



Mohamed Khider University of Biskra
Faculty of exact sciences and natural and life sciences
Material sciences department

MASTER MEMORY

Material sciences department
Physics
Material Physics

Prsented by:
Amina Guesmia
On:
../06/2023

Effect of “La” and “Ba” Doping on the physical propeties of CuO thin films

Jury:

Mrs	Bencharef Zahia	MA"A"	University of Biskra	President
Mrs	Almi Kenza	MC "B"	University of Biskra	Supervisor
Mr	Belahssen Okba	Professor	University of Biskra	Examiner

Academic Year : 2023/2022



Dedications

Oh, Allah, praise and thanks be to you until you feel satisfied and I thank you always and forever for your blessings. I thank God that he helped me to accomplish this modest work.

The trip was not short nor should it be. the way was fraught with obstacles, The dream was not closebut I managed to achieve it. I dedicate this success:

*To the one who raised my head high and I am proud of him, my first idol, who removed the thorns from my path to pave the path of knowledge. for my “dear father **Saleh**” Allah protecthim for me, the man who struggled all his life to make me better than him.*

*To the most precious gift from God, my great mother, to the invisible hand that removed the thorns from my path, that bore every moment of pain I suffered and supported me in my weakness and fragility, my beloved mother **Fadhila**, Allah preserve her for me.*

*To my beloved sisters, whose presence in my life eases many difficulties: **Wissal** and **Hanine**.*

*To my dear grandmothers **Merabiti El Zohraa** , may Allah have mercy on her soul, and **Yamina**.*

I do not forget to mention all my extended family, friends and colleagues over the years and everyone who has helped and supported me in this matter, everyone who knows Amina Guesmia.



Thanks And Acknowledgement

*I would like to express my gratitude and appreciation to the supervisor, **Dr. Almi Kenza** for her support in completing the memory. Her constant guidance, and her patience and constant encouragement during difficult times and willingness to share her vast knowledge made me understand this project and helped me to complete my assigned tasks ontime.*

*I also extend my sincere gratitude to the board members, **Dr. Bencharef Zahia**, President, and **Pr. Belahssen Okba**, Examiner, for accepting to examine of the memoray and evaluating this work.*

*I would like to thank **Amina, Pr. Tibermacine Toufik** for all the optical electrical measurements made of our thin films.*

thanks and appreciation to the laboratory of Physics and chemical Applications in Mohamed Khider university, and all the members and staff who have willingly helped us.

LIST OF FIGURES

Chapter I: Bibliographic research.

Figure (I.1): State conductor, semiconductor and insulator.....	7
Figure (I.2): Energy band in the pure (a) and inlaid state (b).....	8
Figure (I.3): Spectrum of TCO (reflectance, transmittance, absorption).....	10
Figure (I.4): Applications of transparent conductive oxides.....	12
Figure (I.5): Copper metal.....	12
Figure (I.6): Crystalline structural diagram of Cu ₂ O.....	14
Figure (I.7): Crystalline structural diagram of CuO.....	15
Figure (I.8): Barium metal.....	17
Figure (I.9): Lanthum metal.....	18
Figure (I.10): Synthesis of various forms of materials by the sol-gel method.....	20
Figure (I.11): Steps of spin coating.....	20
Figure (I.12): Dip-coating stages: (a) immersion; (b) start-up; (c) deposition; (d) drainage;(e)evaporation.....	21
Figure (I.13): The main steps of deposition by the CVD method.....	22
Figure (I.14): General schematic of a spray pyrolysis deposition process.....	23
Figure (I.15): Physical vapor deposition method.....	24
Figure (I.16): Thermal evaporation in a schematic.....	25
Figure (I.17): Schematic diagram of the position of ions in thin films.....	26
Figure (I.18): Schematic diagram of the docking phase.....	27
Figure (I.19): Schematic diagram showing the growth (a) and docking (b) phases of the growth phase of the thin films.....	27
Figure (I.20): Diagram of different growth patterns of thin films.....	27

Chapter II: Experimental study and characterization technique

Figure (II.1): Visible and ultraviolet Spectroscopy.....	34
Figure (II.2): Schematic diagram showing the operation of the UV Vis Spectroscopy device.....	35
Figure (II.3): Diagram illustratin ($\alpha h\nu$) 2 indicatively $h\nu$	37
Figure (II.4): Drawing showing the four probes technique.....	39

Chapter III: Result and discussion

Figure (III.1): Transmittance Ba doped of CuO.....	41
Figure (III.2): Transmittance La doped of CuO.....	41
Figure (III.3): Absorbance Ba doped of CuO.....	42
Figure (III.4): Absorbance La doped of CuO.....	42
Figure (III.5): Band gap of CuO (0%).....	43
Figure (III.6): Band gap of La (1%).....	43
Figure (III.7): Band gap of La (3%).....	43
Figure (III.8): Band gap of La (5%).....	43
Figure (III.9): Band gap of La (7%).....	43
Figure (III.10): Band gap of La (9%).....	43
Figure (III.11): Band gap of Ba (1%).....	44
Figure (III.12): Band gap of Ba (3%).....	44
Figure (III.13): Band gap of Ba (5%).....	44
Figure (III.14): Band gap of Ba (7%).....	44
Figure (III.15): Band gap of Ba (9%).....	44

Figure (III.16): Urbach energy of CuO (0%).....	45
Figure (III.17): Urbach energy of La (1%).....	45
Figure (III.18): Urbach energy of La (3%).....	45
Figure (III.19): Urbach energy of La (5%).....	45
Figure (III.20): Urbach energy of La (7%).....	45
Figure (III.21): Urbach energy of La (9%).....	45
Figure (III.22): Urbach energy of Ba (1%).....	46
Figure (III.23): Urbach energy of Ba (3%).....	46
Figure (III.24): Urbach energy of Ba (5%).....	46
Figure (III.25): Urbach energy of Ba (7%).....	46
Figure (III.26): Urbach energy of Ba (9%).....	46
Figure (III.27): Band gap and Urbach Energy as function of Ba concentration.....	47
Figure (III.28): Band gap and Urbach Energy as function of La concentration.....	47
Figure (III.29): Band gap and Urbach energy as function of Ba,La concentration....	48
Figure (III.30): R sheet and conductivity as function of Ba concentration.....	49
Figure (III.31): R sheet and conductivity as function of La concentration.....	49
Figure (III.32): The conductivity as function of Ba,La percentage.....	50

LIST OF TABELS

Chapter I: Bibliographic research.

Table (I.1): Simple and compound oxides	6
Table (I.2): Some transparent oxides	8
Table (I.3): The band gap energy for some transparent conductive oxides	11
Table (I.4): Some properties of copper.....	12
Table (I.5): Physical properties of Cu ₂ O	13
Table (I.6): Physical properties of CuO.....	14
Table (I.7): Properties of CuO and Cu ₂ O	15
Table (I.8): Properties of Barium	17
Table (I.9): Properties of Lanthum.....	18

Chapter III: Result and discussion.

Table (III.1): Band gap and Uerbach energy of concentration doping.....	47
Table (III.2): R Sheet and Resistivity, Conductivity of Ba,La concentration.....	48

SYMBOLS

TCO	Transparent conducting oxides
E_g	Band gap energy
J	Density
σ	The electrical conductivity
E	Electric field
ρ	Electrical resistance
n	Concentration of charge carriers
q	The elemental electric charge of an electron
μ	Electrokinetic.
R_s	Sheet resistance
d	Film thickness
T	Transmittance
A	Absorption
R	Reflectance
I_t	The transmitted light intensity
I_0	The intensity of the incident light
I_R	The reflected light
I_A	Absorbed light
PVD	Physical vapor deposition
CVD	Chemical vapor deposition
UV	Ultraviolet
α	Absorption coefficient
Δm	The difference in substrate weight
$h\nu$	Photon energy
E_u	Urbach energy
Å	Angstrom
C_p	Specific thermal capacity
CVD	Chemical vapor deposition
CuO	Copper demonoxide
Cu ₂ O	Copper monoxide
PVD	Physical vapor deposition
λ	Wave length
λ_{Eg}	wavelength of the band gap
λ_p	wavelength of plasma
m	Mass of material
C	Solution concentration
M	The molar mass of the substance
V	The volume of the solution

TABLE OF CONTENTS

Dedications
 Thank and acknowledgement
 List of figure..... I-II
 List of tabels..... III
 Symbols..... IV
 General introductuion..... 1

Chapter I: Bibliographic research

I.1 Introduction.....6
 I .2. transparent conducting oxides.....6
 I .2.1 definition of transparent conducting oxide.....6
 I.2.2 the structure of transparent conducting oxides.....6
 I.2.2.1 Transparent conducting oxides in the intrinsic states.....7
 I.2.2.2 Transparent conducting oxides in the doped states.....7
 I.2.3.characteristion of transparent conducting oxides.....8
 I.2.3.1 Electrical properties of transparent conducting oxides.....8
 I. 2.3.1.1. Electrical conductivity.....9
 I. 2.3.1.2. Sheet resistance.....9
 I. 2.3.1.3 Electrokinetic μ9
 I. 2.3.2 Optical properties of transparent conducting oxides.....10
 I. 2.3.2.1 Transmittance.....10
 I. 2.3.2.2 Reflectivitance.....10
 I. 2.3.2.3 Absorption.....10
 I. 2.3.2.4 Absorbance coefficient.....11
 I. 2.3.2.5 Band gap energy.....11
 I.2.4 Applications of transparent conductive oxides.....11
 I.3 copper.....12
 I.3.1 Metal Oxides.....13
 I.3.2 Copper oxide.....13
 I.3.2.1 physical properties of copper monoxide (Cu_2O).....13
 I.3.2.2 Structural properties of copper monoxide.....13
 I.3.2.3 Physical properties of copper demonoxide (CuO).....14
 I.3.2.4 structural properties of copper demonoxide.....15
 I.3.3 Comparison between copper oxide properties.....15
 I.3.4 copper oxide applications.....16
 I.4. doping copper oxide.....16
 I.4.1 Barium.....16
 I.4.2 Barium properties.....17
 I.4.3 Previously study on barium.....17
 I.4.4 Lanthanum.....17
 I.4.5 Lanthanum properties.....18
 I.4.6 Previously study on Lanthum.....18
 I.5. The thin films.....18
 I.5.1.1 Chemical methods.....19
 I.5.1.1.1 Sol Gel Method.....19
 Spin coating.....20
 Dip coating.....21
 I.5.1.1.2 Chemical vapor deposition (CVD).....21
 I.5.1.1.3 Spray pyrolysis technique.....23

I.5.1.2 Physical method.....	23
I.5.1.2.1 Physical vapor deposition.....	23
I.5.1.2.2 Thermal (or vacuum) evaporation.....	24
I.5.1.2.3 Catholytic spray.....	25
I.5.2 The principle of thin film deposition.....	25
I.6 Thin films growth mechanisms.....	26
I.7 Stages of thin film growth.....	26
I.7.1 positioning phase.....	26
I.7.2 docking phase.....	26
I.7.3 growth phase.....	27

Chapter II: Experimental study and characterization techniques

II.1 Introduction.....	29
II.2 Materials and Experimental Methods.....	29
II.2.1 Material used in the experimental work.....	29
II.2.2 The chemical products used	30
II.3 Preparation of the Substrates.....	32
II.3.1 The choice of substrate.....	32
II.3.2 Cleaning of the substrate.....	32
II.4 The solution’s preparation.....	33
II.4.1 Undoped CuO solution.....	33
II.4.2 Doping solution	33
II.4.3 Deposition by method spin coating.....	33
II.4.4 Annealing Thin Films.....	34
II.5 Analysing Methods of the thin films.....	34
II.5.1 Optical properties.....	34
II.5.1.1 Ultraviolet Visible Spectroscopy.....	34
II.5.1.2 Determine the absorption coefficient.....	35
II.5.1.3 Determine the thickness of the samples.....	35
II.5.1.4 The extinction coefficient K.....	36
II.5.1.5 Refractive index n.....	36
II.5.1.6 Determine the band gap.....	36
II.5.1.7 Determine the Urbach energy.....	37
II.5.2 Electrical Characteristics.....	38
II.5.2.1 Four Probes Technology	38

Chapter III: Result and discussion

III.1 Introduction.....	41
III.2 Optical Properties.....	41
III.2.1 Transmittance.....	41
III.2.2 Band gap and Urbach energy.....	42
III.3 Electrical Properties.....	48
References.....	50
General conclusion.....	58
Abstract.....	60

A decorative border with a repeating geometric pattern surrounds the entire page.

GENERAL INTRODUCTUION

General Introduction

Thin films have been historically used for more than a half century in optical coatings, making electronic devices, instrument hard coatings, and decorative parts.

The thin film is a traditional material technology. However, is still being developed on a daily basis since it is a key in the twenty-first century development of new materials such as nanometer materials.

One of interested thin films is transparent conductive oxides (TCO); they have received great attention from researchers because of their dual characteristic of both high transparency in the visible range of light and good conductivity close to that of metals. Such as cadmium telluride and copper oxide (I), zinc oxide (ZnO), indium oxide (In_2O_3)..., etc).

Copper oxide possess two phases of copper oxide I and copper oxide II which are extensively attracting many researcher attention, and it belongs to a p-type semiconductor category and p-n heterojunction of n-type materials. Its p-type conduction arises from the presence of holes in valance band due to the process of doping or annealing. CuO is for promoted for solar energy harvesting because of its smaller optical band gap and it can absorb the whole spectrum of visible light, in addition to bemoore stable in atmospheric air, gas sensors. Copper oxide thin films is the one of the best material in photovoltaic devices such as light emitting diode and electrode materials for battery and catalysis, and it is non-toxicitic, low cost, natural abundance, easy processing.

In order to improve CuO optical and electrical properties, researchers study the possibility of doping using different elements. Many studys shows that Baruim and lanthanum are effective enhance of optical and electrical properties of many semiconductors, thereby the choice of La and Ba for doping copper oxide in the present study.

The objective of this work is the development of copper oxid thin films doped whit baruim and lanthanum deposited on a glass substrates by spin coating, and the study of the influence of the Ba, La dopant on CuO thin films optical and electrical properties.

The dissertation is divided in three chapters in addition to the general introduction and conclusion:

In the first chapter, we present a background about transparent conductive oxides, kinds, propeties and applications, a particular kind, application and then we talk about of definition technique of growth principle of thin films and principle deposition focusing on copper oxide. Then we mention the dopent we used. Then we talk about the previous studies La and Ba.

The second chapter presents the experimental details and characterization techniques, which were used in this study. It includes knowledge about the chemical components and methods involved in the preparation and characterisation of doped and undoped CuO thin films.

The third chapter is devoted to study the influence of the Ba, La doped on CuO thin films optical and electrical properties. It contains summarizes the results of these study and discussion.

Finally, we end with a general conclusion displays the most important results obtained in this work.

Chapter I

Bibliographic research

I.1 Introduction

In this chapter, we will present a background the properties of transparent conductive oxides, kinds and applications, focused on copper oxide on which we investigated. Then we mention the dopent we used. Then we studied the thin films in terms of definition and techniques growth, principle of deposition.

I.2. Transparent conducting oxides

I.2.1 Definition of transparent conducting oxide

Transparent conducting oxides is a semiconductor compound with oxygen, and has a certain transparenc, Such as copper oxide (CuO), nickel oxide (NiO) and zinc oxide (ZnO). [1]

Transparent conductive oxides they have white energy separation, and have good conductivity and they have a wide energy separation and have a good electrical conductivity and they are transparent in the visible range. [2]

They are metallic oxides consisting of metal atoms and oxygen atoms and are symbolized by M_xO_y , where M represents the chemical symbol for metal, and O the chemical symbol for oxygen and x, y are natural numbers. [3] Metal oxides may be simple, meaning they contain one metal, or they may be complex, meaning they contain more than one metal. Table (I-1) shows some examples of these oxides. [4]

Table (I.1): Simple and compound oxides.

simple oxides	CuO	ZnO	NiO
compound oxides	BaTiO ₃	CdInO ₄	Cnd ₂ SnO ₄

I.2.2 The structure of transparent conducting oxides :

Materiels generally classified in terms of their electrical conductivity into three classes: conductors, semiconductors, and insulators. [5]

- Conductor: An overlap between the transport band and the valence band, which allows free electrons to move.
- Semiconductors: A forbidden band separates the valence and transport bands.
- Insulators: Have an energy gap greater than 5ev.

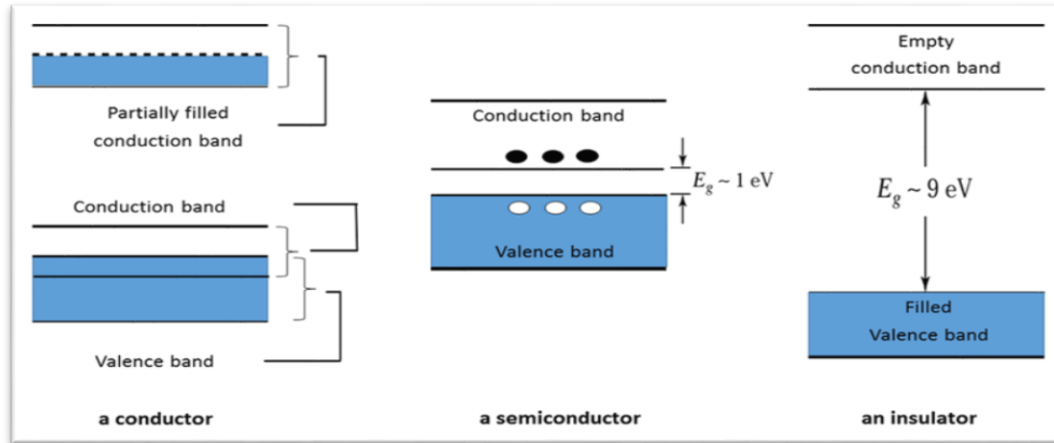


Figure (I.1): State conductor, semiconductor and insulator diagram.[6]

I.2.2.1 Transparent conducting oxides in the intrinsic states

Pure semiconductors without impurities are called self-semiconductors from an ideal point of view, the valence band will be completely filled with electrons, while the transport band will be completely empty of electrons at zero temperature, and for this reason, semiconducting materials are considered insulators in this states. [7]

On the other hand, a transparent carrier oxide is freestanding or pure when it satisfies this condition ($n = p = n_i$).

Which represents self-focusing, and in order to improve the electrical conductivity, the number of charge carriers is raised by impurities sites for donors and takers, which is related to the parity of the grafts or cultivation sites (donors or takers), and we obtain the conductivity of type (N) or type (p)[8]. The impurity atoms in the crystal lattice exist in two states, either they occupy atomic sites of the lattice and are known as substitutional impurities, or between atomic sites and are known as interstitial impurities. [9]

I.2.2.2 Transparent conducting oxides in The doped states

The conductivity of pure semiconductors can be increased by adding trivalent or pentavalent impurities to the pure semiconductor material carefully and at a controlled rate. The semi-carrier is divided into two types, according to the impurities added to it

- Type n: In this type of transparent conductive oxides, electrons are the majority charge carriers, and in the pure state most of the known TCOs are of type-n-, and thus are most commonly used in practical applications.
- Type p: Many applications require a type-p- transparent conductive oxide. Therefore, there have been large studies in the recent period in order to make this type of (TCO). An advantage of this type is that holes are the predominant charge carriers. Table (I-2) shows some transparent oxides .[10]

Table (I.2): Some transparent oxides. [3]

TCO type n	TCO type p
SnO ₂	PdO
Ta ₂ O ₅	Ag ₂ O
In ₂ O ₃	BaTiO ₃
TiO ₂	TeO ₂
ZnO	NiO
WO ₃	La ₂ O ₃

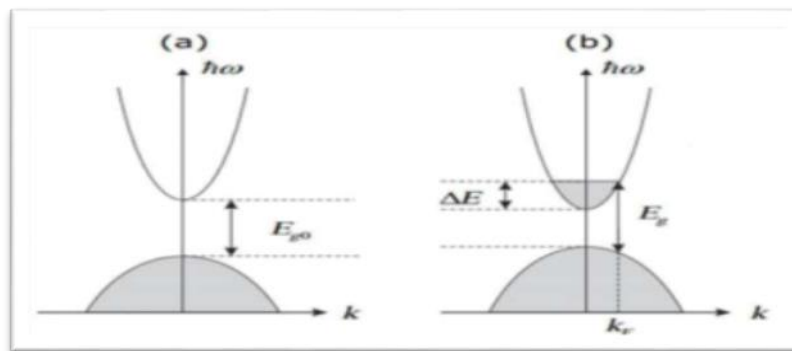


Figure (I.2): Energy band in the pure (a) and doped state (b). [11]

I.2.3 Characteristic of transparent conducting oxides

Transparent conducting oxides are considered semiconductors, and they possess a large number of characteristics that make them extremely important in scientific applications, and the most prominent of these characteristics are the following: [12]

- High transparency at visible wavelengths (400 - 800 nm).
- Its electrical conductivity increases with increasing temperature, and this characteristic is one of the characteristics that distinguishes it from other conducting materials, and at low temperatures it becomes semi-insulating.
- The semiconductor has a high sensitivity that may lead to an increase in its conductivity when it contains impurities or defects.
- They can result in one type of charge carrier and this means the decrease or disappearance of the other type.

I.2.2.1 Electrical properties of transparent conducting oxides

We explain the specific electrical properties of TCO films by the basic theory of electrical transport phenomena in thin film semiconductor.

Transfer phenomenon is the movement of charge carriers under the influence of a charge internal or external domain. In the case of a zero electric field, the electron field in a

semiconductor are in an equilibrium, which arise as a result of the interaction of electrons with lattice defects (impurity atoms, refractories Grid vibrations "phonons").

If an electric field E is applied to a material, an electric current will flow, whose density J , usually expressed in A/m^2 by:

$$J = \sigma E \quad (I.1)$$

Where: σ is called the electrical conductivity of a material usually expressed in Siemens per cm ($S.cm^{-1}$).

1. 2.2.1.1. Electrical conductivity:

Semiconductor physics for large energy separation describes and prepares the electrical properties of transparent conductive oxides. The conductivity is the most important quantity indicating these properties, which is expressed by the symbol (σ), and its unit is $(\Omega.cm)^{-1}$. The conductivity is determined by the relation [13]:

$$\sigma = n q \mu \quad \text{or} \quad \sigma = p q \mu \quad (I.2)$$

σ : electrical conductivity.

n, p : concentration of charge carriers.

q : The elemental electric charge of an electron.

μ : Electrokinetic.

Resistivity ρ is also known as the reciprocal of conductivity [12] by the relation :

$$\rho = \frac{1}{\sigma} \quad (I.3)$$

ρ : electrical resistance ($\Omega.cm$).

σ : electrical conductivity ($\Omega.cm$)⁻¹.

1. 2.2.1.2. Sheet resistance:

Transparent conductive oxides are prepared and used in the form of thin films. One of its important electrical properties is the sheet resistance R_s . It is expressed as the ratio of the resistance over the thickness of the oxide film, and its unit is Ω . [14]

$$R_s = \frac{1}{\sigma d} \quad (I.4)$$

R_s : the sheet resistance of the sample (Ω).

d : film thickness (cm).

1. 2.2.1.3 Electrokinetic μ :

The mobility of charge carriers (electrons and holes) is an important and influential factor in the electrical conduction phenomenon, so that an increase in this factor leads to the improvement of the electrical properties of the transparent conducting oxide.

Mobility depends mainly on the spread of charge carriers in the material crystal lattice. [15]

I. 2.2.2 Optical properties of transparent conducting oxides

The importance of studying the optical properties of transparent conducting oxides lies in its wide exploitation in many applications (optical fibers and reflective coatings, which require accurate knowledge of their optical constants over a wide range of wavelengths). [17]

The optical properties of materials are embodied in three basic phenomena: transmittance, reflectivity and absorption. We express these phenomena by the following quantities: [20]

Permeability or penetration coefficient T, reflectivity or reflection coefficient R, absorbance A and absorption coefficient α .

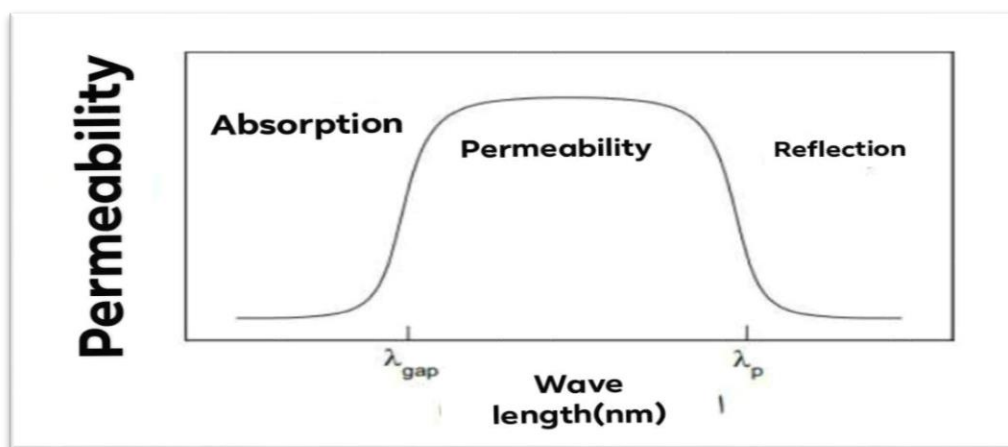


Figure (I.3): Spectrum of TCO (reflectance, transmittance, absorption). [21]

I. 2.2.2.1 Transmittance:

Transmittance symbolizes T is the ratio of the transmitted light intensity I_t and the intensity of the incident light I_0 , given by the following relation:

$$T (\%) = \frac{I_t}{I_0} * 100 \quad (I.5)$$

The transmittance spectrum is highly dependent on the magnitude of the energy levels, which in turn is related to the chemical composition, crystalline structure as well as film thickness, temperature, and atom doped kind.

I. 2.2.2.2 Reflectivity:

Reflectivity named R. It is the ratio of the intensity of the reflected light I_R and the intensity of the incident light I_0 . The following relation gives it: [12]

$$R (\%) = \frac{I_R}{I_0} * 100 \quad (I.6)$$

I. 2.2.2.3 Absorption:

Absorption A. it is the ratio of the intensity of the absorbed light I_A and the intensity of the incident light I_0 . It is given by the following relation: [18]

$$A (\%) = \frac{I_A}{I_0} * 100 \quad (I.7)$$

The overall flow is conserved .We can write:

$$I_A + I_T + I_R = I_0 \quad (I.8)$$

$$T + R + A = 1 \quad (I.9)$$

I. 2.2.2.4 Absorbance coefficient :

It is denoted by a symbol α .In order to determine it, we use the Beer_Lumber law [22], which allows the connection between the permeable flow and the thickness of the film thickness.

I. 2.2.2.5 Band gap energy:

The most transparent conductive oxides is characterized by the energy separation the TCO large band gap between (3.01-4.6 ev) and varies according to the technique used in sedimentation and the experimental conditions. It also depends on the type of compound used. The table shows the band gap for some transparent conductive oxides. [14]

Table (I.3): the band gap energy for some transparent conductive oxides

TCO	The band gap (ev)	References
SnO ₂	4.2-3.6	
ZnO	3.3-3.2	[17]
NiO	4 -3.6	
ITO	4.2	[18]

I.2.4 Applications of transparent conductive oxides

They are widely used because many applications recourse this combination between of optical transparency with electrical conductivity [23]

1. Laser cavity.
2. Mirrors and photoelectricity.
3. Electromagnetic protection.
4. Gas sensor.
5. Heat-reflecting windows (buildings and ovens).
6. Touch control screen.
7. An organic diode.
8. Solar cells as the front contact through which light must pass to enter the cell solar.
9. Flat screens.



Figure (I.4) :Applications of transparent conductive oxide.[24]

I.3 Copper

Copper is a chemical element that is included in the composition of many alloys. For example, it is added to gold to give it hardness, a well-known transition metal characterized by an important conductivity. This makes it important for electrical applications such as conductive coatings, and is used especially in microelectronics [25]. Some properties of copper are shown in the Table (I.4).

Table (I.4): Some properties of copper. [26]

The chemical formula	Cu
Molar mass	63.54 g/mol
Point vaporation	1273 °C
Volumetric mass	8.935(g.cm ⁻³)
Point boiling	2855 °C

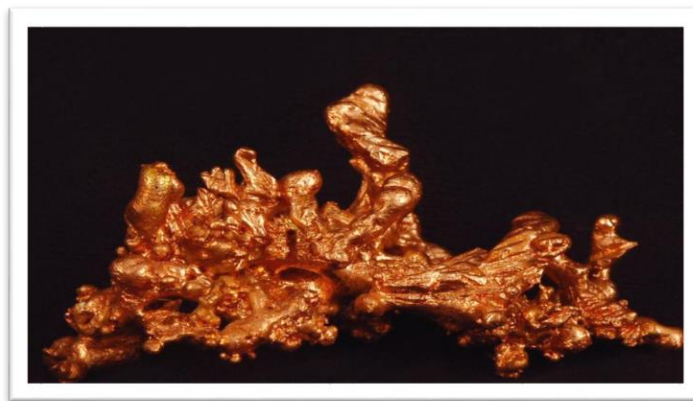


Figure (I.5): Copper metal.[27]

I.3.1 Metal oxides

We can classify metal oxides either according to the nature of conduction with electrons and holes (type n or type p), or depending on whether they are simple or compound, which it gives them an important role in different fields such as, microelectronics. Knowing the structural and electronic properties of oxides is a very important step to achieve more efficient materials.

Metal oxides are heterogeneous catalysts and are used for acid-base and redox reactions. Certain groups of metals, especially transition metals, have attracted a lot of attention because of their properties.

I.3.2 Copper oxide

There are two phases of copper oxide

- Copper monoxide.
- Copper demoxide.

I.3.2.1 physical properties of copper monoxide (Cu₂O):

Copper monoxide is a reddish solid with a density of 6.0 g/cm³. Its melting point is 1235 °C and it does not dissolve in water [28]. Unlike most other metal oxides, Cu₂O is a p-type semiconductor [29].

The energy gap is (1.9~2.6) eV [28, 26] and can be prepared by thermal oxidation [30, 31], anodic oxidation [32], spray deposition [33] and electrochemical deposition [34]. The electrical properties of copper oxide films vary to a large extent with the methods of preparation, which result from the great variation in Cu₂O films resistivity [29]. Moreover, it exhibits interesting properties such as rich excitation architecture, which allows the observation of a well-defined series of exciting properties in the absorption and photoluminescence spectra of Cu₂O in bulk [28]. Other physical properties of the material are given in the following table:

Table (I.5): Physical properties of Cu₂O [29]

Density	6.0 g/cm ³
Molecular weight	143.092 g/mol
Point melting	1235°C
Cu-O bond length	1.85 Å
O-O bond length	3.68 Å
Cu-Cu bond length	3.02 Å
Band gap energy at temperature ambient (E _g)	2.09 eV
Specific thermal capacity (C _p)	70 J/(K mol)
Thermal conductivity (k)	4.5 W/(K m)
Relative Permittability	7.5

I.3.2.2 Structural properties of copper monoxide

Cu₂O has a simple cubic structure. It is described as a cubic cell with a lattice constant $a = 0.427$ nm.

In the lattice, each copper atom coordinates with two oxygen atoms and each atom the oxygen atom is surrounded by four copper atoms.

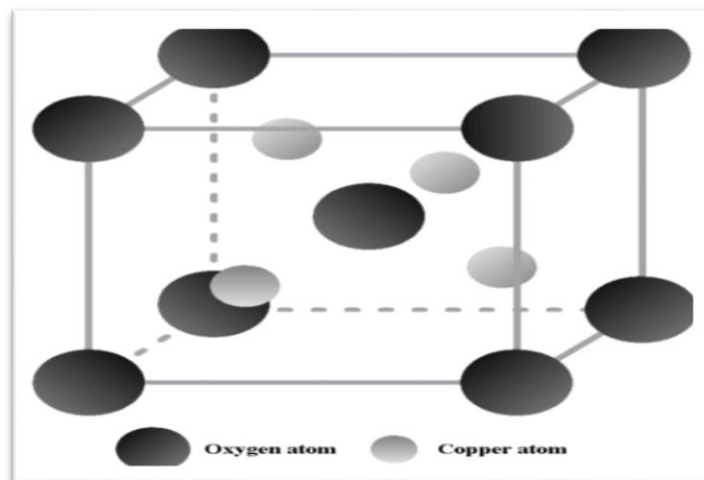


Figure (I.6): Crystalline structural of Cu₂O.[35]

I.3.2.3 Physical properties of copper demonoxide (CuO)

Copper demonoxide is a black solid with a density of 6.4 g/cm³. Also has a high melting point

(1330 °C) and is insoluble in water as well Copper oxide, which is a p-type semiconductor. It has a wide band gap energy (1.4 eV to 1.9 eV). [36, 37] Many methods can be used to prepare copper oxide such as:

Thermal oxidation, spraying and electrochemical deposition. [38]

Other physical properties of the material are shown in the following table:

Table (I.6): Physical properties of CuO. [29]

Density	6.4 g/cm ³
Molecular weight	79.55 g/mol
Point melting	1330°C
Cu-O bond length	1.95 Å
O-O bond length	2.62 Å
Cu-Cu bond length	2.90 Å
Band gap energy at temperature ambient (E _g)	1.4eV
Relative Permitability	12.0

The refractive index of CuO in the form of a thin film and its absorption coefficient differ according to the production conditions.

- The refractive index is between (1.2-3) depending on the deposition method.[39]
- Absorption coefficient in the visible field and a good range of stability.[40]
- Super conductivity at high temperatures.[41]

I.3.3 structural properties of copper demonoxide :

Copper monoxide forms a more complex tenorite crystal. It is are Monoclinic contains four CuO molecules. These lattice constants are: $a = 0.47 \text{ nm}$, $b = 0.34 \text{ nm}$, $c = 0.51 \text{ nm}$ and $\beta = 99.54$.Each atom has four neighbors from the other kind. In the (110) level, each copper atom is bonded to four planar O atoms, at the corner of a rectangular parallelogram approx ,the O atom is coordinated into four atoms copper to form a deformed tetrahedron [29].

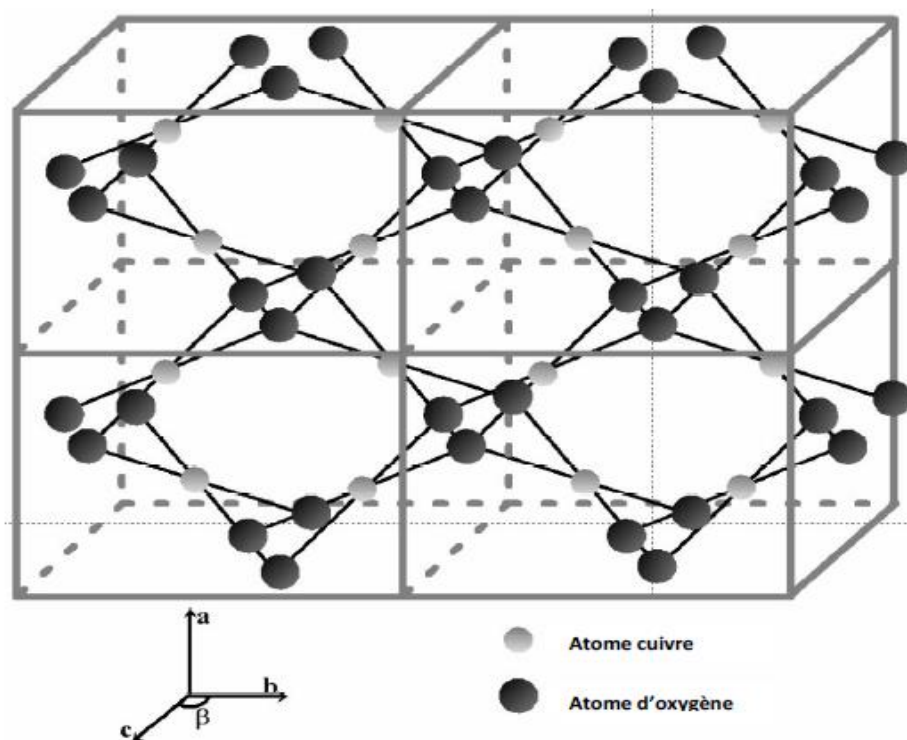


Figure (I.7): Crystalline structural of CuO. [35]

I.3.4 Comparison between copper oxide properties

We mention some properties of CuO and Cu₂O:

Tabel (I.7): Properties of CuO and Cu₂O. [26,28,36]

		CuO	Cu ₂ O
Chemical properties	Molecular weight	79.55 g/mol	143.092 g/mol
	boiling temperature	2000 C°	1800 C°
	Density	6.4 g/cm ³	6.0 g/cm ³
optical properties	the color	Black	brown red
Electrical properties	energy gap	(1.4- ,19) ev	(1.9- 2.6) ev

I.3.5 Copper oxide applications

Copper oxide has become of interest in many applications including :[42]

- ❖ Gas sensors.
- ❖ Energy applications (used in photovoltaic complexes).
- ❖ Pigment to produce blue lights in fireworks.
- ❖ Participates in the production of Schweizer reagent solutions.
- ❖ Abrasive in optics and in the manufacture of some electric batteries.
- ❖ Substitute iron oxide in thermite to make it a low-energy explosive rather than an incendiary.

I.4. Doping copper oxide

Doping of copper oxide is the penetration of outer atoms into the intrinsic (pure) state that are not of the same type of material. They take the position of some of the original atoms and bond with their neighbors and form new energy levels which lie in the copper oxide energy interval and are called impurities. Therefore, doped copper oxide is classified into two main types, according to the type of atoms added.[43]

P type doping This type of defect is called the positive type because the majority of charge carriers are holes and the minority are electrons (taking on atoms). To obtain this type, defectes are added to the copper oxide, this tayp of defect atoms formns an separation energy very close to the valence band.[43]

N type doping This type of defect is called the negative type because the majority of charge carriers are electrons and the minority are holes .To obtain this type, defectes are added to the copper oxide, this tayp of defect atoms formns an separation energy very close to the conduction band

I.4.1. Barium

Barium, is a chemical element with symbol Ba and atomic number 56. It is a soft, silvery-white metal of alkaline earth metals. Its salts are used in making glass, paints, and fireworks. Barium is never found in a pure state.

It combines easily with many other chemicals to form compounds with many uses in the field of industry, such as Barium carbonate (BaCO_3) is a toxic substance like all water-soluble barium compounds. [44] Barium titanate (BaTiO_3) is used in sonar detection and other electrical devices.

- Barium Nitrate $\text{Ba}(\text{NO}_3)_2$ The signal lights flash green
- Barium ferrite ($\text{BaO} \cdot 6\text{Fe}_2\text{O}_3$) in the magnet industry



Figure (I.8) :Barium metal.[45]

I.4.2. Barium properties

Explain the general properties of Barium

Tabel (I.8): Properties of Barium. [46]

Element symbol	Ba
Atomic number	56
Element status	Solid
Point melting	1000 k (727 C ° - 1341° F)
Point boiling	2170 K (1897 °C -3447 °F)
The group	2

I.4.3. Previously study on barium

- "S Santhosh Kumar Jacob, S Yahia ", in this work barium (Ba) doped cuprous oxide (Cu₂O) films were prepared using spray technique by taking different doping concentration (0%, 3%, 5%, and 7%) of Ba. The Optical analysis was revealed the decreasing in band gap with increasing barium doping concentration.[47]
- The two researchers "Ashour Mohammed , Ahmed Mohammed Shaban", studied the preparation of CuO and Ba-doped CuO thin films on glass substrates using a simple ion cascade adsorption and reaction (SILAR) method for hydrogen production. The band gap of the CuO film in pure form was set to be 1.63 to 1.87 eV after incorporation of 6% Ba. CuO 2% Ba-doped films showed high catalytic performance as a photoelectrode for efficient hydrogen generation.[48]

I.4.4. Lanthanum

Lanthanum is a chemical element belonging to rare earths. Its atomic number is 57. In the classical model, lanthanum contains 1 electron in the 5d subshell (or subshell) and 2 electrons in the 6s subshell. In this calculation, lanthanum is considered to have a 3 valence atom. group 3 but outside the periodic representation of groups represents the bulk of the chemical elements in the deterministic quantum model the lanthanum instead has +2 electrons in the 4f sublevel in this calculation the lanthanum could be its maximum valence 5. The lanthanum is a silver-grey metal, malleable, ductile, soft enough to be cut with a knife, it oxidizes in air and water.



Figure (I.9) : Lanthanum metal.[49]

I.4.5. Lanthanum properties

Explain the general properties of Lanthanum:

Table (I.9): Properties of Lanthanum. [50]

Element symbol	La
Atomic number	57
Element status	solid
Element description	lanthanide
The group	3
Point of melting	1193 K (920 °C, 1688 °F)
Point of boiling	3737 K (3464 °C, 6267 °F)
Point of evaporation	400 kJ/mol

I.4.6. Previously study on Lanthum

- " Naveena, & Bose, A. C ", in this work studied the properties analysis of unsaturated and La doped CuO (LCO) thin films as a potential absorber for photovoltaic application. A chemical spray pyrolysis technique was used to prepare the dissociated thin films and LCO with different weight ratios (2, 4, 6, 8 and 10). From the UV spectra, La doped films show high optical absorption and the band gap value decreases from 1.62 eV to 1.49 eV up to 6 wt%.[51]
- "Arslan Masood ,....., and Muhammad Isa Khan" photocatalysis is a promising technique for remediation and decontamination of waste water. This research work focuses on the synthesis of pure and lanthanum (La)- (1, 2 and 3 wt%) doped copper oxide nanoparticles (CuO-NPs) via a simple, cost effective and efficient sol-gel process. Quite interestingly, doping of rare earth element La has reduced the particle size , the band gap and electron hole recombination rate is also reduced. Band gap has shifted towards visible region (3.13ev to 2.85 ev) which makes it an excellent material for photocatalysis.[52]

I.5 The thin films

The term thin films is used to describe one or more layers of material atoms that are less than one micrometer, or several nanometers thick, and because they are thin and brittle (easy to break) must be deposited on a solid material such as glass, silicon, and polymers [53]

The primary difference between thin and thick film deposits is the thickness of the deposited layers. A thin film of a given material is an arrangement of the elements of that material in two dimensions with a thickness of the third dimension. We ignore the role of boundaries (surfaces) in some properties, but in the case of thin films the opposite is the effect of surfaces on properties. Often, the greater the decrease in thickness, the greater the effect of surfaces on physical properties [54].

The second major advantage of layering is that thin film condensation is always obtained regardless of the method used.

Thin films are also distinguished by their large surface area, and their physical and chemical properties differ from the properties of the material they are composed of, and the change of their optical and electrical properties depends on the methods and conditions of their preparation, such as changing the type or percentage of impurities added or changing the temperature of the base. [55]

I.5.1 Thin film deposition methods

With the increase in scientific and technological development, the techniques used in the preparation process varied, and this was due to the great expansion in the uses of transparent conductive oxides as thin films, which prompted researchers to devise and develop different methods in order to prepare these membranes. , and the use of only one method depends on several factors, the most important of which [56]

The type of material used ,The field of using the prepared membranes, preparation cost.

Where some methods are suitable for certain materials and not suitable for other materials, some are easy, and others are more complex or less available. These methods are classified into two main categories according to the sedimentation methods: physical and chemical

I.5.1.1 Chemical methods:

I.5.1.1.1 Sol gel method:

This technology has known significant developments over the past three decades. It is a wet chemical synthesis technique for the preparation of oxide gels, glass, and ceramics at low temperature [57]. The basic principle of this technique is to convert the solution into a gel. This is based on a set of chemical reactions, as a first stage, the powders of the raw material are dissolved in a solution that consists of water, acid, base or alcohol, so we have a sol solution as a result of the dissolution reactions, and after removing the water from the sol, which dries quickly, a gel is formed for us.

The sol-gel method is effective for surface modification of the substrates. Obtaining a high surface area and essentially stable surfaces is the most important advantage of the sol-gel method. The chemical and physical properties of the materials acquired by the sol-gel method are related to the applied experimental conditions [58]. It is possible to manufacture ceramic or glass materials in a variety of shapes, such as ultra-fine powders, fibres, thin films. Since then, powders, fibers, thin films, and monolithic optical lenses have been made from sol-gel glass. [59]

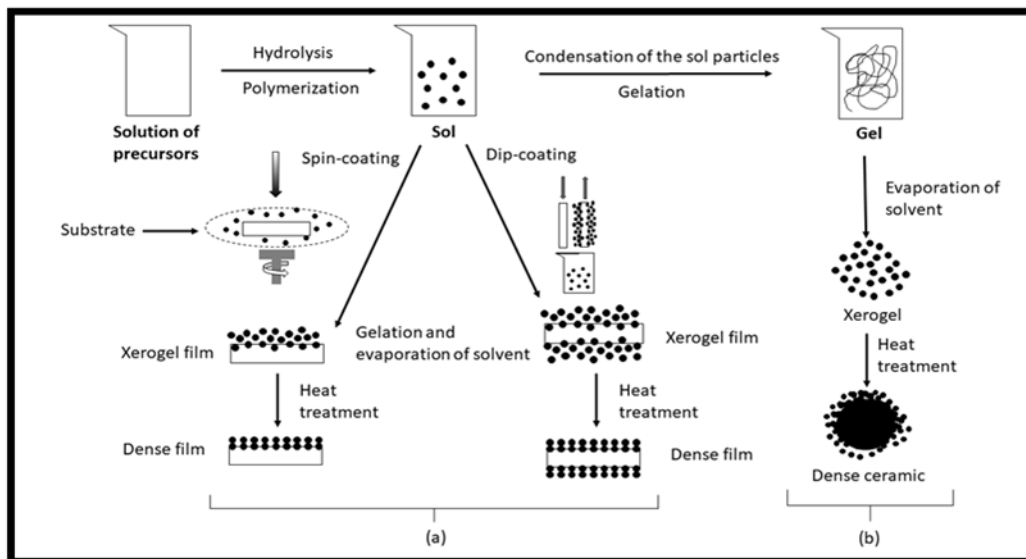


Figure (I.10): Synthesis of various forms of materials by the sol-gel method.[60]

Spin coating:

Spin coating is used for the thin films' fabrication to deposit uniform coating of organic materials on flat surfaces [61]. This method consists of centrifuging a solution deposited in excess on a substrate. It has the advantage of being easily implemented, and it provides very good results on flat substrates of small areas (a few cm^2) for moderate investments. We can distinguish four main steps in this technique, as presented in Figure

- The deposition of the solution.
- At the start of the rotation, the acceleration phase causes the liquid to flow towards the outside of the support. The constant speed rotation allows the ejection of excess liquid in the form of droplets and the reduction of the thickness of the film uniformly.
- Evaporation of the more volatile solvents, which enhances the reduction in the thickness of the deposited film. [62]

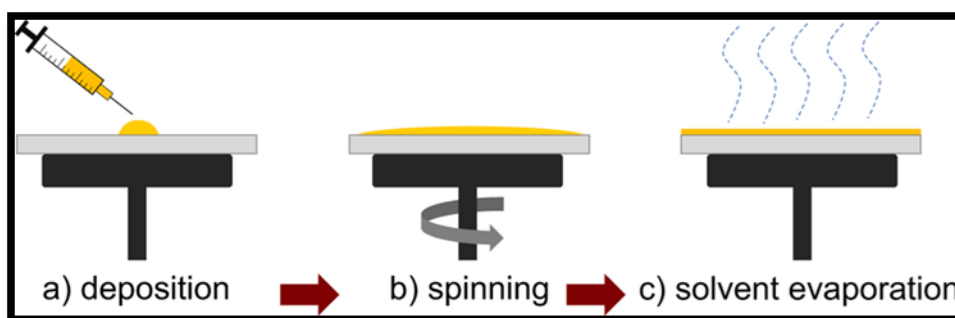


Figure (I.11): Steps of spin coating.[63]

Final film thickness and other properties will depend on the nature of the fluid material (viscosity, drying rate, percent solids, surface tension...) and the parameters chosen for the spin process. Factors such as final rotation speed, acceleration, and fume exhaust affect the properties of the coated films. [64]

Among the advantages of this technology:

- A small amount of sedimentation liquid is sufficient to wipe the entire surface of the sample.
- Easy access to crisis equipment.
- The sedimentation mechanism is very fast.
- It is used to deposit different successive layers on the same bond.
- High purity.
- Low temperature.

Among the disadvantages of this technique:

- The problem of regularity of thickness appears in large supports.
- Specific properties of the solven.

Dip coating:

The dip coating technique can be described as a film deposition process [59]. This simple, flexible and cost-effective coating technique allows the application of a variety of oxide and inorganic-organic hybrids and materials. [65]

Dip coating has been widely used for research purposes due to it being a convenient and easy-to-use approach. However, the quality of coatings produced in this manner is inconsistent. Therefore, it is an unsuitable approach for industrial processes. Critical parameters that can affect coatings produced by dipping. Dip coating consists of five steps, including immersion; start deposit Drainage; Vaporize as shown in figure

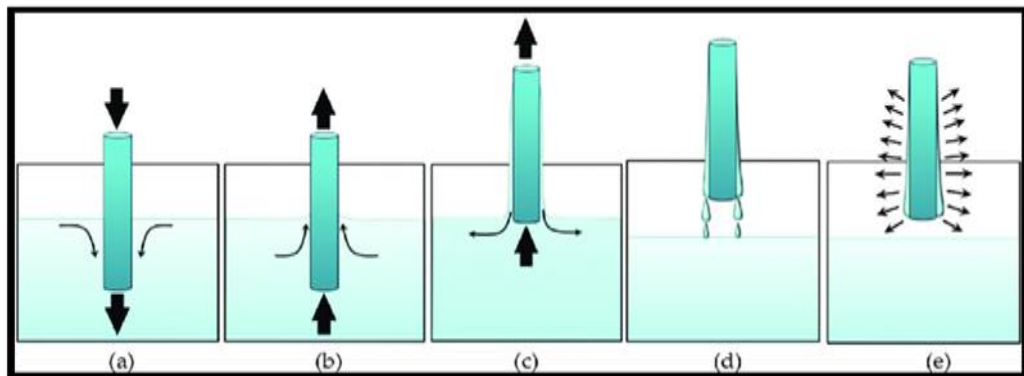


Figure (I.12): Dip-coating stages: (a) immersion; (b) start-up; (c) deposition; (d) drainage; (e) evaporation.[66]

1.5.1.1.2 Chemical vapor deposition (CVD) :

CVD is a thermodynamically complex process consisting of chemical reactions under specific conditions such as temperature, pressure, reaction rates, momentum, mass and energy transfer. Many process factors and the chemical interaction between the reactant and substrate are responsible for the quality of the films produced during CVD, and the film quality can be

controlled and modified using an appropriate set of process parameters such as: flow rates, pressure, temperature, concentration of chemical species, and reactor geometry [67].

This technique can be summarized in five steps:

- Transfer of reactive gas species (or species) to the substrate.
- Adsorption of the reactants on the surface.
- Surface interaction and membrane growth.
- Absorption of volatile by-products.
- Transport and evacuation of gaseous products to the reactor outlet.

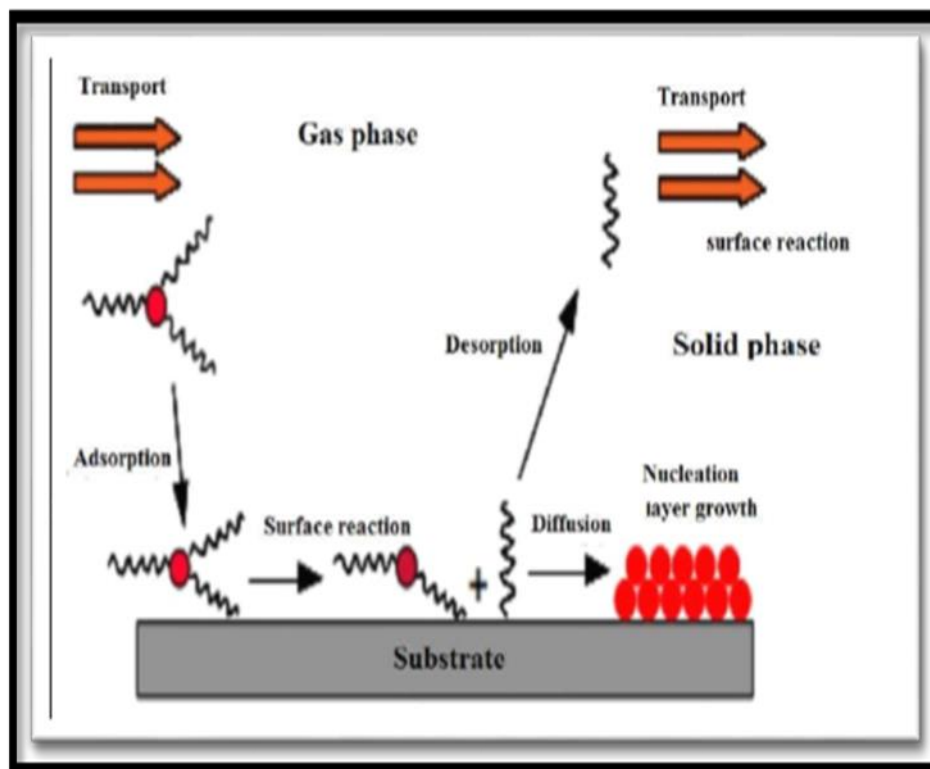


Figure (I.13): The main steps of deposition by the CVD method. [62]

Several CVD type techniques can be given :[68]

- LPCVD: (Low Pressure Chemical Vapor Deposition) Low Pressure Deposition.
- MOCVD: (Metal-Organic CVD) Use of a metal-organic precursor.
- PACVD: (Chemical Deposition of Vapors by Plasma) The role of this method is to improve and activate the reaction speed allowing the material to be deposited at a low temperature. The disadvantage of this method is the possibility of a plasma interaction with the substrate resulting in a homogeneous film.
- APCVD: (Atmospheric Pressure Chemical Vapor Deposition) deposition under atmospheric pressure.

1.5.1.1.3 Spray pyrolysis technique :

The spray pyrolysis is a simple technique based on chemical vapor deposition process (CVD). In this technique, the precursor of the material to be deposited is in solution and sprayed onto a heated substrate using air as carrier gas. [59]

Typical spray pyrolysis equipment consists of an atomizer, precursor solution, substrate heater, and temperature controller. The following atomizers are usually used in spray pyrolysis technique: air blast (the liquid is exposed to a stream of air), ultrasonic (ultrasonic frequencies produce the short wave length necessary for fine atomization), and electrostatic (the liquid is exposed to a high electric field). [69]

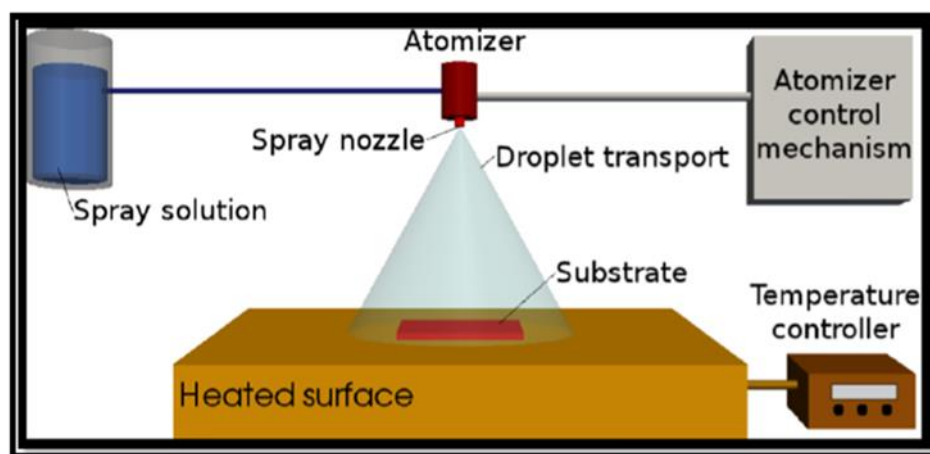


Figure (I.14): General schematic of a spray pyrolysis deposition process. [70]

1.5.1.2 Physical method

Physical methods can be used to precipitate a range of materials, including transparent conducting oxides, and there are several methods, including:

1.5.1.2.1 Physical vapor deposition:

This technique relies on the process of thermal evaporation of materials under low pressure, and it has several advantages compared to the chemical vapor deposition method (CVD).

For the most used vapors: evaporation method under vacuum, cathodic spraying[71] extraction (laser fragmentation) .The thermal evaporation method is one of the suitable methods through which it can be obtained Distinctive properties of the formed membrane, as the membranes are prepared by placing the material to be evaporated in a very low pressure basin less than (10^{-2} Torr) and sometimes up to (10^{-9} Torr), This method is suitable for evaporating most metals and semiconductors [72]

PVD processes are environmentally friendly vacuum deposition techniques consisting of three fundamental steps:

- Vaporization of the material from a solid source assisted by high temperature vacuum or gaseous plasma.
- Transportation of the vapor in vacuum or partial vacuum to the substrate surface.

- Condensation onto the substrate to generate thin films [72].

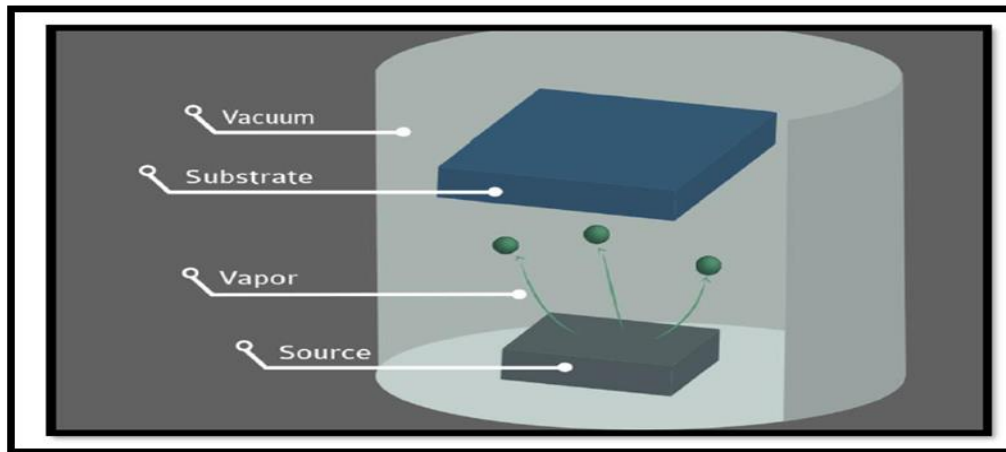


Figure (I.15): Physical vapor deposition method. [73]

Fumigation, spraying in all its forms, and laser ablation [62]. Are essential techniques of physical vapor deposition (PVD). Evaporation and thermal (or vacuum) evaporation are the most common PVD techniques. [74]

1.5.1.2.2 Thermal (or vacuum) evaporation:

An older method of deposition used to generate and build up thin films on the surface of solids is thermal (or vacuum) evaporation. The procedure is still useful in today's environment and is widely used in laboratories and institutions for thin film deposition.

This method is done by evaporating the material to be deposited by heating it to suitable high temperatures inside a vacuum chamber and under pressure ranging from

Pa (10^{-4} and 10^{-3}). [75] After evaporation, this material condenses and is deposited on the surface of the substrate, forming a thin film. Methods include Joule action (for easily soluble substances) or heating with a high-energy condensed electron beam. (refractory materials), and the speed of deposition of these materials depends on:

- source temperature.
- The distance between the evaporated material and the substrate
- The best deposition result is when the surface is perpendicular to the vapor flow

These are the basic sequential steps of thermal or vacuum evaporation:

- The vapor is created from subjecting the target material to very high temperature by subliming or boiling.
- The ejected vapor from the target material is transported to the substrate through a vacuum.
- Condensation of the vapor takes place to form a solid thin film on the substrate's surface, and further repeatability of the deposition cycles result in thin film growth and nucleation. [67]

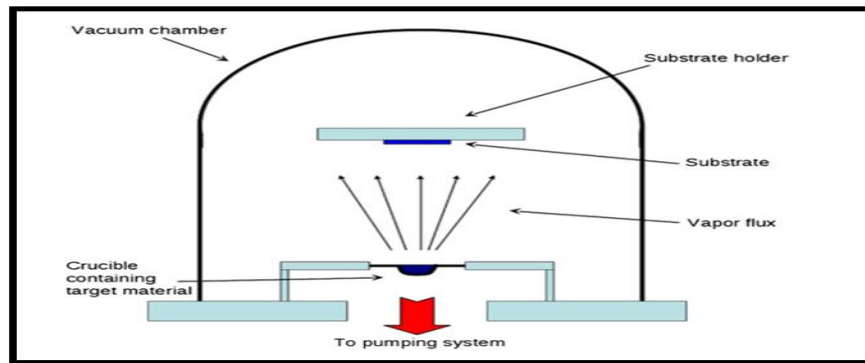


Figure (I.16): Thermal evaporation in a schematic. [76]

1.5.1.2.3 Catholytic spray:

This technique takes place in placing the substrate inside a chamber with an inert gas and low pressure, the latter causing Charge discharge and discharge play an important role in the ionization of gas atoms, and the resulting ions are accelerated by a potential difference (3 and 5 kv) To fall on the cathode with great energy under the influence of the ions of the accelerating gas falling on the cathode, the atoms are removed from it and placed on the surface of the substrate. We can add the gas of the other with the inert gas if we want to precipitate a compound with the extracted self and the added gas, where the added gas interacts with the extracted atoms to form a compound that is placed on the substrate and precipitates .[77]

I.5.2 The principle deposition of thin film

To deposit a thin film on the surface of a solid substrate, the particles of the film-forming material must pass through a carrier medium such that this medium is in direct contact with the substrate. Either ions or molecules, and it may be atoms, as for the transport medium, it may be liquid, solid, gaseous, or vacuum.[78]

- The state of the transmission medium is liquid: This method is relatively easy. As an example, we mention the method adopted in our study, which is liquid gels.[78]
- The state of the transport medium is solid: In this case, the substrate is in contact with the material to be deposited, but only the particles spread out on the substrate to form a thin film. It is often very difficult to obtain thin films by particle contact.[52]
- The state of the transport medium is gaseous or vacume: this medium is more used in various sedimentation methods, such as many techniques and methods are used to achieve these purposes. [79]

I.6 Thin films growth mechanisms

Thin films are deposited on a substrate by thermal evaporation, chemical decomposition, or evaporation of the source material by irradiation of active species or photons. Any thin film deposition process involves three main steps:

- Production of sedimented materials that differ in terms of types (atoms, molecules or ions).
- Transfer of the material from the source to the substrate.
- Condensation and growth of a film on the substrate, either directly or by means of a chemical and/or electrochemical reaction, to form a solid precipitate. The thin film forms according to the thermodynamic parameters of placement and the condition of the glass surface

I.7 Stages of thin film growth

I.7.1 Positioning phase

This phenomenon accompanies the changes that occur in the state of matter, and is represented in the emergence of a turning point for the evolution of the state of matter into a new physical or chemical structure, and the conversion of these materials into aerosols and adhesion to the surface. from the substrate and physically adsorbed by the surface of the substrate so that the ions of this substance react with the substrate and form what are known as groups also called fixed nuclei , This figure represents the placement of ions in the thin films.[80]

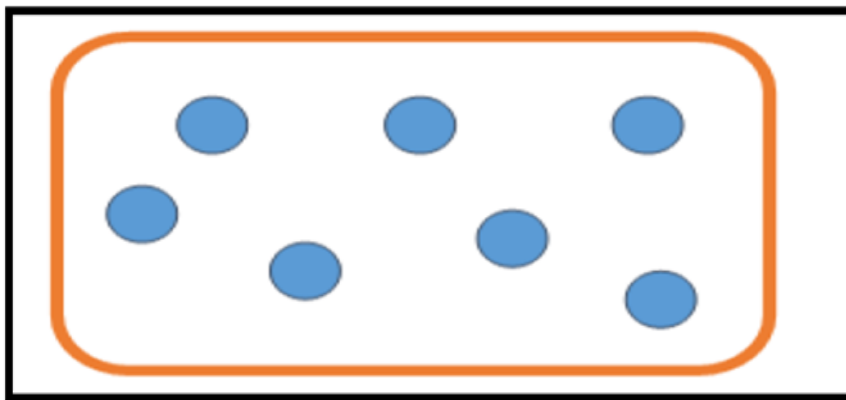


Figure (I.17): Schematic diagram of the position of ions in thin films. [80]

I.7.2 Docking phase

This phase is characterized by the docking of the groups among themselves to form a layer that gradually covers the film. Figure shows this phase.[64]

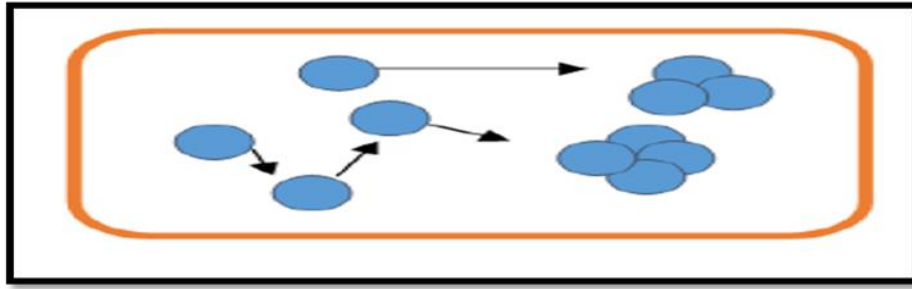


Figure (I.18): Schematic diagram of the docking phase. [64]

I.7.3 Growth phase

The growth phase is the last stage in the thin film installation process, and this phenomenon is considered as a complement to the adhesion process, so that a continuous layer is formed by filling the gaps (voids) by increasing the temperature of the substrate. Figure shows growth phase. [80]

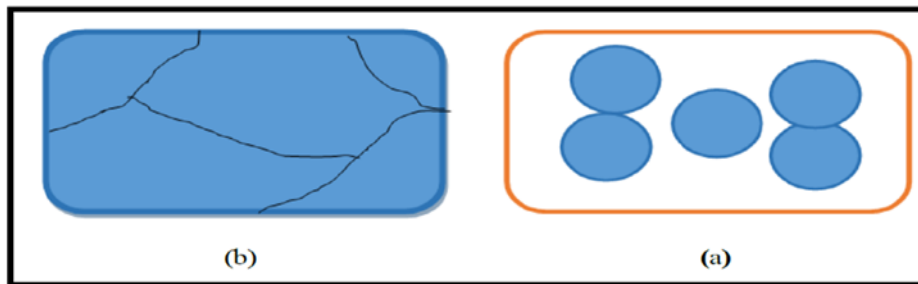


Figure (I.19) : Schematic diagram showing the growth (a) and docking (b) phases of the growth phase of the thin films. [80]

It has been observed experimentally that three growth patterns of thin layers appear, namely: a two-dimensional (2d) growth pattern, in which atoms are deposited layer by layer on the substrate, usually called the (Frank-Van der Merwe) pattern, and then followed by a three-dimensional (3d) growth pattern in which they grow. The thin layers are in the form of groups, and it is called the (weber-volmer) pattern, and finally the mixed pattern, and it is usually called the (Stranski-Krastanov) pattern, which is a mixture between the two previous patterns. [64]

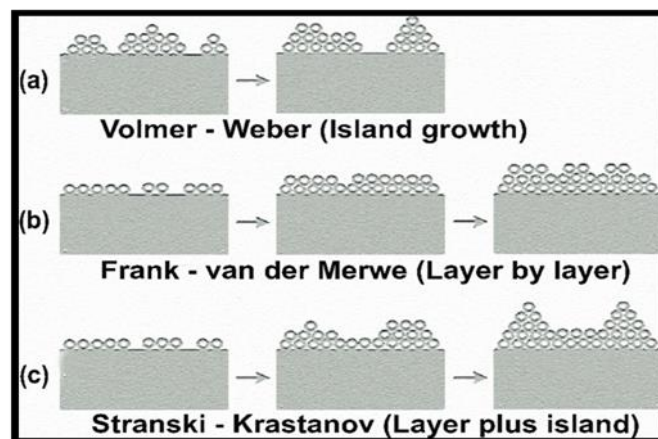


Figure (I.20): Diagram of different growth patterns of thin films. [81]

..

Chapter II

Experimental study and characterization techniques

II.1 Introduction

This chapter presents the experimental details and characterization techniques, which were used in this study. It includes knowledge about the chemical components and methods involved in the preparation and characterisation of doped and undoped CuO thin films.

II.2 Materials and Experimental Methods

II.2.1 Material used in the experimental work

- Diamond cutting pen.
- Etuve.
- Oven.
- Magnetic hotplate stirrer.
- Spin Coating apparatus.



Oven.



Diamond cutting pen.



Magnetic hotplate stirrer.



Spin Coating apparatus.

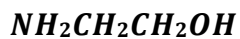


II.2.2 The chemical products used

For the preparation of undoped and barium, lanthanum doped copper oxide we have used the following chemical products:

Ethanolamine

Molecular formula :



Molar mass : 61.08 g/mol

Physical state: liquid

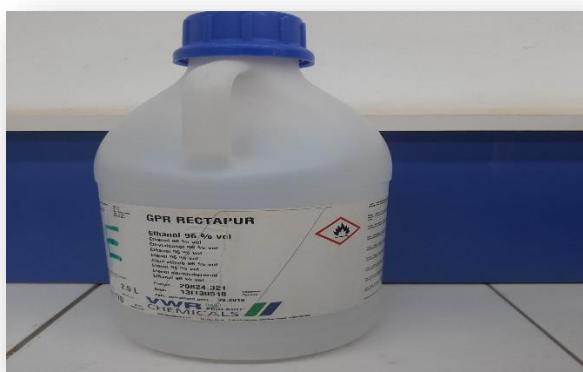


Ethanol

Molecular formula : $\text{C}_2\text{H}_5\text{OH}$

Molar mass : 46.07 g/mol

Physical state: liquid



<p>Baryum Chloride dehydrate</p> <p>Molecular formula : $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ Molar mass : 244.25 g/mol Physical state: solid powder</p>	
<p>Copper acetate</p> <p>molecular formula : $\text{Cu}_2(\text{CH}_3\text{COO})_4$ molar mass : 199.65 g/mol Physical state: solid powder</p>	
<p>Lanthanum Chloride Heptahydrate</p> <p>molecular formula : $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$ molar mass : 371.37 g/mol Physical state: solid powder</p>	

II.3 Preparation of the Substrates

II.3.1. The choice of substrate

The choice of the substrate is very important for preparation of the thin films, because it affects the crystalline quality as well as the optical and electrical properties of the thin films [1]. In this work, CuO thin films were deposited on glass slides in a size of (25 x 25) mm and a thickness of (1 to 1.2) mm this choice was due to these reasons:

- This glass performs a good optical characterization of our films, due to its transparency in UV-Visible wavelength range.
- It is an isolator layer so it will not affect the conductivity measurement.
- For economic

II.3.2. Cleaning of the substrate

The properties of the deposited film depend on the cleanliness of the substrate surface on which the film is deposited, dust, and Impurities on this surface can result in reduced adhesion of the film to the substrate, thus it is necessary to remove all kind of dirty, which include finger prints, dust, oil, and lint particles, and verify that the surface of substrate does not have any damage.

The steps of cleaning substrate surface are:

- Washing it with distilled water and soap.
- Drying using absorbent paper.
- Placing in acetone bath during 10 min to eliminate the organic impurities. Then washing it with distilled water.
- Placing in Ethanol bath during 10 min. Then washing it with distilled water.
- Drying using a drier.

II.4 The solution's preparation

In order to deposit thin films of undoped and doped CuO on glass substrate, we prepared two kinds of solutions.

II.4.1. Undoped CuO solution

A solution of the concentration $C = 0.2$ mol/L was prepared using 15 ml of ethanol and 0.5989 g of copper acetate which was calculated using the following formula :

$$m = M.C.V \quad (\text{II.1})$$

m : Mass of material used (g)

C : Solution concentration (mol/L)

M : The molar mass of the substance (g/mol)

V : The volume of the solution (L)

II.4.2 Doping solution

To prepare the doping solution, we use the same previous conditions (mass, concentration, volume), and calculate the barium and lanthium mass corresponding to the determine pourcentage (1%, 3%, 5%, 7% and 9%) using the following formulas:

$$m_{\text{Lanthanum Chloride Heptahydrate}} = X_{\text{mass}} \% * (M_{\text{Lanthanum Chloride Heptahydrate}} / M_{\text{acétatedecuire}}) * m_{\text{acétatedecuire}} * (M_{\text{Cu}} / M_{\text{La}})$$

$$m_{\text{Baryum Chloride dihydrate}} = X_{\text{mass}} \% * (M_{\text{Baryum Chloride dihydrate}} / M_{\text{acétatedecuire}}) * m_{\text{acétatedecuire}} * (M_{\text{Cu}} / M_{\text{Ba}})$$

	1%	3%	5%	7%	9%
ACu (g)	0.5989	0.5989	0.5989	0.5989	0.5989
La (g)	0.005	0.015	0.025	0.036	0.046
Ba (g)	0.003	0.01	0.017	0.024	0.031

II.4.3. Deposition by method spin coating

This is done by:

- Place the glass substrat on the device.
- Put some drops of the prepared solution on the surface of the substrat.
- Turne on the device, the slide rotates for 30 seconds, and thereby the solution was distribute evenly on the substrate.
- Stop the device.
- Remove the substrat and put it in an etuve at 200 °C to dry.
- We repeat the process 6 times.

II.4.4 Annealing Thin Films

This is the last step in the deposition of thin films. After the drying step of the last film, the sample undergoes an annealing heat treatment at a fixed temperature of 500°C for 1 hour. At the end, the samples are ready to be analyzing.

II.5 Analysing Methods of the thin films

The analysing techniques and description of the thin films is an important step through which thin film properties can be known such as : electrical, optical and structural properties . In this work, we have used UV-vis spectroscopy for the optical characterization and Four probes device for the electrical characterization .

II.5.1 Optical properties:

They refer to a number of optical constantes related to the thin films such as: transmittance, absorption coefficient, gap-energy, refractive index...etc

II.5.1.1. Ultraviolet Visible Spectroscopy:

The transmission spectrometer used is Perkin Elmer LAMBDA 25 UV/ VIS Spectrometer (Figure) with double beam one for their reference (glass) the other with the sample (glass – film). Their spectral range extends from wavelength $\lambda= 200$ nm to 1400 nm. Spectra obtained give the variation of transmittance expressed as a percentage according to their wavelength. [82, 83]



Figure (II.1): Visible and ultraviolet Spectroscopy.

Working principle:

It depends on a light source consisting of two lamps (tungsten-deuterium), where the light beam passes through a uniform wavelength to determine the wavelength of the sample to be

studied and the other pass through a reference glass, and then the two beams are directed towards a collector in order to compare and draw the results. [84]

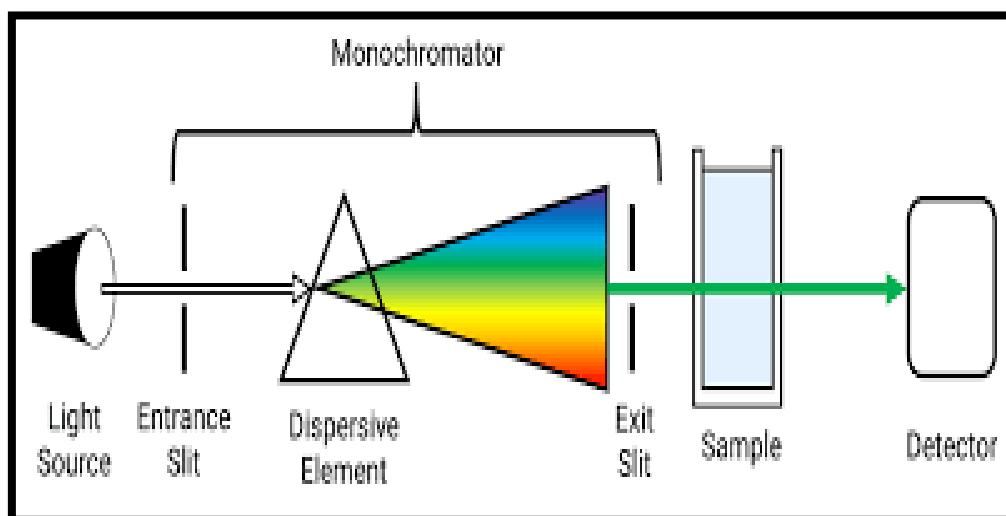


Figure (II.2): Schematic diagram showing the working principle of the UV Vis Spectroscopy device. [85]

II.5.1.2 Determine the absorption coefficient:

The transmittance spectrum enables us to determine the absorption coefficient, using the relationship (beer-Lambert) which is written as follows: [2]

$$T = e^{-\alpha d} \quad (\text{II.2})$$

α : absorption coefficient (cm^{-1}).

d: thickness of the thin film(cm)

From the given transmittance relationship, the expression for the absorption coefficient can be written as follows:

$$\alpha = \frac{1}{d} \ln \frac{100}{T(\%)} \quad (\text{II.3})$$

$$\alpha = 2.303 A \frac{1}{d} \quad (\text{II.4})$$

A: Absorbance

II.5.1.3 Determine the thickness of the samples:

There are several techniques for measuring the thickness, including:

Gravimetric method:

This method is considered somewhat inaccurate, as the substrate is weighed using a sensitive balance beforehand deposition and after deposition, and then we calculate the difference between them and we can calculate the thickness by the relationship: [86]

$$d = \frac{\Delta m}{\rho S} \quad (II.5)$$

Δm : The difference in substrate weight (g)

ρ : thin films density (g/cm³)

S: Substrate area (cm²)

Programming method:

It is allowed to determine the thickness and the refractive index of the prepared sample. This is done based on the transmittance values, which is the frequently used method due to its accuracy and speed compared to its predecessor.

II.5.1.4 The extinction coefficient K

Is the amount of energy absorbed in the material, or the extinction of an electromagnetic wave. The loss due to the interaction between wave and matter which causes the loss of wave energy.

It is possible to express the extinction coefficient through the following relation:

$$K = \frac{\alpha \lambda}{4\pi} \quad (II.6)$$

Where α is the absorption coefficient, and λ is the wavelength

II.5.1.5. Refractive index n

The refractive index of the prepared thin film samples can be expressed by the relation:

$$n = \left(\frac{(R+1)/(1-R)}{2} - (K^2+1) \right)^{1/2} + \frac{(R+1)/(1-R)}{2} \quad (II.7)$$

Where R is the reflectance and K is the extinction coefficient

II.5.1.6 Determine the band gap:

The energy gap is considered one of the important optical constants, as it is considered the energy required to transport electrons from the top of the valence band to the bottom of the transport band. [87]

The value of the energy gap can be calculated through the Tauc method as follows:[90]

$$(\alpha h\nu)^2 = B (h\nu - E_g) \quad (II.8)$$

B: Constant

E_g : The band gap (eV)

$h\nu$: Photon energy (eV)

By drawing a curve $(\alpha h\nu)$ as a function of the photon energy $h\nu$ and drawing the tangent to the linear part of this curve, we can get the value of the band gap by determining the intersection of this line with the $h\nu$ axis.

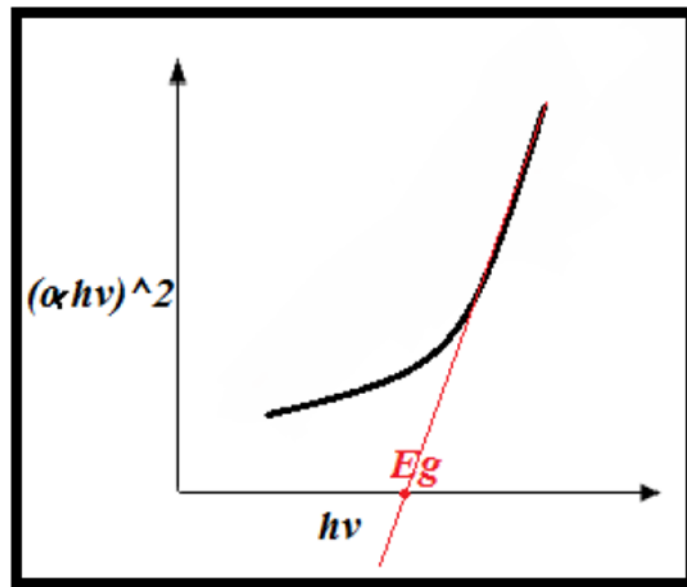


Figure (II.3) :Diagram illustrating $(\alpha h\nu)^2$ as a function of $h\nu$.

II.5.1.7. Determine the Urbach energy:

The Urbach energy E_u is one of the important constants that characterize the optical properties of the thin films. The relationship between the Urbach energy and the absorption coefficient is expressed as follows: [87, 88]

$$\alpha = \alpha_0 e^{\frac{h\nu}{E_u}} \quad (\text{II.9})$$

α_0 : Absorption coefficient for which the absorption value is minimum

E_u : The Urbach energy

$$\ln \alpha = \ln \alpha_0 + \frac{h\nu}{E_u} \quad (\text{II.10})$$

The Urbach energy can be determined from this relationship by calculating the slope of the curve : $\frac{1}{E_u}$

II.5.2 Electrical Characteristics

The electrical properties of undoped and doped copper oxide thin films are studied by a technical method the of four probes to determine the resistivity and specific conductivity of the sample

II.5.2.1 Four Probes Technology

This technique aims to find out the surface resistivity of thin films and determine the value of conductivity, and its device consists of four probes connected to the sample evenly spaced in a straight line and equal distances, a current I is sent passes through the two external probes and the potential difference V is measured between the two internal probes. if The distance s between the probes is much greater than the thickness of the thin film, so we consider the dimensions of the ends to be infinite, and the sample is considered a binary model therefore, the resistance of the sample can be calculated from the relationship:[89]

$$\frac{U}{I} = K \frac{\rho}{d} \quad (\text{II. 11})$$

ρ : Thin films resistivity ($\Omega \cdot \text{cm}$)

d : Thin films thickness (cm)

$\frac{\rho}{d}$: This ratio represents the resistance sheet of the thin film (ohms)

K : It represents the proportionality coefficient

This technique is considered more accurate compared to the traditional two-probe method because the voltage and the current are measured through separate probes; it negates the effect of contact resistance and wire resistance depending on the geometry of the probes and their spacing.

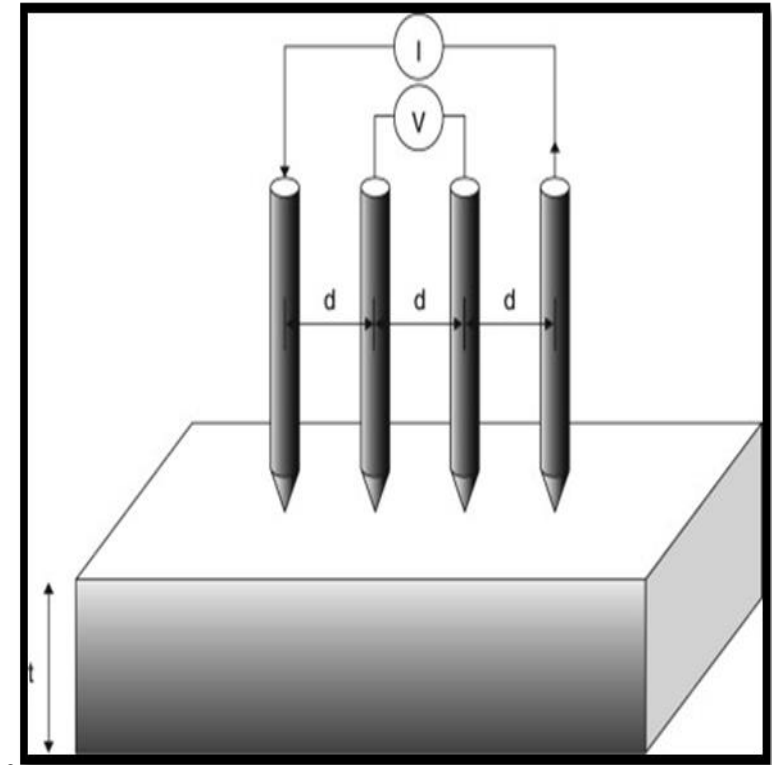


Figure (II.4) : The four probes technique.

Chapter III:

Result and discussion

III.1. Introduction

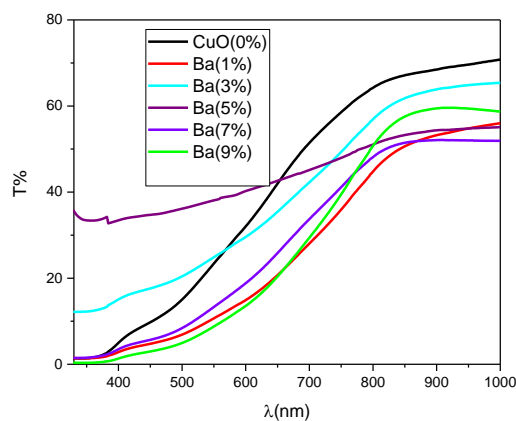
In this chapter, we will obtain results, present, analyse and discuss the obtained results of La-doped CuO and of Ba-doped CuO, then we will compare between them.

III.2. Optical Properties

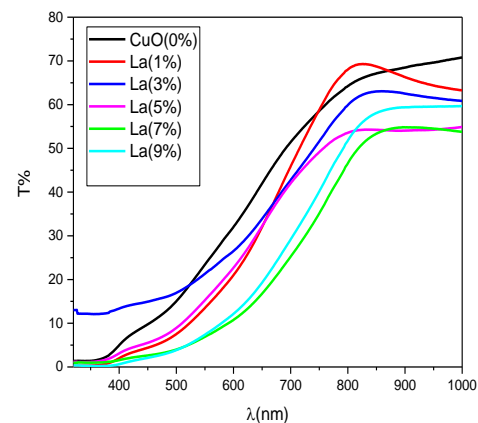
III.2.1. Transmittance

Optical properties of CuO thin films are investigated by spectrophotometer in the wavelength range [300-1000 nm]. Figure (III.1), Figure (III.2) display the optical transmittance spectra as a function of the wavelength of La and Ba doped CuO thin films respectively.

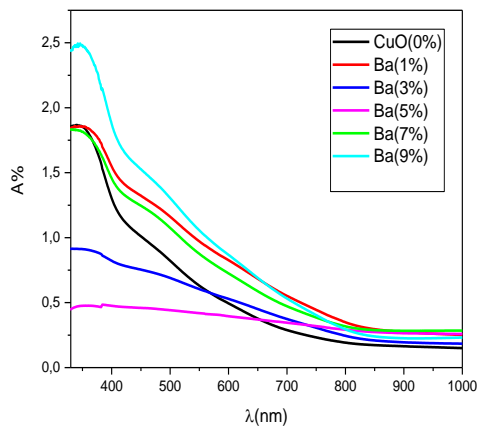
The results showed that the transmittance increases with increasing wavelength, as it appears that the values of the transmittance are the lowest possible in the ultraviolet wavelengths region of the spectrum within the range (300 -400 nm) and increases - rapidly in the visible region (400-700 nm) then it reaches the highest value in the range of (700-900 nm). It also can be noticed that the transmittance decreased in both cases of La and Ba dopant. Figure (III-1) and (III-2) show that the transmittance is inversely proportional to the increase of La and Ba concentrations. As for Ba dopant CuO thin films, the transmittance ranges between (58.69 to 56.02)%, where the highest value belongs to 3% Ba doped-CuO sample and for La dopant CuO thin films, it ranges between (59.69 to 63.29)% , where the highest value belongs to 1% La doped-CuO sample. It is clear from the obtained spectra that the two dopants did not improve the transmittance of CuO in the visible range.



Figure(III.1) : Transmittance Ba doped of CuO

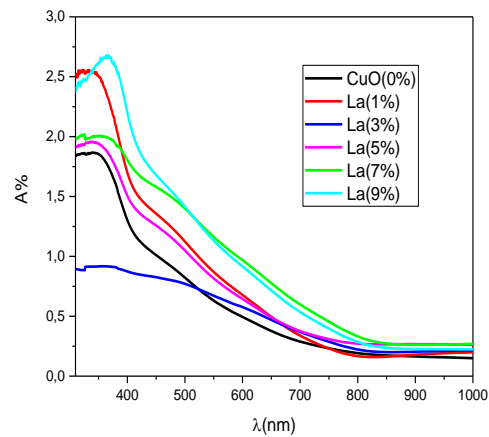


Figure(III.2) : Transmittance La doped of CuO



Figure(III.3) : Absorbance Ba doped

Of CuO



Figure(III.4) : Absorbance La doped

of CuO

The absorption spectra confirm what it is said in the transmittance results as the absorption behavior goes inversely with the transmittance behavior.

III.2.2 Band gap and Urbach energy

Figure (III.5,10) and Figure (III.11,15) present the curves used to determine the gap energy La doped-CuO and Ba doped-CuO respectively.

The band gap E_g and Urbach energy E_u of the undoped thin films and La and Ba doped CuO thin films are shown in Table (III.1) and illustrated in Figure (III.5)-(III.15) overall, It is observed from figure that the band gap decreases with increasing doping concentration for both dopants, AS for La dopant, E_g decreases from (2.85 to 2.09) eV then increases again at 9% with 2.29 eV corresponds to for lanthanum doping ,and decreases from (2.6 to 1.87) eV then increases again at 9% with 2.07 eV compared to barium doping. This decrease in the band gap is confirmed by the increasing width of the band tail presented with Urbach energy Figure (III.27 ,28), the latter may be a consequence of the structural defects seen in the film. We also notice through the results that barium leaves more defects.

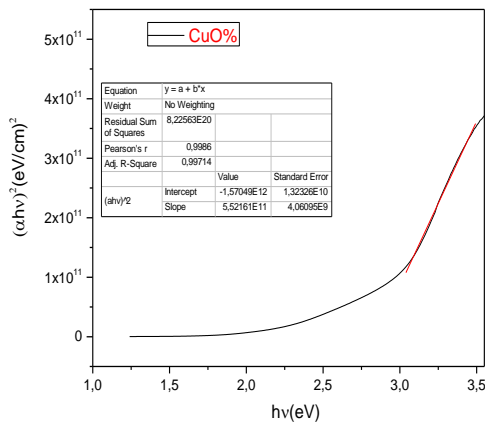


Figure (III.5): Band gap of CuO (0%)

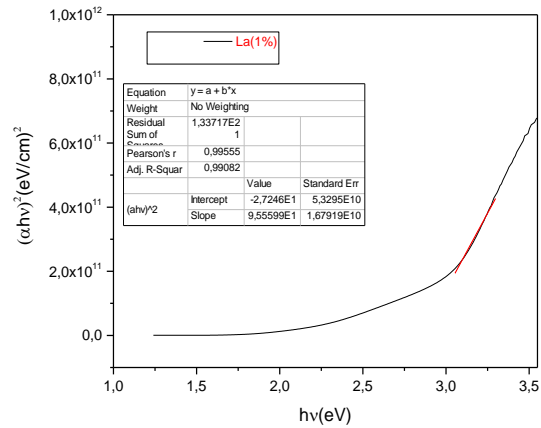


Figure (III.6): Band gap of La (1%)

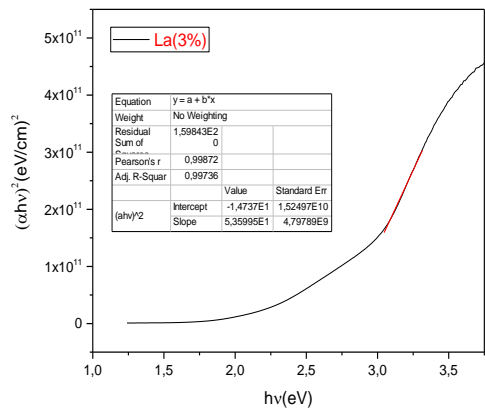


Figure (III.7): Band gap of La (3%)

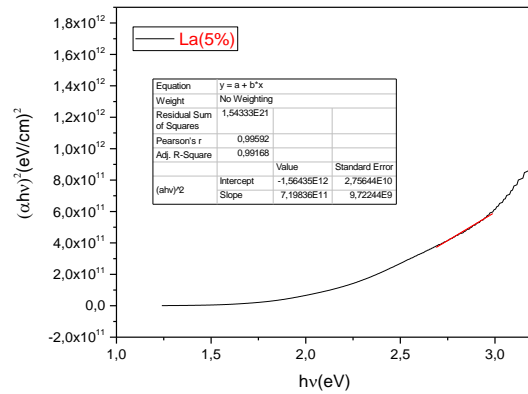


Figure (III.8): Band gap of La (5%)

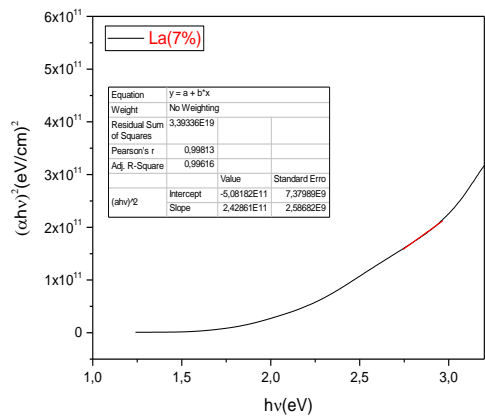


Figure (III.9): Band gap of La (7%)

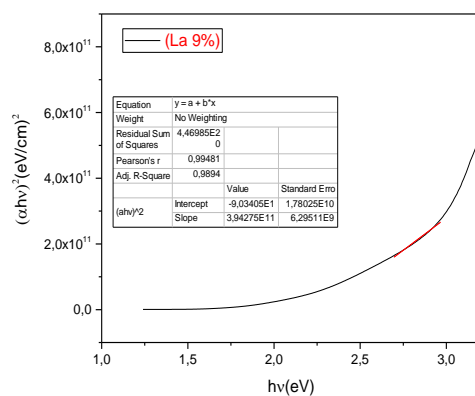
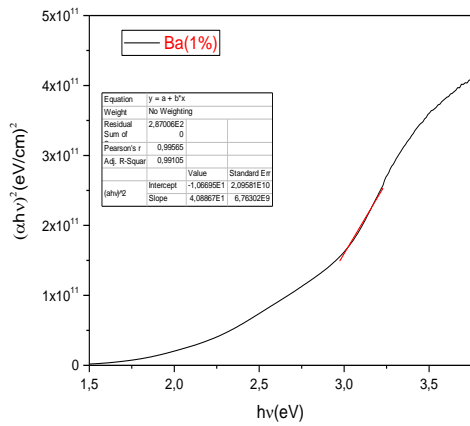
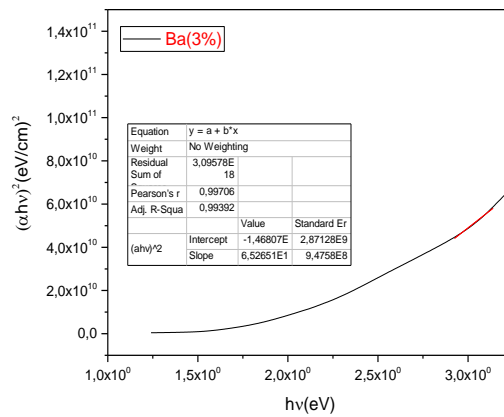


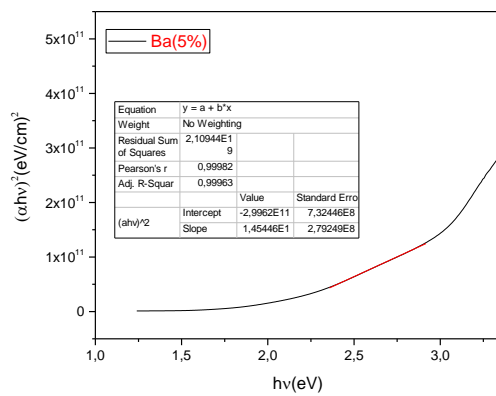
Figure (III.10): Band gap of La (9%)



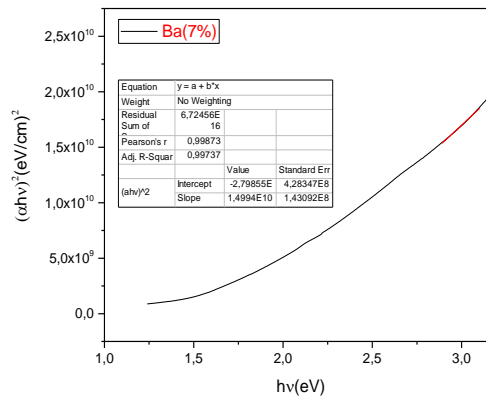
Figure(III.11): Band gap of Ba (1%)



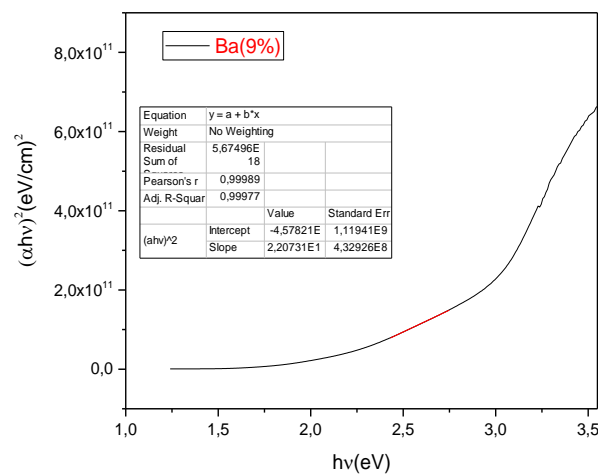
Figure(III.12) : Band gap of Ba (3%)



Figure(III.13) : Band gap of Ba (5%)

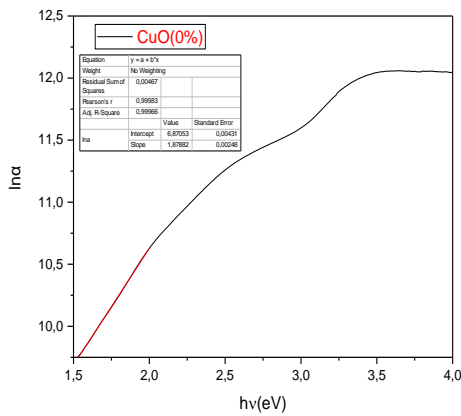


Figure(III.14) : Band gap of Ba (7%)

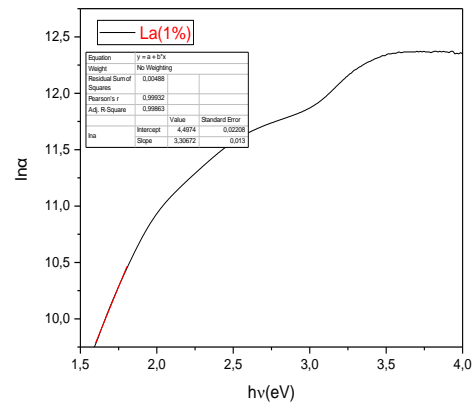


Figure(III.15) : Band gap of Ba (9%)

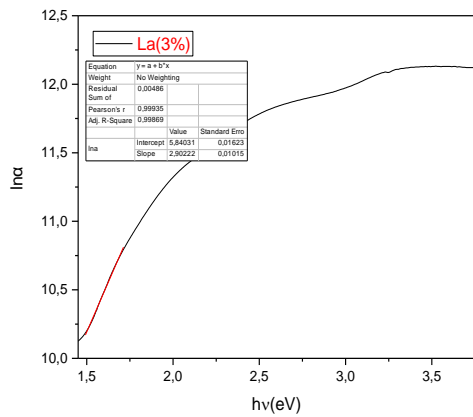
Figure (III.16, 21) and Figure (III.22, 26) present the curves used to determine the Urbach energy of La doped-CuO and Ba doped-CuO respectively according to Tauc law.



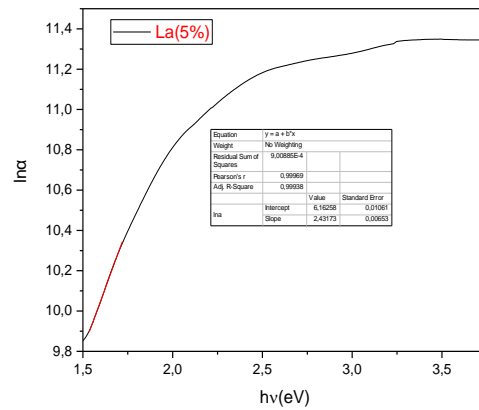
Figure(III.16) : Urbach energy of CuO(0%)



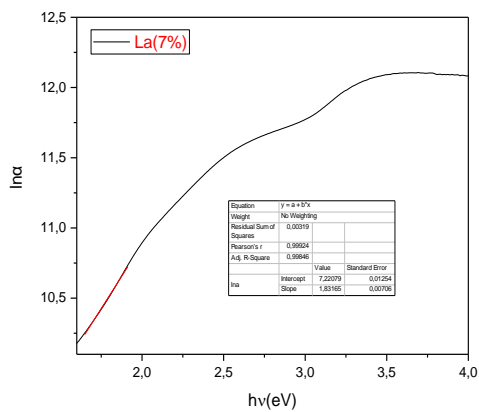
Figure(III.17) : Urbach energy of La(1%)



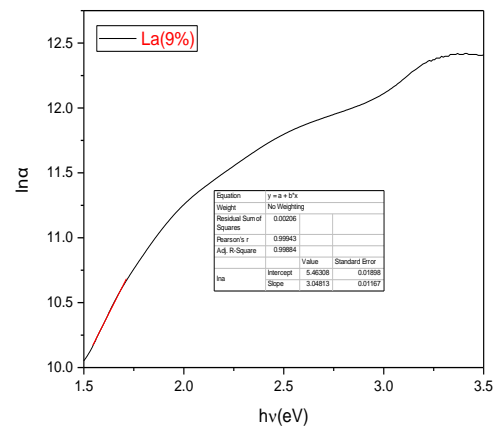
Figure(III.18):Urbach energy of La(3%)



Figure(III.19):Urbach energy of La(5%)



Figure(III.20) : Urbach energy of La(7%)



Figure(III.21) : Urbach energy of La(9%)

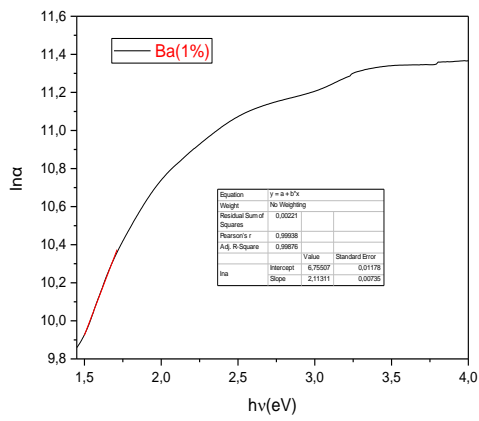


Figure (III.22): Urbach energy of Ba(1%)

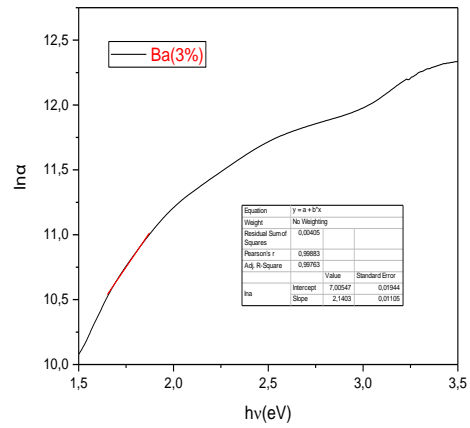


Figure (III.23): Urbach energy of Ba (3%)

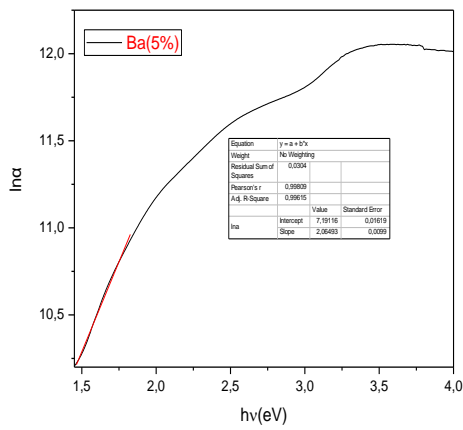


Figure (III.24): Urbach energy of Ba (5%)

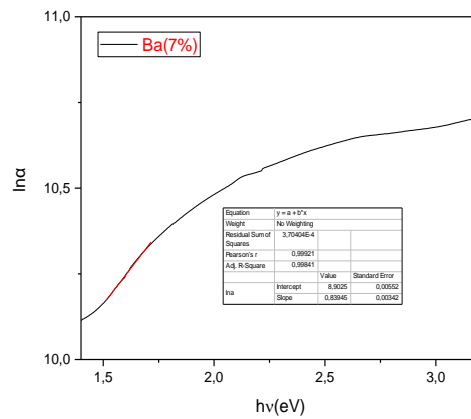


Figure (III.25): Urbach energy of Ba (7%)

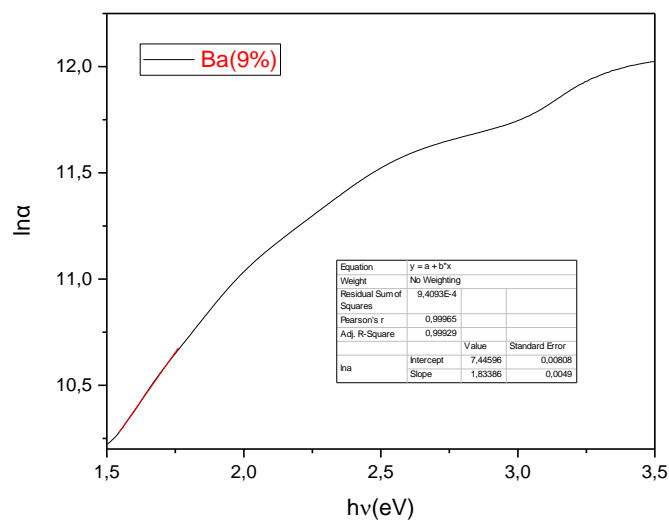


Figure (III.26): Urbach energy of Ba (9%)

The results of gap energy and Urbach energy are summarized in Table (III-1)

Table (III.1): Band gap and Urbach energy of concentration doping.

CuO	Eg(eV)					Eg(eV)				
	2.84					3.66				
Concentration	1%	3%	5%	7%	9%	1%	3%	5%	7%	9%
La	2.85	2.74	2.17	2.09	2.29	1.36	2.01	2.53	3.94	0.81
Ba	2.6	2.24	2.06	1.87	2.07	3.2	3.27	3.48	10.61	4.06

Figure (III.27) and Figure (III.28) illustrate the band-gap and Urbach energy of undoped, Ba doped-CuO and La doped-CuO respectively.

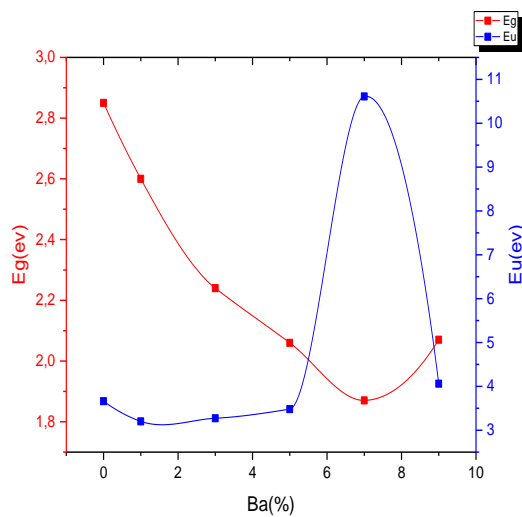


Figure (III.27): Band gap and Urbach energy as function of Ba concentration

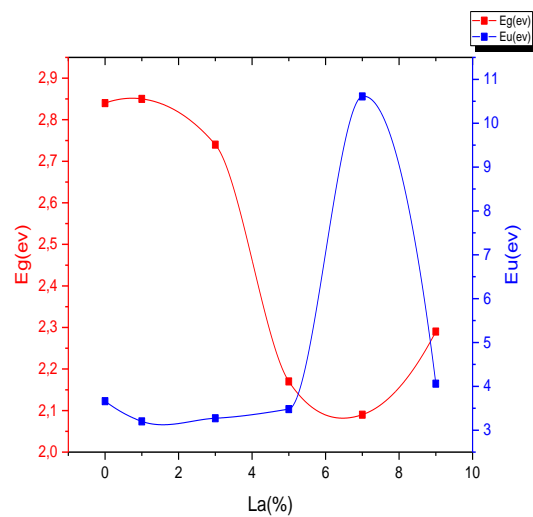


Figure (III.28): Band gap and Urbach energy as function of La concentration

Overall, It is observed from figure (III.27,28) that the band gap decreases with increasing doping concentration for both dopants whereas the Urbach energy increases as the dopant concentration . increases. In the case of La dopant, Eg decreases from 2.85 to 2.09 eV corresponds to 1% and 7% respectively, then increases again at 9% to reach 2.29 eV, while Eu increases from 1.36 to 3.94 eV and decreases to 0.81 eV for the same concentrations of La (see table III.1). therefore, the lowest value of band-gap energy returns to 7% La doped CuO. As for Ba dopant, Eg decreases from 2.6 to 1.87 eV corresponds to 1% and 7% respectively, then it increases again at 9% to reach 2.07 eV, while Eu increases from 3.2 to 10.61eV and decreases to 4.06 eV for the same concentrations of Ba(table III.1). Thus, 7% Ba doped cuo is also the lowest value of the band-gap energy. This result has a good agreement with the literature the films specifies the direct allowed band gap (Eg) with the values of 2.17 to 1.9 eV for all the films. It was observed that the band gap values are decreasing with Ba doping percentage.[47]

Although both doping reach the lowest value of E_g for the same concentration (7%), Ba doping compared to La doping (figure III.29), decreases more effectively the band gap energy of CuO from 2.84 eV (undoped CuO) to 1.87eV (7% Ba). This can be attributed to the structural defects created by Ba more than those created by La and which are responsible of the increasing the disorder in the band gap and increasing the width of the band tail presented by Urbach energy behavior.

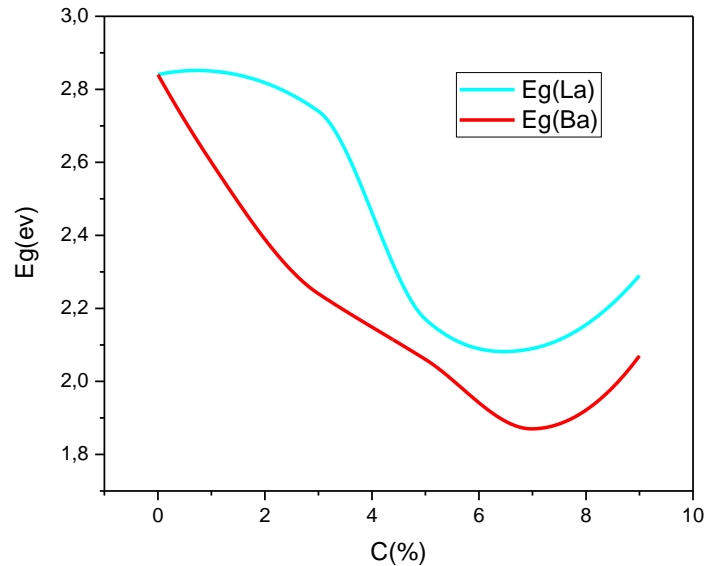


Figure (III.29): Band gap as function of Ba,La concentration

III.3 Electrical Properties

The results of the sheet resistance, the resistivity and the electrical conductivity values of undoped CuO, La and Ba doped-CuO thin films measured by the four-point method are presented in table (III.2).

Table (III.2): R sheet and Resistivity, conductivity of Ba,La concentration.

	R sheet $\times 10^3$ (Ω)					Resistivity ($\Omega.cm$)					Conductivity ($\Omega.cm$) ⁻¹				
	1%	3%	5%	7%	9%	1%	3%	5%	7%	9%	1%	3%	5%	7%	9%
CuO	6.18					0.7					1.43				
La	4.14	1.6	1.17	6.35	18.43	0.5	0.18	0.13	0.72	2.08	2.14	5.59	7.59	1.4	0.5
Ba	8.73	1.83	2.9	1.14	1.06	0.98	0.21	0.33	0.13	0.12	1.02	4.84	3.06	7.77	8.36

The results in table (III.2) reveal a decrease in the resistance (R_{sheet}) and the resistivity values with the increasing percentage corresponding to an increase in the conductivity values of La dopant till 5% where they change the behavior and mark a monotonous increase in the resistance and decrease in the conductivity profile (Figure III.30), whereas in the case of Ba dopant starting from 5%, we can notice a monotonous decrease in the resistance corresponding to a monotonous increase in the conductivity profile (Figure III-31) . 9% of Ba dopant corresponds to the lowest value of the resistance ($R_s= 1.06 \times 10^3 \Omega$, $\rho=0.12 \Omega.cm$) and to the highest value of the conductivity $\sigma= 8.36 (\Omega.cm)^{-1}$. Table (III.2).

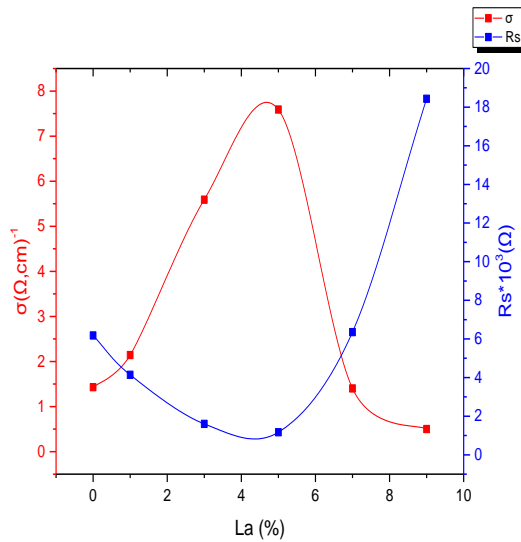


Figure (III.30): R sheet and the conductivity as function of La concentration

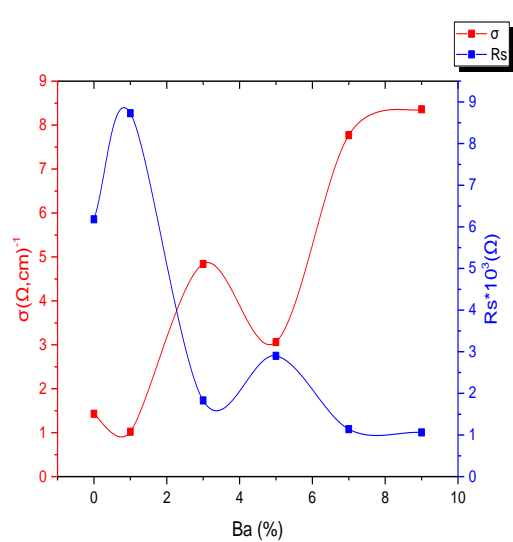


Figure (III.31): R sheet and the conductivity as function of Ba concentration

The comparison between the effect of La and Ba on the conductivity of the samples shows that:

- The conductivity of La doped CuO thin films increases for low La percentages (less than 5%), while that of Ba doped CuO thin films increases for high Ba percentages (more than 5%).
- Moreover, La dopant improves the conductivity of CuO thin films from (1.43 to 7.6) $\Omega.Cm^{-1}$, and Ba dopant improves from (1.43 to 8.36) $\Omega.Cm^{-1}$.
- Ba dopant increases effectively the conductivity compared to La dopants.

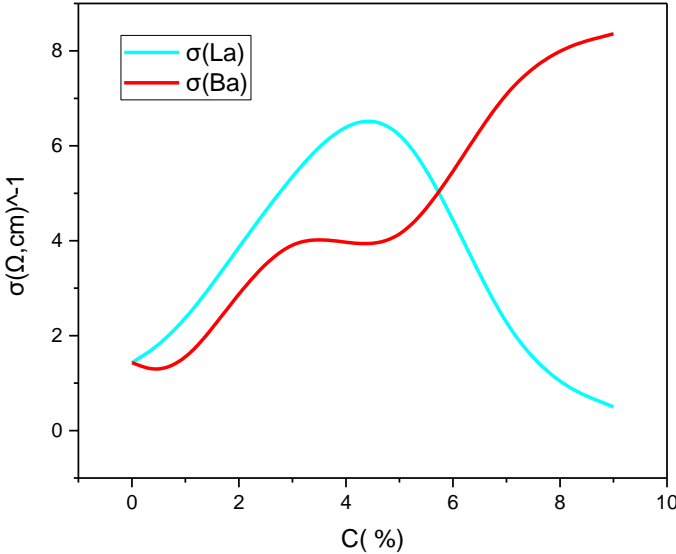


Figure (III.32) : The conductivity as function of Ba,La percentage.

REFERENCES

REFERENCES

- [1] N, BOUFAA, Elaboration et caractérisation des nano poudres d'oxyde d'étain (SnO₂), MEMOIRE DE MAGISTER, UNIVERSITE MENTOURI CONSTANTINE, 2012
- [4] A, Douayar, Contribution à l'étude des propriétés structurales, optiques et électriques des couches minces de l'oxyde de zinc (ZnO) dopé (fluor, indium, aluminium et néodyme), These de doctorat, Université Mohammed V-AGDAL, 2013.
- [6] I. Tunahan. Solar Cells review. 10.13140/RG.2.1.4298.6404,(2015).
- [8] T. Floyd «Electronic Devices, Conventional Current Version »7th edition, perason prentice hall, (2005).
- [10] A. B, Azzoum "etude des couche minces du monoxyde nickel NiO", mémoire de magister, Université d'Oran, 2014.
- [11] J. M. Dekkers, Transparent Conducting Oxides on Polymeric Substrates by Pulsed Laser Deposition, Ph.D. thesis Univ of Twente, Enschede, The Netherlands, Vol. 24, N° 4, (2007).
- [13] S. Boulmelh, " Elaboration Et Caractérisation D'un Dépôt De Couches Minces D'oxyde De Zinc Par Spray Pyrolyse", Mémoire De Magister, Univ .Frères Mentouri Constantine,(2015).
- [14] El .H. CHAREF , "Détermination des Caractéristiques Optiques des Couches Minces du ZnO Elaborées par Spray Ultrasonique" ,CENTRE UNIVERSITAIRE D'EL-OUED,(2012).
- [15] T. K. Subramanyam, B. Srinivasulu Naidu and S. Uthanna « Physical Properties of Zinc Oxide Films prepared by dc Reactive Magnetron Sputtering Pressures»Crystal Research and Technology,VoL266.issue.10.p.1193,(2000).
- [16] J. WANG, V. SALLET, F. JOMARD, A.M.BOTELHO, E. ELAMURUGU, R. MARTINS, E. FORTUNATO, "Influence of substrate temperature on N-doped ZnO films deposited by RF magnetron sputtering " , Thin Solid Films, vol515, p8785-8788, (2007).
- [17] M. Kihel, & A. E. Berbadj ,Etude des oxydes transparents conducteurs: exemple l'oxyde de zinc (ZnO) (Doctoral dissertation,University of Jijel), (2018).
- [22] K .L .Menour ,Etude et réalisation d'une cellule solaire multicouches du type Si-SiO₂-SnO₂-ZnO par APCVD , Mémoire de Magister ,Université Mouloud Mammeri , Tizouzou, 2011.
- [23] A. Tabet , Optimisation des conditions d'élaboration (température de substrat distance bac-substrat) des films minces de ZnO par spray .Mémoire de Magistère Université Mohamed Khider, Biskra , 2013.
- [24] G. K. Dalapati, H.Sharma, A.Guchhait, Chakrabarty, N. Bamola, ... & M.Sharma, Tin oxide for optoelectronic, photovoltaic and energy storage devices: a review. Journal of Materials Chemistry A, 9(31), 16621-16684, (2021).
- [25] S.Triboulet, «Etude des effets de deux types de nanoparticules métalliques sur des macrophages murins par une approche protéomique», Thèse de doctorat, Université de Grenoble, (2013).

- [27] <https://www.britannica.com/science/copper>.
- [28] D.D. Arhin, Thèse de doctorat, Université de Trento, Italie, 2006.
- [29] M.F. Al-Kuhaili, Vacuum, Volume 82, Issue 6, , Pages 623–629,19 February 2008.
- [30] V. Figueiredoa, E. Elangovana, G. Gonçalvesa, P. Barquinhaa, L. Pereiraa, N. Francob, E. Alvesb, R. Martinsa and E. Fortunato, Applied Surface Science Volume 254, Issue 13, , Pages 3949–3954,30 April 2008.
- [31] M. Kaur, K.P. Muthe, S.K. Despande, S. Choudhury, J.B. Singh, N.Verma, S.K. Gupta, J.V. Yakhmi, Journal of Crystal Growth Volume 289, Issue 2, , Pages 670–675,1 April 2006.
- [32] L. Zhang, J. Li, Z. Chen, Y.Tang, Y. Yu, Applied Catalysis A: General Volume 299, , Pages 292–297,17January 2006.
- [33] S. Ghosh, D.K Avasthi, P. Shah, V. Ganesan, A. Gupta, D. Sarangi, R. Bhattacharya, W. Assmann, Vacuum Volume 57, Issue 4, , Pages 377–385 ,June 2000.
- [34] X.M. Liu and Y.C. Zhou, Applied Physics A: Materials Science & Processing Volume 81, Number 4, 685-689(2005).
- [35] A.Kirdous, & A.Bouchekhchoukh, Élaboration et caractérisation des couches minces d'oxyde de cuivre: application electrocatalytique sur l'acide ascorbique, Mémoire de Master, Université A. MIRA–Bejaïa, (2012).
- [36] L. Wang, Thèse de doctorat, Université de Texas Arlington, 2006.
- [37] K. Woo, D. Kim, J. Sub Kim, S. Lim and J. Moon, Langmuir, 25 (1), pp 429–433,2009.
- [38] F. Bayansal, S. Kahraman, G. Çankaya, H.A. Çetinkara, H.S. Güder, H.M. Çakmak, Journal of Alloys and Compounds Volume 509, Issue 5, 3 February 2011, Pages 2094–2098.
- [39] P.K. Ooi, S.S. Ng, M.J. Abdullah, H. Abu Hassan, Z. Hassan Materials Chemistry Journal of Physics D: Applied Physics, vol. 38, pp. 266-271, 2005a.and Physics,140_243,(2013).
- [40] J. B. Forsyth, S.Hull, "The effect of hydrostatic pressure on the ambient temperature structure of CuO", J.Phys.Condens.Matter,3(1991)5257.
- [42] M.Noreen, M. Khan, N. M, A.Ahmed, , & G.Hussain, A perspective study on copperoxide nanoparticles and their role in different fields of biomedical sciences. Int J Sci Res Eng Dev, 3, 1246-56, (2020).
- [44] <https://www.feedo.net/environment/EnvironmentalProblems/Problems/HeavyMetals.htm>.
- [45] <http://clearlyexplained.com/chemical-elements/barium/index.html>.
- [46] <https://www.britannica.com/science/barium>.
- [47] S.Jacob, S. . . , I.S.Yahia, Investigation on structural, optical and photovoltaic properties of Barium doped cuprous oxide thin films by nebulizer spray technique. Materials Research Express, 6(11), 115055, (2019).

- [48] A. M.Ahmed, E. M.Abdalla, & M.Shaban, Simple and low-cost synthesis of Ba-doped CuO thin films for highly efficient solar generation of hydrogen. *The Journal of Physical Chemistry C*, 124(41), 22347-22356, (2020).
- [49] <https://en.wikipedia.org/wiki/Lanthanum>
- [50] <https://chemicalengineeringworld.com/lanthanum-element-properties-and-information/>
- [51] D.Naveena, R. Dhanabal & A. C. Bose, Investigating the effect of La doped CuO thin film as absorber material for solar cell application. *Optical Materials*, 127, 112266,(2022).
- [52] A. Masood, T. Iqbal, S. Afsheen, K.Riaz, G. Nabi, & M. I. Khan, Simple synthesis of novel Lanthanum doped Copper oxide nanoparticles for wastewater treatment: A comparison between Experiment and COMSOL simulation , (2022).
- [56] R. Gheriani, Thèse de Doctorat D'Etat,(2445)
- [57] R. Messemche, Elaboration and characterization of undoped and doped titanium dioxide thin layers by sol gel (spin coating) for photocatalytic applications. Doctoral Thesis, University of Biskra, Algeria (2021).
- [58] E.Yilmaz, M. Soylak, Functionalized nanomaterials for sample preparation methods, Chaudhery Mustansar Hussain, Handbook of Nanomaterials in Analytical Chemistry, Elsevier, ,375-413, (2020).
- [59] M. Dahnoun, Preparation and characterization of Titanium dioxide and Zinc oxide thin films via Sol-Gel (spin coating) technique for optoelectronic applications. Doctoral Thesis, University of Biskra, Algeria (2019).
- [60] L. Znaidi. Sol–gel-deposited ZnO thin films: A review, *Materials Science and Engineering. B* 174, 18–30,(2010).
- [61] B. S. Yilbas, Abd Al-Sharafi, H. Ali, Chapter 3 - Surfaces for Self-Cleaning, Self-Cleaning of Surfaces and Water Droplet Mobility, Elsevier, (2019), 45-98.
- [62] N. Abdelouahab, Preparation and characterization of thin films nanostructures based on ZnO and other oxides. Doctoral Thesis, University of Oum El Bouaghi, Algeria (2019).
- [63] S. Obregón, & V.Rodríguez-González, Photocatalytic TiO₂ thin films and coatings prepared by sol–gel processing: A brief review. *Journal of Sol-Gel Science and Technology*, 1-17, (2021).
- [65] J. Puetz, M.A. Aegerter, Sol-gel technologies for glass producers and users; Dip coating technique, (2004).
- [66] G. Ji, & M. Zhao, Membrane separation technology in carbon capture. *Recent advances in carbon capture and storage*, 59-90, (2017).
- [67] O. Olayinka Abegunde, Esther Titilayo Akinlabi, Oluseyi Philip Oladijo, Stephen Akinlabi, Albert UchennaUde, Overview of thin film deposition techniques, *AIMS Materials Science*, 6(2), 174-199, (2019).
- [68] A. Mennad, “Les techniques de dépôt de couches minces et leurs applications,” *Revue des Energies Renouvelables*, vol. 18, pp. 713–719 (2015).

- [69] Y. Benkhetta, Elaboration and characterization of thin layers of zinc oxide (ZnO) deposited by ultrasonic spray for photovoltaic and optoelectronic. Doctoral Thesis, University of Biskra, Algeria (2019).
- [70] M. Othmane, Synthesis and characterization of Zinc Oxide (ZnO) Thin films deposited by spray pyrolysis for applying: electronics and photonics. Doctoral Thesis, University of Biskra, Algeria (2018).
- [71] G.Hass and R. E. Thun, "Physics of thin Films", Academic Press, NewYork, (1966).
- [72] E.Salonen, Swift chemical sputtering of amorphous hydrogenated carbon , Physical Review, vol. 63, no. 19, P. 195, (2001).
- [73] Overview Metallization Technology, Physical Vapor Deposition PVD (2015).
- [74] K.Wasa, M.Kitabatake, H.Adachi, Thin Film Processes, In: Wasa K, Kitabatake M, Adachi H, Thin Film Materials Technology, Norwich, NY: William Andrew Publishing, 17–69; (2004).
- [75] D,Influence Des Défauts Sur Les Propriétés Optiques Et Tainoff Electroniques De Nanoparticules De Zno",Thèse De Doctorat, Université De Claude Bernard-Lyon 1,(2009).
- [76] A.Bashir, T. Awan, I.Tehseen, A. Tahir, M. B., & M.Ijaz, Chapter 3—Interfaces and Surfaces. Chemistry of Nanomaterials; Awan, A. Bashir, T.Tehseen, A., Eds, 51-87, (2020).
- [77] S.Benramache,Elaboration et caractérisation des couches minces deZnO dopées cobalt et indium ", Univ Mohamed Kheider, Biskra,(2012).
- [78]A. Rahal, Elaboration des verres conducteurs par déposition de ZnO sur des verres ordinaires, mémoire de magister ,université d'eloued, (2013) .
- [79] A. Hafdallah, Etude du Dopage des Couche Mince de ZnO Elaborées par Spray Ultrasonique, Mémoire de magister, université de Constantine, (2007).
- [81] R.Pérez-García, Controlled deposition of fullerenes: effects of topological nano-modifications of a surface on aggregation and growth phenomena (Doctoral dissertation, Technische Universität Berlin). (2018).
- [82] H. Villavicencio Garcia, M. Hernandez Vélez, O. Sanchez Garrido, J.MMartinez Duart, J.Jiménez, CdS doped-MOR type zeolite characterization,Solid State Electronics, Vol. 43, N.6, P. 1171-1175, (1999).
- [83] G. Huertas, "Etude de Nouveaux Matériaux D'électrode Positive et d'électrolyte Solide Vitreux Sous Forme de Couches minces pour des Couches Minces Micro batteries au Lithium", thèse de doctorat, université of Bordeaux, (2006).
- [85]<https://jascoinc.com/learning-center/theory/spectroscopy/uv-visspectroscopy/instrumentation/>
- [87] Y. SIROTIN, AND Y. M. SHASKOLSKAYA, "Fundamentals of crystal physics Mir publishers Moscow 198

[88] A. S. Hassanien, A. A. Akl, Effect of Se addition on optical and electrical properties of chalcogenide CdSSe thin films, Journal of Superlattices and Microstructures (Elsevier), 89, P. 153-169 (2016).

[89] S. J. Ikhmayie, R. A. Bitar, A study of the optical bandgap energy and Urbach tail of spray deposited CdS:In thin films, Journal of Material Research and Technology (Elsevier), 2(3), P. 221-227 (2013).

[2] م . بن خالد، دراسة بعض الخواص البصرية لأغشية لكبريتيد الرصاص المحضر بطريقة التحلل الكيميائي الحراري، مجلة الهندسة والتكنولوجيا، المجلد 30 ، العدد60 ، 2012،

[3] م. بن خليل، دراسة بعض الخواص البصرية والكهربائية لأغشية أكسيد الزنك المحضرة بطريقة الرش الكيميائي الحراري،مجلة الهندسة والتكنولوجيا، المجلد 30 ، العدد6 ، جامعة بغداد، العراق، 2012

[5] ر. عبد الله منيف، ر. عبد الوهاب إسماعيل، ص. جاسم محمد ، دراسة الخواص التركيبية والبصرية لغشاء أكسيد الزنك الرقيق نانوي التركيب بطريقة الترسيب بالحمام الكيميائي، 2012،

[7] م.بن طالب، دراسة الخصائص التركيبية و البصرية لأغشية أكسيد النيكل المطعمة بالنحاس و الكوبالت" ص. بوعيشة ، جامعة محمد خيضر بسكرة، 2020،

[9] ب.حمصي، "دراسة الخصائص الضوئية و الكهربائية و البنيوية لشرائح أكسيد القصدير المطعم الأنتيموان موضه بطريقة الأمواج الصوتية " ،مذكرة ماستر، فرع فيزياء، جامعة الوادي ، 2014.

[12]أ.زيد عبد، "دراسة الخصائص التركيبية و البصرية لأغشية (أكسيد النيكل)" ، رسالة ماجستير، جامعة ديالى،العراق،2012،

[18] ن. فرحات، & ش. لخضر،دراسة بنيوية وضوئية لشرائح أكسيد النحاس لمطعم بالنيكل ،ماستر أكاديمي ،جامعة الوادي، 2020.

[19]ع. ردينة صديق، "دراسة الخصائص التركيبية و البصرية لأغشية $Ni(1-x)Zn_xO$ ،

المحضرة بطريقة التحلل الكيميائي الحراري، رسالة ماجستير، جامعة بابل، العراق

[20] م. حزين بلقاسم ،دراسة الخصائص البنيوية و الضوئية و الكهربائية لأكسيد القصدير المطعم بالفلور المتوضع بتقنية الأمواج فوق الصوتية، مذكرة ماستر اكاديمي، جامعة الوادي، 2014

[21] ل. سقني،"تحديد خصائص أكسيد القصدير المطعم بالحديد"،مذكرة ماستر أكاديمي ،جامعة الشهيد حمه لخضر الهادي 2016.

[26] ن.حمروني،ع.بليلة،الدراسة البنيوية والضوئية والكهربائية لشرائح أكسيد القصدير المطعم بالنحاس، مذكرة ماستر أكاديمي،جامعة الوادي،2017

- [41] أ.د. زياد محمد عبود، أ. خضير عباس مشجل آيه عبد الكريم جاسم، تأثير درجة حرارة القاعدة على الثوابت البصرية الأغشية. أكسيد النحاس المحضرة بتقنية التبخر الكيميائي الحراري الجامعة المستنصرية (كلية التربية) قسم الفيزياء، 2017
- [43] ن، محمد، علي الكرخي، "دراسة خصائص التركيبية لأغشية المحضرة بطريقة التحليل الكيميائي الحراري"، جامعة ديالى، العراق، 2012
- [53] ع. صلاح حسن، ن. بخيت حسن، ع. جمعة حيدر، دراسة تأثير التطعيم بالمغنيزيوم على الخصائص الطبوغرافية وبعض الخواص البصرية لغشاء كبريتيد الخارصين المحضر بتقنية الترسيب بالليزر النبضي، مجلة جامعة كربلاء المؤتمر العلمي الأول لكلية العلوم، الحجم 1، 2013.
- [54] ص. جاسم محمد، أ. اسعد حمدي، "دراسة تأثير التشويب بالنحاس على الخصائص البصرية لأغشية... الرقيقة" ،كلية التربية جامعة تكريت، العراق، 2013 .
- [55] ن. مصباحي، الدراسة البنيوية والضوئية والكهربائية لأكسيد القصدير.. المطعم بالألمنيوم .. بطريقة الرش الحراري، ماستر أكاديمي، جامعة الشهيد حمه لخضر، الوادي، 2019
- [64] ع. دقة، ا. مصباحي، تحديد بعض خصائص أغشية أكسيد النيكل المطعم بالحديد ، مذكرة ماستر اكاديمي، جامعة الوادي، 2017
- [80] م. حزيز بلقاسم ،دراسة الخصائص البنيوية و الضوئية و الكهربائية لأكسيد القصدير المطعم بالفلور المتوضع بتقنية الأمواج فوق الصوتية، مذكرة ماستر اكاديمي، جامعة الوادي، 2019.
- [84] المؤسسة العامة للتدريب التقني والمهني، "طرق التحليل الطيفي"، المملكة العربية السعودية ص2-5، 1429.
- [86] ح. عبد شهاب، ، تصنيع ودراسة الخواص الكهربائية لخلايا الأغشية الرقيقة الشمسية من نوع Cu_2S , Cds الصرفة، مجلة تكريت للعلوم، المجلد16، العدد30، 2011.

GENERAL CONCLUSION

General conclusion

This work is based on the elaboration and characterization of undoped, and La, Ba doped CuO thin films by sol-gel via spin-coating technique on a glass substrate, it aims to study the effect of La and Ba doped CuO on the properties of CuO thin films. The optical properties were investigated by visible and ultraviolet spectroscopy, and the electrical properties were obtained using the four probes method. The main results can be recapitulate as follows

The transmittance of Ba dopent CuO thin films, ranges between (58.69 to 56.02)%, where the highest value belonged to 3%, and that of La dopent CuO thin films ranges between (59.69 to 63.29)%, where the highest value belonged to 1%. The band gap decreases with increasing dopant concentration of each dopant while the Eurbach energy increases with dopant concentrations. The lowest value (1.87 eV) of band gap energy, In the case of Ba dopant, belongs to 7%. The same concentration gives the lowest band gap energy value (2.09 eV) for La dopant. Ba doping increases effectively the conductivity more than La doping and 9% corresponds to the highest value of the conductivity ($\sigma = 8.36 (\Omega.cm)^{-1}$).

ABSTRACT

Abstract

The present work is a comparative study between La, and Ba effect on the optical and electrical properties of CuO thin films at the following concentrations (1%, 3%, 5%, 7%, 9%). Samples were prepared using sol-gel via spin-coated technique on a glass substrate, visible and ultraviolet spectroscopy was employed to characterize the optical properties and the four probes method was used to characterize the electrical properties. The main results reveal that La dopant decreases the band gap of CuO to (2.09 eV) corresponds to 7% and improve the conductivity to $7.59 (\Omega.cm)^{-1}$ corresponds to 5% .while, Ba dopant decreases the band gap of CuO to (1.87 eV) corresponds to 7% and improve the conductivity to $8.36 (\Omega.cm)^{-1}$ corresponds to 9%.

Keywords: CuO, thin films, sol-gel, spin-coating, baruim, properties, lanthanum.

ملخص

العمل الحالي عبارة عن مقارنة بين تأثير الباريوم و اللانثيوم على الخصائص البصرية و الكهربائية للشرائح الرقيقة لأكسيد النحاس بالتراكيز التالية (1%,3%,5%,7%,9%) باستخدام تقنية الطلاء الدوراني بالمحلول الهلامي على الركيزة الزجاجية, تم استخدام التحليل الطيفي المرئي والأشعة فوق البنفسجية لتوصيف الخصائص البصرية، واستخدام طريقة المجسات الأربعة لتوصيف الخواص الكهربائية. أشارت النتائج الرئيسية أن التطعيم باللانثيوم يقلل من طاقة فجوة النطاق لأغشية أكسيد النحاس إلى 2.09 إلكترون فولت عند 7%، ويحسن الناقلية إلى $7.59 (\Omega.cm)^{-1}$ عند 5%. بينما التطعيم بالباريوم يقلل من طاقة فجوة النطاق لشرائح أكسيد النحاس إلى 1.87 إلكترون فولت عند 7%، ويحسن الناقلية إلى $8.36^1 (\Omega.cm)^{-1}$ عند 9%.

الكلمات المفتاحية: الأغشية الرقيقة، أكسيد النحاس، المحلول الهلامي، تقنية الطلاء الدوراني، الباريوم، اللانثيوم، الخصائص.