by a vertical upward arrow. 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 which is given as:

$$\mathbf{(Ahv) = k(hv-E_g)^{n/2}} \quad \text{.....3.10}$$

Where A is absorbance, hν is the incident photon energy, K is a constant, and the exponent n assumes the values 1, 4, 3 and 6 for allowed direct, allowed indirect, forbidden direct and forbidden transitions, respectively.

The energy band gap can be obtained by extrapolating the linear portion of $(Ahv)^2$ versus hv to the energy axis at $(Ahv)^2 = 0$ [24].



a. b.

Figure 3.8: E-K diagrams showing (a) direct and (b) indirect inter- band transition[24] .

3.9 Chemical and Experimental Procedures

3.9.1 Materials used

In order to prepare manganese doped copper oxide thin films by varying the concentration of manganese and to identify the effect of this concentration on the formation of the required thin film the following materials were used. To synthesize manganese doped copper oxide thin films the researcher used the following materials Glass substrates in different size used to deposit the films ,test tube brush to clean test tube, Electronics beam balance to determine the mass of the solid in gram, spoon to transfer small amount of solid, Volumetric flask to make solution of specific concentration, Magnetic stirring to mix chemicals and deionized water, thermometer to measure temperature gradient, A beaker to heat and stirring the chemicals with the deionized water, Substrate holders to support the substrate during the coating process, electromagnetic stands to take out the used stirs from the beakers, ordinary water, distil water was used to clean flasks, beakers and the spoon, a substrate holder for supporting substrates during coating processes includes an expandable outer frame and Petridis used to hold the deposited thin films

3.9.2. Reagent Preparation

The chemical used for the preparation of copper manganese oxide thin film as shown below in the table .

Table 3.1 The chemical used for the preparation of copper manganese oxide thin films

No	Chemical Name	Chemical formula	Brand (manufactured by)	Percentage purity	Molar weight
1	Copper acetate monohydrate	$(CH_3COO)_2Cu.H_2O$	Blulux laboratories	98%	199.65
2	Hydrazine hydrate	N_2H_5O	LOBA CHEMIE	99%	50.06
3	Ammonia solution	NH_4OH	LOBA CHEMIE	25%	35.05
4	Manganese sulphate	$Mn_2SO_{4.}H_2O$	LOBA CHEMIE	98%	169.02

3.9.3 Preparation of O.4M Copper Acetate ((CH3COO) 2Cu.H2O)

To prepare the mass of the reagents like copper acetate the researcher used the following relation .This relations are:- Mass (m) =concentration(C) of the chemicals x volume (V) of deionized water x

It's molar weight (Mw) x its percentage purity (Pp)

Mass=C.V.Mw.pp

To prepare 7.82628g of 0.4M of copper acetate($(CH_3COO)_2Cu.H_2O$) in 100ml of distilled water as follow **Mass=C.V.Mw.Pp**=0.4Mx0.1Lx199.65g/MLx0.98=7.82628g

where M is molar, g is gram and L is liter of copper acetate is prepared firstly and then which was dissolved in small amount of distilled water and then transferred into 250ml volumetric flask using funnel. The solution was then topped up to 250ml mark with distilled water and thoroughly shaken to dissolve the copper acetate completely and the resulting solution had a concentration of 0.4M. The

formed 0.4M copper acetate having a light blue color in 250ml volumetric flask .

3.9.4 Preparation of 0.01M manganese sulphate Mn_2So_4, H_2O

To prepare the mass of the reagents Manganese sulphate the researcher used the following relation .This relations are:-

Mass (m) =concentration(C) of the chemicals x volume (V) of deionized water x It's molar weight (Mw) x its percentage purity (Pp)

Mass=C.V.Mw.pp

To prepare 0.1656396g of 0.01M of manganese sulphate Mn_2So_4,H_2O in 100ml of distilled water as follow

Mass=C.V.Mw.Pp=0.01Mx0.1Lx 169.02g/MLx0.98=0.1656396 g

where M is molar, g is gram and L is liter of manganese sulphate Mn_2So_4,H_2O is prepared firstly and then which was dissolved in small amount of distilled water and then transferred into 250ml volumetric flask using funnel. The solution was then topped up to 250ml mark with distilled water and thoroughly shaken to dissolve the manganese sulphate Mn_2So_4,H_2O completely and the resulting solution had a concentration of 0.01M.The formed 0.01 M manganese sulphate Mn_2So_4,H_2O color less in 250ml volumetric flask .

3.9.5 Cleaning of the Substrates

A substrate is a surface on to which a thin film sample is deposited on the slide. The type, nature and finish on a substrate surface are extremely important because they influence properties of thin films deposited onto them [32]. Before the deposition process was performed the glass slides of dimension (75×25×2)mm degreased in acid overnight and subsequently kept in alcohol more than 20 minute, after that, cleaned with distilled water and again dried under ambient conditions.

3.9.6 Preparation of the Mother Solution (Manganese Copper Oxide Thin Film)

Manganese Copper oxide thin films were deposited onto the substrates by CBD using manganese sulphate, copper acetate, ammonia, hydrazine and deionized water as precursor materials. The preparation conditions were optimized by adjusting concentration of dissolved chemicals, bath temperature, and bath solution and the deposition time to obtain homogeneous films with good adherence to the substrate. The deposition were carried out by adjusting the final temperature at 50^oC on the heater ,deposition time 30 minute by varying the concentration of manganese starting 1.5 ml,3ml,4.5ml and 6ml by the interval of 1.5 ml for four samples. In this thin film preparation the volume concentration of copper acetate, the bath temperature, deposition time, the volume concentration of hydrazine, the concentration of ammonia are restricted while the amount of deionized water and the volume concentration of manganese are changing. The mother solution prepared by 0.4M of 5ml of copper

acetate, 0.01M of 1.5 ml of manganese sulfate the 5ml of ammonia, 3ml of hydrazine, and 55.5ml of deionized water, totally 70ml and continues by varying the concentration of manganese by the interval of 1.5ml up to four trials. The initial color of the mother solution is light blue, purple and brown, these color change occurs due to the addition of copper acetate, ammonia and hydrazine but the addition of manganese does not change the color of the solution. After each deposition cycle, the thin films were taken out from the reaction vessel after the adjusted time and cleaned with de-ionized water to remove powdery residue and less- adherent particles. The deposited films were golden in color, partially transparent and well adherent to the substrate. Visual observation shows that the thickness of deposited sample on the glass slide was increased by decrement of the deposition of manganese sulphate. Samples were dried in ambient conditions and kept inside the desiccate or until they were annealed and characterized by various techniques . The films were annealed at 300^0C for 1:30 hours before characterization.

The sample and the total volume through each concentration for copper manganese oxide thin film preparation as shown below table 3.2

Table 3 .2 sample and the total volume through each concentration for copper manganese oxide thin films

Sample Code	Copper acetate(ml)	Manganese sulphate (ml)	Ammonia (ml)	Hydrzine (ml)	Distilled water(ml)	Total volume(ml)	Time (minute)	Temperature (C^0)
Df 4	5ml	1.5 ml	5 ml	3 ml	68.5 ml	70 ml	30	50 C^0
Df 1	5 ml	3 ml	5 ml	3 ml	67 ml	70 ml	30	50 C^0
Df 3	5 ml	4.5 ml	5 ml	3 ml	65.5 ml	70 ml	30	50 C^0
Df 2	5 ml	6 ml	5 ml	3 ml	64 ml	70 ml	30	50 C^0

The Preparation and fabrication process of manganese doped copper oxide thin films were follow as shown in the Figure below

Figure 3.9 the preparation and fabrication processes of manganese doped copper oxide thin films

CHAPTER FOUR

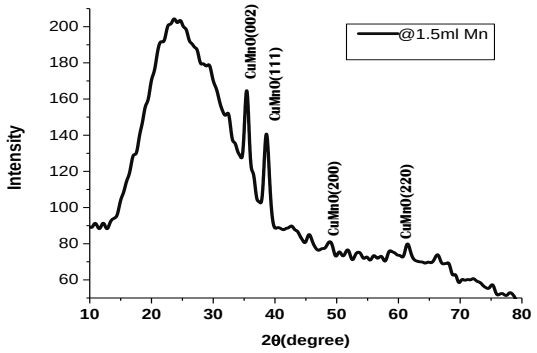
4. RESULT AND DISCUSSION

This chapter basically includes the final reports of the result and discussions carried out in this work. That is the characterization results are discussed. Manganese doped copper oxide (CuMnO) thin films, at 1.5ml,3ml,4.5ml, and 6ml of manganese doped copper oxide deposited on glass substrate at 50℃ in 30 minutes by using CBD technique. The structural and optical analysis of deposited thin films was investigated.

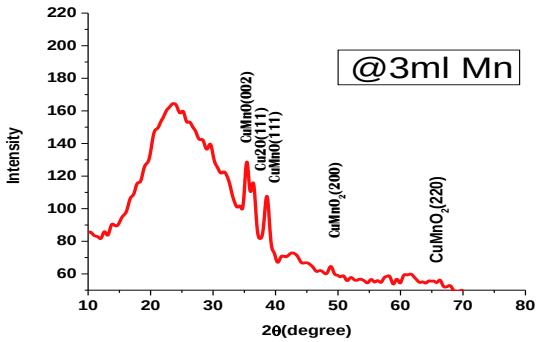
4.1 Structural Analysis

The structural analysis of the thin films were carried by Shimadzu XRD diffractometer. The XRD diffraction pattern of the thin film is represented the horizontal axis of the graph is 2θ, twice the Bragg angle and the vertical axis is the intensity count rate. In the field of material characterization, X-ray diffraction is used to determine the degree of crystallite of the materials that means whether they are crystalline or non-crystalline (amorphous).The structural characterization of the thin film were carried out by XRD pattern. The structural property of copper manganese oxide thin films was scanned by **SHIMADZU XRD-7000** X-Ray diffractometer 2θ ranging from 10° – 80° . A typical XRD pattern for manganese doped copper oxide thin films at 1.5ml,3ml,4.5ml and 6ml of Mn doped copper oxide on a glass substrates are shown in fig 4.1 The XRD pattern of the thin films show that all the films are highly crystalline in monoclinic Copper Manganese Oxide structure **(JCPDS No. 00-014–0184)**and cubic Cu_2O structure **(PDF 00-005-0667)** . Prominent diffraction peaks were observed at 35.5, 36.4 and 38.7 ^{o} . The peaks at 35.5and 38.7 ^{o} are indexed to the (002) and (111) plane of monoclinic phase of copper manganese oxide structure **(JCPDS No 00-014–0184),** respectively. A peak at 2θ values of 36.4 ^{o} is indexed to (111) plane of cubic Cu_2O structure **(JCPDS No 00-005-0667**). The other minor peaks at 24.2, 48.9 and 66.3 also match well with monoclinic copper manganese structure. The corresponding diffraction planes are(110) ,(200) and (220) respectively. The incorporation of the manganese atom in to the CuO structure is observed for all volume of manganese sulphate.

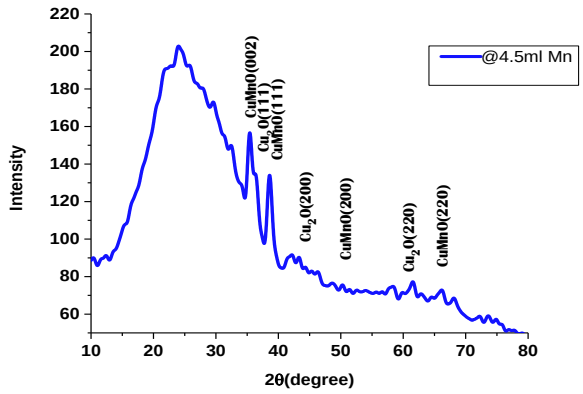
The X-ray diffraction pattern of manganese doped copper oxide thin films at 1.5ml,3ml,4.5ml and 6ml of manganese as shown in the figure below



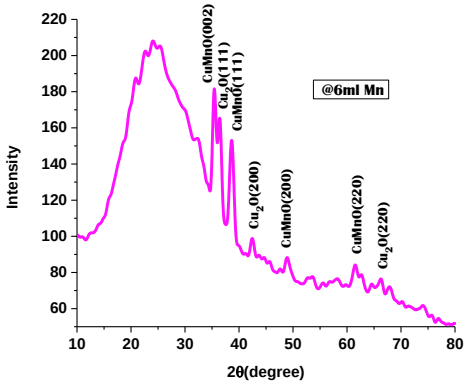
a.



b.



c.



d.

Figure 4.1 a-d shows the X-ray diffraction pattern of manganese doped copper oxide thin films at 1.5ml,3ml,4.5ml and 6ml of manganese

Some of the structural parameters of the thin films were calculated as follow.

The d-spacing value was obtained by using Braggs law:

$$\mathbf{d = n\lambda / 2\sin\theta} \quad \text{.....4.1}$$

Some structural parameters such as crystal size, strain and dislocation density calculated from XRD data given in table 4.1 .

The average crystalline size (D) for manganese doped copper oxide thin films are evaluated for the preferred planes (hkl)using the Scherer formula.

$$\mathbf{D}=\frac{K\lambda}{B\cos\theta} \quad \text{.....4.2}$$

Where K is a constant which is taken as 0.9,λ=1.5406 Å, β is FWHM in radians, θ is the Braggs angle. The origin of strain is related to lattice 'misfit' which in turn depends upon the growing conditions of the films. The micro strain (ε) developed in the thin films can be calculated from the relation [64]

$$\varepsilon=\frac{\beta\cos\theta}{4} \quad \text{.....4.3}$$

Where Ɛ and β has their usual significances.

A dislocation is a defect in a crystal where there is a misalignment of the lattice between different regions of the crystal. Unlike vacancies and interstitial atoms, dislocations are not considered equilibrium defects. The mechanisms of crystal growth involving dislocations are quite significant. The dislocation density in thin films can be described using Williamson and Small man's relation[65].

$$\delta=\frac{1}{D^2} \quad \text{.....4.4}$$

Where **δ** is dislocation density and D is the crystallite size.

Table4.1 The calculated structural parameters like crystal size, dislocation and strain for copper manganese oxide thin film in monoclinic structure

Sample	hkl	2 θ(degree)	θ(degree)	FHWM (degree)	FHWM (radian)	Crystallite size(D)(nm)	Strain (ε) 10^{-3}(nm)	dislocation (δ) $(n^{-2})(m^{-2})$
at 1.5 ml Mn	002	35.5	17.75	0.944	0.0164	8.8	3.92	0.0128
at 3ml Mn	002	35.5	17.75	0.934	0.0162	8.9	3.87	0.0125
at 4.5ml Mn	002	35.5	17.75	0.815	0.0142	10.2	3.38	0.00953
at 6ml Mn	002	35.5	17.75	0.878	0.0153	9.4	3.65	0.01109

From the XRD studies it can be observed that

The crystallite size increased from 8.8 nm to 8.9 nm to 10.2 nm as the deposition concentration of manganese increased from 1.5 mL to 3 mL to 4.5 mL. However, it then decreased from 10.2 nm to 9.4 nm when the deposition concentration of manganese reached 6 mL. This aligns with the results reported by *Ganesan, K. et al. (2019)* [32], who found that an increase in manganese concentration leads to a corresponding increase in the crystallite size of copper manganese oxide thin films. The crystallite size initially increases

with Mn concentration, reaching a maximum at 4.5 ml Mn, and then slightly decreases at 6 ml Mn. This behavior is consistent with typical observations where dopant concentration affects crystal growth dynamics. The strain decreases with increasing Mn concentration up to 4.5 ml, then increases slightly at 6 ml. This suggests that the doping level affects lattice distortion, potentially due to changes in crystal quality or the formation of new phases. The dislocation density decreases with increasing Mn concentration up to 4.5 ml, then increases at 6 ml Mn. This trend implies that while higher doping levels enhance crystal quality to a certain extent, further increases in concentration may result in more defects. Manganese doped in CuO thin films can lead to significant changes in structural parameters, including crystallite size, micro strain phases and dislocation density . The d- spacing calculated from Bragg's equation **(nλ=2dsinθ)** and the lattice parameter is obtained from the relation $\mathbf{a_{hkl}} = \mathbf{d}(\sqrt{\boldsymbol{h^2 + k^2 + l^2}})$where h, k and l are miller indices[59].

Table 4.2 The calculated structural parameters like inter planer space and lattice parameter for copper manganese oxide thin film in monoclinic structure

sample	hkl	2θ(degree)	θ (degree)	Interplaner space (d)Å	Lattice parameter(a)Å	Intensity
At 1.5 ml of Mn	002	35.48401	17.742	2.5280	5.0561	38
At 3 ml of Mn	002	35.44594	17.722	2.5309	5.0619	30
At 4.5 ml of Mn	002	35.45679	17.728	2.5301	5.0602	32
At 6 ml of Mn	002	35.45046	17.725	2.5305	5.0611	52

From the XRD studies it can be observed that

The lattice parameter increases slightly from 1.5 ml to 3 ml of Mn, then decreases slightly at 4.5 ml and remains relatively stable at 6 ml. This indicates that Mn doping affects the lattice parameter, which could be due to the size difference between Mn and Cu ions and the local strain in the lattice. Changes in the d-spacing can indicate variations in the lattice parameter.. It seems to fluctuate with different Mn concentrations, which suggests that Mn doping affects the lattice parameter. The lattice parameter generally

shows small increases or decreases based on the Mn concentration, indicating that Mn is substituting or interstitially occupying positions in the lattice. The intensity values vary for different Mn concentrations. This might indicate variations in the crystallites or phase purity of the films. Higher or lower intensities can be related to changes in the structural integrity or the relative abundance of the (002) planes. The small shifts in lattice parameters and 2θ values indicate that Mn is being incorporated into the CuO lattice, possibly substituting for Cu or creating interstitial positions.

4.2 Optical Analysis

To study the optical property of materials we need to note the optical parameters such as absorbance and band gap .The band gap energy is the most important parameter of semiconductor thin films. The optical analysis of the manufactured thin film made by using UV-Vis Spectroscopy .The UV-Visible spectroscopy used to measure the absorption or transmission of light that passing through the samples as the function of wave length. It also measures how much a chemical substance absorbs light. Using UV-Visible spectroscopy, the optical characteristics and the optical band gap were identified by measuring the UV-Vis absorption spectroscopy in the wavelength range 400-800 nm. The parameters, like absorbance, transmittance and band gap are very important parameters to be considered while studying the some properties of the materials. The optical absorption of manganese doped copper oxide thin films are as shown in Figure 4.2 a-d.

Plot of wavelength versus Absorbance for manganese doped copper oxide thin films deposited at 1.5ml,3ml,4.5ml and 6ml of manganese annealed at $300C^0$ for one and half hour is as shown in figure 4.2 a-d

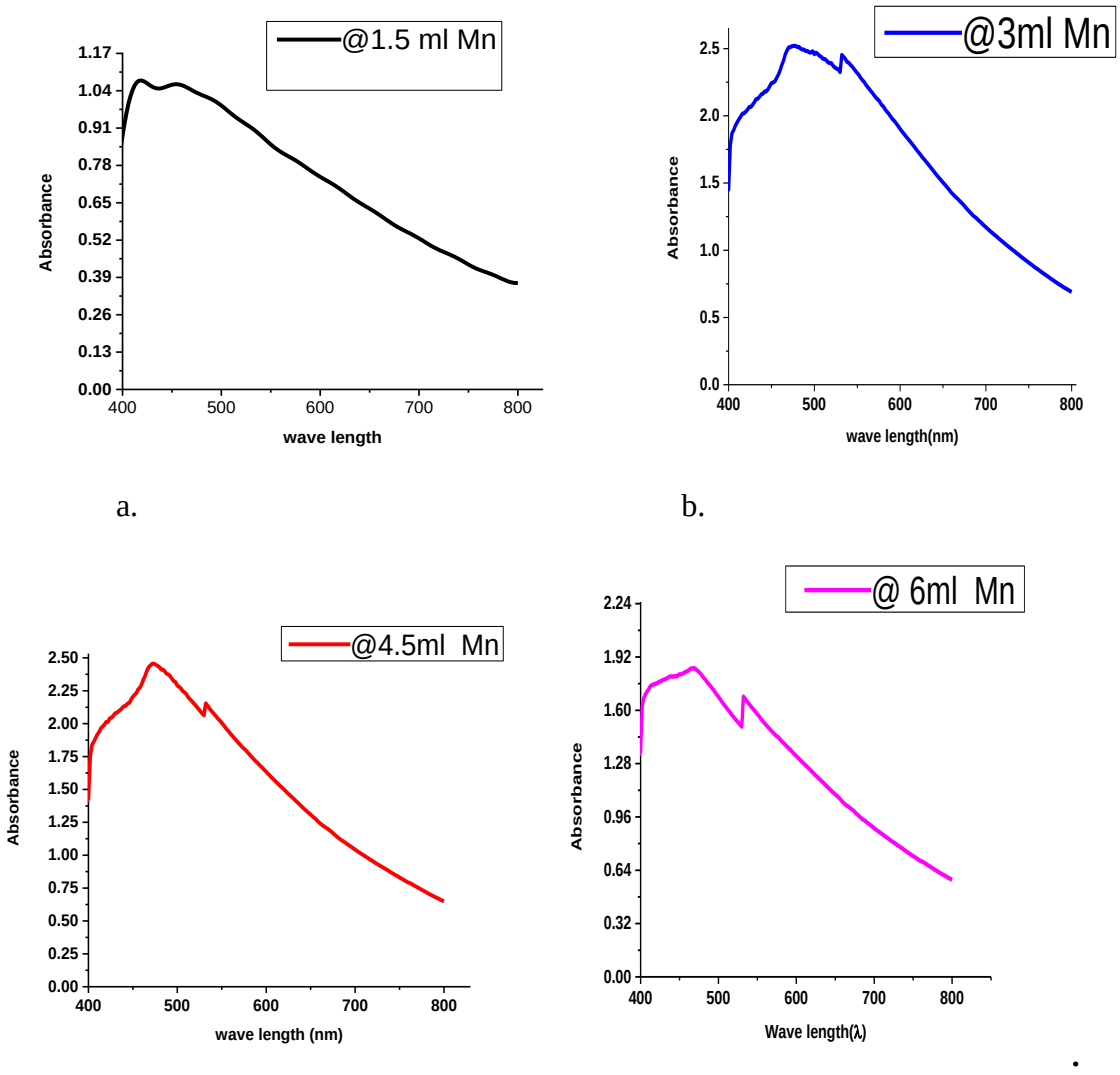


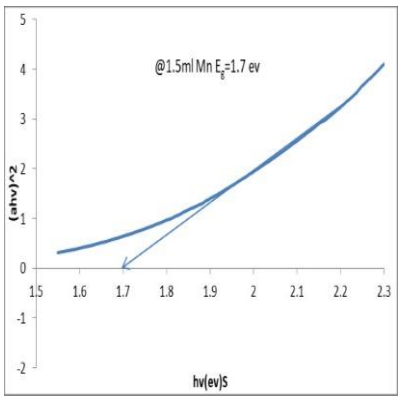
Figure 4.2 a-d Plot of wavelength versus Absorbance for manganese doped copper oxide thin films deposited at 1.5ml,3ml,4.5ml and 6ml of manganese annealed at $300C^0$ for one and half hour

The absorption of the films increased with increasing the manganese precursors concentration and decays exponentially with an increase in wave length.

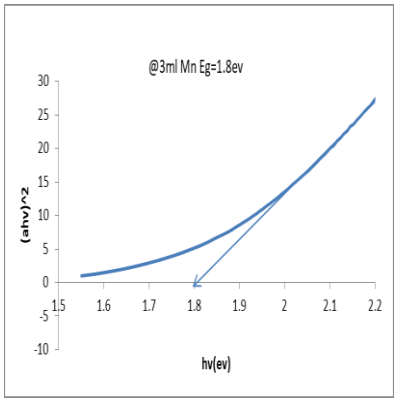
The optical absorbance of the films also increased with manganese concentration, showing a higher absorbance at shorter wavelengths.

The band gap of the thin film was obtained by plotting $(Ahv)^2$ versus (hv) of copper manganese oxide thin films. The extrapolation of the straight line portion of the plot toward the energy axis (hv-axis) gives the band gap at the intercept of hv axis .

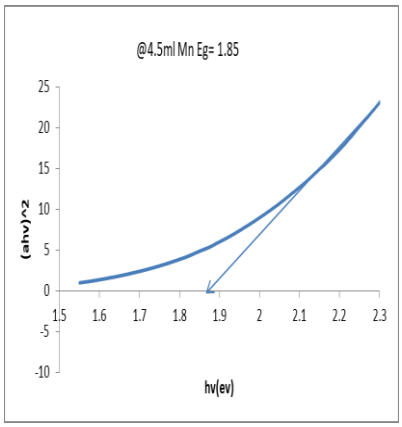
A plot of$(Ahv)^2$ $(ev)^2$ versus photon energy (hv)(ev) of CuMnO graph is as shown in figure 4.3 a-d



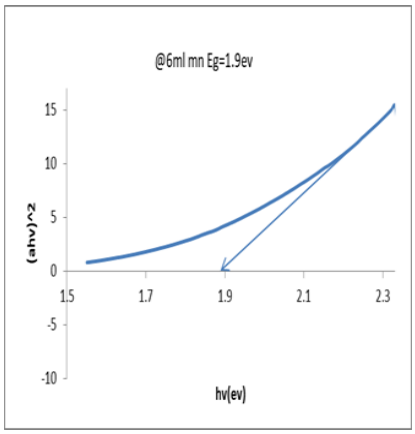
a.



b.



c.



d.

Figure 4.3 Plot of(Ahv)2 (ev)2 versus photon energy (hv)(ev) of manganese doped copper oxide thin films deposited at 1.5ml,3ml,4.5ml and 6ml of manganese annealed at $300C^0$ for one and half hour .

The band gap of the prepared copper manganese oxide thin films increases from 1.7ev to 1.8ev , 1.85ev and 1.9ev at 1.5ml,3ml,4.5ml and 6ml deposition of manganese precursors concentration . These energy band gap value were in good agreement with the results reported by Gao, W. et al. (2010) [33], who found that an increase in manganese concentration leads to a corresponding increase in the band gap of copper manganese oxide thin films. The $(Ahv)^2$ versus hv (ev) graph indicates that the energy band gap increases from 1.7eV to 1.9ev for a thin film with increasing of manganese precursors concentration from 1.5 ml of manganese to 6ml.

Table 4.3 UV-Vis analysis of CuMnO thin films

Sample code &amount of manganese concentration	Energy band gap(E_g)	Deposition time in minute	Deposition temperature in C^0
Df4 at 1.5 ml Mn	1.7 ev	30 minute	50 C^0
Df1 at 3 ml Mn	1.8ev		
Df3 at 4.5 ml Mn	1.85ev		
Df2 at 6 ml Mn	1.9 ev		

The energy band gap (E_g) of each sample increases when the concentration of the dopant increases for all samples annealed at a constant temperature of $300C^0$ for 1:30 hours .The increase in the band gap with increasing Mn concentration that you observed in your UV-Vis analysis is consistent with these possible mechanisms. It indicates that the Mn doping is likely influencing the electronic structure of the CuO thin films in a way that increases the band gap, possibly through mechanisms like the Burstein-Moss effect, band structure modification, or strain-induced changes. The possibility for optical band gap variation in CuMnO thin films presents the opportunity for the design of a suitable material for photovoltaic absorbance as well as for other optoelectronic devices.

CHAPTER FIVE

5. CONCLUSIONS AND RECOMMENDATION

5.1 Conclusion

CBD method is the best method to form a solid from aqueous solution and it is simple, inexpensive and easy method to deposit qualified uniform thin film with large scale production at low temperature with little infrastructure. In this research, manganese doped copper oxide thin films were successfully deposited by chemical bath deposition method on the glass substrate at different deposition of manganese concentration (1.5ml,3ml,4.5ml and 6ml)of manganese sulfate, bath temperature of 50 C, a time of 30 minutes , 5 ml copper acetate,3ml of hydrazine,5ml of ammonia and distilled water with a total volume of 70ml . The samples annealed a temperature of 300 C for 1:30 hour . The structural and optical property of the obtained thin films was characterized and analyzed by XRD and UV-VIS characterization techniques. The XRD showed coexistence of monoclinic copper manganese oxide and cubic Cu_2O. The band gap of the thin film increased from 1.7 ev to 1.9ev with increasing manganese concentration from 1.5ml manganese to 6ml manganese. The result shows the increment of band gap with increasing deposition of manganese concentration . However the band gap and crystalline size show correlation. The variations of Manganese concentration causes a significant changes in the optical and structural properties of copper manganese oxide thin films. The study demonstrates that manganese doping significantly influences the structural and optical properties of copper oxide thin films. The increase in band gap with higher Mn concentration suggests potential tenability of the material's optical properties for specific applications.

5.2 Recommendation For Future Work

Even though the deposition carried out was successful, however some investigation couldn't carried out. so that further investigation will carry out to investigate the following areas. Further studies are needed:

- ✓ Conduct additional characterization techniques such as scanning electron microscopy (SEM), transmission electron microscopy (TEM), and photoluminescence (PL) spectroscopy to gain a deeper understanding of the film morphology, defect structure, and optical properties.
- ✓ To further needs elemental analysis of copper manganese oxide thin films by using Energy Dispersive X-ray Spectroscopy (EDX/EDS**)**:
- ✓ To explore the specific application of the currently synthesized manganese doped copper oxide thin films

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