

**THE EFFECT OF TIN DOPING ON THE STRUCTURAL AND OPTICAL  
PROPERTIES OF COPPER OXIDE THIN FILMS SYNTHESIZED BY  
USING CHEMICAL BATH DEPOSITION METHOD**



**MSC: IN SOLID STATE PHYSICS**

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**HAWASSA UNIVERSITY, HAWASSA, ETHIOPIA**

**NOVEMBER 2024**

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**ATHESIS IS SUBMITTED TO THE DEPARTEMENT OF PHYSICS,**

**COLLAGE OF NATURAL AND COMPUTATIONAL SCIENCE, SCHOOL  
OF GRADUATE STUDIES**

**HAWASSA UNIVERSITY**

**HAWASSA, ETHIOPIA**

**IN PARTIAL FULFILLMENT OF THE REQUAIREMENTS FOR THE  
MASTER OF SCIENCE IN PHYSICS**

**(SPECIALIZATION: SOLID STATE)**

**NOVEMBER 2024**

## **Declaration**

**I declare that this thesis has not been submitted to any other institution for award of an academic degree, diploma or certificate' In the preparation, data collocation. Data analysis and compilation of this work .I have followed all ethical and technical principles of thesis. This work was submitted in practical fulfillment of the requirement for MSC degree in physics specialization in solid state at Hawassa University. The experimental work is my own work and the collaborative contributions have been clearly identified and acknowledged.**

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**The undersigned here by certify that they have read and recommend to the collage of Natural and computational Science school of graduate studies for acceptance MSC.A thesis entitled the effect of tin doping on the structural and optical properties of copper oxide thin films synthesized by using chemical bath deposition method author by Ahmed Hussien in partial fulfillment of the requirements for the degree of masters in solid state physics.**

**Approved by**

**Advisor DR, TIZAZU ABZA      Signature -----date-----**



## **Acknowledgments**

**First and for most, thanks you Allah. The challenge was too much during this work. Next and foremost, I would like to express my sincere Advisor Dr. Tizazu Abza, for his patient guidance, support and encouragement. I am very much admire and thankful to Hawassa University for support of thesis materials and financial encouragements to complete my thesis work and also I am thankful to Tokuma Secondary School for support of thesis materials to complete my thesis work .I appreciate my wife Aadde Dadisu Habib for her sincere support and help during my research work and for being with me as a companion to make the late night works flavored and memorable to the end of my life and I take this thesis paper to here memory who go off by car accident in the journey of these work. I record my deep and most gratitude to my mother Adde Hinsene Manjaa who supported me with her prayer and financial support and also for my children Samira Ahmed ,Imran Ahmed,Mubarak Ahmed,Riyad Ahmed and my brothers for their selfless support, motivation, encouragements, patience and tolerance. Finally I thank all my well-wishers.**

# TABLE CONTENT

<b>CONTENTS</b>	<b>page</b>
Declaration.....	i
advisors approval sheet one .....	ii
examiners approval sheet two .....	iii
acknowledgments.....	iv
table content.....	v
listof table .....	vii
list of figure -----	viii
Abbreviations.....	ix
Symbols .....	x
Abstract.....	xi
CHAPTER ONE .....	1
1. INTRODUCTION .....	1
1.1. Semiconductors.....	1
1.1.1. Intrinsic semiconductors .....	2
1.1.2. Extrinsic semiconductors: .....	2
1.2. Thin films.....	3
1.3. Doping of semiconductor.....	3
1.6. Objectives of the study.....	6
1.6.1. General objectives of study.....	6
1.6.2. Specific objectives of study.....	6
1.7. Beneficiary of the study .....	6
1.8. Significance of the study.....	6
1.9. Thesis structure.....	7
CHAPTER TWO .....	8
2. LITERATURE REVIEW .....	8
2.1. Definition of the thin film .....	8
2.1.3 Thin film characterization techniques.....	10
CHAPTER THREE .....	13
3. EXPERIMENTAL METHODS AND TECHNIQUES .....	13
3.1. Chemical bath deposition (CBD) technique .....	13

3.2. Thin film characterization techniques.....	14
3.2.1 X-ray diffraction (XRD) .....	15
3.2.2. UV-Visible spectroscopy .....	16
3.3.1 Material used.....	17
3.3.2. Chemical used.....	17
3.3.3. Cleaning the material .....	17
3.4. Preparation of precursor solution.....	17
3.4.1. Preparation of copper acetate.....	17
3.4.2. Preparation of tin chloride solution.....	18
3.5. Preparation of mother solution and deposition of Un doped copper acetate thin film.....	19
<u>CHAPTER FOUR</u> .....	22
RESULT AND DISCUSSION .....	22
4.1 structural characterizations .....	22
4.1.1. XRY diffraction .....	22
4.1.2. Optical properties.....	24
CHAPTER FIVE.....	26
CONCLUSION AND RECOMMENDATION .....	27
5.1 Conclusion.....	27
5.2. Recommendation .....	28
Further studies on this thesis to makes the materials closer to commercial application. ....	28
The following further investigations are recommended: .....	28
Reference .....	29

LISTOF TABLE-----	Page
Table 3.1.The Chemical Used In The Deposition Of Thin Film.....	19
Table 3 .2 Sample And The Total Volume Of Tin Doped Copper Oxide Thin Film Preparation .....	20
Table 4.1 Crystal Size, Dislocation, Density And Micro Strain For Cubic Copper Dioxide (Cu <sub>2</sub> O) Structure.....	23
Table 4.2 Crystal Size, Dislocation, Density And Micro Strain, For Copper Mono Oxide (CuO) .....	24

<b>LIST OF FIGURE</b>	<b>-----Page</b>
Figure 1.1 unit cell of cubic $\text{Cu}_2\text{O}$ and mono clinic of $\text{CuO}$ .....	4
Figure 1.2 thin film deposited on a glass substrate 2.1.1. thin film deposition methods .....	8
Figure 1.3 the chemical deposition processes 2.1.2 application of thin film .....	9
Figure 3.1 experimental set up of chemical bath deposition.....	14
Figure 3.2 derivation of bragg's law using the reflection geometry and applying trigonometry. ....	16
Figure 3.3 image of the physical appearance of chloride.....	18
Figure 3.4.a the color of chemical solution of copper acetate and ammonia before adding hydrazine.....	20
Figure 3.4.b shows the color of chemical solution of copper acetate and ammonia after adding hydrazine.....	20
Figure 3.4.c shows the color of the deposition of thin film formed after 25 minute at temperature 50. ....	20
Figure 4.2 x-ray diffraction patterns of tin doped and un doped copper oxide thin film.....	22
Figure 4.3 plot of photon energy $h\nu(\text{e.v})$ vs $(ah\nu)^2(\text{e.v})^2$ for the (sn: $\text{CuO}_2$ ) deposited by doping level from 0ml to 6ml tin doped copper oxide thin film.....	25
Figure 4.4 plot of wave length versus absorption for tin doped copper oxide thin film.....	26

## **Abbreviations**

<b>AFM</b>	<b>a atomic force microscope</b>
<b>CVD</b>	<b>chemical vapor deposition</b>
<b>DMSS</b>	<b>dilute magnetic semiconductors</b>
<b>EDX</b>	<b>energy dispersive x-ray spectroscopy</b>
<b>HRTEM</b>	<b>high resolution transmission electron microscopy</b>
<b>JCPDS</b>	<b>joint council for powder diffraction standard</b>
<b>MBE</b>	<b>molecular beam epitaxy</b>
<b>MEMS</b>	<b>micro electromechanical systems</b>
<b>MO</b>	<b>metal organic</b>
<b>MOS.</b>	<b>Metal oxide semiconductor.</b>
<b>OER</b>	<b>oxygen electro reaction</b>
<b>PVD</b>	<b>physical vapour deposition</b>
<b>ALE</b>	<b>atomic layer eptexy</b>
<b>RHEED</b>	<b>reflection high energy electron diffraction</b>
<b>SEM</b>	<b>scanning electron microscope</b>
<b>SNO</b>	<b>tin oxide</b>
<b>TOMS</b>	<b>transition metal oxide</b>
<b>UV</b>	<b>visible spectroscopy</b>
<b>VRS</b>	<b>visible reflectance spectroscopy</b>
<b>XPS</b>	<b>x-ray photoelectron spectroscopy</b>
<b>XRD</b>	<b>x-ray diffraction</b>

## Symbols

$C$	Speed of light
$\lambda$	wave length
$D$	crystal size
$\alpha$	Exception coefficient
$\beta$	Full wave half maxima
$\rho$	Density
$\delta$	$d$ Islocation density
$\varepsilon$	Microstrain
$\theta$	Central angle
$\mu$	Micro

## ***Abstract***

*This thesis studied the effect Tin doping copper oxide thin films synthesis by chemical bath deposition method. The deposition of thin film was done on glass substrate by changing the tin chloride solution as 0ml, 2ml, 4ml and 6ml. The deposition of thin film was done by using 0.4M of copper acetate as Cu source and 5ml Ammonia to control the PH value 3ml of Hydrazine as a complexing agent at constant temperature of 50°C and constant time of 25 minute. The structural and optical properties were studied by using XRD and UV VIS technologies. The XRD patterns show two phase that  $Cu_2O$  which have cubic crystal structure and Copper mono oxide which have monoclinic crystal structure. The crystallite size of the cubic  $Cu_2O$  phase deposited at 0 ml, 2 ml and 4 ml  $SnCl_2$  was 38.51, 33.44 and 37.74 nm respectively. The crystallite size of the  $CuO$  phase deposited at 2 ml, 4 ml and 6 ml  $SnCl_2$  are 11.75, 77.6 and 15.99 nm respectively. The intensity was decrease as the doping level increase in both  $Cu_2O$  and  $CuO$ . The UV-VIS investigation revealed the three energy band gap result when 2ml, 4ml and 6ml of tin chloride added to the solution the energy band gap observed between wave length of 400-800 nm shows at 2ml 1.7ev, at 4ml 1.9ev .and at 6ml 2.05ev.*

*Key words: chemical bath, thin film copper die oxide, copper mono oxide*

# CHAPTER ONE

## 1. INTRODUCTION

Metal oxides are the basis of modern diverse smart and functional materials and devices. Because physical and chemical properties of these oxides can be tuned. Functional properties of metal oxides depends on many chemical and structural characteristics such as chemical composition, various kinds of deficiencies, morphology, particle size, surface-to-volume ratio, etc. By varying either of these characteristics, the electrical, optical, magnetic, and chemical properties can be regulated, giving the possibility of fabricating smart devices. Such unique characteristics make oxides the most diverse class of materials, with properties covering almost all aspects of material science and physics in areas such as semi conductivity, superconductivity, Ferro electricity, and magnetism. It is known that the reversible chemisorption of reactive gases on the surface of the oxide semiconductor is accompanied by reversible changes in conductivity.

This makes semiconductors the most attractive materials for the manufacture photosensitive electronic converters based on them. Conductivity of semiconducting oxides caused by deviations from stoichiometry and also defects such as interstitial cat ion or anion vacancies. Depending on type of determinate impurity (electron acceptor or electron donor) and conduction type (n- or p-type), the resistance of the sensitive layer of the sensor is increased or decreased. Oxidizing gases or electron acceptors such as  $\text{NO}_2$  produce a decrease in the conductance of n-type semiconducting materials (i.e., electrons are the major carriers, such as  $\text{ZnO}$  and  $\text{SnO}_2$ ) and an increase in the conductance of p-type semiconducting materials (i.e., holes are the major carriers, such as  $\text{CuO}$ ); reducing gases or electron donors such as  $\text{H}_2\text{S}$ ,  $\text{CO}$ ,  $\text{H}_2$  and water vapor act in a reverse manner.[1].

### 1.1. Semiconductors

A semiconductor material is one whose electrical properties lie in between those of insulators and good conductors. Examples are: germanium and silicon. In terms of energy bands, semiconductors can be defined as those materials which have almost an empty conduction band and almost filled valence band with a very narrow energy gap (of the order of 1eV) separating the two. In general, depending on the level of doping, semiconductors can be classified under/into two main groups such as intrinsic semiconductors and extrinsic semiconductors.[2]

### **1.1.1. Intrinsic semiconductors**

An intrinsic semiconductor was one which 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 0.72eV and 1.1eV respectively [2]. 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 [3].

### **1.1.2. 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. Depending on the type of doping material used, extrinsic semiconductors can be sub-divided into two classes: N-type semiconductors and P-type semiconductors [2]. N-type of semiconductor is obtained when a pentavalent material like antimony (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. P-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 [4--7].

## **1.2. Thin films**

**Thin film technology is the basic of astounding development in solid state electronics. The usefulness of the optical properties of metal films and scientific curiosity about the behavior of two-dimensional solids has been responsible for the immense interest in the study science and technology of the thin films. Thin film studies have directly or indirectly advanced many new areas of research in solid state physics and chemistry which are based on phenomena uniquely characteristic of the thickness, geometry and structure of the film [8].**

**The phenomenal rise in thin film researches is no doubt due to their extensive applications in the diverse fields of electronics, optics, space science, aircrafts, defenses and other industries. These investigations have led a numerous inventions in the forms of active devices and passive components, piezo-electric devices, micro-miniaturization of power supply, rectification and amplification, sensor elements, storage of solar energy and its conversion to other form, magnetic memories, super conduction films, interference filters, reflecting and antireflection coatings and many others[9] . Thin film materials are the key elements of continued technological advances made in the fields of optoelectronic, photonic and magnetic devices. The processing of materials into thin films allows easy integration into various types of devices. The properties of material significantly differ when analyzed in the form of thin films. Most of the functional materials are rather applied in thin film form due to their specific electrical, magnetic, optical properties or wear resistance.**

**Thin film technologies make use of the fact that the properties can particularly be controlled by the thickness parameter. Thin films are formed mostly by deposition, either physical or chemical methods. Thin films, both crystalline and amorphous, have immense importance in the age of high technology. Few of them are: microelectronic devices, magnetic thin films in recording devices, magnetic sensors, gas sensor, A. R. coating, photoconductors, IR detectors, interference filters, solar cells, polarizer's, temperature controller in satellite, superconducting films, anticorrosive and decorative coatings[10].**

## **1.3. Doping of semiconductor**

**By themselves, intrinsic semiconductors are not of particular use. They are neither good conductors nor insulators, and their conduction is largely dependent on temperature .Doping in semiconductors is the processes of introducing impurities into an intrinsic**

semiconductors to modulate its electrical, optical and structural properties. A crystal with an added dopant is referred to as an extrinsic semiconductor or doped material. The amount of impurity added is generally small, perhaps in the neighborhoods of one part per million [11]. The dopant may be added through a gaseous diffusion process where the crystal is heated in an oven and the dopant added in gaseous form. Over a period of time the impurities will diffuse or “seep into” the target crystal. An alternate approach is ion implantation. In this method the impurities are accelerated and quite literally smash into the target, dislodging and replacing some of the original atoms in the crystal.

#### 1.4. General properties of copper oxide and tin oxide

Copper is a first-row transition metal. The electron configuration of copper is  $[\text{Ar}] 3d^{10} 4s^1$  and common compounds of Cu exist at oxidation states of +1 and +2. The oxides corresponding to  $\text{Cu}^+$  and  $\text{Cu}^{2+}$  are  $\text{Cu}_2\text{O}$  and  $\text{CuO}$ , respectively. In ternary and quaternary cuprite's, copper can exist also as  $\text{Cu}^{3+}$  [12]. Of the binary copper oxides,  $\text{Cu}_2\text{O}$  crystallizes in a simple cubic structure, while  $\text{CuO}$  assumes the monoclinic structure.

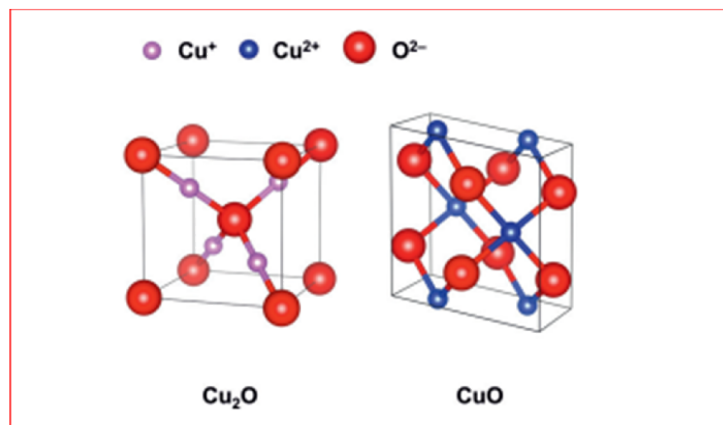


Figure 1.1 unit cell of cubic  $\text{Cu}_2\text{O}$  and mono clinic of  $\text{CuO}$

$\text{Cu}_2\text{O}$  and  $\text{CuO}$ , a mixed valence copper oxide,  $\text{Cu}_4\text{O}_3$ , is also known.  $\text{Cu}_4\text{O}_3$  is considered to be a metastable material, as  $\text{CuO}$  and  $\text{Cu}_2\text{O}$  impurity phases are easily formed during its synthesis and post-synthesis annealing. Copper oxide which is considered as one of the most important p-type semiconductor transition metal oxide which exists in two general phases: cupric oxide ( $\text{CuO}$ ) and cuprous oxide ( $\text{Cu}_2\text{O}$ ) [13]. Cupric Oxide belongs to the monoclinic crystal structure with energy band gap of (1.2-2.1) eV. On the other hand, cuprous oxide belongs to the cubic crystal structure with energy band gap of (2.2- 2.9) eV [14]. Copper ions in high temperature superconductor have a square planar coordination as

in CuO and the antiferromagnetic behavior of these systems shows striking similarities cupric oxide is an organic compound with the formula of Cu O ABLAK solid it is one of the two stable oxide of copper (1) oxide cuprous oxide as a mineral nontoxicity natural abundance of starting materials and remarkable physical and chemical properties

.The copper oxide classified into three phase there are:

- ✓ Cuprous oxide or cuprite ( $\text{Cu}_2\text{O}$ )
- ✓ Cupric oxide or tenorite. ( $\text{Cu O}$ ).
- ✓ Parameleconite ( $\text{CU}_4\text{O}$ )

Among the three cuprous oxide and cupric oxide are the most stable phase exhibiting p-type semiconductor. The melting point of cupric oxide is  $1326^\circ\text{C}$  in soluble in water and soluble in ammonium chloride and potassium cyanide.  $\text{Cu}_2\text{O}$  was the first p-type's semiconductor studies in the early 20<sup>th</sup> century and was used recertifies in radio receivers. Later copper oxide were used in photo voltaic device, solar cell and catalysis .The inorganic compound tin (IV) oxide, also known as stannic oxide, has the formula  $\text{SnO}_2$ . Cassiterite is a tin oxide mineral,  $\text{SnO}_2$ , and it is the most common tin ore. Tin metal is burned in the air to create synthetic tin (IV) oxide. The annual production is in the kilotons scale. In a reverberator furnace at  $1200\text{--}1300^\circ\text{C}$ ,  $\text{SnO}_2$  is reduced to metal with carbon. Tin(iv) oxide is a crystalline solid or powder that is white or off-white. Sublime:  $1800\text{--}1900^\circ\text{C}$ , mp:  $1127^\circ\text{C}$ , density:  $6.95\text{ g/cm}^3$  Water doesn't remove it. It can dissolve in hydrochloric acid and concentrated sulphuric acid. Tin oxide is Odour less and insoluble in water heavy atom count and hydrogen bond acceptor. Sulfate is formed when  $\text{SnO}_2$  dissolves in sulphuric acid. Tin oxide, which has a Sn +4 oxidation state, can be used to make ceramic bodies opaque, as a mild abrasive, and as a fabric weighting agent. The cosmetics ingredient review has determined that tin oxide is a healthy ingredient, based on the fact that it is not easily absorbed through the skin. Tin oxide is used in dentistry and to render a precious metal polishing paste for high polishing of amalgam and precious metals when combined with water.

### 1.5. Statement of the problem

Transition metal oxides (TMOs) consider as an important and promising materials which have attracted large attention in many technological applications due to their outstanding electronic, optical, magnetic, and catalytic properties [15]. Copper oxides are one of the most important transition metal oxides which have huge interest in several fields. To

improve the electrical conductivity, transmission stability and feasibility for the practical use, various processes like doping, annealing and ageing are employed [16]. Among these methods, doping is one of the excellent ways to improve the above mentioned properties. There are very limited reports on tin doped copper oxide thin films deposited by chemical bath deposition method. Due to this the researcher was interested to synthesize tin doped copper oxide thin films deposited by CBD method using different molar ratio of tin chloride solution. The film was characterized for their structural and optical properties using XRD-diffraction, UV-VIS spectrometer spectroscopy.

## **1.6. Objectives of the study**

### **1.6.1. General objectives of study**

The main objective of this thesis was to study the effect of Tin Doping on the structural and Optical Properties of Copper Oxide thin Films Synthesized by Using Chemical Bath Deposition Method.

### **1.6.2. Specific objectives of study**

- To synthesize tin doping copper oxide thin film by chemical bath deposition method by varying tin chloride concentration
- TO investigate the effect of tin doping on copper oxide on structural and optical characteristics using XRD and UV-Vis spectrometer.

## **1.7. Beneficiary of the study**

The following are the main beneficiary of the study:-

- ✓ It is important for scientific community
- ✓ It will help for those industry that manufacture semiconductor devices
- ✓ It will serve as reference for the future researcher who will be conduct their thesis paper on similar title

## **1.8. Significance of the study**

The research will fill the gap of knowledge and providing clear information on the **study** related to tin doped copper oxide thin films synthesized by using chemical bath deposition (CBD) method. The findings of this research could be used in technologies that use (Sn: CuO<sub>2</sub>) thin films. It give clear information on to the gap on doped and un doped semiconductor like (Sn: CuO<sub>2</sub>).Inspire other researchers to make further investigation and use this document as a reference

## **1.9. Thesis structure**

**The thesis is organized in five chapters. The first chapter gives why the researcher needs to study about the semiconductor materials such as  $\text{CuO}_2$  and  $\text{SnO}_2$ . The second chapter deals with reviews of literature on copper oxide ( $\text{CuO}_2$ ) and tin ( $\text{SnO}_2$ ). The third chapter deals experiments and method of the experimental procedure. The fourth chapter deals with the result and discussion of final work using method of figure, graphical representation and list of data in the table. The fifth chapter deals with conclusion and recommendation. List of the reference used in the work placed at the end.**

## CHAPTER TWO

### 2. LITERATURE REVIEW

#### 2.1. Definition of the thin film

Thin films are ubiquitous and they are found more or less everywhere. Thin films are applied to modify the surface of a material or to build functional devices. It is its thickness is greatly possible to define a thin film of a material that is an element of this material so that reduced, which is expressed with nanometers. The small distance between the two boundary surfaces gives a disturbance of the physical, chemical and mechanical properties (Figure 1.2). The small distance between the two boundary surfaces gives a disturbance of the physical, chemical and mechanical properties but in the thin state, on the contrary, the effects related to the boundaries are preponderant and very important. It is quite obvious that the lower the thickness, the greater the dimensionality effect. Conversely, when the thickness of a thin layer exceeds a certain threshold, the effect of thickness will become minimal and the material will return to the well-known properties of the solid state of material. The second essential characteristic of a thin layer is that, whatever the procedure used for its manufacture, a thin layer is always integral with a substrate on which it is built (even if it sometimes happens that one separates the thin film of said substrate). Consequently, it will be imperative to take into account this major fact in the design, namely that the substrate has a very strong influence on the structural properties of the layer deposited therein [17].

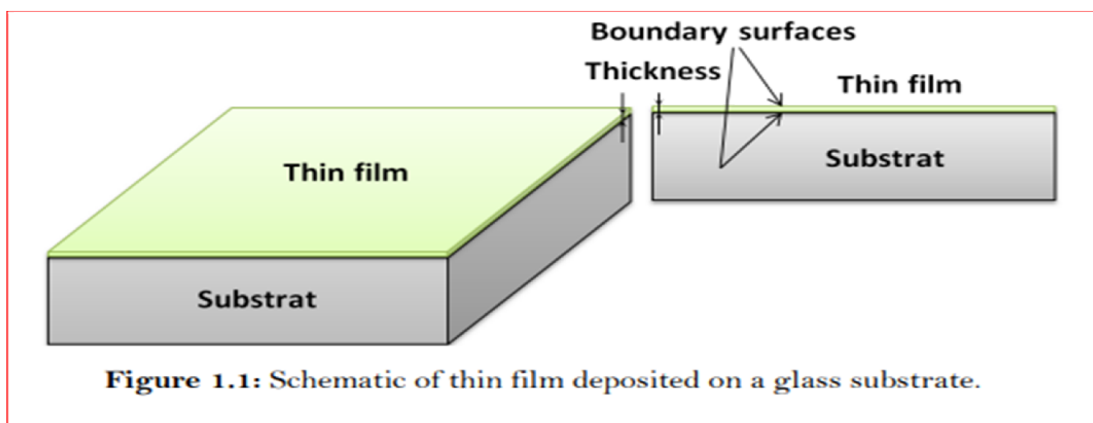


Figure 1.2 thin films deposited on a glass substrate

### 2.1.1. Thin film deposition methods

Over the years, various materials have been synthesized in the form of thin films due to their prospective technological significance and scientific interest in their properties. They have very extensive range of applications and extend from nanostructures to coatings of several square meters on window glasses. Based on the nature of the deposition process, the techniques employed for thin film deposition can be classified into two groups, namely, physical and chemical deposition processes.

The physical methods include physical vapor deposition (PVD), laser ablation, molecular beam epitaxy and magnetron sputtering. While the chemical methods comprise gas phase and liquid phase deposition methods (Figure 1.3). The gas phase methods are chemical vapor deposition (CVD) and atomic layer epitaxy (ALE), while spray pyrolysis, sol-gel, electro deposition, chemical bath deposition (CBD), liquid phase epitaxy (LPE), spin-coating and dip-coating are liquid phase methods.

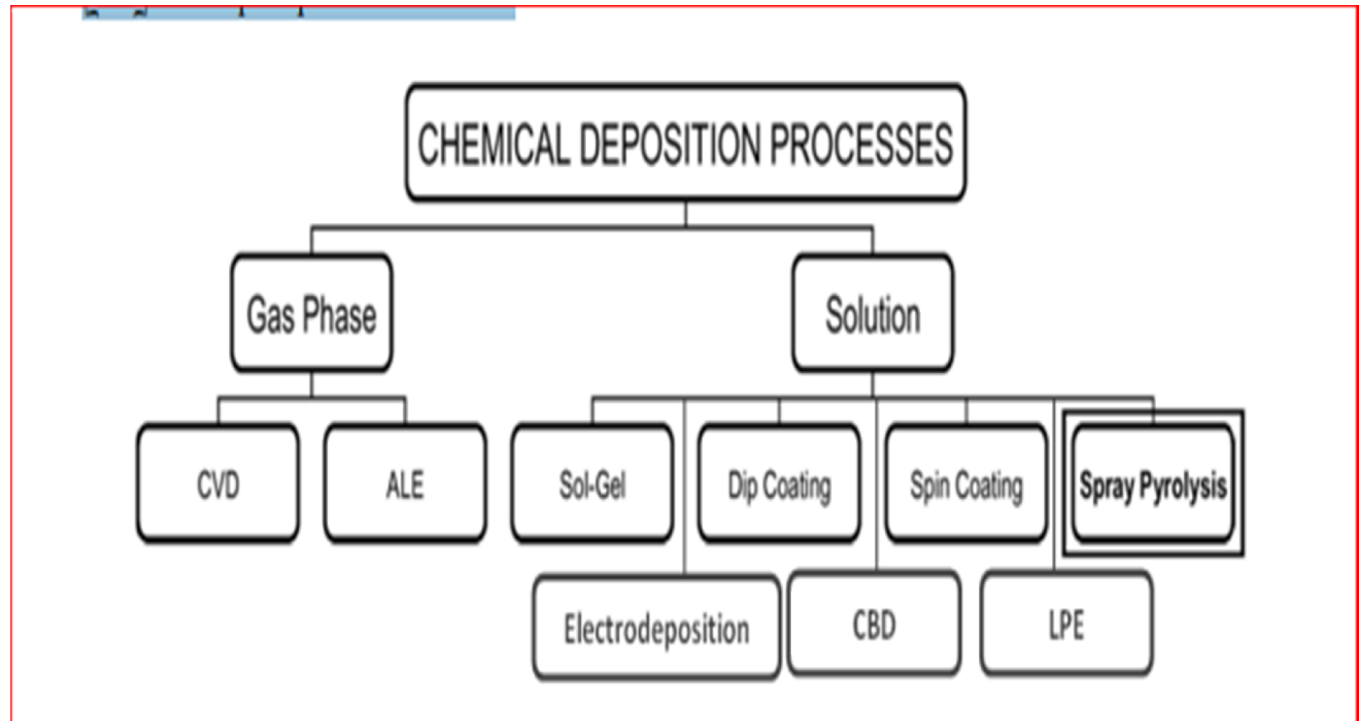


Figure 1.3 the chemical deposition processes

### 2.1.2 Application of thin film

Thin film materials have already been used in semiconductor devices for wireless communications, telecommunications, integrated circuits, rectifiers, transistors, solar cells, light-emitting diodes, photoconductors, light crystal displays, magneto-optic memories, audio and video systems, compact discs, electro-optic coatings, memories, multilayer

capacitors, flat-panel displays, smart windows, computer chips, magneto-optic discs, lithography, micro Electromechanical systems (MEMS), and multifunctional emerging coatings, as well as other emerging cutting technologies

### **2.1.3 Thin film characterization techniques**

Characterization techniques are used to evaluate the physical properties of the semiconductor thin films, such as crystal structure, micro structural details, composition of the film, surface morphology, optical, chemical binding configuration and electrical properties to optimize the preparation conditions. The characterization of these thin film materials are the prime and key step in the fabrication and development of the devices. The properties of these thin film materials can be studied by using various characterization tools and techniques.

## **2.2. Review literature**

Saadaldin N [2015] prepared thin films of copper oxide by chemical bath deposition (CBD) method on substrates of glasses by Alternate immersions method (AI) at room temperature for 20 second using heated liquid of sodium hydroxide up to 70°C and copper thiosulfate complex. The substrates were annealed at different temperatures (200-300-400°C) in the air; the crystalline structure of prepared samples was studied by using XRD and (SEM) technologies. The results were indicated to; the crystalline structure of prepared films was related to temperature of annealing of copper-oxide (Tenorite), cubic of Cu<sub>2</sub>O (Cuprite). Optical studies showed that the prohibited rang between (1.3-2.4) e.V were related to annealing temperature (monoclinic). Therefore, application of solar cells is very promising as a suitable material for conversion of photovoltaic energy with high absorbency solar and low thermal issue. Real and imaginary dielectric constants were calculated. Significant improvement in structure as a follower of annealing temperature required by oxide layer, SEM image showed that porous structure were distinctive materials for the manufacture of gas sensors.[18] M. D. Shined [2019] prepared Cu O thin films carried out by simple chemical bath (CBD) technique. The thin films on glass substrate were deposited at 80°C by varying the deposition time. CuO thin film were prepared by using copper acetate (CH<sub>3</sub>.COO)<sub>2</sub>.Cu.H<sub>2</sub>O as Cu precursor, triethanolamine (TEA) as complexing agent and sodium hydroxide (NaOH) as pH regulator. They were later annealed at temperature (400°C) for 2hour. The Structural characterizations of the films were carried out by studying X-ray diffraction (XRD) patterns. The optical

properties of CuO thin film were studied via UV-Visible spectroscopy in the range of 400-900 nm X-ray diffractograms of the CuO thin film. The optical properties of CuO thin film were studied using UV-Visible spectroscopy and the band gap value was calculated to be 1.5 to 1.8 e.V by varying deposition time. Optical and structural properties of the deposited CuO thin films were studied which revealed formation of CuO on the glass substrate. Such films are useful for gas sensing studies [19].

Wanjala et al. [2016] reported that the CuO thin films prepared by DC magnetron sputtering technique at 350 W and 400 W deposition powers. Reflectance of less than 40% in the wavelength range of 250-2500 nm was reported in all deposited films. Band gaps obtained by simulation were 1.25 and 2.06 e.V. These values of the band gap show that the obtained copper monoxide (CuO) films are good absorbers. They also observed that the deposited thin films exhibited high absorbance of above 80% in the Ultra-Violet (UV) region of the electromagnetic spectrum which was decreased below 30% towards the Near Infrared Region (NIR)[20].

Muhammad Imran [2023]. Was investigate that by using Copper Oxide (CuO) thin films deposited on glass substrates by chemical bath deposition (CBD) and effects of annealing at 300, 350, 400, 450, and 500 C for 1 h . XRD spectra matched well with monoclinic nature of CuO. XRD results revealed that with increasing annealing temperature, crystallite size increased. Raman spectroscopy confirmed development of CuO phase. UV-vis spectroscopy showed excellent photo absorption in the visible region of incident sun light and absorption coefficient remained high. Optical band gap energy decreased in the range of 1.45 to 1.52 e.V with increasing annealing temperatures. The obtained results suggest that CuO thin films with excellent optical junction for solar cell structures.[21]. G Papadimitropoulos et al [2005] reported that thin films of copper oxide that was deposited by oxidation of copper thin films on silicon substrates in temperatures varying from 150 up to 450°C. Copper films were deposited by vacuum evaporation and their thickness was estimated from the evaporated mass. X-rays diffraction (XRD) patterns showed that in the copper oxide films coexist two phases: CuO and Cu<sub>2</sub>O their proportion varying with oxidation temperature. At temperatures up to 225°C Cu and Cu<sub>2</sub>O is formed while above this temperature CuO forms. Pure Cu<sub>2</sub>O was obtained at 225°C while pure CuO above 350 °C[22]. Necmi Serin, Tülay Serin [2005] reported by annealing effect on the structural, optical and electrical properties of copper oxide films prepared on glass

substrates by chemical deposition. The films were annealed in air for different temperatures ranging from 200 to 350°C. X-ray diffraction patterns shows that the films as-deposited and annealed at 200 and 250°C was of cuprite structure with composition Cu<sub>2</sub>O. Annealing at 300 converts these filto CuO. This conversion is accompanied by a shift in the optical band gap from 2.20 e.V to 1.35 e.V. [23].

The above literature review show that the effect of copper oxide deposition of the thin film synthesized by chemical bath deposition on the structural and optical properties.

The method was used in their work was annealing temperature chemical bath deposition method and deposition of copper oxide on glass substrate by chemical bath deposition technique. How ever there was no work use the effect of Tin Doping on the structural and Optical Properties of Copper Oxide thin Films Synthesized by Using Chemical Bath Deposition Method by the same consternation.

## CHAPTER THREE

### 3. EXPERIMENTAL METHODS AND TECHNIQUES

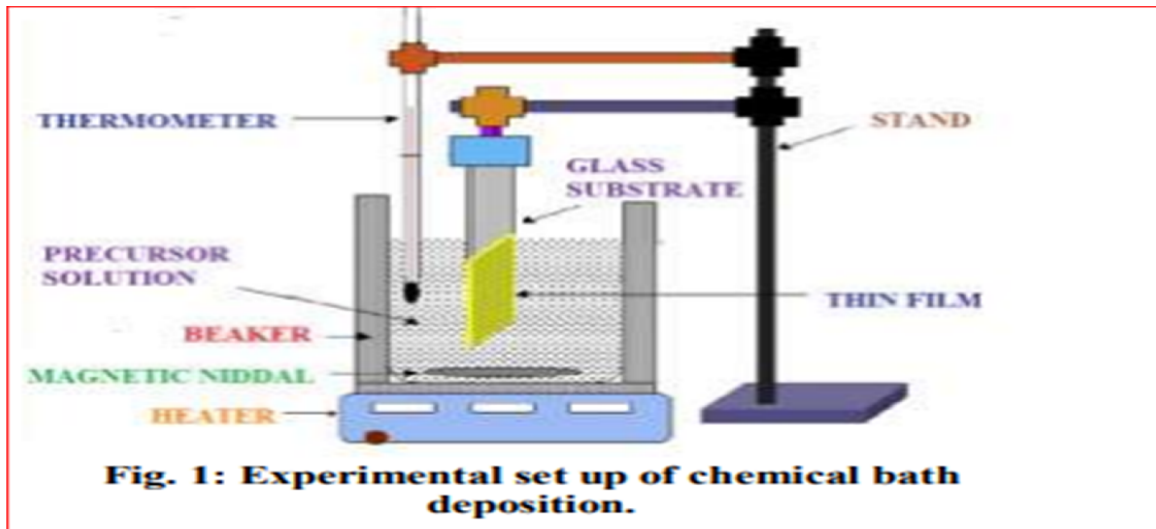
#### 3.1. Chemical bath deposition (CBD) technique

In this technique it is possible to control the film thickness and chemical composition by varying the deposition parameters such as temperature, precursor concentration, complexing agents used and the pH of the solution. The ability of this method to coat large areas in a reproducible and low-cost process is the most attractive advantage. This method depends on the deposition of thin films from aqueous solutions either by passing a current or by chemical reactions under appropriate conditions. By the nature of their preparative conditions, these films are generally not of high purity [24]. With appropriate control of the deposition parameters definite composition of thin films can be obtained.

In CBD process, thin films are deposited on a solid substrate when it is immersed into a dilute solution of one or more metal salts ( $MP^+$ ), a source of chalcogenide, X (X=S, Se, Te) ion and a suitable complexing agent in an aqueous solution. Using this method the metal chalcogenide films will form on the substrate via four steps as follows:-

- ✓ Establishment of equilibrium between water and the complexing agent
- ✓ Formation of metal- complex species
- ✓ Hydrolysis of the chalcogenide source
- ✓ Formation of the solid film on the substrate

The deposition of the film occurs on the substrate when the value of ionic product exceeds the solubility product, otherwise it is precipitated out. The metal ions are usually complexes by a suitable complexing agent, which would then gradually release metal ions during the course of reaction. The formation of metal-complex ion controls the rate formation of solid metal hydroxides which leads to the formation of solid film. Thus, the metal ion must be complexes in order to prevent precipitation of metal hydroxide. The strength of the complexing agent should not be too weak or too strong in ordered to prevent bulk precipitation or to deposition of the desired film. The basic principle of CBD is to control the chemical reaction so as to effect the deposition of thin film by precipitation. The process depends on the slow release of chalcogenide ion into an alkaline solution in which the free metal ion is buffered at a low concentration.



The figure 3.1 Experimental set up of chemical bath deposition

The solution chemistry must choose such that a spontaneous reaction from the liquid phase is possible. The advantages of using this method over all other various methods is as follows:-

CBD method is presently attracting considerable attention as it does not require sophisticated instrumentation like vacuum system and other expensive equipment's. The simple equipment's like hot plate with magnetic stirrer are sufficient for deposition needed. The starting chemicals are commonly available and cheap. With this method a large number of substrates can be coated in a single run. No electrical conductivity of the substrate is required for deposition. The low temperature deposition avoids oxidation and corrosion of metallic substrates. Chemical deposition results in pin hole free and uniform deposits are easily obtained since the basic building blocks are ions instead of atoms.

### 3.2. Thin film characterization techniques

Many techniques are used to determine the shape, size morphology of copper oxide thin films such as XRD, SEM, UV, Infrared (IR) spectroscopy and HRTEM (High resolution transmission electron microscopy). From the above thin Film Characterization Techniques the materials that the researcher used to characterize thin film was:

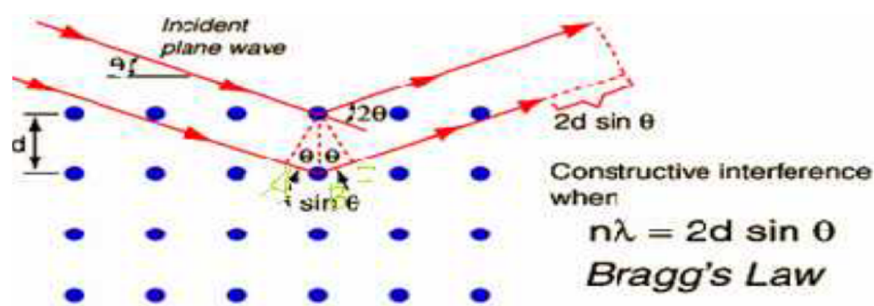
- XRD (X- ray diffraction)
- UV (visible spectroscopy)

Characterization of the deposited thin films has a crucial role in the production of any device. The growth mechanism and properties of the films can be well understood by their

characterizations using a variety of investigative techniques. Appropriate techniques were employed for investigation to evaluate the properties of thin films. The optimization is the most important aspect to control material processing and regularize sensor performance. Before using prepared films in applications, one has to characterize the films to achieve optimum performance. The complete characterization of any material consists of phase analysis, compositional characterization, structural elucidation, micro-structural analysis and surface characterization, which have strong bearing on the properties of materials. This has led to the emergence of a variety of advanced techniques in the field of thin film technology. This subtopic discussed about the commonly used characterization techniques of the deposited (Sn:CuO<sub>2</sub>) thin films. The structural, optical and electrical properties of tin doped copper oxide (Sn: CuO<sub>2</sub>) thin film by using X-RAY diffraction and UV (Visible spectroscopy).

### 3.2.1 X-ray diffraction (XRD)

The researcher that used for phase identification material was X-Ray machine or X-Ray spectroscope Apparatus that named by X-Ray Diffractometer (XRD). XRD is most powerful and primary analytical technique used for phase identification of crystalline materials. The breakthrough work of XRD was developed by Bragg's father and son pair in 1913. It is rapid and non-destructive method which determines phase, size, cell parameters, strain and anisotropic growth involved in nanomaterial-ray diffraction (XRD) is a very powerful experimental technique for studying crystal structures of solids and thin films. An XRD technique is important method to identify non molecular and crystalline substances. It can be used to determine the crystal structure, unit cell parameters and content, including crystallite size. This structural data is useful in the explanation of trend in many properties.



**Figure 3.2 Derivation of Bragg's Law using the reflection geometry and applying trigonometry.**

Appropriate techniques were employed for investigation to evaluate the properties of thin films. The optimization is the most important aspect to control material processing and regularize sensor performance. Before using prepared films in applications, one has to characterize the films to achieve optimum performance. The complete characterization of any material consists of phase analysis, compositional characterization, structural elucidation, micro-structural analysis and surface characterization, which have strong bearing on the properties of materials. This has led to the emergence of a variety of advanced techniques in the field of thin film technology. [25]

XRD in thin films is helps for the phase identification. This identification is done by comparing the measured' spacing in the diffraction pattern and, to a lesser extent, their integrated intensities with known standards in the JCPDS Powder Diffraction File (Joint Committee on Powder Diffraction Standards, Swath more, Pennsylvania, 1986) and the reflections can be indexed with Miller indices. However, if the size of the diffracting tiny crystal is small, there is no more complete destructive interference at  $\pm$  which broadens the peak corresponding to diffracted beam in proportion to the size of the tiny crystal. This can be used to calculate the particle size. The relation for the same is given by Debye-Scherrer and formulated as;

$$D=k\lambda/\beta\cos\theta\text{..... (3.1)}$$

Where k is a constant  $k=0.94$  (k is the shape coefficient for the reciprocal lattice point),

$\lambda$  -is the wavelength of the X-ray source,

$\beta$  -(FWHM) is full width at half maxima..XRD is used to determine the size by using scherrer equation.

### **3.2.2. UV-Visible spectroscopy**

Ultraviolet-visible Spectroscopy (UV-VIS) is vital and non-destructive tool for characterization of optical properties of semiconductors. It deals with absorption/reflectance/ transmittance spectroscopy in UV-Visible region. In this electromagnetic region molecules undergo electronic transition and are related with color of the sample after interaction with light. In solid state physics and in nanomaterial when incident light is greater than the band gap of semiconductor then it absorbs light and UV-VIS spectrum is obtained of absorbed region through spectrometer.

The researcher was used Ultraviolet-visible Spectroscopy (UV-VIS) to determine the band gap of the prepared film by using UV spectrometer.

### **3.3. Experimental procedure**

#### **3.3.1 Material used**

The following materials were used during in the process of deposition of thin films. Electronic beam balance (FA224),Magnetic stirrer ,water distilling apparatus ,spoon, beakers ,measuring cylinders ,long metallic picker ,Tweezers, electronic heater ,chemical bath beaker , water bath beaker ,washing bush ,soap, glass substrate ,thermometer ,glove, water holding beakers, plastic hand pump, 250ml and 50ml of cylinder for holding prepared solution.

#### **3.3.2. Chemical used**

Copper acetate with 199.5 MW and 98% of purity percentage , tin chloride ( $\text{SnCl}_2$ ) with 225.63MW and 97% of purity percentage , Ammonia solution ( $\text{NH}_3$ )with 35.05MW and 25% of purity percentage to control the PH value of the solution, hydrazine( $\text{N}_2\text{H}_4$ ) solution with 50.05 MW and 98% of purity percentage

#### **3.3.3. Cleaning the material**

Cleaning the laboratory equipment is very important before doing any work. Because if we do not cleaned the substrate and beakers very well the result that need to understand was not give pure result. Before started the deposition of thin film glass substrate were immersed in the beakers contain nitric acid ( $\text{HNO}_3$ ) and hydrochloric acid (HCL), But the acid that we used in the laboratory was nitric acid to clean the glass substrate in our laboratory work over the time .After that glass substrate must be immersed in the alcohol for about an hour .finally cleaned the glass substrate with distilled water and dried in light condition of the atmosphere of a place.

### **3.4. Preparation of precursor solution**

The separate preparations of appropriate solution of the starting chemicals are very important before the preparation of the actual reaction of the solution.

#### **3.4.1. Preparation of copper acetate**

Copper (II) acetate was prepared by heating copper (II) hydroxide or basic copper (II) carbonate with acetic acid. The chemical formula of copper acetate ( $(\text{CH}_3\text{COO})_2\text{Cu} \cdot \text{H}_2\text{O}$ )

which have molar mass of 181.63g/mol of hydrate The physical appearance is dark green crystallize solid.

The preparation of copper acetate solution each precursor solution was measured the copper acetate using the relation

$$M = C \times V_{H_2O} \times MW \times PP \text{ -----Where } M = \text{ mass of the precurese in gram}$$

$$C = \text{ the concentration of precursor , } V_{H_2O} = \text{Volume of water } Mw = \text{molar weight}$$

$$PP = \text{Purity percentage}$$

To prepare the solution of 0.4M of copper acetate(  $(CH_3 COO)_2 CU, H_2 O$  ) in the 250ml of distilled water ..Frist by using the above equation must be found the mass of copper acetate

$$M = C \times V \times MW \times PP$$

$$M = 0.4M \times 0.25L \times 199.65g/ML \times 0.98 = 19.5657g$$

Then we measure 19.7654g of copper acetate powder and dissolve in 250ml distilled water and shake very well unstill the solution become to uniform colour solution ,lastly the solution of copper acetate forms light blue color was formed.

### 3.4.2. Preparation of tin chloride solution

To prepare 0.005M of Tin chloride ( $(SnCl_2), 2H_2 O$  ) in the 50 ml of water

$$M = C \times V_{H_2O} \times MW \times PP$$

$$0.005M \times 0.05L \times 225.63g \times 0.97 = 0.05471g \text{ of Tin chloride prepared}$$

Then we measure 0.05471g of Tin chloride and dissolve in 50 ml of distilled water and shake very well un still the solution become to uniforme colour solution.



Figure 3.3 image of the physical prance of TIN chloride (lab. Observatoin)

The following chemicals or solutions were like Hydrazine and Ammonia were directed used by measuring the amount of the solutin needed to make the diposition of thin film in the expermental step. Because the solutins were industrial prepared.

**Table 3.1. The chemical used in the deposition of thin film**

<b>NO</b>	<b>Chemical Name</b>	<b>Chemical Formula</b>	<b>Band manufacture</b>	<b>Percentage purity</b>	<b>Molecular Weight</b>
<b>1</b>	<b>Copper acetate monohydrate</b>	<b>(CH<sub>3</sub>COO)<sub>2</sub>CU.H<sub>2</sub>O</b>	<b>BULUX LABURATOR</b>	<b>98</b>	<b>199.65</b>
<b>2</b>	<b>TIN(111) Chloride Sncl</b>	<b>Sncl<sub>2</sub> 2H<sub>2</sub>O</b>	<b>BULUX LABURATOR</b>	<b>97</b>	<b>225.63</b>
<b>3</b>	<b>Ammonia solution</b>	<b>NH<sub>4</sub> OH</b>	<b>LOBA CHEME PVT-LTP</b>	<b>25</b>	<b>35.05</b>
<b>4</b>	<b>HYDRAZINE</b>	<b>NH<sub>2</sub> OH<sub>5</sub></b>	<b>LOBA CHEME</b>	<b>99</b>	<b>50.05</b>

### **3.5. Preparation of mother solution and deposition of Un doped copper acetate thin film**

The preparation of mother solution of un doped copper oxide was started by measuring the 0.4M and 5ml of copper acetate solution, then stirring for few minute and drop 5ml of ammonia to control the PH value to the deposited solution and adding 3ml of hydrazine to the solution to control the deposition of thin film and lastly 57ml of distilled water added to the solution to full 70ml of total volume of the solution. The deposition of thin film was started by adjusting the heater and taking the room temperature as initial point and recording the initial time to the final deposition time of 25 minute and total constant temperature of 50°C. As the deposition of chemical solution started the color of deposited solution was gradually change its color and its look like brown after 10 minute from starting point. Finally the deposition of thin film was formed at total deposition time of 25 minute and total temperature of 50°C .The substrates were removed after 25 minutes and washed several times with distilled water and allowed to dry under ambient condition before film characterization .The deposition of thin film formed was golden in color well bright and uniform.

**Table 3.2 Sample and the total volume of tin doped copper oxide thin film preparation**

Sample code	Copper acetate(ml)	Tin chloride (ml)	Ammonia(ml)	Hydrazine(ml)	Distilled water (ml)	Total volume	Temperature °C	Time minute
AS <sub>25</sub> '	5ml	0ml	5ml	3ml	57ml	70ml	50	25
CT-1	5ml	2ml	5ml	3ml	55ml	70ml	50	25
CT- 2	5ml	4ml	5ml	3ml	53ml	70ml	50	25
CT-3	5ml	6ml	5ml	3ml	51ml	70ml	50	25

In the process of deposition when the amount of the solution of tin chloride doped to copper acetate increase by two the amount of distilled water decrease by two the other parameters was kept constant. The color of chemical solution shown in the figure below



**a**



**b**



**.c**

**Figure 3.4 .preparation of the solution**

**Figure 3.4.a the color of chemical solution of copper Acetate and Ammonia before adding hydrazine.**

**Figure 3.4.b the color of chemical solution of copper Acetate and Ammonia after adding hydrazine.**

**Figure 3.4.c the color of the deposition of thin film formed after 25 minute at temperature 50.**

### 3.5.1 Preparation of mother solution and deposition of tin doped copper oxide (sn: cuo2) thin film.

The preparation of tin doped copper oxide thin film were prepared by adjusting the molar ratio of 0.4M of CuAc<sub>2</sub> to 0.005M of SnCl<sub>2</sub> using the molar ratio of:-

$X_{ratio} = \frac{V.C \text{ SnCl}_2}{v.c \text{ copper acetate}}$

0.002L/0.4 (Copper acetate=0.005M.

The all step of the result was done by the same method. And the final result of ( X =0.000, 0.005,0.01and 0.015. The experiment was done by using 0.4M and (5ml) of copper Acetate and (2ml,4ml and 6ml ) 0.005M of tin chloride, 5ml of Ammonia solution, 3ml of hydrazine and 55ml of distilled water to full the total volume of 70ml of chemical solution in 100 ml of breakers which was used to deposited thin film. The value of X are x=0.000,0.005,0.01,0.015.The thin film that formed after 25 minute deposition time was very bright and gold in color, then after washed using distilled water dry in well air condition lastly taken to the laboratory to characterized by using XRD and UV VIS machine to see its structural , optical properties of the thin film.

## CHAPTER FOUR

### RESULT AND DISCUSSION

In this chapter basic all listed the final work of the researcher result and discussion which supported by experimental equipment's and there result. The experimental result of tin doped copper oxide (Sn:Cu<sub>2</sub>O) thin film at (x=0.000,0.005,0.01,0.015 ) deposited on glass substrate at a temperature of 50°C and time of 25' with different concentration percentage by using chemical bath deposition method(CBD) technique characterized by XRD and UV VIS spectroscopy

#### 4.1 structural characterizations

##### 4.1.1. XRD diffraction

The structural analysis of the thin film was carried by XRD. To investigate the structural properties of tin (Sn) doped copper oxide (Cu<sub>2</sub>O) thin films, SHAMIDUZ XRD -7000 diffract meter 2 ranging between 10-80 with cu k $\alpha$  ( $\lambda=0.15406$ ) radiation working by using the current of 30mA and the voltage of 40kv was used in the experiment .

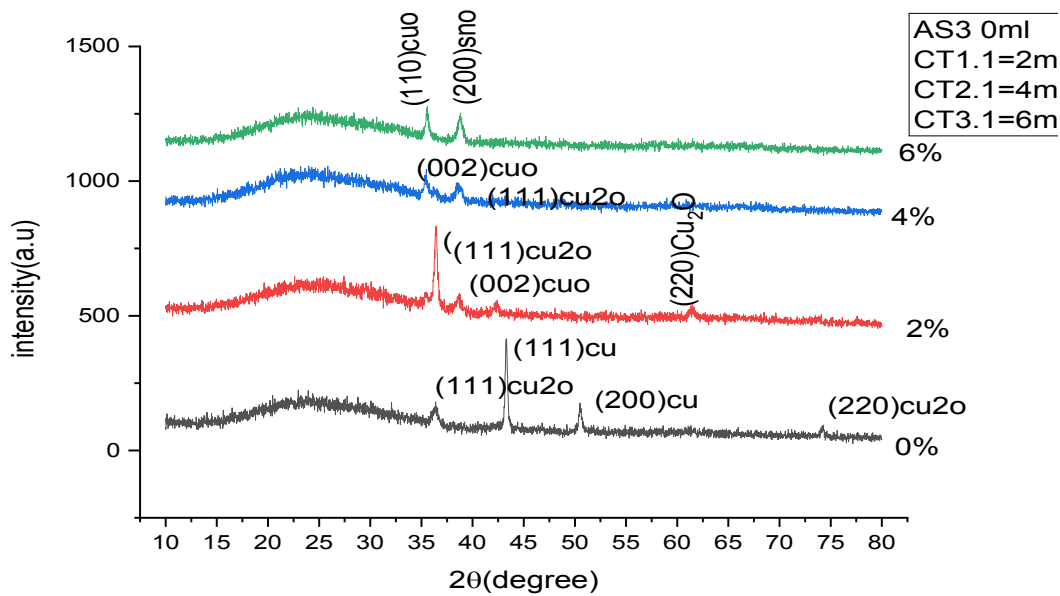


Figure 4.1 X-ray diffraction patterns of tin doped and un doped copper oxide thin film

The XRD patterns of the thin film at 2 ml tin chloride shows a single intensity peak at 2θ value of 36.5° which is indexed to ( 111) plane of cubic Cu<sub>2</sub>O structure (JCPDS reference code 00-005-0667). It has three other weak peaks at 38.6° indexed to (111) plane of

monoclinic phase of CuO structure (JCPDS reference code 00-048-1548) and at 42.3° and at 61.4° indexed to (200) and (220) plane of cubic Cu<sub>2</sub>O phase (JCPDS reference code 00-005-0667) respectively. For 4 ml and 6ml tin chloride the XRD patterns show two peaks at 36.5° and 38.6° indexed to (002) and (111) plane of monoclinic phase of CuO structure respectively. However, the intensity of the peaks for 6 ml tin chloride is higher than that of 4 ml tin chloride. The crystal size (D) was calculated using the Scherrer equation:

$$D = k\lambda / \beta \cos\theta \dots\dots\dots (4.1)$$

Where k is a constant k = 0.94 (k is the shape coefficient for the reciprocal lattice)  
 $\lambda = 0.15406$  is the wavelength of the X-ray source,

$$\beta = (\text{FWHM}) \text{ is full width at half maxima.}$$

The micro strain ( $\epsilon$ ), dislocation density ( $\delta$ ) has been calculated using the following relations and their values are given in the table 4.1. The origin of strain is related to lattice misfit which in turn depends upon the growing conditions of the films. The micro strain ( $\epsilon$ ) developed in the thin films was calculated from the relation.

$$\epsilon = \beta \cos\theta / 4 \dots\dots\dots (4.2)$$

The dislocation density ( $\delta$ ), which is defined as the length of dislocation lines per unit volume (lines/m<sup>2</sup>), is a measure of the amount of defects in the grown Nano-crystalline powder. It was calculated from the average values of the crystallite size (D), where D is the crystallite size from Debye–Scherer equation

$$\delta = 1/D^2 \dots\dots\dots (4.3)$$

**Table 4.1 Crystal size, Dislocation, density and micro strain for cubic copper dioxide (Cu<sub>2</sub>O) structure**

Sample Code(cu <sub>2</sub> o)	2 (deg)	Hkl	FWHM (rad)	CRSYTAL SIZE (nm)	dislocation density 10 <sup>-3</sup> (nm <sup>-2</sup> )	micro strain(unit)
AS3((0ml)	43.3	(111)	0.0013	38.51	6.7	5.3
CT1.1(2ml)	43.3	(111)	0.0015	33.44	8.94	6.2
CT2.1(4ml)	43.3	(111)	0.0013	37.74	7.1	5.4
CT3.1(6ml)		-	-	-		

As it can be observed from Table 4.1, the crystallite size of the cubic Cu<sub>2</sub>O phase deposited at 0 ml, 2 ml and 4 ml SnCl<sub>2</sub> are 38.51, 33.44 and 37.74 nm respectively. Similarly, the dislocation density of cubic Cu<sub>2</sub>O deposited at 0 ml, 2 ml and 4 ml SnCl<sub>2</sub> are 6.7 × 10<sup>-3</sup>,

$8.94 \times 10^{-3}$  and  $7.1 \times 10^{-3} \text{ nm}^{-2}$  respectively . No trend was observed for the XRD parameters with changing SnCl<sub>2</sub> solution volume. At 6ml Cu<sub>2</sub>O was not observed.

**Table 1.2 Crystal size, Dislocation, density and micro strain, for copper mono oxide (CuO)**

Sample of CUO						
AS3 (0ml)	-	-	-	-	-	-
CT 1.1(2ml)	36.3307	(200)	0.0042	11.75	7.2	1.8
CT 2.1(4ml)	36.7502	(200)	0.0063	77.6	1.6	3
CT 3.1(6ml)	36.1222	(200)	0.0030	15.99	3.91	1.3

As it can be observed from the Table 4.2, the crystallite size of the CuO phase deposited at 2 ml, 4 ml and 6 ml SnCl<sub>2</sub> are 11.75, 77.6 and 15.99 nm respectively. Similarly, the dislocation density of monoclinic CuO phase deposited at 2 ml, 4 ml and 6 ml SnCl<sub>2</sub> are  $7.2 \times 10^{-3}$ ,  $1.6 \times 10^{-3}$  and  $3.91 \times 10^{-3} \text{ nm}^{-2}$  respectively. No trend is observed for the XRD parameters of monoclinic CuO phase with changing SnCl<sub>2</sub> solution volume. At 0ml CuO was not observed. In a similar manner G.papadimitropoulos [2005] reported the two phase of copper dioxide by oxidation of copper thin film on silicon substrate by temperature varying from 150°C to 450°C. The XRD result reported shows the coexist two phase CuO and Cu<sub>2</sub>O their proportion varying with oxidation temperature and [23] also reported the two phase of copper dioxide by annealing temperature of the sample.

#### 4.1.2. Optical properties

The optical properties of the thin films were studied by UV-visible spectroscopic measurements. The optical study concerns with transmission, absorption, reflection, refraction, polarization, interference and etc. From these properties it is possible to calculate the optical constants such as: absorption coefficient ( $\alpha$ ), direct and indirect band gap, refractive index (n), extinction coefficient(k), optical conductivity. From the above many duty of the UV-VIS spectroscopy in researcher studies only band gap energy and absorption coefficient included by using the wave length between 400nm-800nm. The band gap ( $E_g$ ) is the energy needed to move a valence electron into Conduction band. For a

semiconductor it is the energy needed to free an electron from nucleus of the parent atom. The highest energy band occupied by electrons is called valance band (VB) and lowest unoccupied band is called conduction band (CB). The energy gap between the two levels is called band gap energy.

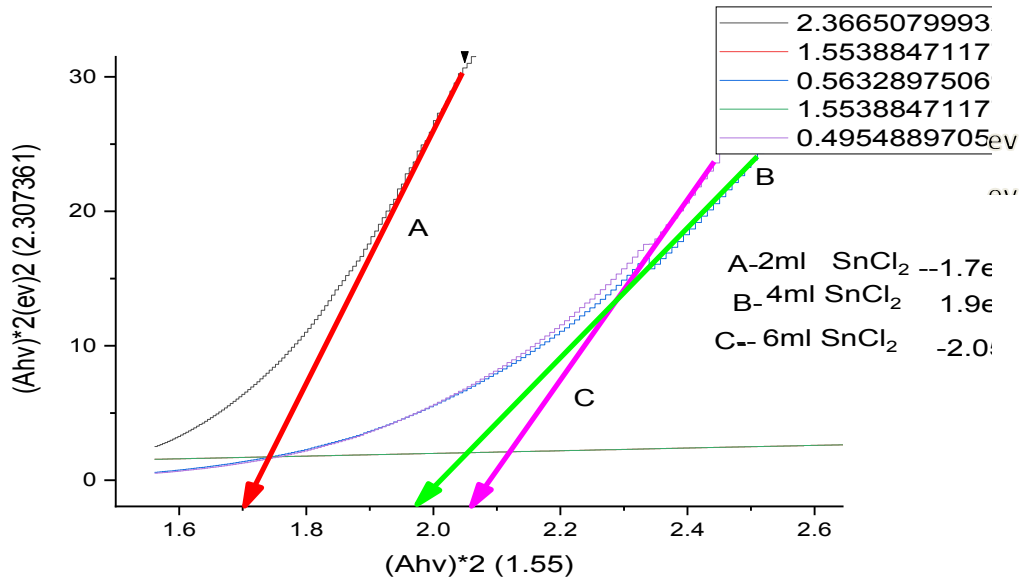
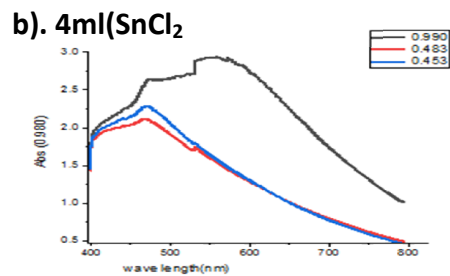
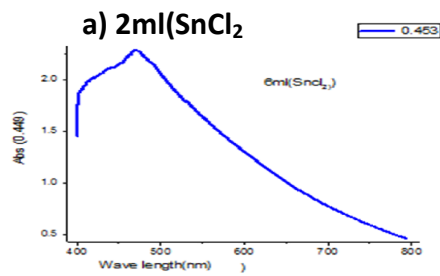
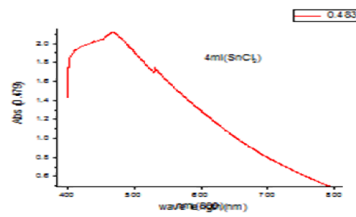


Figure 4.3 plot of photon energy  $h\nu$ (e.V) VS  $(Ah\nu)^2$ (e.V)<sup>2</sup> for the (Sn:CuO<sub>2</sub>) deposited by doping level from 0ml to 6ml tin doped copper oxide thin film.

As shown in the above graph the energy band gap of the 0, 2, 4 and 6 ml SnCl<sub>2</sub> solution were 1.7eV, 1.9eV and 2.05 e.V respectively. Similar result was reported by [26] to Cu<sub>2</sub>O and CuO. In a similar manner M.D.Shined [2019] reported the band gap of CuO by using simple chemical bath (CBD) method the UV visible spectroscopy shows in a range of 400-900nm and the result of the band gap calculated 1.5e.V-1.8e.V by varying deposition time and also [20] reported the band gap of CuO 1.25e.V-2.06e.V with wave length range 250-2500nm and shows the good absorber of CuO.



c) 6ml(SnCl<sub>2</sub>)

d) 2-6ml(SnCl<sub>2</sub>)

**Figure 4** plot of wave length vers us absorvation for tin doped copper oxide thin film AS the graph of wave length vs. absorption shows, the films have high absorption in the 400nm- 800 nm.

## CHAPTER FIVE

### CONCLUSION AND RECOMMENDATION

#### 5.1 Conclusion

The thesis was studied the effect of Tin Doping on the structural and Optical Properties of Copper Oxide thin Films Synthesized by Using Chemical Bath Deposition Method. The deposition of thin film synthesis on glass substrate by chemical bath deposition technique. The deposition was done by doping tin chloride solution into copper acetate by using 5ml Ammonia to control the PH value and 3ml Hydrazine as a complexing agent at temperature of 50°C at a time of 25 minute.. The thin film was characterized by XRD and UV VIS spectroscopy. The XRD result shows when 2ml of tin chloride solution added to pure copper oxide solution the patterns of the thin film shows two phase that was pure copper oxide (Cu<sub>2</sub>O) which have cubic crystal structure and Copper mono oxide (CuO) which have monoclinic crystal structure. The single intensity peak at 2θ value of 36.5° which is indexed to (111) plane of cubic Cu<sub>2</sub>O structure (JCPDS reference code 00-005-0667). It has three other weak peaks at 38.6° indexed to (111) plane of monoclinic phase of CuO structure (JCPDS reference code 00-048-1548) and at 42.3° and at 61.4° indexed to (200) and (220) plane of cubicCu<sub>2</sub>O phase (JCPDS reference code 00-005-0667) respectively. The crystallite size of the cubic Cu<sub>2</sub>O phase deposited at 0 ml, 2 ml and 4 ml SnCl<sub>2</sub> was 38.51, 33.44and 37.74 nm respectively but at 6ml there was no copper dioxide observed. Similarly, the dislocation density of cubic Cu<sub>2</sub>O deposited at 0 ml, 2 ml and 4 ml SnCl<sub>2</sub> was  $6.7 \times 10^{-3}$ ,  $8.94 \times 10^{-3}$  and  $7.1 \times 10^{-3}$  nm<sup>-2</sup> respectively.. The crystallite size of the CuO phase deposited at 2 ml, 4 ml and 6 ml SnCl<sub>2</sub> are 11.75, 77.6 and 15.99 nm respectively. Similarly, the dislocation density of monoclinic CuO phase deposited at 2 ml, 4 ml and 6 ml SnCl<sub>2</sub> are  $7.2 \times 10^{-3}$ ,  $1.6 \times 10^{-3}$  and  $3.91 \times 10^{-3}$  nm<sup>-2</sup> respectively. At final peak of 2θ= 36.5° and 38.6° oriented by (200) and (002) plane orientations that was CuO copper oxide (Tenerife) and SnO<sub>2</sub> tin oxide (Cassiterite) structure respectively observed. The micros strains have no uniform value in bath case. The intensity was decrease as the dopinglevelincreaseinbothCu<sub>2</sub>OandCuO. The UV-VIS investigation revealed the three energy band gap result when2ml,4mland 6ml of tin chloride added to the solution the energy band gap indicates observed between wave length of 400-800 nm shows at 21.7ev,at 4ml 1.9ev .and at 6ml 2.05ev which the result of the energy gap of copper mono oxide.

## **5.2. Recommendation**

**Further studies on this thesis to makes the materials closer to commercial application.**

**The following further investigations are recommended:**

**To investigate the morphological and composition of (Sn: cu<sub>2</sub>o) thin films using SEM (scanning electron miscopy) were recommended**

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