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Elaboration and characterization of Co doped CuO thin films prepared by spin coating technique

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Note :……. Mention :……..……

ملخص

في هذا العمل تم ترسيب الأغشية الرقيقة من أكسيد النحاس المطعم بالكوبالت باستخدام تقنية الطلاء الدوراني وباعتماد طريقة محلول-هلام على ركائز زجاجية. تم بداية استخدام كل من أسيتات النحاس (II) أحادي الهيدرات وخلات الكوبالت (II) رباعي هيدرات كمصادر أساسية، والإيزوبروبانول كمذيب وأحادي إيثانول أمين كمثبت. تم تجفيف الأغشية المطلية عند 200 درجة مئوية لمدة 10 دقائق ثم لدنت عند 500 درجة مئوية لمدة ساعة واحدة. كان متوسط نفاذية أفلام Co doped CuO أعلى من 50٪. من الجدير بالملاحظة حدوث تحول أزرق في حافة الامتصاص لـ CuO مع زيادة تركيز Co في الفيلم لأنه يؤدي إلى انخفاض عرض الإرسال البصري. من ناحية أخرى، اتبعت فجوة نطاق وقرينة الانكسار اتجاهًا معاكسًا وتغيرت من 1.99 إلى 2 فولت ومن 2.697 إلى 2.692 على التوالي.

الكلمات المفتاحية: **Co:CuO شرائح رقيقة، محلول-هلام ، الخصائص البصرية، فجوة النطاق، معاملات الانكسار**

Abstract

In this work, Co doped CuO thin films were deposited by sol gel spin-coating technique on glass substrates. Copper (II) acetate monohydrate and Cobalt (II) acetate tetrahydrate were used as the starting salt materials source, isopropanol as solvent and monoethanolamine as stabiliser. The as-coated films were dried at 250 °C for 10 min and then annealed at 500 °C for 1 hour. Average transmittance of the Co doped CuO films was above 50%.A bleu shift in the absorption edge of CuO with increasing Co concentration in the film is noteworthy as it leads to decrease in the width of the optical transmission. On the other hand, the two parameters band gap and refractive indices followed an opposite trend and changed from 1.99 to 2.01 eV and from 2.13 to 2, respectively.

Key-words: ***Co:CuO thin films, Sol gel, optical properties, Band gap, refractive indices***

Résumé

Dans ce travail, des films minces de CuO dopé Co ont été déposés par la méthode Sol-Gel /centrifugation sur des substrats de verre. L'acétate de cuivre (II) monohydraté et l'acétate de cobalt (II) tétrahydraté ont été utilisés comme (précurseurs) source de sel de départ, l'éthanol solvant et la monoéthanolamine comme stabilisant. Les films ainsi revêtus ont été séchés à 250 °C pendant 10 minutes puis recuits à 500 °C pendant 1 heure. La transmission moyenne des films de CuO dopé Co était supérieure à 50 %. Un décalage vers le bleu du bord d'absorption de CuO avec l'augmentation de la concentration de Co dans le film est remarquable car il entraîne une diminution de la largeur de la transmission optique. En revanche, les deux paramètres bande interdite et indices de réfraction ont suivi une tendance opposée et ont évolué respectivement de 1,99 à 2,01 eV et de 2,13 à 2.

Mots clés : ***Co:CuO, Sol gel, propriétés optiques, Bande interdite, indices de réfraction***

Acknowledgements

*First and foremost, we are grateful to « **ALLAH** », the Almighty, for giving us the patience, bravery, and faith to complete this task. Then, we pray to Allah to facilitate our scientific endeavors and grant us the knowledge to aid others and advance humankind.*

This work was carried out at the EchahidCheikhLarbi University Tébessi-Tébessa's Applied and Theoretical Physics Laboratory.

*We would like to thank Dr. **F. HANINI,** lecturer 'A' at the Echahid Cheikh Larbi University Tébessi-Tébessa's Department of Material Sciences, Faculty of Exact Sciences and Natural and Life Sciences,for allowing us to work under his direction as our academic supervisor, as well as for his insightful advice and ideas, all of which were very helpful to us while we conducted research for our master's thesis.*

*We are particularly grateful to **D. ZITOUNE** PhD student for his help during sample preparation.*

We also want to express our gratitude to the evaluation committee members who honored us by agreeing to review and improve this work.

Finally, but just as importantly, we want to express our gratitude to our loving parents, relatives, and friends for their encouragement and support.

DEDICATION

With pride and gratitude, I dedicate this thesis to myself.

This achievement is the result of allah's guidance and hard work and determination.

I thank everyone who supported me along the way.

IHSEN RAMDANI

DEDICATION

I wanna thank me, I wanna thank me for believing in me, I wanna thank me for doing all this hard work, I wanna thank me for having no days off, I wanna thank me never quitting, I wanna thank me for always being a giver and trying to give more than I receive, I wanna thank me for tryna do more right than wrong, I wanna thank me for just being me of all times..

SELSABIL BERRAHAL

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Introduction

Copper Oxide (CuO) is a compound that has garnered significant interest in recent years due to its remarkable properties and wide-ranging applications in various scientific and technological domains. Also known as Cupric Oxide or Copper (II) Oxide, this binary compound comprises Copper and Oxygen. Classified as a p-type semiconductor, it exhibits interesting electrical, optical, and magnetic properties. CuO has attracted interest for its potential applications in fields such as electronics, optoelectronics, catalysis, energy storage, and sensing. Its favorable characteristics include chemical stability, low toxicity, cost-effectiveness, and high optical absorption in the visible and near-infrared regions.It is also a black color compound with slight translucence is a promising candidate for many applications owing to the abundance of its components in nature, low-cost production, good thermal stability, and electrochemical properties.

Thin films of this semiconducting material have attracted considerable attention in recent years due to their unique properties. They find wide applications in solar cells as an absorber material, gas sensors, biosensors, catalysts, and as electrodes in lithium-ion batteries [1].

So we can prepare CuO thin films using various techniques such as Sol-Gel, wet-chemical synthesis, magnetron sputtering, pulsed laser deposition, molecular beam epitaxy, electro deposition etc. Among these, the Sol-Gel is especially suitable since it has proved to be a simple and inexpensive method, particularly useful for large area applications. This method has also the advantage that the final properties of the films can be tailored by the type and concentration of precursors as well as the annealing temperatures

In this work, we delve into the elaboration and characterization of cobalt (Co) doped CuO thin films fabricated using the spin coating technique. Afterwards, the films undergo annealing at 500°C to enhance their crystallinity and optimize their characteristics. UV-Vis spectroscopy is used to analyze the optical properties of these films.

In addition to an introduction and a conclusion, this present work is structured around three distinct chapters.

- In Chapter I, a brief overview of thin films is provided, followed by a particular focus on the Sol-Gel process used for the elaboration of our thin films. Furthermore, in this regard, a bibliographic study is presented concerning the various properties of copper oxide (CuO) and their areas of application,

- Chapter II presents a comprehensive overview of the different stages involved in the elaboration of our thin films using the Sol-Gel technique, along with various methods and different characterization techniques,

- Finally, in the last chapter, the experimental results related to the samples prepared by the Sol-Gel method are presented along with their interpretations.

Chapter I

Copper Oxide and sol-Gel method

I.1.Thin films

Thin film devices typically have a thickness not exceeding 1µm thick in contrast to bulk devices, which are about 50 to 250 µm thick. If the growth is atom by atom or molecule by molecule it is called thin film and if the growth is grain-by-grain it is thick film [1].

The limit between "thin" and "thick" films cannot generally be defined, although literature sometimes gives an arbitrary value of 1 µm, basically, a film can be considered as "thin" when its properties are significantly different from the bulk. Thin films can be prepared from a nearly infinite range of compositions such as conductive materials, insulators, refractory (Oxides, Nitrides, Carbides) and polymers among others. The structure of the deposited films can be mono or multilayer. Which explain the wide several of their applications: microelectronics, optics, chemistry and mechanics...etc[1].

The formation of thin film is carried out by a combination of coalescence, nucleation and growth process. Firstly, the absorptive species are not in thermodynamic balance with the substrate, and thus move on its surface until their temperature reach to substrate temperature. During these displacements, and when they arrive in favorable sites (crystalline defects, impurities...) which are called sites of nucleation they creating germs, which will be growth to forming the film [1].

I.2. Thin films applications

Since ancient times, thin films have been employed in a wide range of industries, including chemistry with protective layers, electrical fields with metallic conductive layers, mechanics with abrasive or wear-resistant layers, and optics with reflecting and anti-reflective layers[2].

In the middle of the 20^{th} century, thin films saw a huge industrial development, primarily in optical and electrical applications. These days, thin films are employed in the logic of component miniaturization in a variety of domains, including magnetism in its applications for sensors, micro-actuators, and magnetic recording (storage), electronics, optics, and photonics [2].

I.3. Thin films growth process

The formation of a thin film always involves three steps [3, 4]:

1. Production of the appropriate atomic, molecular, or ionic species,
2. Transport of these species to the substrate,
3. Deposition and growth of the layer on the substrate; the state of the substrate surface plays an obtaining optimal properties of thin films largely depends on the following parameters:(i) nature of the deposition technique, (ii) matching lattice parameters between film and substrate, (iii) quality of the substrate, (iv) deposition temperature.

The unit species, on impacting the substrate, lose their velocity component normal to the substrate (provided the incident energy is not too high) and are physically adsorbed on the substrate surface.The adsorbed species are not, initially, in thermal equilibrium with the substrate initially and move over the substrate surface. In this process, they interact among themselves forming bigger clusters. The clusters or the nuclei, as they are called, are thermodynamically unstable and may tend to desorb in time, depending on the deposition parameters. If the deposition parameters are such that a cluster collides with other adsorbed species before getting desorbed, it starts growing in size. After reaching a certain critical size, the cluster becomes thermodynamically stable and the nucleation barrier is said to have been overcome[2,4].

This step involving the formation of stable, chemisorbed, critical-sized nuclei is called the nucleation stage. The critical nuclei grow in number as well as in size until a saturation nucleation density is reached. The nucleation density and the average nucleus size depend on a number of parameters such as the energy of the impinging species, the rate of impingement, the activation energies of adsorption, desorption, thermal diffusion, and the temperature, topography, and chemical nature of the substrate. A nucleus can grow both parallel to the substrate by surface diffusion of the adsorbed species, and perpendicular to it by direct impingement of the incident species. In general, however, the rate of lateral growth at this stage is much higher than the perpendicular growth [2,4].

The grown nuclei are called islands. The next stage in the process of film formation is the coalescence stage, in which the small island start coalescing with each other in an attempt to reduce the substrate surface area. This tendency to form bigger islands is termed agglomeration and is enhanced by increasing the surface mobility of the adsorbed species, larger islands grow together, leaving channels and holes of uncovered substrate [4].

I.4. Copper Oxide (CuO)

Copper have two oxidation states +1 and +2, while under special circumstances some compounds of trivalent are also reported. It was shown that this trivalent copper survives not more than few seconds. Consequently, cuprous oxide (Cu_2O) and Cupric Oxide (CuO) are the two stable forms of Copper Oxide. However, only Cupric Oxide (CuO) phase is reported as a gas-sensitive material and exhibits a number of interesting properties [5].

CuO has attracted particular attention because it is the simplest member of the family of copper compounds and exhibits a range of potentially useful physical properties, such as high temperature superconductivity, electron correlation effects, and spin dynamics.This led to a rapid research expansion in theoretical studies, fabrication, characterization and applications of CuO based devices in the latter half of the 20th century [5].

Cupric Oxide can be obtained easily by heating cuprous oxide (Cu_2O) or Copper in air at 1000-1100°C nearly, Cupric Oxide is formed as follows:

$$Cu_2O + \frac{1}{2}O_2 \rightarrow 2CuO \;/\; 2Cu + 2\,O_2 \rightarrow 2CuO$$

But in industrial method it is prepared by heating malachite ore, CuO is produced according the reaction below:

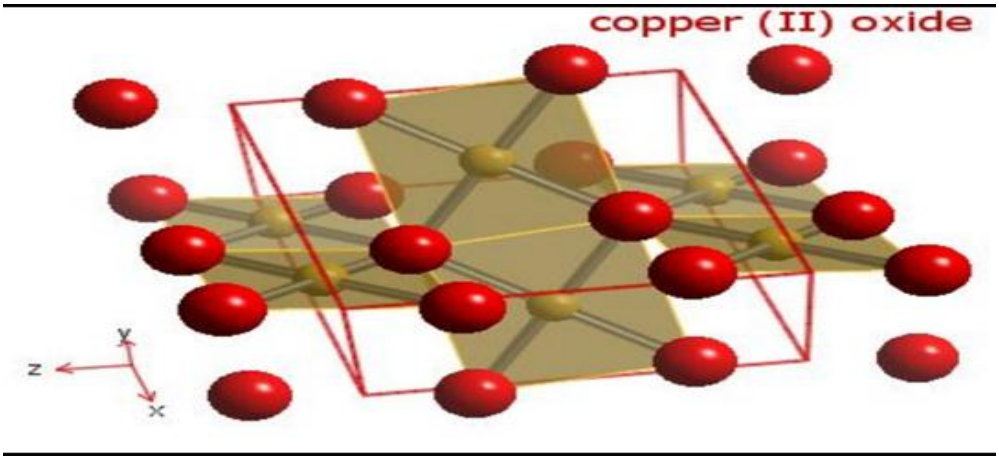
$$CuCO_3 + Cu\,(OH)_2 \rightarrow 2CuO + CO_2 + H_2O + O_2$$

CuO had been studied extensively for a number of decades, with electrical and optical properties reviews, available as early since the 1960's. The first period of notable growth in CuO research interest occurred in the mid of 1980's with a series of highly-cited research works.CuO thin films have been successfully deposited by several deposition techniques including thermal evaporation, Spray Pyrolysis (SP), plasma evaporation, dc magnetron sputtering, elctrodeposition, Sol-Gel .Work in the early part of the 2000s were mainly focused on growth mechanisms and parameters influence. Several review articles dealing with the state of the art of CuO have been published with extensive discussion on band structure, thermal, magnetic, optical and electrical properties, doping, growth and devices [5].

I.5. Copper oxide propreties

Studies on tenorite (CuO) have been carried out since the first decade of last century. Cupric oxide is a narrow energy bandgap (1.2 - 1.9 eV) p-type semiconductor, with a C2/c monoclinic crystalline structure. The unit cell of CuO (a = 4.6837Å, b = 3.4226 Å, c = 5.1288 Å, β = 99.54°), comprises Cu^{2+} ions which are coordinated by four '4' O^{2-} ions in

anapproximately square planar configuration (Figure **I**.1) [6]. Some of the physical features of the material are summarised in Table**I**.1[5].



Figure**I**.1. Crystal structure of CuO. Large spheres (red) are Oxygen atoms and small spheres (yellow) are Cu atoms [6].

TableI.1. Physical properties of CuO [5].

Cupric oxide (CuO)	
Chemical names	Copper (II) oxide Cupric oxide Copper monoxide Copper oxide (CuO) Oxocopper
Molecular Formula	CuO
Appearance	Black powder
Solubility in water	Insoluble
Molecular Mass	79.55 g/mol
Density	$\rho = 6.32$ g/cm^3
Relative permittivity	12
Melting point	1134°C
Boiling point	2000 °C

1.5.1. Electrical properties

CuO is an antiferromagnetic p-type semiconductor with a magnetic moment of 0.65μB (symbol μB, the Bohr magneton = 9.274×10^{-24}) [7,8].and a direct gap (Figure **I**.2) reported interval from 1.2 to 1.9 eV. CuO has low conductivity in general (Table **I**.2)[9].

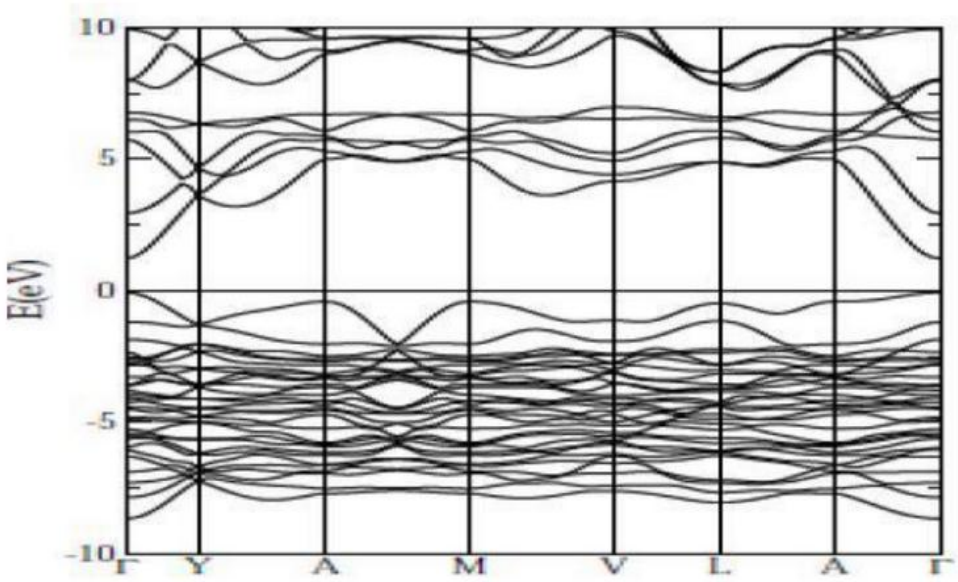


Figure I.2. CuO band structure calculated using DFT Method [10].

Table I.2: Some Electrical Properties of CuO[8 -11].

Properties	CuO
Nature of the Bandgap	Direct
relative dielectric constant	12
Electron effective mass	0.16 à 0.46 m_e
Effective mass of the hole	0.54 à 3.7 m_e
conductivity type	P
Electricalconductivity $(\Omega.cm)^{-1}$	10^{-4}à 10^{-3}

1.5.2. Optical properties

Because of their diverse physical characteristics, transition metal oxides are valuable in a wide range of methods and applications. Apart from their physical characteristics, they have been demonstrated to be chemically and thermally stable in air, which has led to their recent focus on them as selective solar coatings (Figure **I**.3) for photo thermal conversion [12]. CuO's optical properties are shown in table **I**.3.

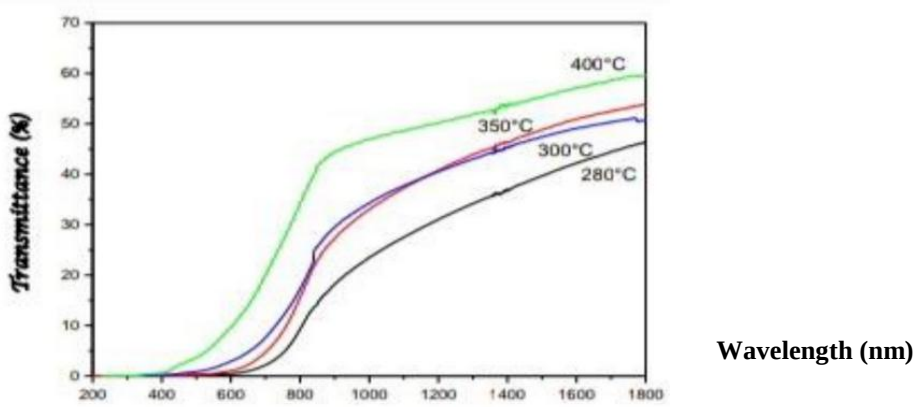


Figure I.3. Transmission in the range of UV-visible regions of CuO prepared with various substrate temperatures [13].

Table I.3: Some optical properties of CuO [14 - 18].

Property	CuO
Transmittance in the visible (%)	20-25
Refractive index	1.5
Absorption coefficient (cm^{-1})	10^4

I.6. Copper Oxide applications

Copper Oxide (CuO) exhibits a wide range of applications across various technological fields. It serves as both an active catalyst and a catalyst support, facilitating crucial chemical reactions such as the degradation of nitrous oxide when combined with ammonia and the oxidation of Carbon monoxide, Hydrocarbons, and Phenol, especially in supercritical water conditions. Additionally, CuO functions as electrode active materials.

Furthermore, CuO finds utility in gas sensing applications, owing to its excellent selectivity. It also serves as a high-efficiency thermal conducting material, contributing to

effective thermal management systems. In the realm of magnetic recording media, CuO's properties are leveraged for enhanced performance.

Moreover, CuO holds promise for solar cell applications, where its characteristics can boost energy conversion efficiency. Overall, its versatility and effectiveness make it indispensable across a spectrum of technological endeavors, from catalysis to energy conversion, sensing and beyond [19, 20].

I.7. The Sol-Gel method

The Sol-Gel method is a wet-chemical synthesis technique for preparation of oxide gels,glasses, and ceramics at low temperature. It's based on control of hydrolysis and condensation of alkoxide precursors. As early as the mid-1800s, interest in the Sol-Gel processing of inorganic ceramics and glass materials has begun with Ebelman and Graham"s studies on silica gels. The investigator recognized that the product of hydrolysis of tetraethoxysilane (TEO_S) under acidic conditions is SiO_2. In the 1950s and 1960s Roy and Co-workers used Sol-Gel method to synthesize a variety of novel ceramic oxide compositions with very high levels of chemical homogeneity, involving Si, Al, Zr…etc, which couldn't be made using traditional ceramic powder methods. It's possible to fabricate ceramic or glass materials in a variety of forms, such as ultra-fine powders, fibers, thin films, porous aerogel materials or monolithic bulky glasses and ceramics. Since then powders, fibers, thin films and monolithic optical lens have been made from the Sol-Gel glass [21].

I.7.1. Sol-Gel process

The Sol-Gel process, as the name implies, involves transition from a liquid **Sol**:(colloidal solution) into a **Gel**: phase. Usually inorganic metal salts or metal organic compounds such as metal alkoxide are used as precursors. A colloidal suspension or a sol is formed after a series of hydrolysis and condensation reaction of the precursors. Then the sol particles condense into a continuous liquid phase (gel). Generally three reactions are used to describe the Sol-Gel process: hydrolysis, alcohol condensation and water condensation. Because water and alkoxides are immiscible, alcohol is commonly used as co-solvent. The twophases which describe the Sol-Gel process are defined as follows[21]:

1. **Sol**: a stable suspension of colloidal solid particles or polymers in a liquid,
2. **Gel**: porous, three-dimensional, continuous solid network surrounding a continuous liquid phase.

I.7.2. Reaction mechanisms of the Sol-Gel method

The chemical transformation mechanism breaks down into two stages:

1. Hydrolysis, which corresponds to the activation reaction.

$$M(OR)_n + xH_2O \longrightarrow M(OR)_{n-x} - (OH)_x + x\ ROH$$

2. Condensation-polymerization which is the stage of chain growth [21].

a) Alcoxolation

$$(OR)_{n-x}M(OH)_n + M(OR)_n \longleftrightarrow (OR)_{n-x}\ (OH)_{n-x}\ M-O-M(OR)_{n-1} + ROH$$

b) Oxidation

$$M(OH)_n(OR)_x(OR)_{n-y} + M(OH)_2 \longleftrightarrow (OR)_{n-x}(OH)_{x-1}M-O-M(OR)_{y-1} + (OR)_{n-x} + H_2O$$

I.7.3. Sol-Gel advantages

- Possibility of obtaining hybrid materials organo-minerals; real nanocomposites of such fate the species (organic and mineral) are mixed at the molecular scale, in the form of thin films or monolithic with specific properties;
- Possibility to manufacture thin films of oxides at room temperature on heat sensitive substrates;
- Possibility of making multi-component deposits in an operation;
- Deposition of thin films on both substrate faces in each operation [3].

I.7.4.Different Sol-Gel techniques

Several techniques can be used for the deposition of thin films on a given substrate: the"spin-coating", the "drain-coating" and "dip-coating". Each having their own characteristics, the choice of method of deposition depends on the characteristics of the substrate such that its geometry or size. The two methods presented below are the most commonly used. In this thesis, we will delve into the spin coating technique [21].

I.7.4.a.dip-coating process

In dip coating process, film formation takes place by evaporation of the solvent from a polymer solution. The substrate is dipped into the polymer solution, taken out at a constant speed and dried by allowing the solvent to evaporate, leaving behind a solid polymer film on the substrate. Scriven et al. divided the dip coating process into five stages: (a) immersion, (b)

start-up, (c) deposition, (d) drainage and (e) evaporation, shown in Figure **I**.4. The thickness of the deposited film is related to the position of the streamline dividing the upward and downward moving layers. There are five forces in the film deposition region governing the thickness of the film and the position of the streamline:(1) viscous drag upward on the liquid by the moving substrate, (2) force of gravity, (3) resultant force of surface tension in the concavely curved meniscus, (4) inertial force of the boundary layer liquid arriving at the deposition region, and (5) surface tension gradient [22].

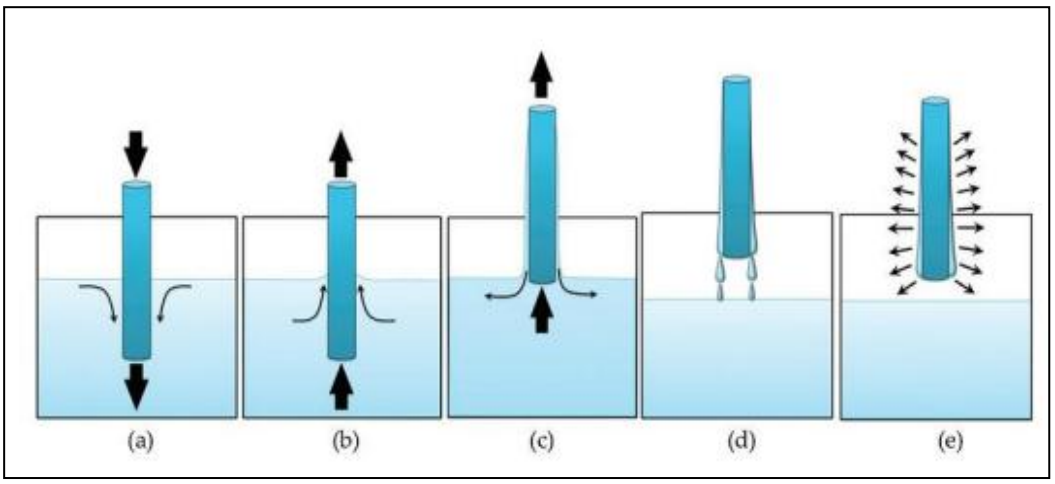


Figure I.4. Dip-coating stages: (a) immersion; (b) start-up; (c) deposition; (d) drainage and (e) evaporation [23].

The thickness of the coating layer depends on the following factors[22]:

1. The speed at which the substrate is taken out;
2. The concentration of the solution;
3. The viscosity of the solution;
4. The rate of solvent evaporation;
5. The angle at which the substrate is taken out;
6. The surface tension of the solution;
7. The vapor pressure ;
8. Temperature and relative humidity above the coating bath;
9. The precise control of air velocity, and the temperature of substrate and solution.

I.7.4.b.Spin-Coating

Spin coating is a simple technique for creating uniform thin films. A substrate spins rapidly while a coating solution is applied, causing excess solution to be thrown off, leaving behind a thin, even coating. Film thickness can be controlled by adjusting rotation speed and duration, along with solution viscosity and solvent evaporation rate. Its affordability, homogeneity, and speed make spin coating widely used in sol-gel thin film production [24].

This deposition technique can be divided into four phases, shown schematically in Figure **I**.5.

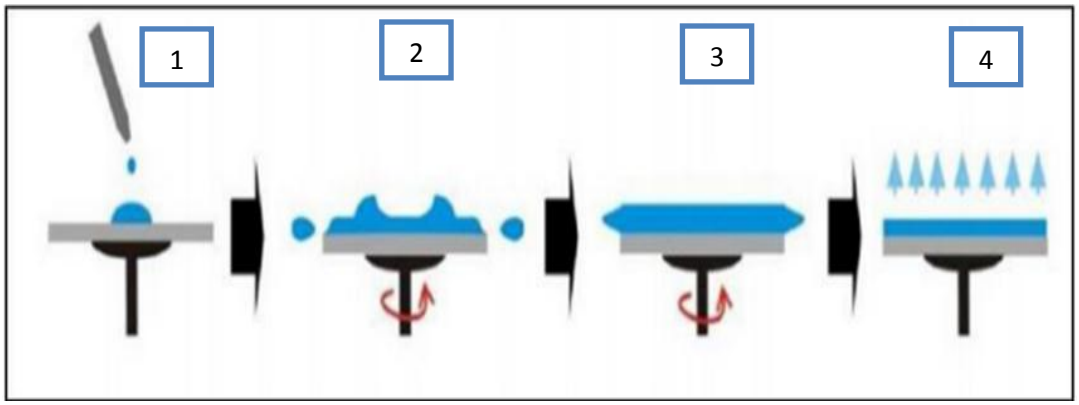


Figure I.5. The four steps of spin coating [1].

1) The deposition of the solution;

2) The start of rotation: the acceleration step causes the flow of liquid outwardly of the substrate;

3) Rotating at a constant speed allows the ejection of excess liquid in the form of droplets and the reduction of the thickness of the film uniformly;

4) Evaporation of the more volatile solvent which increases the reduction of the thickness of the deposited film.

Final film thickness and other properties depend on the parameters chosen for the spin process [21].

I.7.4.b.1. The advantages of spin coating

This technique has the advantage of being easily implemented. It also allows the manufacture of excellent quality layers on flat substrates with dimensions of the order of a few cm^2 [3].

Chapter II

Experimental procedures

II.1. Preparation of the substrate

II.1.1. The choice of substrate

Is crucial due to several factors: (i) firstly, the substrate should have good thermal stability to withstand the deposition process, especially if high temperatures are involved; (ii) additionally, the substrate needs to have a compatible crystal structure with CuO to minimize lattice mismatch and ensure good adhesion between the deposited film and the substrate; (iii) furthermore, the substrate should have a smooth surface to promote uniform and defect-free film growth; (iv) lastly, considerations such as cost-effectiveness, availability, and compatibility with subsequent processing steps also influence the choice of substrate for CuO deposition.

II.1.2. Choice of glass substrate for depositing CuO

The studied films were deposited on substrates of solid glass which have a length of ~ 2.5 cm and a width of ~ 2.5cm (figure II.1).

Figure II.1. Photo of the glass substrate used.

The choice of glass like substrate of depot was adopted because of the following reasons:

1. For their transparency which adapts well for the optical characterization of films in the visible one;
2. For economic reasons.

II.2. Cleaning substrate

Cleaning the substrates is an essential process so that the work is fully successful. Cleaning it is therefore necessary to remove traces of dust and impurities and to ensure that there are no flattening impurities or defects on the surface of substrates. The protocol (process steps) cleaning is selected according to the type of substrates used.

II.2.1.Glass substrate

The quality of thin films deposited on glass substrate depends on purity and surface state of the used substrate. Firstly using a pen with diamond point to cut the substrates and the process of cleaning surface for the glass substrate is as follows:

1) Rinsing with the water distilled and then with acetone during 5 min;
2) Rinsing with distilled water;
3) Washing in methanol at ambient temperature in a bath with the ultrasound for to eliminate the traces from greases and impurities stuck to surface of substrate then they are to clean in a water bath distilled with the ultrasound.

II.3. Deposition device: Centrifugation or spin-coating

The centrifugation device (also known as spin-coating) utilized for depositing our thin layers obtained through the Sol-Gel method was developed and assembled at the Laboratory of Applied and Theoretical Physics, Echahid Cheikh Larbi Tebessi University - Tebessa. A visual representation of the centrifugation apparatus is depicted in figure.II.2.

Figure II.2. Experimental spin coating device for thedeposition of layers used at the Laboratory of Applied and Theoretical Physics, Echahid Cheikh Larbi Tebessi University - Tebessa.

II.4. Preparation of the solution

This work aims to investigate the effect of mass doping with cobalt (Co), on the optical characteristics of copper oxide thin films elaborated by Sol-Gel method. The table II.1 below shows the different chemical compounds used to deposit Co-doped CuO thin films,

Table II.1. Different products used for the preparation of our thin films by sol-gel method (spin coating).

Product	Formula	Mark	Purity (%)
Copper (II) acetate monohydrate	(CH3CO2)2Cu·H2O	Aldrich	99,9
Monoethanolamine (MEA)	C_2H_7NO	Biochem	99
Isopropanol	$CH_3CHOHCH_3$	Prolabo	99,9
Cobalt(II) acetate tetrahydrate	$(CH_3COO)_2Co \cdot 4\ H_2O$	Prolabo	99,9

Copper (II) acetate and cobalt (II) acetate tetrahydrate was first added in isopropanol to prepare the Co doped CuO for various mass ratios of Co/Cu were 0, 3, 5 and 10%wt (figure II.3). After 15 min of stirring at room temperature, the hot plate temperature was ramped up to 80°C and the MEA was added drop by drop and the mixture was stirred for 1 h at 80°C to obtain a transparent and homogenous blue solution (figure II.4).

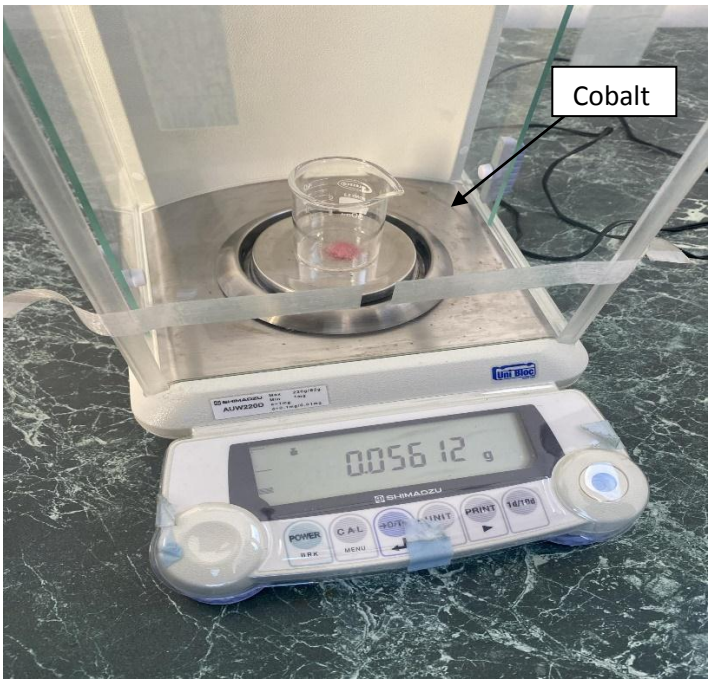


Figure II.3. Electronic Analytical Balance (SHIMADZU AUW 220D)

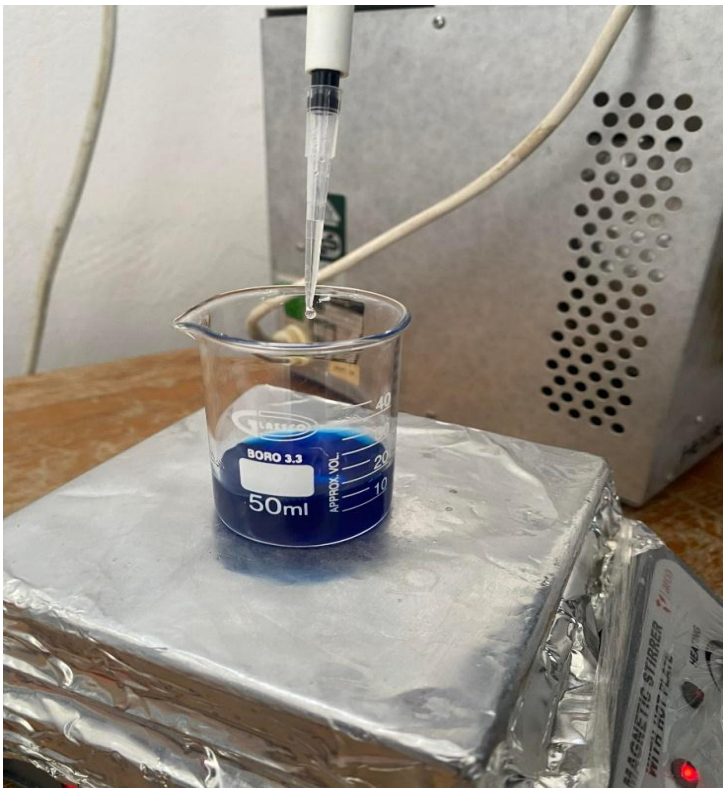


Figure II.4. Photograph of a Sol-gel (CuO)

To summarize the above, the sol-gel preparation was carried out according to the protocol described in figure II.5, at a temperature of 80°C and with stirring using a magnetic stirrer.

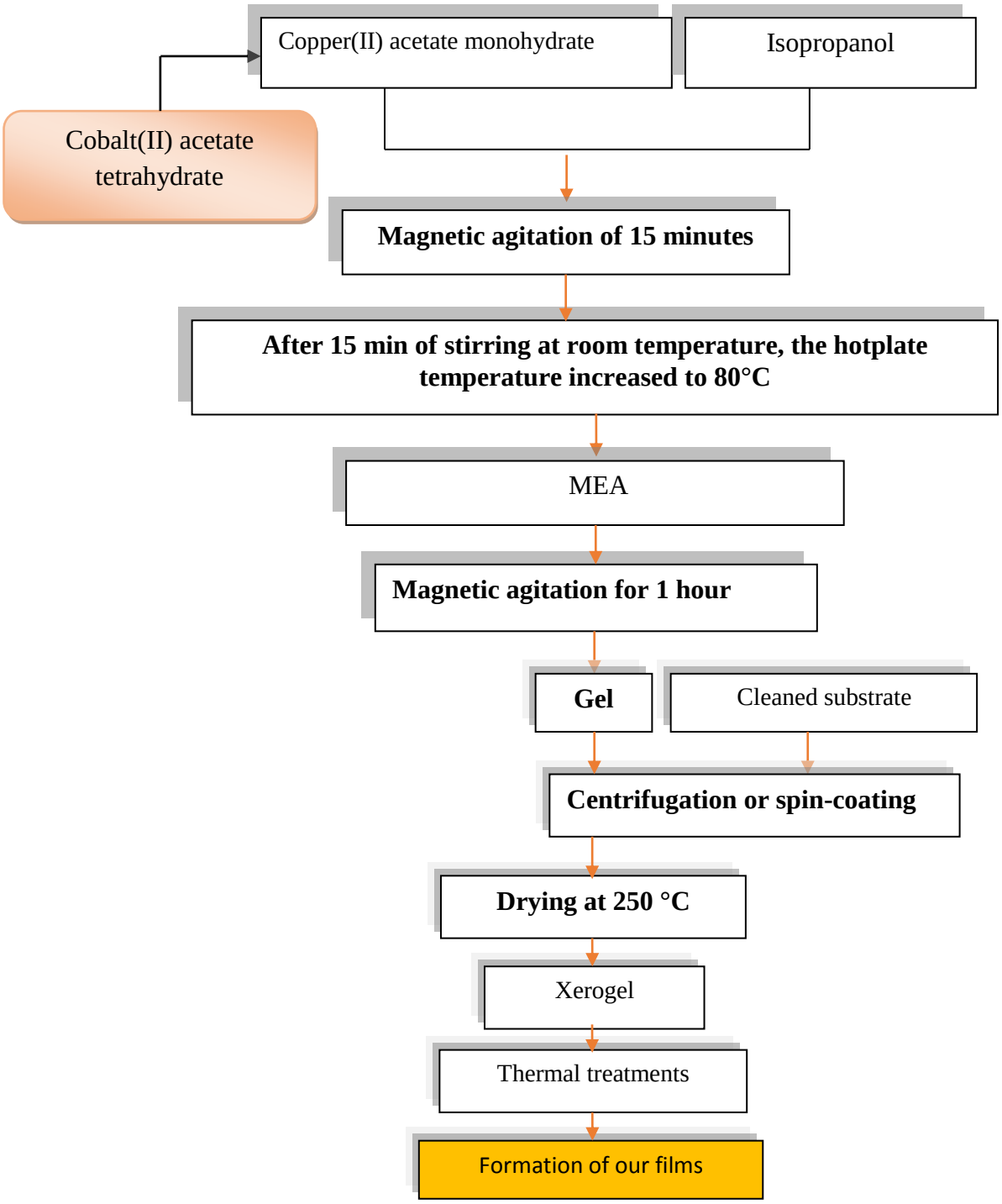


Figure.II.5. Diagram of the fabrication process of our thin films.

Before deposition, glass substrates were successively cleaned with acetone, methanol, and distillated water. All thin films were coated onto glass substrates at a speed of 3000 rpm for 30 s and dried for 10 minutes on a hot plate at 250°C. This procedure was repeated 9 times and at the end the samples were annealed at 500°C for 1 hour under air. Figure II.6 illustrates some of the samples prepared before the annealing process.

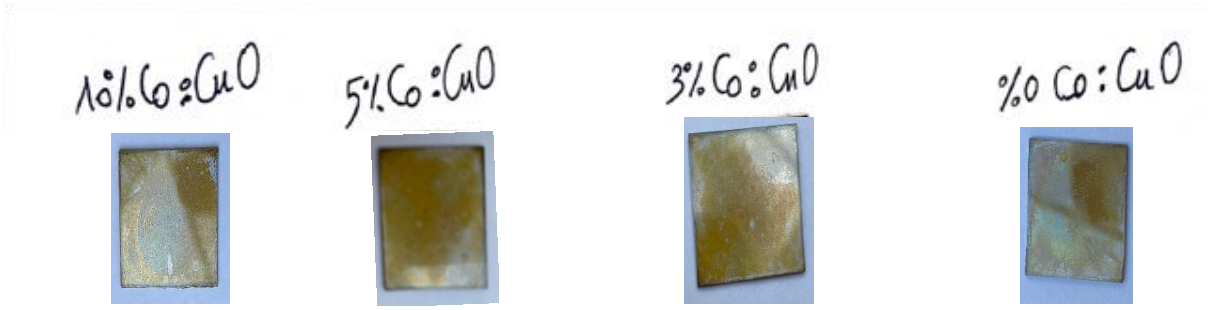


Figure.II.6. The samples prepared before the annealing process represent.

II.5. The annealing or heat treatment

The annealing or heat treatment process is considered the final stage in the preparation of thin films, where the samples are placed in an oven at a temperature of 500 °C for one hour. This process eliminates the organic species present in the initial solution and promotes the condensation and crystallization of the material. Figure II.7 illustrates some of the samples prepared after the annealing process.

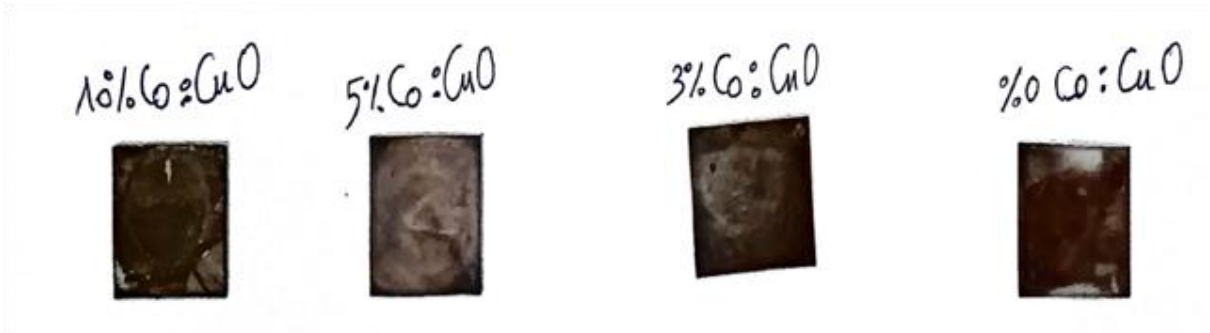


Figure II.7. The samples prepared after the annealing process represent.

II.6. Characterization techniques

Below we will present a rigorous and well-tailored technique that we used to study the optical properties of these prepared thin films.

II.6.1. UV-visible spectroscopy

UV-visible spectroscopy is the atomic spectroscopic technique used to investigate electronic transitions. This technique rests on the knowledge of the distances between interference rings in the spectra of transmission in the visible and the near infra-red. One uses a recording spectrophotometer with double beams, of which its principle of operation is represented on Figure.II.8 [1, 25].

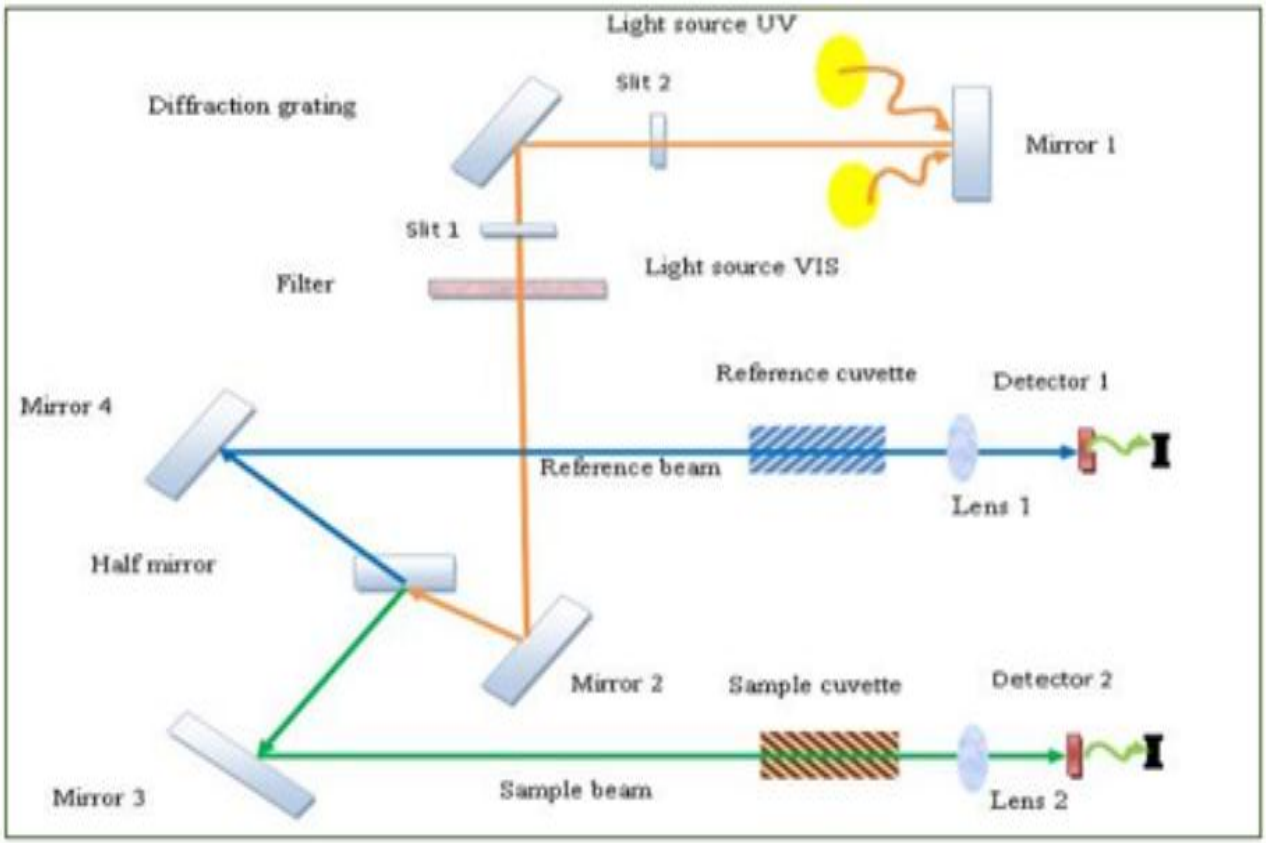


Figure II.8. The principle of operation of UV-visible [1].

The obtained spectra give the variation of transmittance expressed as a percentage $T(\%)$ according to their wavelength λ (nm). Thanks to the interferences, one can determine the

following parameters: thickness of the film, optical gap, absorption coefficient and the refraction index which can be calculated using the following relations [1]:

1. The thickness of the film $\boldsymbol{d}$ (Swanepoel method) :

$$d = \lambda_1\lambda_2/2(\lambda_2 n_1 - \lambda_1 n_2) \quad \text{II.1}$$

Where: n_1 and n_2 are the refraction index of the film for the wavelength λ_1 and $\lambda_2$respectively; we can calculate n_1 and n_2 from the following relation:

$$n_{1(2)} = [N_{1(2)} + (N_{1(2)}^2 - S^2)^{1/2}]^{1/2} \quad \text{II.2}$$

Where: s is the refraction indexes of the substrate and $N_{1(2)}$ can be obtained using this relation:

$$N_{1(2)} = 2S(T_M - Tm_{1(2)})/T_M Tm_{1(2)} + (S^2 + 1)/2 \quad \text{II.3}$$

With: $Tm_{1(2)}$ is the minimum transmittance corresponds with $\lambda_1(\lambda_2)$ and T_M is the maximum transmittance confined between Tm_1 and Tm_2

II.6.1.a. Absorption coefficient α

In the spectral field where the light is absorbed, and by knowing the film's thickness, we can determine the absorption coefficient for each value of transmittance T (%) as follows:

$$\alpha\ (cm^{-1}) = [1/d] \times ln\ [100/T(\%)] \quad \text{II.4}$$

This approximate relation is established, by neglecting the reflexions with all interfaces; air/film, air/substrate .

II.6.1.b. Optical Gap Eg

In high energy, absorption results from electronic transitions between wide states of band to band. It is usually described by Tauc law:

$$(\alpha\ h\nu) = C^{te} \times (h\nu - Eg)^m \quad \text{II.5}$$

Where: $h\nu$ is the photon energy, Eg is optical gap m and A are constants, m characterizes the optical type of transition and takes the values 2, 1/2 (2 for allowed direct transitions or 1/2 for allowed indirect transitions). In order to determine the nature of the transition from the films

produced in this study, we will plot the curves $(\alpha hv)^m = f\ (hv)$ .We can obtain Egvalue as it showing in figure II.9 [1].

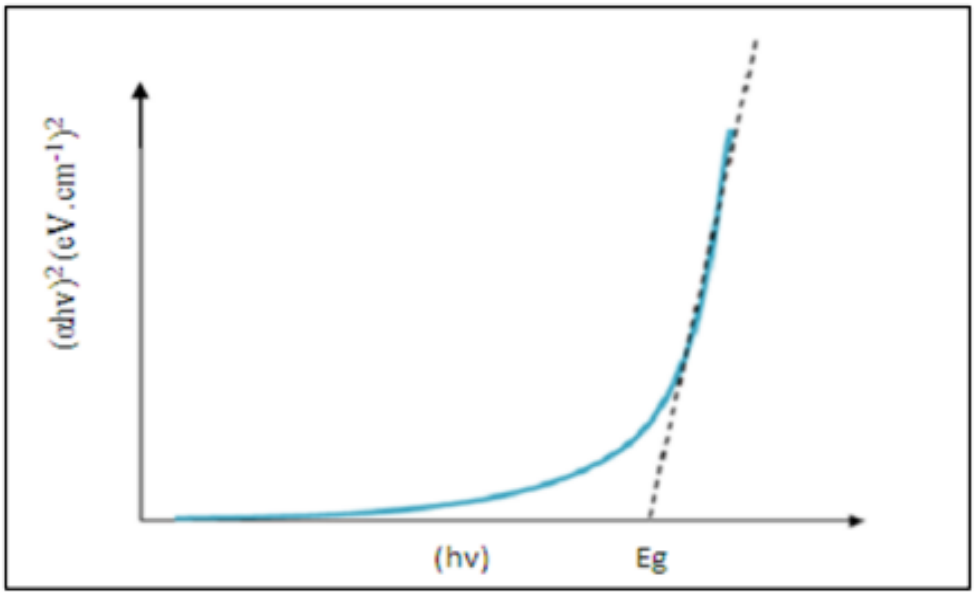


Figure II.9. determination of Eg [1].

The transmission curves of the studied thin films are obtained using a dual beam recording spectrophotometer, UV-Vis of UV-Visible type JASCO V630.

The transmission coefficient, or transmittance T, is defined as the ratio of the transmitted light intensity to the incident light intensity.

To have the transmittance curves, our CuO films, were deposited on the glass substrates. The latter is essential because it does not absorb light in the studied spectral domain. A blank substrate in the reference beam of the spectrophotometer was used. For spectra tracing, a computer connected to this apparatus reproduces the spectra representing the transmittance, according to the wavelength of the incident beam. By exploiting these UV-Visible spectra, it is possible to calculate the thickness of the films, as well as the optical characteristics; the absorption coefficient, the value of the width of the gap and the refractive index.

Chapter III

Experimental results and discussion

III.1. Studies of optical properties by UV-Vis spectroscopy

III.1.1.The transmittance

Figure.III.1.shows the room temperature transmittance spectra as a function of wavelength for both undoped CuO film and Co-doped CuO films with different Co content.

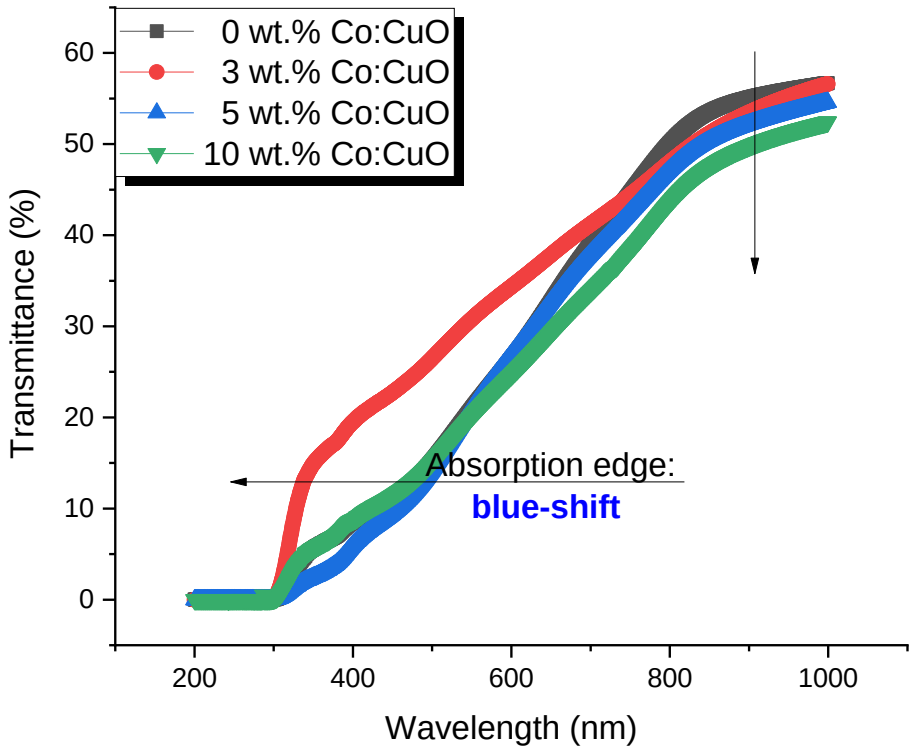


Fig.III.1. UV-vis transmittance spectra of Co-doped CuO.

The optical transmission of Co-doped CuO film was the highest, especially in the visible region. Therefore, the decrease in transmittance (from 1000 to 700 nm) with increasing Co concentration, which have plausible application in optoelectronic devices. The decrease of optical transmittance at higher Co doping contents may be attributed to the increased scattering of photons by crystal defects by employing Co doping. The free carrier absorption of photons may be also conducing to the reduction in the optical transmission of heavily transitional metal doped thin film same results reported by ***Babu et al.***[26].in effect of Co doping in tailoring the crystallite size, surface morphology and optical band gap of CuO thin films prepared via thermal spray pyrolysis.

It can be observed that the maximum transmittance in the visible light wavelength range is over 55% for undoped CuO film. The transmission decreases substantially with the increase of Co content. However, the maximum optical transmission in the visible region is still beyond 50% for the Co:CuO films with 3 wt.% Co, which is important for the applications of the Co:CuO films as transparent conducting oxide (TCO). The deduced absorption edge (Figure III. 2) of films shows a pseudo- 'blue shift' with the increasing addition of Co.

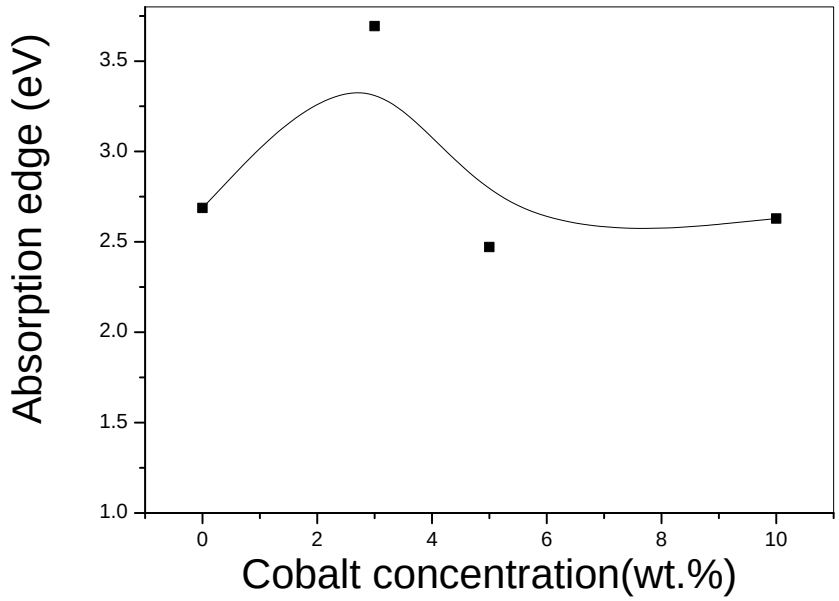


Figure III.2. The absorption edge derived from transmittance data vs cobalt concentration.

III.1.2.The absorbance

Figure.III.3 shows the room temperature absorbance spectra as a function of wavelength for both undoped CuO film and Co-doped CuO films with different Co content.

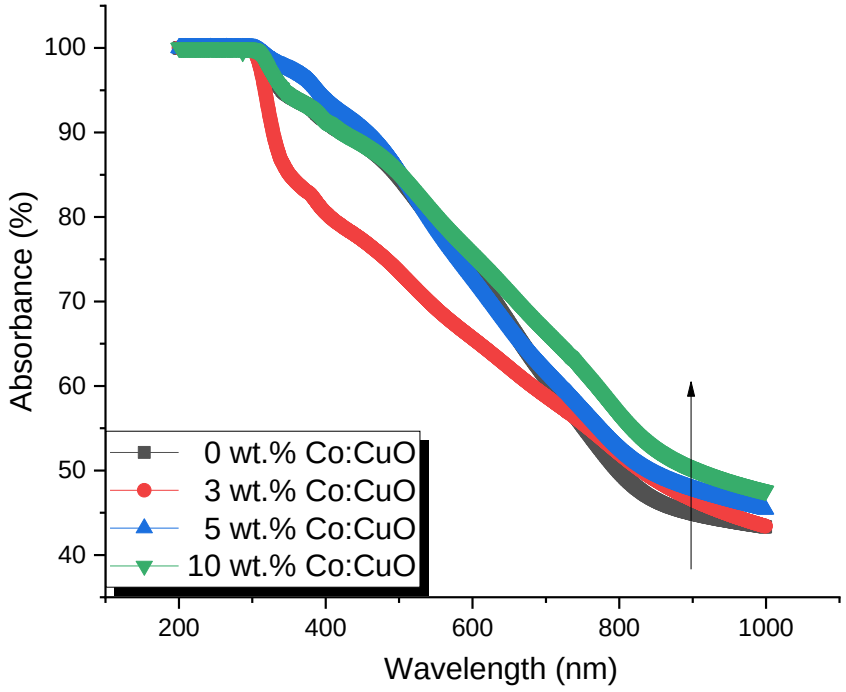


Figure III.3. Absorbance spectra of Co-doped CuO.

From figure.III.3.the highest absorbance was obtained at wavelength from 600 to 1000 nm for sample 10 %wt. Co doped CuO. Because, the absorption was occurred when electron made the transition from a lower energy state in valence band to high energy state in conduction band while absorbing the excess energy as photon. There is a possibility of increasing of absorbance caused by scattering at grain size This behavior agrees well with the earlier results published by ***Halin et al.***[27] in characterizations of cuprous oxide thin films prepared by sol-gel spin coating technique with different additives for the photo electrochemical solar cell. The absorbance of samples 3% and 5 % shows the same trend and the absorbance can be improved by increasing the cobalt concentration of films.

III.1.3.The optical band gap

The optical band gap 'Eg' of the Co doped CuO thin films annealed at 500°C were calculated using the Tauc model equation III.1.

$$(\alpha h\upsilon)^2 = C^{te}(h\nu - E_g) \qquad \text{III.1}$$

Where, absorbance coefficient, α = 2.303A (A = Absorbance), $h\nu$ = photon energy,was calculated using equation.III.2

$$h\nu = hc/\lambda \qquad \text{III.2}$$

where h is the Plank constant which is 6.63×10^{-34} (J/s) , c is the light constant that is 3×10^{8} (m/s) and λ is wavelength.

C^{te} is a constant and Eg refers optical band gap energy. while "n" represents a number indicating the type of transition. For a direct transition, n=2 and for indirect transition, n = 1/2. for the CuO, we have n = 2. The tangent to the curve on $(\alpha h\nu)^2$ versus hv plot intersects the 'Photon Energy' axis giving the band gap energy (figure III.4).

The optical band gap of undoped CuO film was calculated to be 1.99 eV. As seen from figure III.4 (a-d) the optical band gap of Co-doped CuO films increased with the increasing of Co concentration. The Eg values were found to be 2.01, 2.13, and 2 eV for films that were doped with 3%, 5% and 10% wt. Co respectivley.

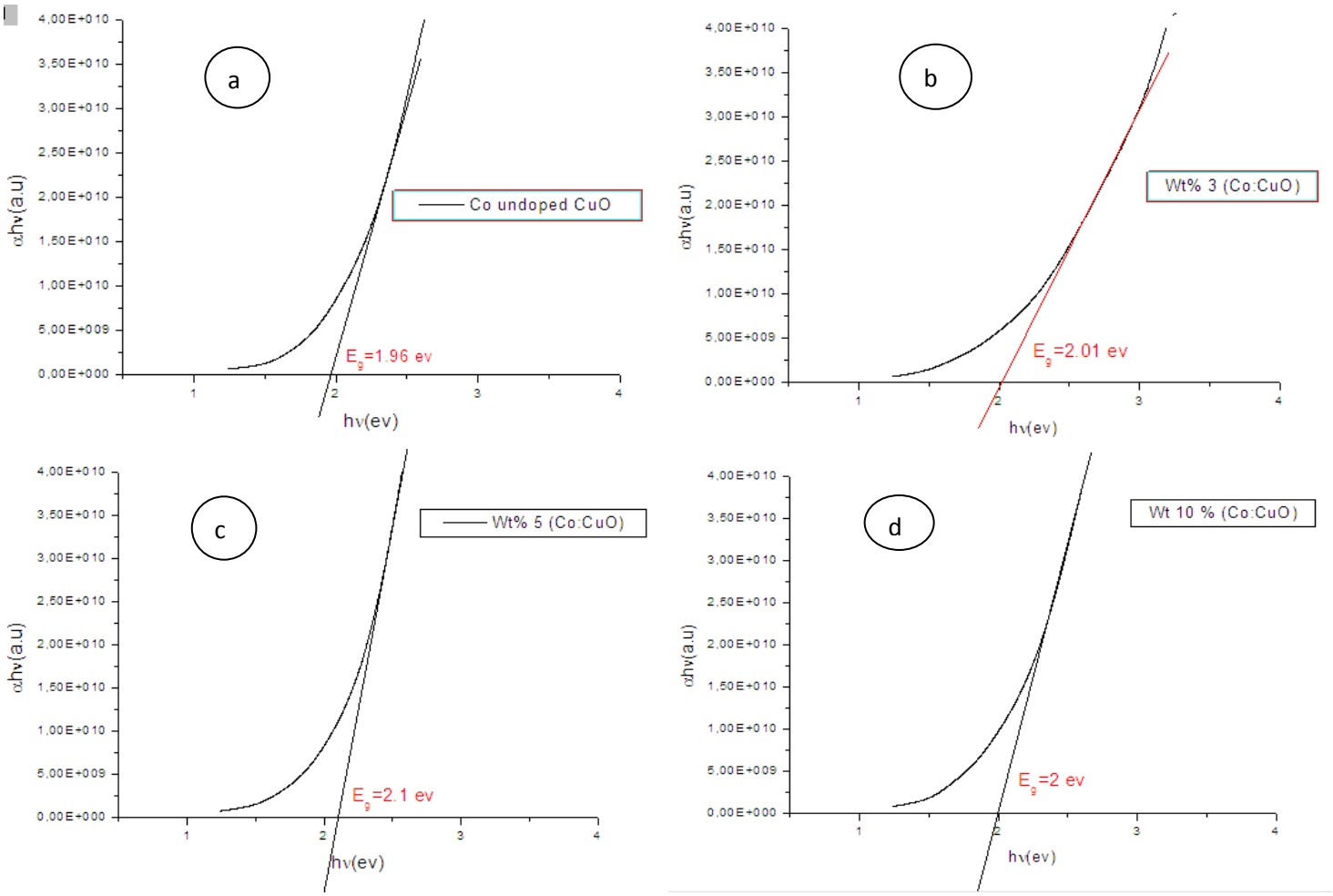


Figure III.4. Measurement of direct optical band gap vs cobalt concentration.

Bulk CuO exhibits much lower band energy value (~1.2 eV) than that of these observed values for CuO thin films. So that increasing According to quantum confinement effect theory, band gap energy for nanostructured material increases with decreasing particle size. The nanostructured thin films are tightly confined compared to the bulk material. So, the material needs more energy to excite an electron from valence band to conduction band. Hence, the band gap energy of nanostructured CuO is more than that of the bulk. the same conclusion has been reported by ***Muhamed et al.***[28]in Effect of stabilizer on sol ageing for CuO thin films synthesized by sol-gel spin coating technique, and by ***Talbi et al.***[29] in Pb-doped CuO thin films synthesized by the Sol-Gel method.

In this study, band gap was increased with increasing Co concentration. This increase in the band gap is probably due to the lower quality of the films with higher structural defects (e.g. increased point defect annihilation & dislocation) which is evident from the increasing dislocation density with increasing cobalt concentration. The same conclusion has been reported by ***Muhamed et al***.[28]. The quantum confinement effect and decreased crystallinity of the thin films directly contribute towards the bleu shift of direct optical band gap.

III.1.4.Reflective index

Figure.III.5.shows the reflective index as a function of different Co concentration for both undoped CuO film and Co-doped CuO films. This refractive index having described the inverse relationship between the refractive index and the band gap, was estimated following the model proposed by ***Kumar and Singh*** [30]:

$$n = 3.3668 \times \left(E_g\right)^{-0.32234} \qquad \text{III.3}$$

Table.III.1. Values of the estimated refractive index in addition to their band gap (Eg).

Co (Wt %)	Eg (eV)	n
0	1.99	2.69703
3	2.01	2.68835
5	2.13	2.63856
10	2	2.69267

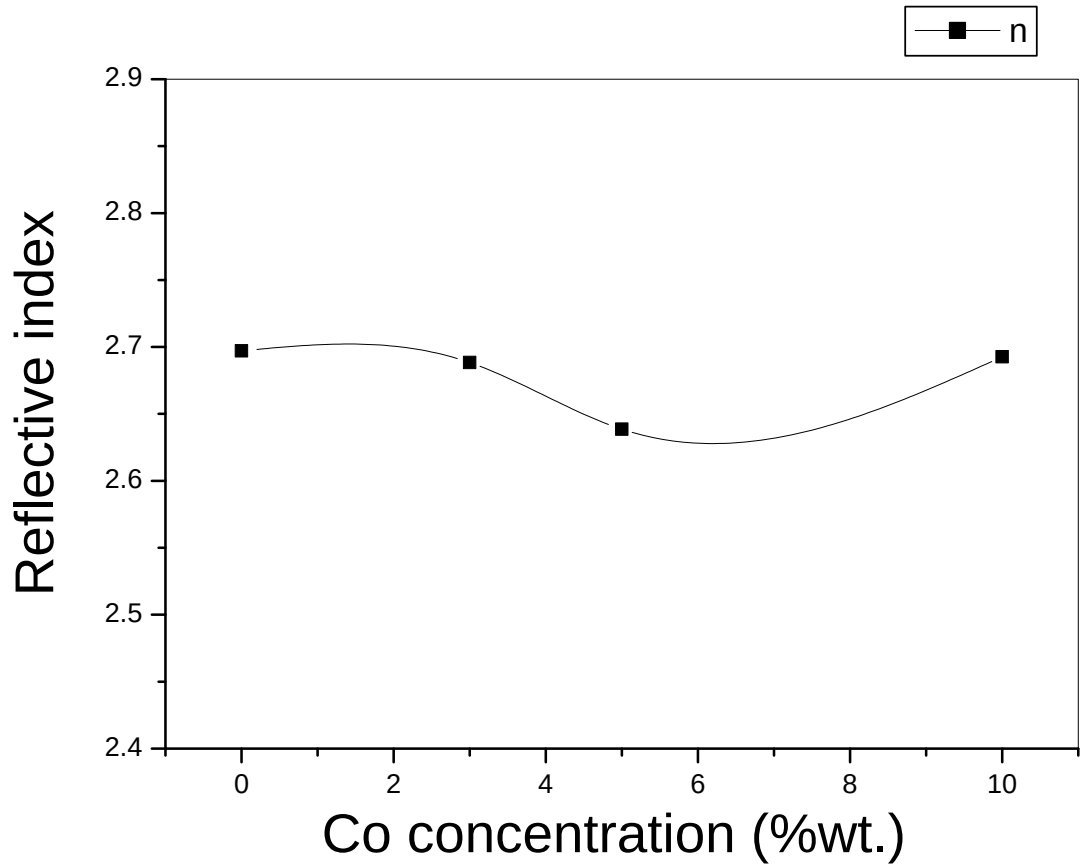


Figure III.5. The reflective index as a function of different Co concentration

Figure III. 5 and table III.1 show that the reflective index '*n*' values decrease slightly with increasing of Co concentration. The reflective index of undoped CuO film was calculated to be 2,670. The n values were found to be 2.688, 2.638 and 2.692 for films that were doped with 3%, 5% and 10%wt. Co respectively. This is probably related to the crystallization of the material and the elimination of pores as well as microstructural changes [31].

Conclusion

Conclusion

Undoped and doped CuO (3, 5, 10% wt. Co/Cu) with different concentrations of Cobalt, the subject of our study, were prepared by the Sol-Gel method. These materials were deposited in thin films using a spin-coating technique on glass substrates, using a rotation speed equal to 3000 rpm.

After completing this study on the influence of cobalt doping on the optical properties of thin CuO films, it is evident that the films exhibit significant alterations in their optical features. These features are characterized using a UV-visible spectrophotometer, in which we observe: **(i)** thin films of copper oxide doped with cobalt have lower transparency compared to thin films of undoped copper oxide in the visible region (600-1100 nm); When the cobalt doping increases from 0 to 10%wt.Co, the transmittance is decreased by 10%; **(ii)** the absorbance of the undopedCuO thin film was higher than the Co-doped CuO thin films. This is a clear effect of cobalt doping, on the optical properties of the CuO thin films; **(iii)** the 10% wt.Co doped CuO sample showed a higher absorption layer than the others; **(iv)** the optical gap is approximately 1.99 eV for the undopedCuO film. However, the gap of the doped CuO thin films are 2.01 eV, 2.13 eV and 2.0 eV for CuO doped 3, 5 and 10 wt%. Co respectively; **(v)** the refractive index decreases slightly with the cobalt concentration.

Based on the optical properties of Co doped CuO thin films in this study, it was therefore recommended that these thin films are recommended for use in several optoelectronic applications such as...

Recommendation for Further work

1. Firstly, as a continuation of this research, the degree of crystallinity in the thin layer should be investigated in a future study utilizing X-ray diffraction (XRD) or/and Raman spectroscopy,
2. Introduction of Co inCuO led to a reduction in the film transmittance. However there is need to study and understand the charge transport in Co doped CuO thin films it i?
3. The optical properties study confirmed that all the CuO films changed with concentration. However, detailed analysis on how different concentration of Co doping affected the film roughness?

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REFERENCES

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Echahid Cheikh Larbi Tebessi University- Tebessa
Faculty of Exact Sciences and Natural and Life Sciences
Department: Material Sciences

Master Thesis

Domain: Material Sciences
SPECIALTY
Materials Physics

THEME

Elaboration and characterization of Co doped CuO thin films prepared by spin coating technique

By:

RAMDANI Ihsen *BERRAHAL Selsabil*

Jury committee:

President:	**BECHIRI Abderrachid**	**Prof.**	**Echahid Cheikh Larbi Tebessi University- Tebessa**
Advisor:	**HANINI Faouzi**	**M.C.A.**	**Echahid Cheikh Larbi Tebessi University- Tebessa**
Examiner:	**BELGHIT Hana**	**M.A.B.**	**Echahid Cheikh Larbi Tebessi University- Tebessa**

Defended on: 09/06/2024

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Année universitaire 2023/2024

Formulaire de levée de réserves après soutenance d'un Mémoire de Master

Données d'identification du candidats(es) :

Nom et prénom du candidat : …… **RAMDANI Ihsen**……

…… **BERRAHAL Selsabil** ……

Intitulé du Sujet : **Elaboration and characterization of Co doped CuO thin films prepared by spin coating technique**

……

Données d'identification du membre de jury :

Nom et prénom : …… **BECHIRI Abderrachid** ……

Grade :……**Professeur**……

Lieu d'exercice : Université Larbi Tebessi- Tébessa

Vu le procès-verbal de soutenance de la thèse sus citée comportant les réserves suivantes :

1. Grade du membre (MAB)
2. Co ; s'écrit en arabe, (في الملخص باللغة العربية)
3. قواعد تصبح ركائز, (في الملخص باللغة العربية)
4. matrial→ matrials, (في الملخص باللغة الانجليزية)
5. were→ was, (في الملخص باللغة الانجليزية)
6. مؤشرات تكتب قرينة (في الملخص باللغة العربية)
7. تكتب مختصرة كما في ملخص الفرنسي والانجليزي , (في الملخص باللغة العربية) أغشية أكسيد النحاس الرقيقة
8. Les interlignes et la taille, le type de police ne sont pas homogénéisés (table de matière)
9. symbol μB !
10. Les formes des références ne sont pas homogènes + références 5, 26 et 27 n'existent pas en texte
11. Chapitre 3, ajouter les unités
12. Corriger Fig. III 1→ Fig. III 2

Et après constatation des modifications et corrections suivantes :

1. Correction de grade du membre (MCB)
2. Co → كوبالت,

3. ركائز, (في الملخص باللغة العربية)
4. matrials, (في الملخص باللغة الانجليزية)
5. was, (في الملخص باللغة الانجليزية)
6. مؤشرات تكتب قرينة
7. Co:CuO شرائح رقيقة
8. Les interlignes et la taille,le type de police ont été homogénéisés
9. On a ajouté la definition symbol μB……magnetic moment of 0.65 μB (symbol μB, the Bohr magneton = 9.274×10^{-24})……
10. Les référence ont été écrit selon le format **Harvard** ; Exp. Chen, J.T., Zhang, F., Wang, J., Zhang, G.A., Miao, B.B., Fan, X.Y., Yan, D. and Yan, P.X., 2008. CuO nanowires synthesized by thermal oxidation route. *Journal of Alloys and Compounds*, *454*(1-2), pp.268-273.(**exp. attaché**) + on a supprimé les références 5, 26 et 28. (27 existe, UV-Vis chapitre 2 ; ancienne version)
11. On a ajouté les unités au chapitre 3.
12. On a coriigé Fig. III. 1→ Fig. III. 2

Je déclare en ma qualité de président de jury de soutenance que le mémoire cité remplit toutes les conditions exigées et permet au candidat de déposer son mémoire en vue de l'obtention de l'attestation de succès.

Le 01/07/2024

Président de jury de soutenance : (Nom/Prénom et signature)

A. Bedrine

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Faculté des Sciences Exactes et des Sciences de la Nature et de la Vie

Déclaration sur l'honneur de non-plagiat

(À joindre obligatoirement au mémoire, remplie et signée)

Je soussigné(e),

Nom, prénom : RAMDANI Ihsen , BERRAHAL Selsabil

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Année universitaire : 2EME Année Master

Domaine : Science de la matière

Filière : physique

Spécialité : physique de materiaux

Intitulé du mémoire :

Elaboration and characterization of Co doped CuO Thin films prepared by Spin coating technique

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