THE EFFECT OF DEPOSITION TIME ON COPPER OXIDE THIN FILMS DEPOSITED BY CBD METHOD

MSc in solid state physics

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JUNE 2024

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A THESIS IS SUBMITTED TO THE DEPARTEMENT OF PHYSICS,

COLLEGE OF NATURAL AND COMPUTATIONAL SCIENCE,SCHOOL OF GRADUATE STUDIES

HAWASSA UNVERSITY

HAWASSA, ETHIOPIA

IN PARTIAL FULFILLMENT OF THE

REQUAIREMENTS FOR THE

DEGREE OF

MASTER OF SCIENCE IN PHYSICS

(SPECIALIZATION: SOLID STATE)

JUNE 2024

DECLARATION

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

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ADVISOR'S APPROVAL SHEET I

SCHOOL OF GRADUATE STUDIES
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The undersigned hereby certify that have read and recommend to the College of Science school of Graduate Studies for acceptance MSc. This thesis entitled **"THE EFFECT OF DEPOSITION TIME ON COPPER OXIDE THIN FILMS DEPOSITED BY CBD METHOD"** by author ASHEBIR WONDAFRASH KIDANE in partial fulfillment of the requirements for the Degree of Masters in **Solid state physics**.

Approved by:	**Signature**	**Date**
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EXAMINERS APPROVAL SHEET TWO

We. The undersigned members of that the broad of examiners of the final open defense by Ashebir wondafrash have read and evaluated his thesis entitled "effect of deposition time on copper oxide synthesis by CBD method" and examined the candidate. This is, therefore, certifying that the thesis has accepted in partial fulfillment of the requirement for the degree,

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

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ACKNOWLEDGMENTS

First and foremost, I would like to thank the almighty God, merciful and passionate who endowed me to succeed in this work during each and every phase of my life and granting me the capability to proceed successfully. Next I would like to express my heartfelt thanks and special and deepest gratitude to my advisor, Dr.Tizazu Abza for his excellent, useful suggestions, inspiration guidance, critical comments, insights, encouragement, willingness and advising until the completion of this thesis work. I am so lucky to meet so nice advisor without his unreserved support and continuous supervision i would not have had reached this stage. I am thankful to Hawassa University department of physics for the provision of all possible facilities and equipment's (apparatus) during this thin film deposition in laboratory. My deepest thanks to my wife Netanet Busho, for her unconditional love and encouragement during the whole dedication toward the present study. And also I would like to express special gratitude to my son Sofoniyas Ashebir and my daughter Absalat Ashebir for their patient and strength enduring the pain of living apart with a lot of challenges. I also thank my family totally for their encouragement during this work. I fully acknowledge my indebtedness to all members of my classmate's well as my group members for their supporting through the whole studies period of hard times in Hawassa University

Finally thanks to Gimbo sec school directors and vice directors and all my department members who encourage me during this work.

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ACRONYMS AND SYMBOLS

A	Absorbance
Å	Angstrom
ATM	Automated Teller Machine
C	concentration
c	molar concentration of the sample
CB	Conduction Band
CBD	Chemical Bath Deposition
DW	Deionized water
Eg	Optical band gap
FWHM	full wave half maxima
h	Planck constant
IR	Infrared
L	liter
l	path length of light through the cell
LED	light emitting diode
M	Molar concentration
Min	Minute
ml	milliliter
mm	millimeter
Mw	molar weight
Pp.	Percentage purity
SEM	Scanning electron microscope
SILAR	successive ionic layer adsorption and reaction
UV	Ultraviolet
UV-VIS	ultra violet- visible spectroscopy
ν	Photon frequency
V	volume
VB	Valence band
VIS	Visible Spectrum
XRD	X-ray Diffraction

Symbols

ε	strain.
δ	dislocation density
θ	theta

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ABSTRACT

This paper reports the preparation of Copper Oxide thin films by Chemical Bath Deposition method .The copper oxide thin films were synthesis on glass slide substrates by chemical bath deposition by varying the deposition time using 0.4M of copper acetate, ammonia solution, and hydrazine hydrate. The thin film were deposited by varying deposition time at 15', 25', and 35' at 50^{o}C having the total volume of 70ml. The deposited thin film were red in color, thick, well adhere and uniform. The samples are annealed at 300^{o}c for 1.5hrs. The thin films were characterized by XRD and UV-VIS spectroscopy to investigate the structural and optical phase properties. The structural property was scanned by SHIMADZU XRD-7000 X-ray difractometer 2θ ranging from 10-80^{o}. The XRD result shows all films prepared with deposition time 15' and 25' are highly crystalline in cubic Cu_2O structure while at the deposition time of 35'additional dominant cubic Cu structure is observed. And the preferred orientation of the film at 15' and 25' has 36.38^{o} along the (111) and at 35' along the (111) plane of metallic copper. The optical characteristics were identified in the wave length ranging from 400-800nm and the band gap decreased with increasing the deposition time from 2.45-1.75eV. The film deposited at 25' has a band gap of the 1.85 eV. Which similar to the band gap of Cu2O reported by [69]. Although XRD result shows a dominant metallic copper phase at deposition time 35', UV-Vis result shows the presence of band gap which is in contradiction of XRD result. Therefore further investigation is required.

The result shows the decrement of band gap with increasing deposition time. However the band gap and crystalline size doesn't show correlation. This could be due to varies factor like deposition method, dopant, defects, diffusion and super saturation. That is as the film thickens diffusion of reactant become slower and the solution become supersaturated with copper ion hindering further nucleation; these factors eventually limit crystal growth. And also Ostwald ripening occurs when larger crystal grows at the expense of smaller ones. Then smaller grain dissolves and their material migrate to larger grains. This process reduces the overall crystal size. Generally initially, increasing reaction time leads to larger crystal; beyond a critical point, Ostwald ripening also dominates, causing a decrease in crystal size. The balance between the

CHAPTER ONE

1. GENERAL INTRODUCTION

Materials are usually classified into three groups according to their electrical conductivity such as conductors, semiconductors and insulators. Semiconductors are materials whose conductivities lie between those of metals and insulators. Metals react with oxygen gives us metallic oxides **.**metallic oxides can adopt a large variety of structural geometries with an electronic structure that may exhibit metallic, semiconductor, or insulator characteristics, endowing them with diverse chemical and physical properties. Therefore, metal oxides are the most important functional materials used for chemical and biological sensing and transduction. Metal oxides are attractive materials for thin film electronic and optoelectronic applications due to their compatibility with synthesis on large area inexpensive glass and flexible plastic substrate. Metal oxides, especially transition metal oxides, comprise a very diverse and fascinating class of compounds with properties covering almost all aspects of material science and physics [1]. Among the transition metal oxides type, copper oxide is abundant on earth and is non- toxic, exhibiting relatively high minority carrier diffusion length, high absorption coefficients in the visible area and large exaction binding energy with low-cost manufacturing processes. It is a p-type, narrow band gap semiconductor. Copper Oxide has two common forms; cupric oxide (CuO) with band gap in the range 1.2-1.9 eV and cuprous oxide (Cu_2O), with band gap of 1.8-2.5 eV [2]. In CuO the lattice structure has monoclinic symmetry, whereas Cu_2O has cubic structure [3].The CuO and Cu_2O thin films are widely used in several device applications such as thin film transistors, photovoltaic, smart windows, IR detector, optical limiters etc [4-8]. The cupric oxide (CuO) is a black solid with a metallic luster while cuprous oxide (Cu_2O), is a red solid with a metallic luster. Copper oxide is harmless to human beings and it is insoluble in water this is because it is a basic due to strong electrostatic interaction between the oxygen atoms with the metal copper.

A thin film is a layer of material ranging from fraction of a nanometer (monolayer) to several micrometers in thickness. The controlled synthesis of material as thin films (a process referred to as deposition) is a fundamental steps in many applications. Semiconductor thin films are produced in one thinner layer. Copper oxide thin film is an inorganic compound that exists as a pitch black solid at room temperature. It is a naturally occurring mineral that is composed of the non-metal (oxygen) and transition metals (copper) .It is found naturally in a mineral ore by the name tenorite. Its formula can be derived by determining the ions that make this compound which are the oxygen ions O^{-2} and the copper ions Cu^{+x} where x is used in the place of copper ion's formula charge because copper has multiple oxidation states. The two possible formed oxidation numbers are +1 and +2, meaning there are two possible copper ions Cu^{+1} and $Cu^{+2.}$The copper (I) ion, cuprous Cu^{+1} is formed when elemental copper Cu gives up one of its valence electrons and the copper (II) ion, cupric ion, Cu^{+2} is formed when elemental copper Cu gives up its two valances electrons .both are p-type semiconductors and CuO is more thermally stable materials

1.1Semiconductor

Semiconductors are materials whose conductivity lies between conductors and insulators [9]. The electrical conductivity of a semiconductor is consequently typically much less than that of a metal [10]. Different semiconductor materials have differ in their properties [11]. The most popular conductors are silken (Si) and Germanium (Ge) as a pure elements and compounds such as GaAs, InAs, InP, GaN, Etc. In the process of doping small amount of impurities are added to pure semiconductor causing large changes in the conductivity of the material. These elements have a partially filled Conduction band and partially filled valence band. The valence band of a semiconductor is full similarly to that of an insulator, but the band gap is much smaller (about 1 eV).In fact, the band gap in several semiconductors is so small that electrons are easily able to be thermally excited in to the conduction band [12]. This means that the electrical conductivity of many semiconductors is strongly reliant on temperature. .

To have practical uses for semiconductor, the conductivity must be greatly increased and raising the temperature is not a very reliable way to achieve this goal. However, it is accomplished by doping (adding a very small amount of other atoms in with the semiconductor), which increases conductivity by adding either n-type (electron) or p-type (holes), to a semiconductor [13]. Semiconductors are the basic building block of modern electronics, including transistors, solar cells, light-emitting diodes (LEDs) [14], and digital and analog integrated circuits

.

1.2. Classification of Semiconductor

. Semiconductors materials can be classified into two types: elemental and compound semiconductors:- Elemental semiconductors are composed of single species of elements found in the group IV of the periodic table, such as silicon (Si) and Germanium (Ge). A compound semiconductor is a semiconductor made from two or more elements. Most compound semiconductors are from combinations of elements from Group III and Group V of the periodic table of the elements (GaAs, GaP, InP and others). Other compound semiconductors are made from Group II and VI (CdTe, ZnSe and others). It is also possible to use different elements from the same group to make compound semiconductors such as SiC. And also Semiconductors can be classified in to two types. These are intrinsic semiconductors and extrinsic semiconductors .Intrinsic semiconductors are pure semiconductors example Si and Ge. They will not have any impurities added to it. Extrinsic semiconductors [15] are semiconductors with impurities like Al, In, P, As, Bi, B, etc. The impurities modify the electrical properties of the semiconductor and make it more suitable for electric device such as diodes and transistors. The conductivity of semiconductors can be greatly improved by adding impurities called doping .Depending on the type of impurity added ,the extrinsic semiconductors is further divided in to two types;-these are N-type semiconductors and P-type semiconductors. In an N-type semiconductor electrons are the majority carriers. When a trivalent impurity is added to the materials it become a p-type semiconductors.in p-type semiconductors holes [16] are the majority carriers and electrons are the minority carrier.

1.3 The Important Properties of Semiconductors

Semiconductors are substances with properties somewhere between conductors and insulators [17]. 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.

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 [18]. 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[19] 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 Semiconductor Thin Films.

A thin film is a layer of material ranging from fraction of a nanometer (monolayer) to several micrometers in thickness. The controlled synthesis of material as thin films (a process referred to as deposition) is a fundamental steps in many applications. Semiconductor thin films are produced in one thinner layer. Common application of such structure includes many electronic materials such as transistor, sensors and photovoltaic devices. Thin film materials have been used in semiconductor devices, wireless communications integrated circuits rectifiers transistors, solar cells, light emitting

diodes, photoconductors and light crystal display's etc. Generally thin films are used to improve the surface properties of solids; transmission, reflection absorption hardness, abrasion resistance; corrosion permeation and electrical behaviors are some of the properties of a bulk material surface that can be improved by using a thin film.

1.6 Copper Oxide

Copper oxide is a p-type transitional basic inorganic semiconductor material [20] with a direct energy gap of about 2 eV and closes enough to the optimum energy gap in the radioactive spectrum [21]. Copper oxides are usually present in two stable forms, copper oxide (Cu_2O) and copper oxide (CuO) [22]. Copper oxide thin films have wide range of applications including energy harvesting and storage as solar cells [23], photo electro-chemical cells [24], photo-catalysts [25], and lithium ion batteries [26]. These also find applications in the domain of catalysts [27], field-emission devices [28], gas sensors [29], photovoltaic devices [30], and super conductors [31].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 [32]. Further, the chemical as well as physical properties of CuO depend significantly on thickness and morphology of the film [33], and therefore, the precise control and thickness optimization along with its morphology is immensely crucial for utilizing such films in Nano-electronics, opto electronics and bio-sensing applications [34]. And it can also be used as a solar absorbent due to its high absorption coefficient and low thermal emission [35]

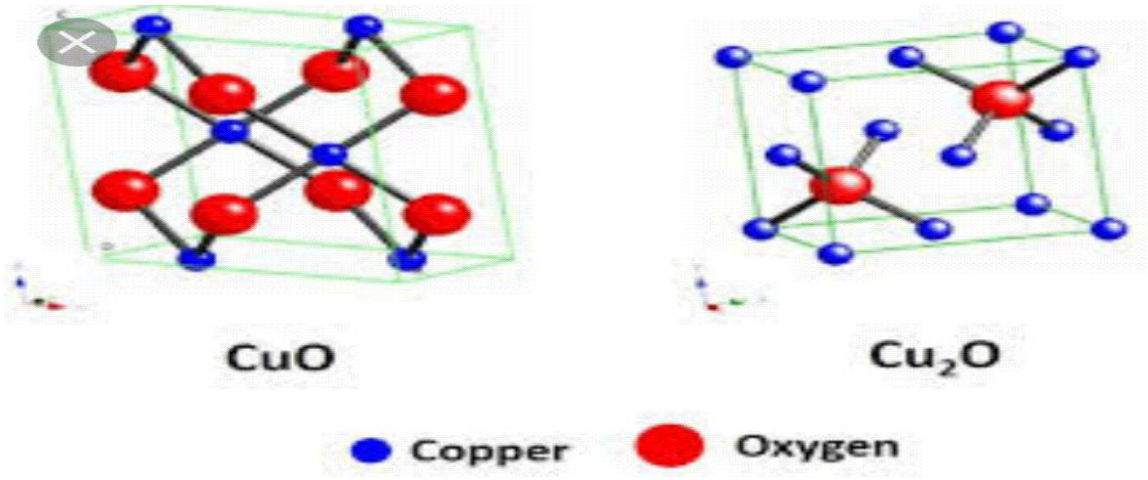


Figure 1. 1. Chemical structure of Copper oxide

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.

1.7 Statement of the Problem

In the preparation of copper oxide thin films using the Chemical Bath Deposition (CBD) method involves the use of specific ingredients, including copper acetate, ammonia, and hydrazine. However, there are some potential drawbacks associated with this approach:

1. **Precursor Concentrations**: The specified concentrations (0.4 M copper acetate, 5 ml ammonia, and 3 ml hydrazine) may impact film quality. If these concentrations are not optimized, it could lead to non-uniform or undesirable film properties.

2. **Film Composition**: The choice of precursors affects the stoichiometry of the resulting copper oxide film. If the proportions are not carefully controlled, the film may deviate from the desired composition (e.g., CuO or Cu_2O).

3. **Deposition Temperature**: The CBD method operates at low temperatures (30-80°C). While this simplicity is advantageous, it can also limit the crystallinity and overall quality of the film. Higher temperatures might yield better results.

4. **Substrate Material**: The substrate plays a crucial role in film growth. If the substrate is incompatible with the deposition conditions, it could affect adhesion, crystallinity, and other properties.

5. **Uniformity and Pinholes:** CBD typically produces pinhole-free films, but variations in solution mixing or deposition conditions could lead to non-uniform coverage or defects.

6. **Oxygen Content**: The oxygen content in the film can impact its properties. Bubbling oxygen during deposition may enhance oxygen incorporation, but excessive oxygen could alter the film's behavior1.

In summary, while CBD is a cost-effective and accessible method, careful optimization of parameters is essential to achieve high-quality copper oxide thin films. Researchers should consider adjusting precursor concentrations, deposition temperature, and substrate choice to address these potential as a drawbacks. There are several techniques used to synthesize copper oxide (CuO) thin films including thermal oxidation, atomic layer precipitation, chemical bath deposition[39], sol-gel method [40], laser

pulse deposition, permeable coating method, activated microwave atomization, magnetic spray [41], chemical vapor deposition[42], vacuum evaporation, electronic beam evaporation [43], oxidation of copper sheets [44], electro deposition [45], ultrasonic spray pyrolysis [46]and reactive sputtering[47]. 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 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 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. As far as the researcher is aware that there is no report on such combination of precursors. We have able to synthesis copper oxide thin films in a short period of time (15-35') at 50c using the aforementioned combination. The thin films were characterized by XRDU and UV-VIS,

.

1.8 The Objective

1.8.1 General Objectives

The general objective of this research is to study the effect of deposition time on properties of copper oxide thin films synthesized by chemical bath deposition (CBD)

1.8.2 The Specific Objectives of the Research

The specific objectives of this research are:-

- To synthesize copper oxide thin films by CBD method by varying deposition time
- To investigate the structural and optical properties of copper oxide thin films for specific application.

1.9 The Significance of the Study.

In this research the researcher would found the gap of the synthesis of copper oxide thin films by varying the deposition time by CBD method which can be used in various applications such as catalysis,

solar energy conversion, gas sensing, etc. [50]. Finally the study may serves as a supporting document for further study in the area.

1.9.1 Thesis Structure

This thesis was arranged into five chapters. The first chapter deals about general introduction, semiconductors, statement of the problem, objective and significance of the study. The second chapter deals about review of literature, deposition technique and application of thin films. The third chapter deals about methodology, 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 TW0
2. REVIEW OF LITRATURE

2.1 Thin Films

Any solid material that possesses at least a two- dimensional order of periodicity is known as a “thin film”. Thin films are significantly different from the bulk in terms of surface behavior and interfacial effects which determine the overall behavior of thin films. A thin film is a layer of a material ranging from fraction of a nanometer (monolayer) to several micrometers in thickness. A thin film is different from thick films. A thin film is defined as a low-dimensional material created by condensing, one-by-one, atomic/molecular/ionic species of matter. The thickness is typically less than several microns and they are differing from thick films. A thick film is defined as a low-dimensional material created by thinning a three dimensional material or assembling large clusters/aggregates/grains of atomic/molecular/ionic species[51].The processing of materials into thin films allows easy integration into various types of devices [52]. The controlled synthesis of material as thin films (a process referred to as deposition) is fundamental steps in many applications. Thin film can be defined as a thin layer of material, where the thickness is varied from several nanometers to few micrometers. Like all materials, the structure of thin films is divided into amorphous and polycrystalline structure depending on the preparation conditions as well as the material nature. Thin films comprise two parts the layer and the substrate where the films are deposited on it. Also, thin films can be composed of different layers such as thin-film solar cells, electro chromic cells, and so on.

Thin film technology:-The Thin film technologies are revolutionized the field of electronics and optics. This technology is used for the manufacturing of electronic component servicing high-speed digital, communications, computing, and automotive markets. It simulates, designs, and manufactures signal integrity solutions worldwide. Thin film technology utilizes thin film processes to build passive components used in data-communication, computer, medical, test equipment, power supplies. It is widely used in variety of products including delay lines both differential and single equalizers force able and backplane equalization, filters for signal conditioning, termination networks, precision resistors, inductors, and capacitors. In order to obtain thin films with good quality, there are two common deposition techniques: physical and chemical depositions. It can be summarized as shown in

Top-down Approach	Bottom up Approach
1.Evaporation techniques	1.Sol-gel technique
1. Vacuum thermal evaporation.	2.Chemical bath deposition
2. Electron beam evaporation	3.Spray pyrolysis technique
3. Laser beam evaporation	4.Plating
4. Arc evaporation	1. Electroplating technique.
5. Ion plating evaporation	2. Electro less deposition.
	5.Chemical vapor deposition (CVD)
2.Sputtering techniques	1.Low pressure CVD(LPCVD)
1.Direct current sputtering(DC sputtering)	2.Plasma enhanced CVD(PECVD)
2.Radiyo frequency sputtering(RF sputtering)	3.Atomic layer deposition(ALD)

Fig 2.1 classification of thin film deposition techniques

2.1.1 Thin Film Deposition Techniques

The act of applying a thin layer to a surface is known as thin-film deposition. It is a technique for depositing a thin film of material onto a substrate or onto previously deposited layers. "Thin" is a relative term, but most deposition techniques allow layer thickness to be controlled within a few tens of nanometers, and some allow single layers of atoms to be deposited at a time. Thin films can be prepared by various methods, which have been reviewed in the literature. Deposition techniques can be divided into two broad categories, depending on whether the process is primarily Top-down Approach and Bottom up Approach as described in table 1

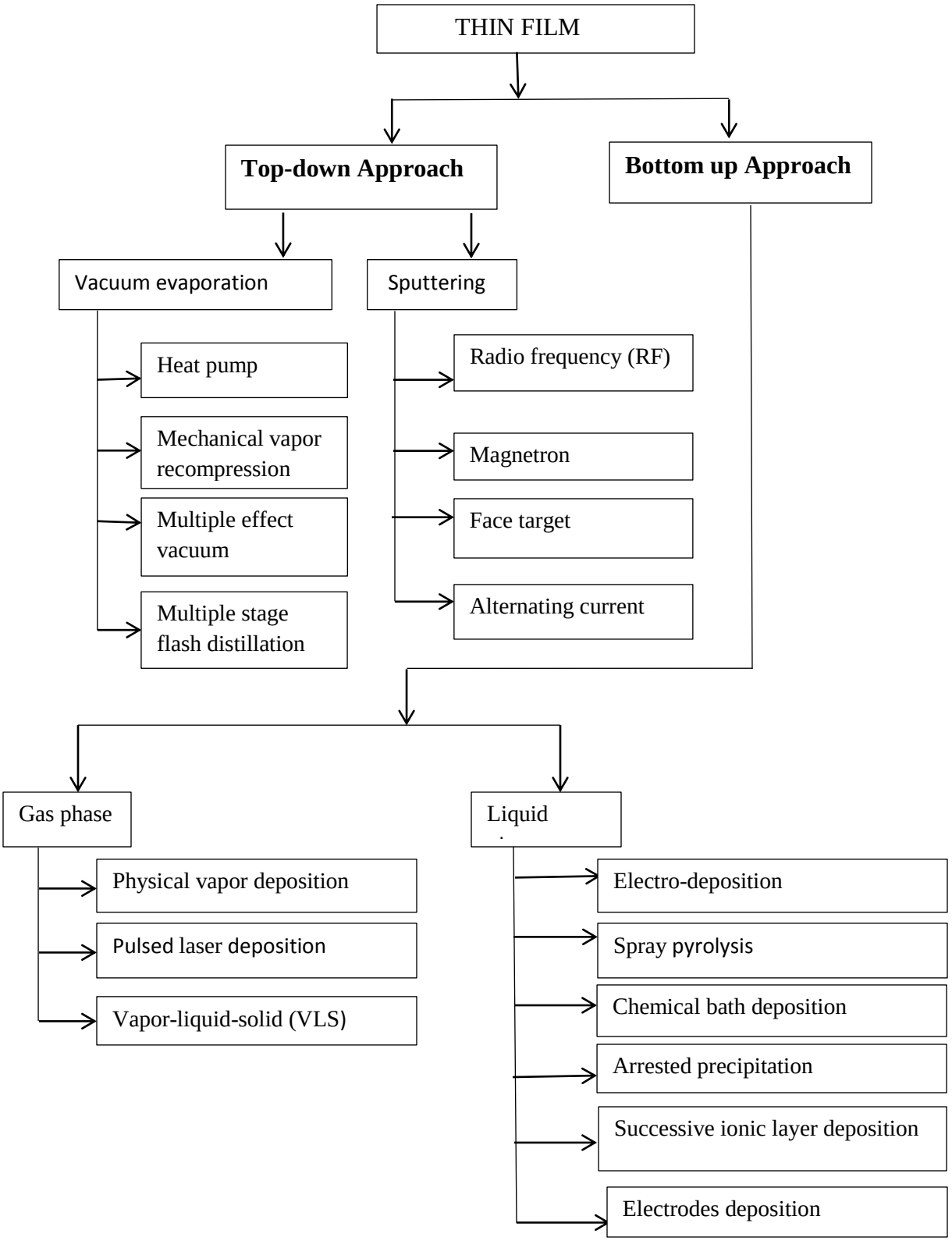


Figure 2. 1. Representations of thin film deposition techniques

2.1.1.1 Top-Down Approach

In physical deposition techniques such as physical vapor deposition, electron beam's evaporation and thermal evaporation techniques, the deposition processed through physically can't take place chemical reaction.

2.1.1.2 Bottom-Up Approach

In chemical deposition techniques contains just like that of chemical vapor deposition, successive ionic layer adsorption and reaction (SILAR) and chemical bath deposition. In chemical deposition techniques which have been used ultrathin film growth. In addition, in chemical deposition method chemical reaction takes place but in physical deposition method doesn't take place chemical reaction. In case of chemical deposition techniques is to produce high quality films.

2.1.2 The Application of Thin Films.

Thin films are everywhere in the modern world, with many of the technologies we depend upon in daily life being, in turn, dependent upon thin film technology. These may range in dimension from an atomic or molecular monolayer perhaps only a few angstroms thick to either mono- or multilayer coatings with a thick-ness of several microns. Such materials may have a huge range of extremely useful properties; they may be, for example, anti-reflective, impervious to oxygen and/or other gases, optically transparently electrically conductive, catalytic, and self-cleaning. Everyday examples featuring thin film technology include, but are not limited to, mobile phones, touch screens, laptops, and tablets [53, 54].Other important applications of thin films include band pass filters as used in gas analysis [55],mirrors used in astronomy[36–38],protective (e.g. Biomedical, anticorrosive, and antimicrobial) coatings [56], architectural glass coatings (e.g., to reflect heat while transmitting visible light) [57], photovoltaic electricity generation [56,58], and a great many others. In the present time, thin films can be fabricated in various ways. Thin film is a very thin layer of a substance or supporting materials specially a coating (as of a one atom/ one molecules. Thin films are generally used to improve the surface properties of solids such as transmission reflection, absorption, hardness, abrasion resistance, corrosion, permeation and electrical behavior surface that can be improved. Materials such as jewelry, wrist watches and knives are often coated to avoid corrosion. Magnetic thin films are useful in making sensors and solar cells. Thin films technology is usefully employed in Smart windows and information storage. In optics, laser mirrors and transmission enhancing coatings are manufactured. In electronics, integrated circuits are made of layers of insulators, semiconductors and conductors. A thin film can be

binary, ternary and quaternary depending on the number of elements that make up the film. Binary thin films are thin films that contain two different elements [59].

2.2. Review of Literature on Chemical Bath Deposited Copper Oxide Thin Films

M.T.S. Nair *et al (march 1999)* deposited copper oxide thin films with thickness ranging from 0.05–0.45 mm on microscope glass slides by successively dipping them for 20 s each in a solution of 1 M NaOH and then in a solution of copper complex. Temperature of the NaOH solution was varied from 50–90^{o}C, while that of the copper solution was maintained at room temperature.
X-ray diffraction patterns showed that the films, as prepared, are of cuprite structure with composition Cu_2 O. Annealing the films in air at 350^{o}C converts these films to Copper oxide.

Nasser[a*] et al [61] (2015) have been deposited copper oxide on glass substrate by CBD alternate immersion method at room temperature for 20 second intervals. They have studied the effect of annealing on the properties of the films. The significant improvement in structure by annealing at different temperature was discussed. The SEM image so obtained showed that porous structure was distinctive materials for the manufacture of gas sensors.

Sultana *et al* [60] (December 2016) Fabricated CuO thin films by the chemical solution, the chemical bath contains an aqueous solution of Copper (II) Chloride Dehydrate as a metal salt and ammonia solution as a complexing agent while the water itself provides oxygen, i.e. a source of chalcogenide, initially in the form of hydroxide ions (OH-).. The special emphasis is given on the varying thickness of grown copper oxide with different reaction time and its subsequent impact on chemical composition on copper oxide, surface morphology, phase formation and grain size of the nanostructures. The electrical and optical properties of the CBD grown thin film varies significantly with thickness. The result conforms that the films with 110nm thickness are promising to use for antireflection coating and solar energy harvesting.

R.S.Pokharkar1 *et al. (May 2019)* Prepared Copper oxide by a modified dip and dry method. 0.2gm copper acetate and 5 drops of NaOH were dissolved into 80ml methanol respectively. The beaker containing above solution kept in aultra-sonicator for 5min.The solution were mixed rapidly.

Dipped the substrate in the resultant solution for 10 second and dried on the hot plate for few second, repeat this procedure for 18 times. Light brown color substrate observed.

.The CuO growth was carried out by suspending the above obtained substrate in the 250ml beaker filled with an aqueous solution of copper acetate 0.02M,0.7ml TEA and NaOH at 80^0C for 2 hours. The pH was adjusted by NaOH, and TEA issued as complexing agent. Subsequently, the substrate was removed from solution, rinsed with distilled water and dried in air at $80\ ^0C$.

T. A. Aswada,*, *et al (*July 12, 2021*)* synthesized Copper oxide thin films by chemical bath deposition (CBD) method on glass slides with dimensions of (25.4*76.2*1) mm3, where aqueous copper sulfate (CuSo4.5H2O) used to obtain copper ions in the solution. The solutions prepared at room temperature with different deposition times (1, 4, 8) days, with fixing the concentration of the solution at 0.1 M. The process done by dissolving the required weight of the substance(1.2484)g in 50 ml of distilled water gradually dissolving using a magnetic mixer at room temperature for 30 minutes to ensure complete dissolution of the solution.

CHAPTER THREE

3. METHIDOLOGY

3.1 Synthesis and Characterization of Thin Films.

3.1.1 Thin Film Synthesis Process

Thin film materials exhibit unique material properties resulting from the atomistic growth process which is clearly dependent on the deposition process and chosen parameters.

3.2 Chemical Bath Deposition Technique

The chemical bath deposition (CBD) is well-suited for producing large area thin films as required in solar energy related applications, as well as storage devices. This technique involves deposition of semiconductor thin films on substrates that are kept in dilute solutions. Chemical Bath Deposition typically forms films using heterogeneous nucleation (deposition or adsorption of aqueous ions onto a solid substrate), to form homogeneous thin films of metal chalcogenides (mostly oxides, sulfides, and selenite) and many less common ionic compounds. Chemical Bath Deposition, also called Chemical Solution Deposition [59], is a method of thin-film deposition (solids forming from a solution or gas), using an aqueous precursor solution. Chemical Bath Deposition produces films reliably, using a simple process with little infrastructure, at low temperature (<100˚C), and at low cost.*[59]* Furthermore, Chemical Bath Deposition can be employed for large-area batch processing or continuous deposition.

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[42][46]

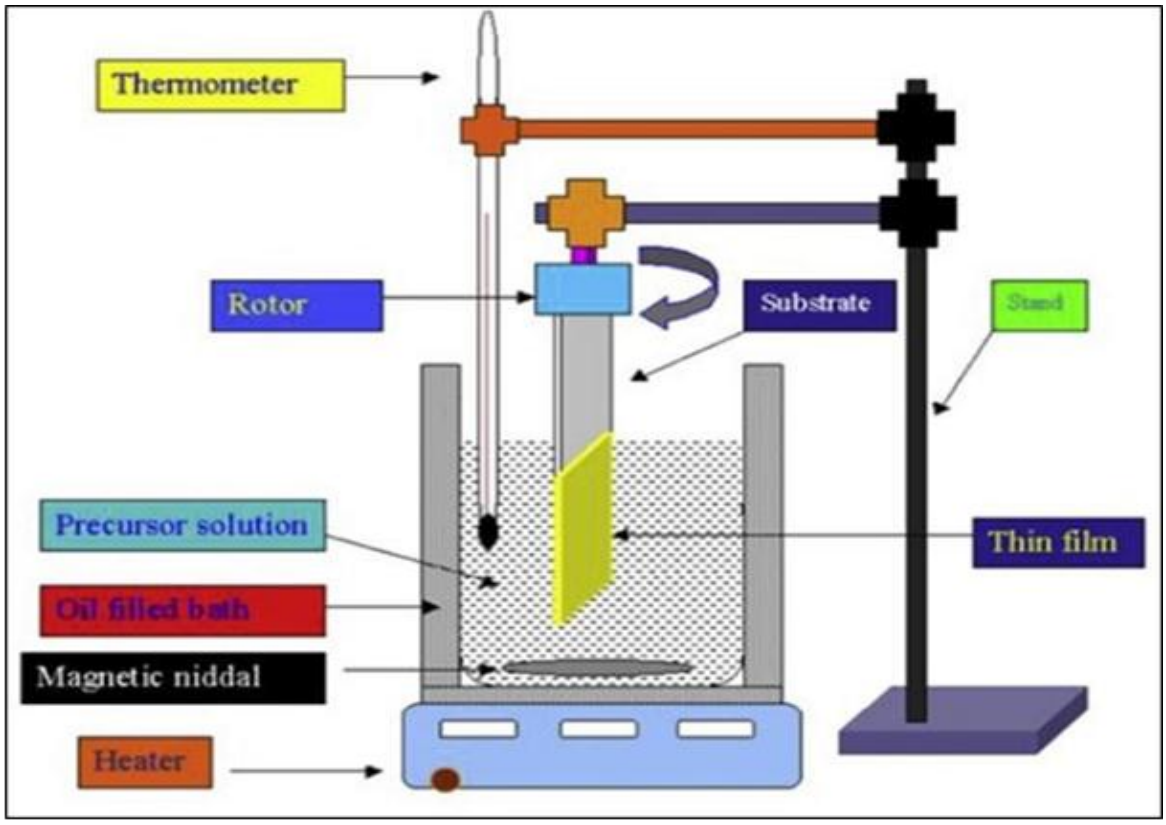


Figure 3. 1. Experimental set up of CBD method

3.2.1 Thin Film Deposition Mechanism in Chemical Bath Deposition

There are four main mechanisms leading to compound formation, whose operation depends on the specific process and reaction parameters. The thin film growth in CBD occurs via the following four possible mechanisms.

A. Simple Ion-by-Ion Mechanism

B. Simple Cluster (Hydroxide) Mechanism

C. Complex-Decomposition Ion-by-Ion Mechanism

D. Complex-Decomposition Cluster Mechanism

3.2.1.1 Simple Ion-By-Ion Mechanism

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

$M^{n+} + X^{m-}$ == MmXn (Adsorbed on the substrate)

3.2.1.2 Simple Cluster (Hydroxide) Mechanism

In most of the CBD's, the preparative conditions are chosen so that the formation of metal hydroxide should be avoided. However, in reality, CBD's 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 (M^mX^n) is formed by reaction of X^{m-} ion with the $M(OH)^n$.

$$M^{n+} + OH \longrightarrow M(OH)_n \text{ followed by } M(OH)_n + X^{m-} \longrightarrow M^mX^n + OH^-$$

3.3 Factors Affecting the Size and Distribution of Thin Films.

The pH of solution, the reactant concentration, concentration of cation and anion, deposition of time, temperature, and composition of the film affect crystal size, and can be used to control the rate of formation and the structure of the film. Other factors affecting crystal size include agitation, illumination, and the thickness of the film upon which the crystal is deposited [59] Agitating the solution prevents the deposition of suspended colloidal crystals [62] creating a smoother and more homogenous film with a higher band gap energy. Agitation also affects the formation speed and the temperature at which formation occurs, and can alter the structure of the crystals deposited [62].

Unlike most other deposition processes, Chemical Bath Deposition tends to create a film of uniform thickness, composition, and geometry (lateral homogeneity) even on irregular (patterned or shaped) substrates because it, unlike other methods of deposition, is governed by surface chemistry. Ions adhere to all exposed surfaces of the substrate and crystals grow from those ions [63] [64].

3.3.1 Deposition Time

In CBD method the deposition of time significantly influences the properties of the resulting copper oxide thin films. Longer deposition time generally leads to thicker thin film due to increased nucleation and growth. As the reaction time increases the crystal size of copper oxide also tends to increases. However there are limiting factors like diffusion and super saturation. That is as the film thickens diffusion of reactant become slower and the solution become supersaturated with copper ion hindering further nucleation these factor eventually limit crystal growth. And also Ostwald ripening occurs when larger crystal grows at the expense of smaller ones. Then smaller grain dissolves and their material migrate to larger grains. This process reduces the overall crystal size. Generally initially, increasing reaction time leads to larger crystal; beyond a critical point, Ostwald ripening dominates, causing a decrease in crystal size. The balance between the nucleation and growth determines the final crystal size.

3.3.2 Nature of Substrates

It plays an important role in the reaction kinetics and adhesion of the deposited films. Hence, cleaning of the substrate surface is the first step in the thin film deposition. Higher deposition rates and thicknesses are observed for those substrates whose lattice parameters were well matched with those of the deposited material.

3.3.3 Effect of PH

When the PH of the reaction bath increases, the metal complex usually becomes more stable reducing the availability of free metal ions. This will decrease the reaction rate resulting in higher thickness of the film. The PH of a solution is a quantitative measure of the acidity or basicity of aqueous or other liquid solutions in which its value of the concentration of hydrogen ion ranges between 0 to 14.The effect of pH on the particle size depends mainly on the reaction mechanism involved. This is especially true when H+ or OH ions are directly involved in the reaction. Reduction and precipitation are also strongly affected by change in the media PH. In a redox reaction, the compound with the highest reduction potential is reduced by oxidizing the compound with the lower reduction potential [67]

3.3.4 Effects of Temperature

From the listed factor that affects the preparation of cobalt oxide thin films by CBD method bath temperature is the most common reaction parameter used to control the reaction kinetics for thin films formation. An important factor that influences the rate of reaction is the 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 [66]

3.3.5 Nature and Concentration of Complex Agent

Nature of the complexing agent has great influence on the final products. Generally the reactant concentration is another important parameter for the control of size thickness. In a reaction, metal ion concentration decreases with the increase of completing ion concentration. As a consequence, the rate of reaction and hence the precipitation is reduced leading to a large terminal thickness of the film [65].

3.4 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.[59].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 [59]

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 [59]. 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 [59]. 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. [59]. 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.

3.5. The Thin Film Characterization Techniques

3.5.1 X-Ray Diffraction (XRD)

X-ray diffraction (XRD) is a powerful technique for determination of crystal structure and phase of material/ lattice parameters. The method is based on the interference of scattered X-rays from a crystal lattice

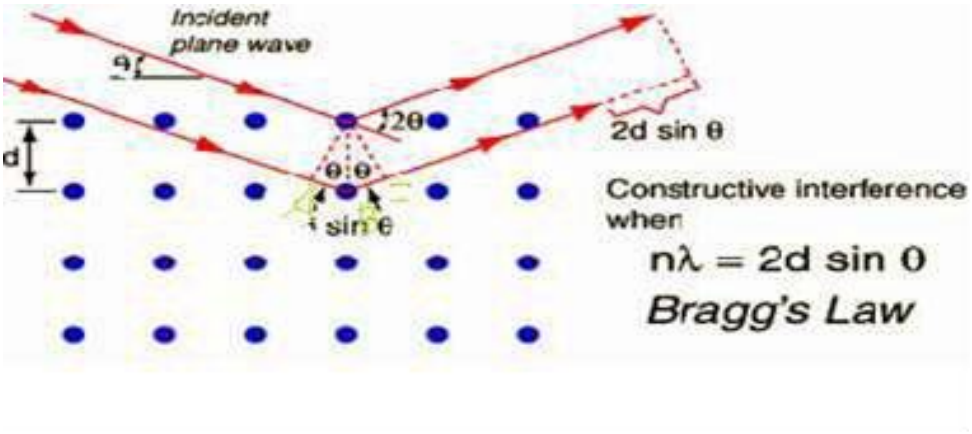


Figure 3. 2.X-ray diffraction diagrams

$n\lambda = 2d \sin\theta$; **n** = 1, 2, 3

where **d** = is interplaner spacing **θ**=is diffraction angle

λ= wavelength of x-ray **n** = is an integer which is the order of diffraction

Fig 3.2 X-ray diffraction diagrams

By measuring the angle 2θ/ the peak position under which constructively interfering x-rays leave the crystal, the Bragg's equation gives the corresponding lattice spacing, which is characteristic for a particular compound. Width of the diffraction peaks signifies the dimension of the reflecting planes. The crystalline sizes of copper oxide thin films can be calculated by using the Scherer equation.

$$t = \frac{0.9\lambda}{\beta cos\theta}$$

Where *t* is the thickness of crystalline sizes (in Å), λ(is the 1.5406 Å) x-ray wave length, θ is the Bragg/diffraction angle and β is the full width at half maxima of the diffraction peak at the diffraction angle 2θ.To synthesized copper oxide thin films by CBD method; The composition of copper oxide thin

films was verified by x-ray diffraction patterns (XRD). X-ray power diffraction is a raped analytical techniques, primary used for phase identification of crystal materials and can provide information on a unit cell dimensions. The analyzed material is finally ground, homogenized and average bulk composing is determined. XRD is a technique used in materials science to determine the crystallographic structure of a material. XRD works by irradiating a material with incident x-rays and then measuring the intensities and scattering angles of the x-rays that leaves the materials. XRD is the most common and first hand instrument used by solid-state scientists. It is a powerful method to investigate the detailed structure, composition and related properties of Nano-materials. This information can be derived from peak position, intensity and the peak profile .A great advantage of X-ray powder diffraction is that it requires virtually no sample preparation, in comparison to the techniques.

3.5.2 Ultraviolet-Visible Spectroscopy (UV-VIS)

Ultraviolet-visible spectroscopy (UV-VIS) is a spectroscopy (absorption or reflectance) in the ultraviolet-visible region. UV/VIS spectra originate from the excitation of electron, and therefore UV-VIS spectroscopy is often also referred to as "electron spectroscopy". The term electron spec-cryoscopy encompasses the excitation of electrons by ultra-violet or visible radiation. The UV-VIS absorption spectroscopy provides information of light absorption as a function of wavelength, which describes the electronic transitions occurring in the measured samples.it detects the light intensity passing through a sample and compares the detected intensity to incident light intensity (light before passes through the sample) . In general it uses a light source to illuminate a sample with light across the UV to the visible wave length range (typically 190-900nm). The instrument then measure the light absorbed transmitted or reflected by the sample at each wave length. The founder of this device is Arnold Beckman and his colleagues at national technologies laboratories in 1940. The diagrammatical representation of the UV-VIS spectrometer device is as follows

3.6. Chemical and Experimental Procedures

3.6.1 Materials

In order to prepare copper oxide thin films by varying the deposition time and to identify the effect of this deposition time on the formation of the required thin film the following materials were used.

- Test tube brush to clean test tube.
- Electronics beam balance to determine the mass of the solid in gram.
- Scapula 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.
- A PH meter is a scientific instrument that measures the hydrogen-ion activity in water-based solutions, indicating its acidity or alkalinity expressed as PH.

3.6.2. Reagent Preparation

The chemicals used for this thin film preparation by varying the deposition time with their chemical names, chemical formula, brand (manufactured by), percentage purity and their molecular weights are given in the table below.

Table 3. 1. The chemical used for the preparation of copper oxide

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	Ammonia solution	NH_4OH	LOBA CHEMIE	25%	35.05
3	Hydrazine hydrate	N_2H_5OH	LOBA CHEMIE	99%	50.06

3.6.3 Preparation of O.4M Copper Acetate ($(CH_3COO)_2Cu.H_2O$)

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 19.5657g of 0.4M of copper acetate($(CH_3COO)_2Cu.H_2O$) in 250ml of distilled water as follow

Mass=C.V.Mw.Pp

=0.4Mx0.25Lx199.65g/MLx0.98=19.5657g

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 seems like as follows.

Figure 3. 3. 0.4M of copper acetate

3.6.4 Cleaning of the Substrates

A substrate is a surface onto 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 [31].

Before the deposition process was performed the glass slides of dimension (75×25×2)mm washed by pure water and soup and then dried under ambient condition then 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.

3.6.5 Preparation of the Mother Solution or Copper Oxide Thin Film

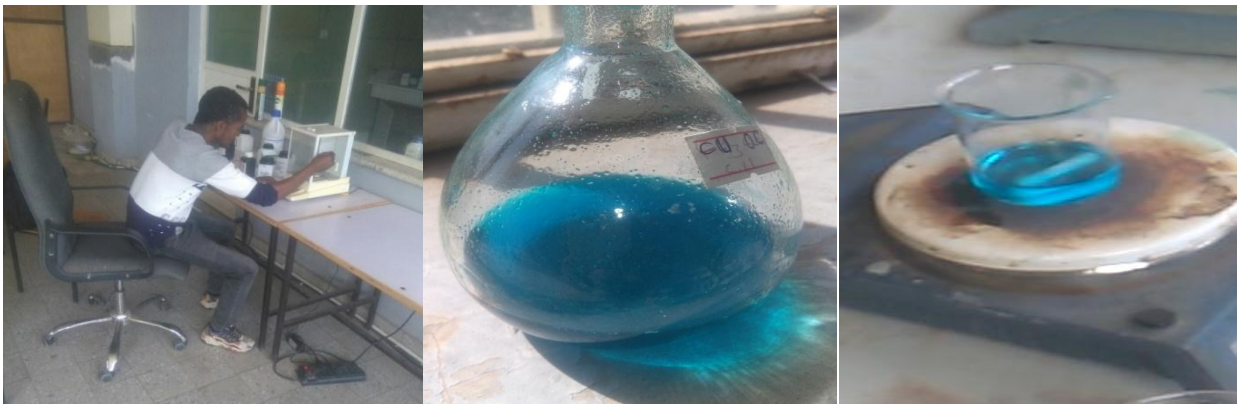
Copper oxide thin films were deposited onto the substrates by CBD using copper acetate, ammonia, hydrazine and deionized water as precursor materials. The preparation conditions were optimized by adjusting concentration of dissolved chemicals, bath temperature, and bath solution and the deposition time to obtain homogeneous films with good adherence to the substrate. The deposition were carried out by adjusting the final temperature at 50^{o}C on the heater by varying the deposition time starting from 15 minutes up to 35 minutes by interval of 10 minutes for three samples. In this thin film preparation the amount of chemical used, the bath temperature and the amount of deionized water are restricted while changing deposition of time. The mother solution prepared by 0.4M (5ml) of copper acetate, the same volume of ammonia, 3ml of hydrazine and 57ml of deionized water, totally 70ml. The initial colour of the mother solution was colourless. As the temperature of the bath increases gradually, the color was changed in to light golden. 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 as-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 increment of the deposition time. Samples were dried in ambient conditions and kept inside the desiccator until they were annealed and characterized by various techniques .The films were annealed at 300℃ for 1.5 hrs before characterization.

Table 3. 2. sample and the total volume through each duration for copper oxide thin film preparation

Sample code	Copper acetate(ml)	Ammonia (ml)	Hydrazine (ml)	Distilled water(ml)	Total volume(ml)	Time in minutes	Initially At room temperature	Temperature (^{o}C)
$As_{15'}$	5ml	5ml	3ml	57ml	70ml	15	,,	50
$As_{25'}$	5ml	5ml	3ml	57ml	70ml	25	,,	50
$As_{35'}$	5ml	5ml	3ml	57ml	70ml	35	,,	50

The fabrication process of copper oxide thin films were follow are shown in Figure 3.4.

A/ *B/* *C/*



D/ *E/* *F/*

G/ *H/* *I/*

Figure 3. 4. Pictorial representation of the preparation of copper oxide thin films

Figure 3. 5.As deposited copper oxide thin films which is adhere on glass slide through each deposition time

CHAPTER FOUR
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.

4.1 Structural Analysis

In the field of material characterization, X-ray diffraction is used to determine the degree of crystalliity 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 oxide thin films was scanned by *SHIMADZU XRD-7000 X-Ray diffractometer* 2θ ranging from 10 - 80°*c*. A typical XRD pattern for deposited copper oxide thin films at 15', 25', and 35' on a glass substrates are shown in fig 4.1 a-c. The XRD pattern of the thin films shows that all the films are highly crystalline in cubic Cu_2O structure (PDF 00-005-0667) and cubic Cu structure (JCPDS No. 003–1018). The films deposited at 15' and 25' has preferred orientation at 36.38°(along the (111) plane), however the film deposited at 35' has preferred orientation at 43.24° (along the (111) plane of the cubic Cu). Similar result is reported by Güneri, E etal (2022) and Lin, Z. D etal (2016) [68]

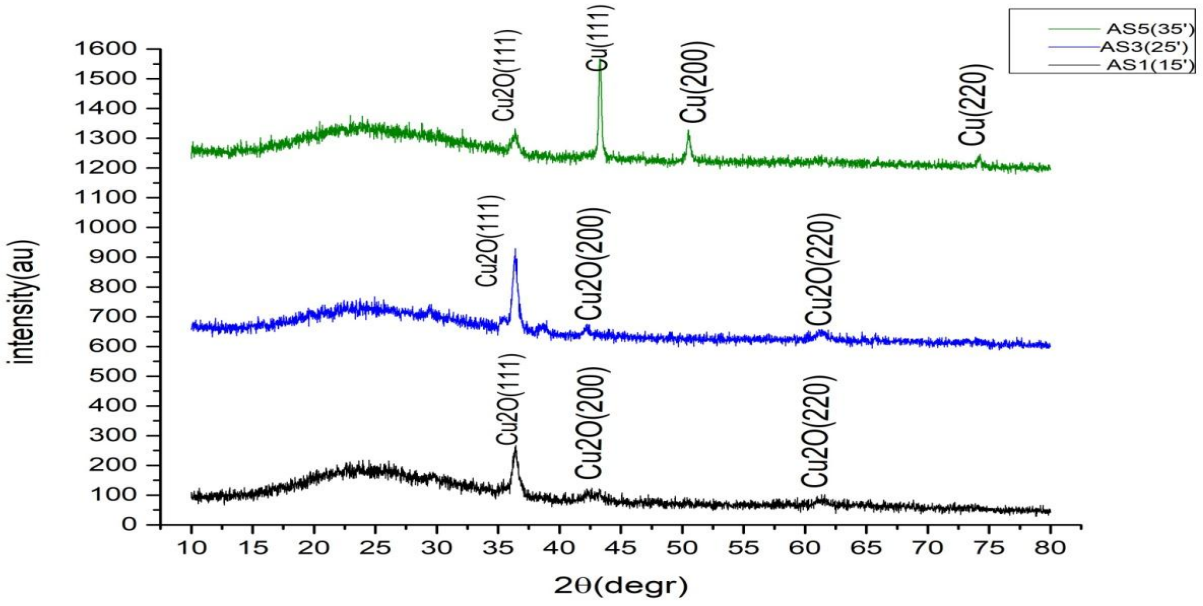


Figure 4. 1.The XRD patterns of the entire merged Copper oxide thin film sample deposited at 15, 25, and 35 minutes annealed at 300℃ for 1.5 hrs

The films deposited at 15' and 25' crystallized in cubic Cu_2O with three peaks at 2θ= 36.38º, 42.42º and 61.48 corresponding to (111), (200) and (220) planes of the Cu_2O structure (PDF 00-005-0667). A film deposited at 35' shows peaks at 36.38, 43.38, 50.56 and 74.3°. The peak at 36.38° corresponds to (111) planes of the cubic Cu_2O structure. The peaks located at 2θ= 43.38º, 50.50º and 74.18º respectively are characteristic of Cu corresponding to the (111), (200) and (220) planes (JCPDS No. 003–1018).

Some of the structural parameters of the thin films were calculated as follow.
The d-spacing value was obtained by using Braggs law:

$d = n\lambda / 2\sin\theta$……4.1

Some structural parameters such as crystal size, dislocation density and strain calculated from XRD data are given in table 4.1. The Scherrer formula given by following relation was used to calculate the crystal size:

$D= K\lambda/ \beta\cos\theta=0.9\lambda/\beta\cos\theta$……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. In addition, the dislocation density (δ) and the crystal size (D) are calculated by using the following relation.

$\delta=1/D^2$……..4.3

The strain (ε), was determine by using the XRD data and following relation:

$\varepsilon = \beta\cos\theta/ 4$……...4.4

Table 4. 1. The calculated crystal size, dislocation and strain for copper oxide thin films

Sample code	2θ(deg)	FWHM(rad)	Crystallite size t(nm)	strain(ε) (10^{-4})	Dislocation Density(δ) (10^{-4}) (m^{-2})
AS1	36.4072	0.0034	48	8.1	4.3
AS3	36.3889	0.0029	56	6.9	3.2
AS5	36.5166	0.0035	46	8.3	4.7

The crystallite sized increased from 48 nm to 56 nm when the deposition time increased from 15' to 25'and then decreased from 56 nm to 46 nm when the deposition time further increased to 35'. The initial increase in crystallite size could be due to the domination of the formation of the Cu2O crystal and decrease in crystallite size for 35' could be due to the domination of decomposition of the Cu2O after the Cu ions are used up.

4.2 UV-Vis Spectroscopy Analysis

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 spectrophotometer in the wavelength range 400-800 nm. The optical absorption of the films is shown in Figure (4.2). The absorption of the films increased with increasing the deposition time and decays exponentially with an increase in wave length. The parameters, like absorbance, transmittance and band gap are very important parameters to be considered while studying the some properties of the materials. The band gap of the thin film was obtained by plotting $(Ahf)^2$ verses (hf) for copper oxide thin films. The extrapolation of the straight line portion of the plot toward the energy axis (hf-axis) gives the band gap at the intercept of hf-axis as shown in Fig 4.3

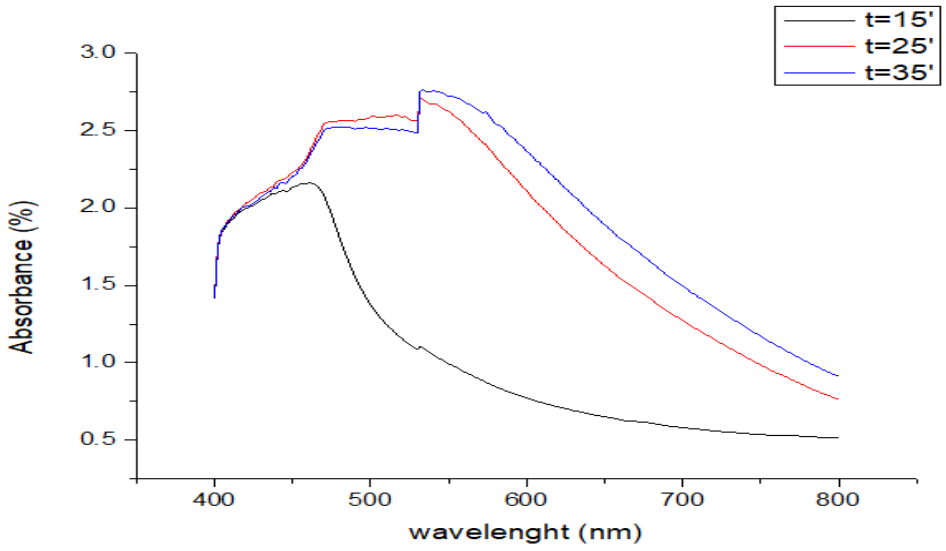
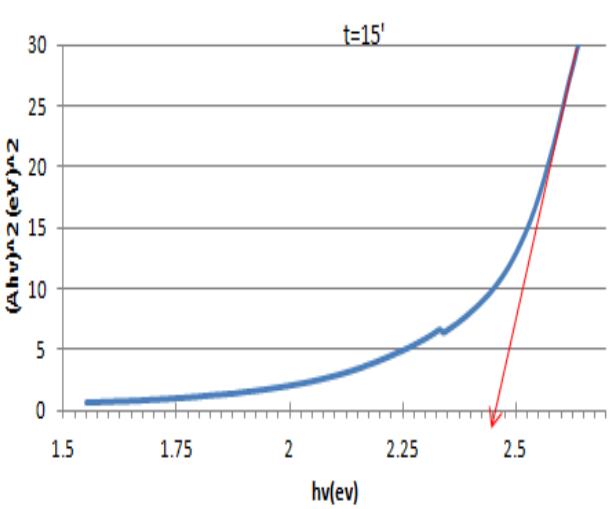
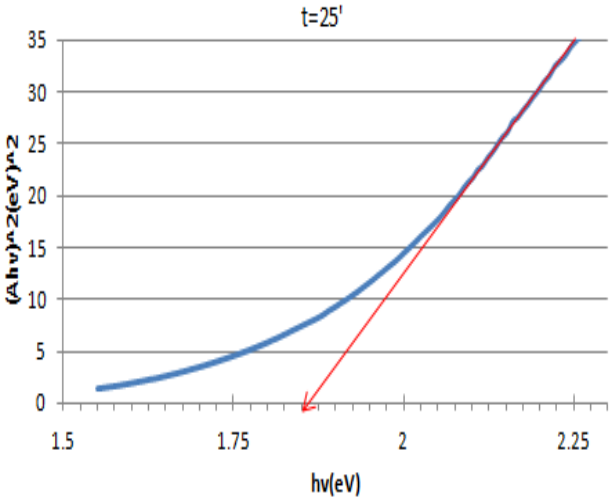


Figure 4. 2. Plot of wavelength versus Absorbance for CuO thin films deposite at 15', 25' and 35' annealed at 300℃ for 1.5 hrs



a/



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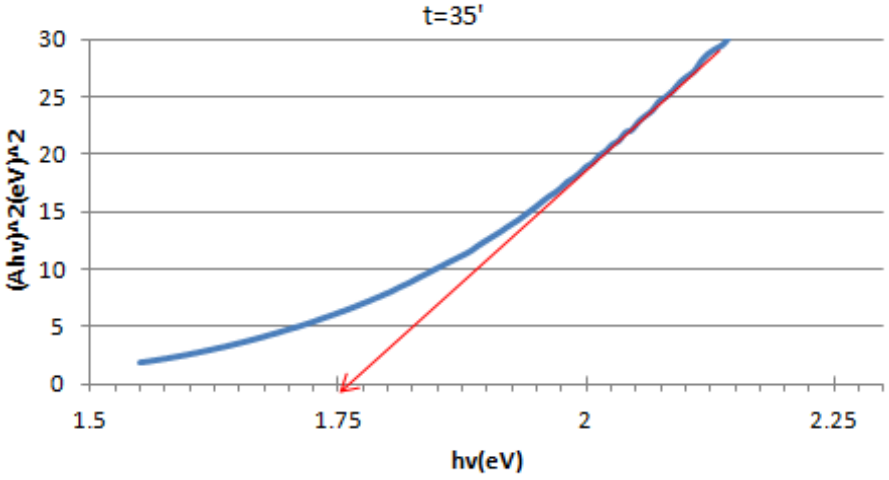

c/

Figure 4. 3. Plot of photon energy, hv (eV) versus (Ahv) 2(eV) 2 for the CuO thin films deposited at 15', 25' and 35' Minutes.

The band gap of the thin films decreased with increasing the deposition time as shown in figure 4.3. It decreased from 2.45eV for a film deposited at 15' to 1.75 eV for the film deposited at 35'. The film deposited at 25' has a band gap of the 1.85 eV. The film deposited at 25' has a band gap of the 1.85 eV.

Which similar to the band gap of Cu2O reported by [69]. Although XRD result shows a dominant metallic copper phase at deposition time 35', UV-Vis result shows the presence of band gap which is in contradiction of XRD result. Therefore further investigation is required.

The result shows the decreament of band gap with increasing deposition time. However the band gap and crystalline size doesn't show correlation. This could be due to varies factor like deposition method, dopant, defects, diffusion and super saturation. That is as the film thickens diffusion of reactant become slower and the solution become supersaturated with copper ion hindering further nucleation; these factors eventually limit crystal growth. And also Ostwald ripening occurs when larger crystal grows at the expense of smaller ones. Then smaller grain dissolves and their material migrate to larger grains. This process reduces the overall crystal size. Generally initially, increasing reaction time leads to larger crystal; beyond a critical point, Ostwald ripening also dominates, causing a decrease in crystal size. The balance between the nucleation and growth determines the final crystal size.

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CHAPTER FIVE

5 CONCLUSIONS AND RECOMMENDATION

5.1 CONCLUSION

The copper oxide thin films were successfully deposited on glass substrate by CBD method at different deposition time. 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. The structural and optical property of the thin films was characterized by XRD and UV-VIS characterization techniques. Longer deposition time generally leads to thicker thin film due to increased nucleation and growth. As the reaction time increases the crystal size of copper oxide also tends to increases. However there are limiting factors like diffusion and super saturation. That is as the film thickens diffusion of reactant become slower and the solution become supersaturated with copper ion hindering further nucleation these factor eventually limit crystal growth. And also Ostwald ripening occurs when larger crystal grows at the expense of smaller ones. Then smaller grain dissolves and their material migrate to larger grains. This process reduces the overall crystal size. Generally initially, increasing reaction time leads to larger crystal; beyond a critical point, Ostwald ripening dominates, causing a decrease in crystal size. The balance between the nucleation and growth determines the final crystal size. The band gap of the thin film decreased with increasing the deposition time from 2.45eV to1.75 eV. The film deposited at 25' has a band gap of the 1.85 eV. Which similar to the band gap of Cu2O reported by [69]. Although XRD result shows a dominant metallic copper phase at deposition time 35', UV-Vis result shows the presence of band gap which is in contradiction of XRD result. Therefore further investigation is required.

The result shows the decreament of band gap with increasing deposition time. However the band gap and crystalline size doesn't show correlation. This could be due to varies factor like deposition method, dopant, defects, diffusion and super saturation. That is as the film thickens diffusion of reactant become slower and the solution become supersaturated with copper ion hindering further nucleation; these factors eventually limit crystal growth. And also Ostwald ripening occurs when larger crystal grows at the expense of smaller ones. Then smaller grain dissolves and their material migrate to larger grains. This process reduces the overall crystal size. Generally initially, increasing reaction time leads to larger crystal; beyond a critical point, Ostwald ripening also dominates, causing a decrease in crystal size. The balance between the nucleation and growth determines the final crystal size.

5.2 RECOMENDATION FOR FUTURE WORK

Further studies are needed:

- To further investigate the film's morphological and electrical properties.
- To explore the specific application of the currently synthesized copper oxide thin films

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