



University Mohamed Khider of Biskra
Faculty of Exact Sciences and Sciences of Nature and Life
Department of Matter Sciences

Master Thesis

Domain of matter physics
Section of physics
Material physics

Réf. : Entrez la référence du document

Presented by :
Benouakhir Hayet
Belmabrouk Naziha

Le : 24-6-2021

The Impact of Co-doping with La and Li on the Physical Properties of Copper Oxide (CuO) Thin Films

To the jury composed by :

Ouahab Abdelouhab	Professor	University Med Khider of Biskra	President
Kanza Almi	M.C « B »	University Med Khider of Biskra	Raporter
Okba Belahssen	Professor	University Med Khider of Biskra	Examiner

Academic Year : 2020-2021

Dedication

Dedicate this work:

To my dear parents for their support

To my brothers and sisters

To my family and to all those who supported me

Dedication

To...

My mother and father and dear aunt

My brothers and sisters

*My deas friends and colleagues in the laboratory
and everyone who supported me in my studies*

Acknowledgements

First of all , I thank **GOD** the whole powerful for having agreed his infinite kindness, courage, the force and patience to complete this modest work.

Next, I make a point of profoundly thanking to our supervisor **Pf. Almi Kenza** Professor at the Department of sciences of matter at Faculty of Exact Sciences and Sciences of Nature and Life in Mohamed Khider University of Biskra. She gives us every opportunity to carry out this work. Her availability, guidance, assistance, sound advice and her contagious optimism have been very valuable to us throughout this work and it has been a pleasure to work alongside it.

We thank **Pf.Ouahab Abdelouhab** , Professor at the University of Mohamed Khider in Biskra, for the interest he has shown in this work and for having accepted the presidency of the jury.

We are grateful to **Pf.Belahssen Okba** , at the department of sciences of matter, who agreed to accept to belong to the jury and to examine my work.

Special thanks go to our **Fathers** and **Mothers**, we are very grateful for what they have done for us and To our family: To our sisters and brothers. our uncles, our aunts, Fort their help and encouragements .

we would also like to acknowledge: Dr. **Tibermacine Toufik and Dr Saad Rahmane** for his generous help in the experimental phase.

Finally, we wish to address our thanks to all the teachers and our friends of the department of sciences of matter especially the **Professor of physics**, everyone by his name.

Table of Contents

Dedication I	
Dedication II	
Acknowledgements	
General Introduction:	1
CHAPTER I:	4
Bibliographical Study on TCO Thin Films and Deposit technique	4
I.1. Introduction:	5
I.2. Physical properties of TCOs	5
I.2.1. Electrical properties	5
I.2.2. Optical properties	6
I.3.1 Gas sensor	8
I.3.2 Solar cells	8
I.4 copper oxide semiconductor	8
I.4.1 Electrical and Optical Properties of Copper Oxide Films.....	9
I.4.1.1 Optical properties	9
I.4.1.2 Electrical properties	10
I.5 The lanthanum	10
I.5.1 Lanthanum Area of Use:	12
I.6 The Lithium:	12
I.6.1 Uses:	13
I.7 Copper oxide Doping:	14
I.8 The effect of co-doping on optical and electrical properties of nanomaterials	16
I.8.1 co-doping of CuO	17
I.9 Thin Film Deposition Processes	17

I.9.1 Physical Processes	18
I.9.1.1 Physical vapor deposition	18
I.9.2 Chemical Process	18
I.9.2.1. Chemical Evapore Déposition	18
I.10 Sol-gel method	19
I.10.1 The different stages of the Sol-Gel procedures	19
I.10.2 Main system states during the soil-gel transition	19
I.10.3 The main techniques for depositing thin films by sol-gel	22
I.10.3.1 Dip-coating	23
I.10.3.2 Spin-coating:(Centrifugation)	23
I.10.4 Drying and annealing thin layers (heat treatment)	24
I.10.5 Advantages and disadvantages of sol-gel method	25
I.11 Applications of the sol-gel technique	26
II.1 Generality on thin film	29
II.2 Mechanism of Thin Films Growth	29
II.2.1 Nucleation	29
II.2.2 Island structure	29
II.2.3 Coalescence	30
II.2.4 Channel and Holes	30
II.2.5 Continuous film	30
II.3 Spin coating technique	30
<i>II.3.1.1 Important guidance and steps during the experiment:</i>	31
II.3.2 products used in the experiment	32
II.3.2.1 The solids elements	32
II.3.2.2 Liquid elements:	33
II.3.3 -Preparation of the solution	34
II.3.4 Depositing of thin films	35
II.4 Experimental techniques for characterizing thin film layers	36

<i>II.4.1 Optical characterization</i>	37
II.4.1.1 UV-Visible Spectroscopy	37
<i>II.4.2 Electrical Characterization</i>	41
III.1 Introduction	44
III.2 Characterization of the prepared films	44
III.2.1 Thin films' thickness Measuring	44
III.2.2 Effect of the dopant rates on the transmittance spectra	45
III.2.3 Effect of the concentration of the co-dopants on the Absorbance	46
III.2.4 Effect of the concentration of co-dopant on the absorption coefficient	46
III.2.5 Optical gap	47
III.2.6 The Disorder (Urbach energy)	49
III.2.7 The reflection	52
III.2.8 The extinction coefficient K	53
III.2.9 The refractive index n	54
III.2.10 Determination of the electrical resistivity	55

Chapter III : Results and Discussion

III.1 Introduction.....	44
III.2 Characterization of the prepared films.....	44
III.2.1 Thin films' thickness Measuring	44
III.2.2 Effect of the dopant rates on the transmittance spectra.....	45
III.2.3 Effect of the concentration of the co-dopants on the Absorbance.....	46
III.2.4 Effect of the concentration of co-dopant on the absorption coefficient	46
III.2.5 Optical gap	47
III.2.6 The Disorder (Urbach energy).....	49
III.2.7 The reflection	52
III.2.8 The extinction coefficient K	53
III.2.9 The refractive index n.....	54
III.2.10 Determination of the electrical resistivity.....	55

List of figure

Figure	Title	Page
Chapitre I :Bibliographical Study on TCO Thin Films and Deposit technique		
I .1	Electrical structure of transparent conducting oxides (TCO' s).	20
I .2	Access Spectrum, Reflection and Absorption of Transparent Carrier Oxide.	21
I .3	Applications of transparent conducting oxide.	22
I .4	3D Copper oxide CuO.	23
I .5	Structural optical and photoluminescence investigations of nanocrystalline CuO thin films at different microwave powers.	24
I .6	Variation of electrical properties of the copper oxide films as a function of annealing temperature.	25
I .7	The Lanthanum in bulk form.	26
I .8	the Lanthane (La) undoped structure crystalline is Hexagonale.	26
I.9	(a): Samples of metallic lithium.	28
I.10	b): Structure of the Li-compound	28
I.11	Diagram of E-Beam Evaporation Process	34
I.12	Main steps in a soil-gel synthesis of a material. Parameters influencing reaction kinetics:	36
I.13	The formation of the polymeric gel.	38
I.14	The formation of the colloidal gel.	38
I.15	Stages of the dip-coating process: a) dipping of the substrate into the coating solution; b) wet layer formation by withdrawing the substrate; c) gelation of the layer by solvent evaporation .	39
I.16	Dip coater.	39
I.17	The four steps of spin coating.	40
I.18	Spin coater.	40

Chapter II : Elaboration and Characterization of CuO Thin Films

II.1	Thesubstrates and a diamond-tipped pen.	48
II.2	cupric acetate.	49
II.3	Lanthanium chloride.	49
II.4	Lithium Nitrate.	50
II.5	Ethanol.	51
II.6	Lithium powder.	52
II.7	Undoped copper oxide.	52
II.8	Lanthanium Powder(La)	52
II.9	La-doped CuO solution.	52
II.10	Lithium Powder (Li).	53
II.11	Li doped CuO solution.	53
II.12	The principe of UV-Visible transmitted spectroscopy with out reference	55
II.13	The principe of UV-Visible transmitted spectroscopy with reference	55
II.14	The transmitted of electrons	55
II.15	(a)SchematicofUV-Visspectrometer.	57
	(b)Schematicofdispersivespectrometer	
II.16	illustrationofbandgapdetermination	58
II.17	illustrationofband Urbachdetermination	59
II.18	Schéma d'un dispositif quatre pointes alignées	60

Chapter III: Rusults and Discussions

III.1	Transmittance spectra of our CuO thin films	65
III.2	Adsorption spectra of pure copper oxide thin films and co-dopant withLa and Li	66

III.3	The absorption coefficient curve for $h\nu$ for copper oxide films	67
III.4	Curve of changes $(A h\nu)^2$ is terms of $(h\nu)$ for copper oxide thin films co-dopant with La and Li.	68
III.5	$\ln(\alpha)$ as a function of $(h\nu)$ for copper oxide thin films co-doped with La and Li.	69
III.6	Band energy and Urbach energy as function of co-doping ratios (CuO : La,Li).	70
III.7	Optical reflection spectrum of La,Li co-doped CuO films as a function of wavelength	71
III.8	shows the change of the extinction factor as a function of photon energy for undoped and co-doped copper oxide thin films.	72
III.9	the refractive index of La and Li co-doped CuO films.	73

List Of Tabela

Table	Titre	Page
-------	-------	------

Chapter I: Bibliographical Study on TCO Thin Films and Deposit technique

I.1	Physic-chemical properties of Lanthanum.	27
-----	--	----

I. 2	physic-chemical properties of Lithium	29
------	---------------------------------------	----

Chapter III: Results and Discussions

III. 1	Thickness of CuO thin films co-doped with La + Li (%) by sol-gel technique.	62
--------	---	----

III. 2	Energy gap value of copper oxide thin films co-doped with La and Li.	63
--------	--	----

III. 3	Urbach value of copper oxide thin films co-doped with La and Li.	69
--------	--	----

General Introduction

General introduction

General Introduction:

Scientists and researchers have studied semiconductors of different types and characteristics since the early nineteenth century because of their significant industrial advantages and applications. In recent decades more attention has been paid to this research. Most electronic industries, which are the nerve of global economic and commercial life and showed important applications in nanotechnology, have shown that materials can be prepared as thin films. In the sense of materials manipulation skills on a scale of a few nanometers, they can be made from conductive, insulating, semiconductor and polymer materials. So that materials produced in the form of thin film have in particular different physico-chemical properties from those of solid. According to most studies confirmed that when the size of the components of an object is reduced to the nanoscale, the physical properties of these objects are altered and even improved.

Transparent conducting thin films are a class of material mostly takes a good side to electrical conductivity whilst maintaining a high transmission in the visible range of the electromagnetic spectrum. Since the realization of this type of material, vast amounts of research and development have gone into commercializing these thin film coatings. P type TCO exist but they still have less performance than n type TCO, particularly in their resistivity, Cu_2O and its composites are one of these materials, specially Delafossite phase [1].

Copper oxide is a transparent oxide, it is of great importance in semiconductor physics, it has different physical properties and it forms two well-known stable oxides; cupric oxide (CuO) and cuprous oxide (Cu_2O). CuO has monoclinic structure belongs to space group $2/m$, it displays a wealth of interesting properties, it is abundant, nonhazardous source materials, and it can be prepared by low cost solution methods which are the key issues for sensing applications [2]. CuO is superior for solar energy harvesting because of its smaller optical band gap and it can absorb the whole spectrum of visible light, in addition to be more stable in air [3]. This makes copper oxide a promising candidate in scientific and technological research. In order to improve CuO optical and electrical properties, researchers study the possibility of doping and co-doping CuO using different elements. Lanthanum and Lithium have proved effective in enhancing optical and electrical characteristics of many

General introduction

semiconductors, hence the choice of La and Li for doping and co-doping copper oxide in the present study.

The elaboration of Copper oxide thin films and nanomaterials can be done using various techniques such as thermal evaporation, sputtering, chemical vapour deposition (CVD), spray pyrolysis and sol-gel technique. Each methodology has associated pros and cons and careful consideration of the resulting film properties such as crystallinity, microstructure and adhesion which must be taken into account considering optical and electrical properties. Gel spin coating (centrifugation a solution deposited in excess on a substrate) is a simple method not expensive and efficient in the production of homogeneous thin layers with high purity for preparing a wide variety of oxides under different configurations (monoliths, fibers, thin films, powders, etc.). This large possibility of manipulating and manufacturing made this process very attractive in technological domains such as optics and electronics [4].

The purpose of this work is the development of copper oxide (CuO) thin films pure and co-doped with Lanthanum (La) and Lithium (Li) deposited on glass substrate by Sol Gel method (Spin Coating) and then we study the impact of these two elements on CuO optical and electrical properties.

The memory is organized in three chapters, in addition to an introduction and a general conclusion, they are presented as follows:

The first chapter: This chapter is devoted to a bibliographic synthesis in which we talk about conductive transparent oxides (TCO), and about un-doped copper oxide; its different properties and applications in form of thin films. Moreover, we display a brief description of the chosen dopants and their properties namely lanthanum and lithium. In the end of this chapter, we will present some research about doping and co-doping copper oxide as well as other well known oxides to find out how extent co-doping process can enhance the material properties.

The second chapter: this chapter tackles the experimental details concerning the elaboration, deposition and the characterization of La, Li co-doped CuO thin films. It presents and describes all the products, the materials, and the methods used in our experimental work in order to achieve our object.

General introduction

The third chapter: This chapter focuses on the presentation of the results namely optical (UV-VIS) and electrical results of the elaborated thin films. The discussion and the interpretation of the obtained results was built in view of what we have learnt from our literature review.

Finally, we end the dissertation with a general conclusion in which we exhibit the main results obtained and we talk about our perspectives and suggestions recommended in this work.

CHAPTER I:

Bibliographical Study on

TCO Thin Films and

Deposit technique

I.1. Introduction:

Transparent conducting oxides (TCOs) are electrical conductive materials with relatively low absorption of light. They are highly flexible intermediate states and nearly lossless conductors of light. Therefore, their conductivity can be .

adjusted from insulating to semiconducting or electrical conducting. As they can be produced as n-type or p-type conductive, TCOs materials are usually prepared with thin film technologies and used in optoelectrical devices such as solar cells, displays, optoelectrical interfaces, and circuitries.

I.2.Physical properties of TCOs

I.2.1.Electrical properties

The specific electrical properties of TCO films could be explained by reference to the basic theory of electrical transport phenomena in semiconductor thin films. Transport phenomenon is the the motion of charge carriers under the action of an internal or external field. In the absence of an electric field, the electron gas in a semiconductor is in an equilibrium state, which is established as a result of the interaction of electrons with lattice defects. Such defects especially include lattice imperfections in the crystallites, grain boundaries, impurity atoms, thermal vibrations of the lattice (phonons). If an electric field E is applied to a material, an electrical current will flow, whose density J , usually expressed in A/m², is given by $J = \sigma E$ (I.1)

Where: σ is called the electrical conductivity of the material usually expressed in Siemens per cm (**S.cm⁻¹**). The reciprocal of electrical conductivity is known as electrical resistivity ρ (in **Ω .cm**), and can be expressed by:

$$\rho = \frac{V}{I} \frac{t}{Ln2} = 4.53 \frac{tV}{I} \text{ (I.2)}$$

Where: t represents the film thickness, the resistivity ρ is correlated to the so-called 'sheet resistance (R_s)' by:

$$R_s = \frac{\rho}{t} \text{ (I.3)}$$

The current density can be also expressed as:

$$J=Ne(I.4)$$

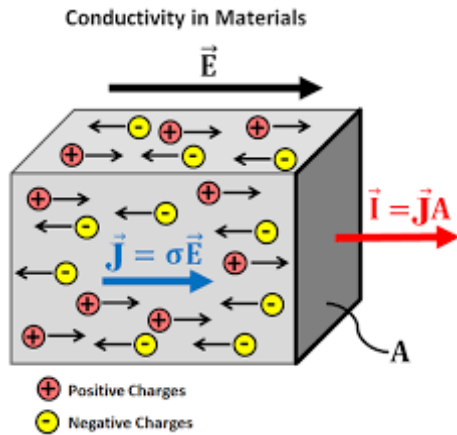


Figure (I.1) : Electrical structure of Transparent Conducting Oxides (TCO' s).

I.2.2.Optical properties

TCOs materials show high optical transmission in the visible range, which requires an energy gap larger than 3.3 eV.

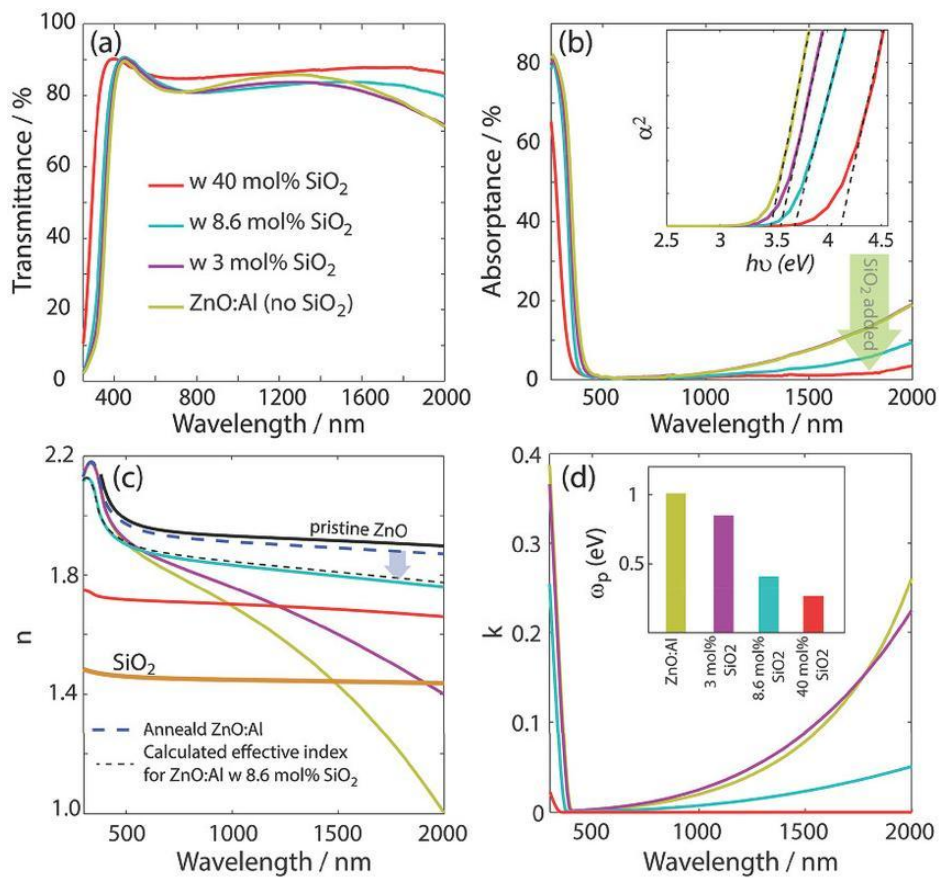
The optical properties of TCO thin films provide powerful tools to known energy band structure, impurity levels, localized defects, lattice vibrations, etc. these properties and thereby the optical constants, strongly related to the elaboration' conditions of TCO thin films such as the deposition parameters, microstructure, level of impurities, and growth technique.

The typical spectral dependence of TCOs on the wavelength of light is represented in Figure I.2. The transmission window is limited between two regions in which no light is transmitted Thus, the absorption dominates.

This could be explained by the quantum phenomenon where the photon energy in UV area is high enough to equal the band gap energy (3 - 4 eV). This energy is used to transit over the gap energy.

However, when wavelength varied in the range of 400 -1000 nm, the photon energy is too low so the absorption in this zone is small.the TCO film is transparent. If the

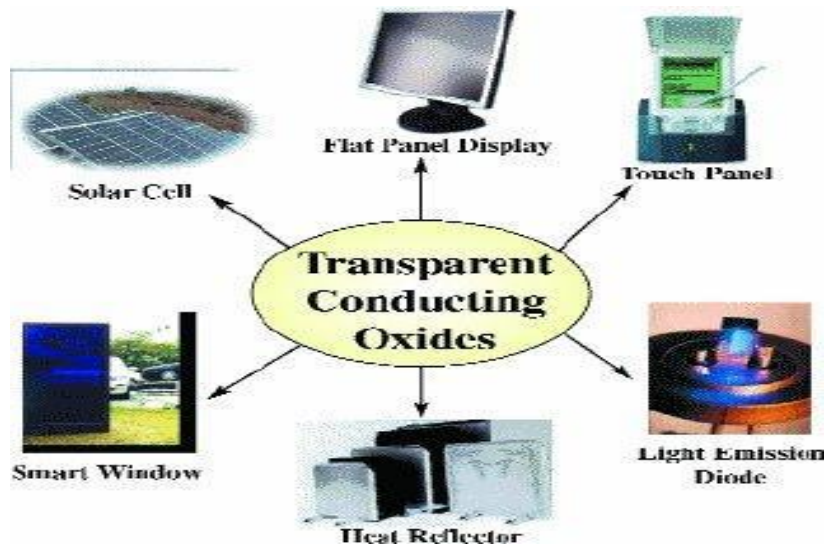
TCO is adequately flat, an interference structure will be observed and related to the thickness of the film and refractive index.



Figure(I.2): Access Spectrum, Reflection and Absorption of Transparent Carrier Oxide.

I.3 Applications of TCOs materials

The TCOs properties previously mentioned have opened a wide range of technological applications, some of these applications are presented in what follows:



Figure(I.3) : Applications of transparent conducting oxide.

I.3.1 Gas sensor

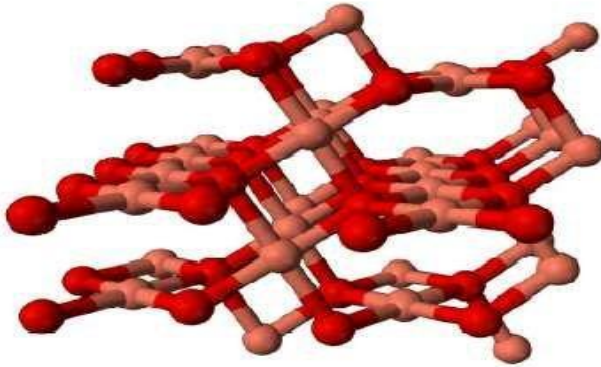
Metallic oxides are known to be highly transparent semiconductor, and can also change their electrical properties. This has been triggered by highly exciting, multi-field research and industrial materials. They have contributed to the gas sensors, which, in turn, reveal to us various sets of pollutants and toxic gases found in nature by absorbing the gas considered to be on the surface of the thin layer for purpose.

I.3.2 Solar cells

One of the most important applications of TCOs is that they are used in solar cell systems, which are the primary component of photovoltaics because they function as the transparent electrical power of solar cells because solar cells are photovoltaic cells and are known to be transformers that convert electromagnetic radiation into electric current.

I.4 copper oxide semiconductor

Copper oxide is a naturally p-type semi-conductor solid material with a single-tilted structure, black shape, classified from important metal oxides, and also has good strength and a narrow energy separation



Fig(I.4):3D Copper oxide CuO.

I.4.1 Electrical and Optical Properties of Copper Oxide Films

I.4.1.1 Optical properties

CuO thin films are highly transparent therefore, their applications are very successful and important in optical properties, which function as a layer in solar cells where they require very high absorption in visual range it can be used in electrodes for optical devices as well.

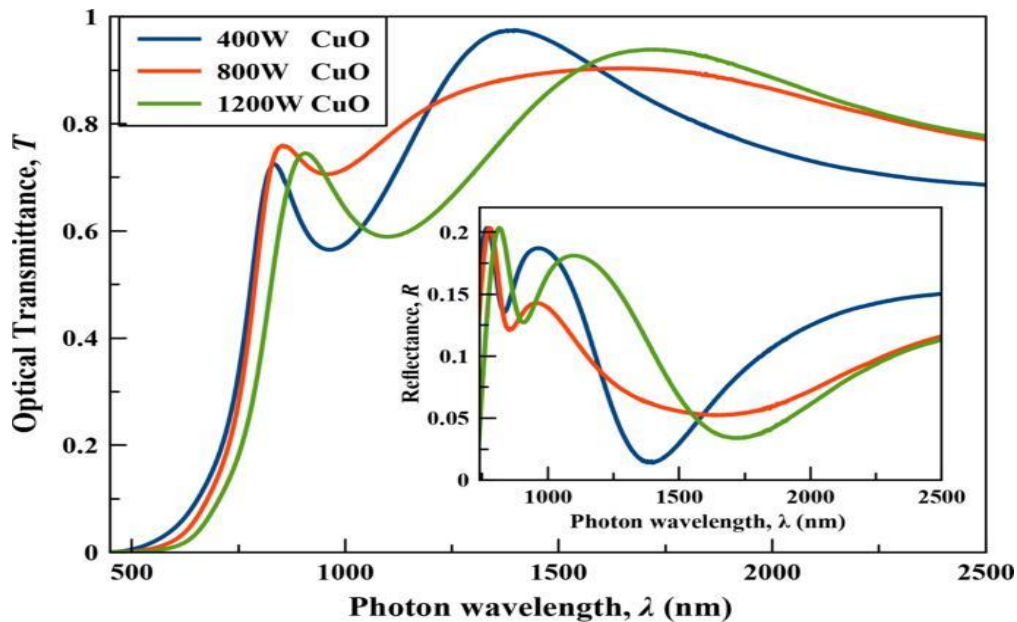


Figure (I.5): Structural, optical and photoluminescence investigations of nanocrystalline CuO thin films at different microwave powers.

I.4.1.2 Electrical properties

Copper oxide is a semiconductor that displays a low conductivity habit, which is due to the reasons for its low impurity concentration or thermal instability, but it can be used as smart windows, in rear car mirrors and in mobile displays a High resolution as an electronic paper, gaz sensor, microwave dielectric materials and heterocontacts.

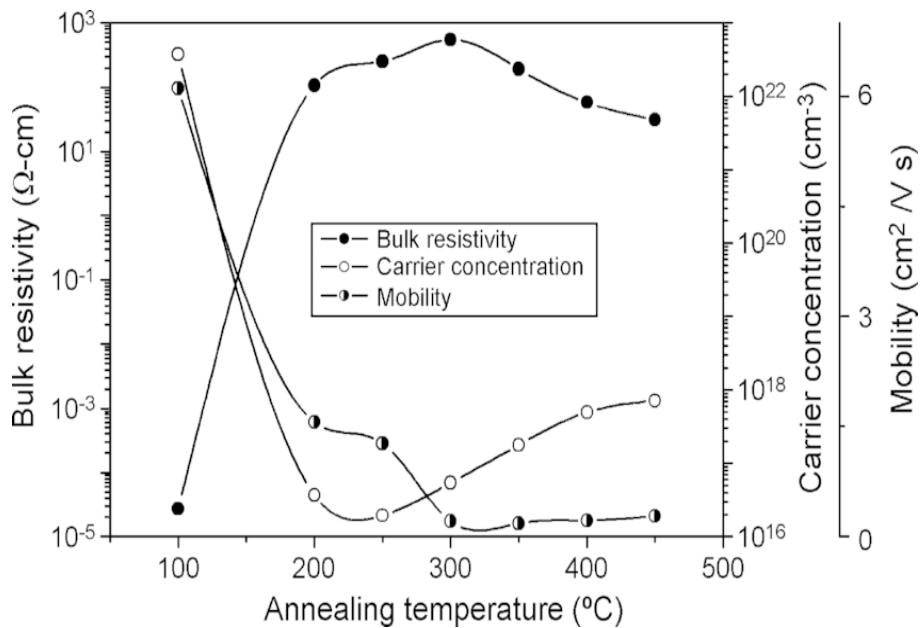


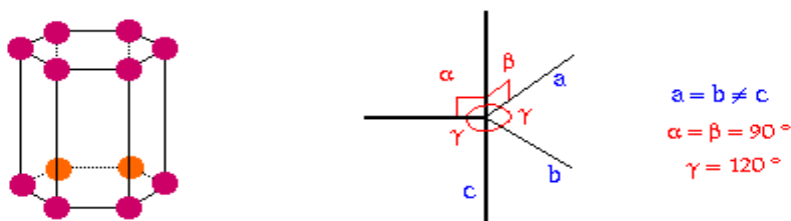
Figure (I.6):Variation of electrical properties of the copper oxide films as a function of annealing temperature.

I.5 The lanthanum

Lanthanum is a chemical element of symbol La and atomic number 57. Lanthanum has given its name to the family of lanthanides that belong to the rare earth; its name derives from the Greek word «lanthanein» which means «hide», lanthanum remained hidden for a long time in cerium oxide. At room temperature, 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.7): The Lanthanum in bulk form.



Figure(I.8) : the Lanthane (La) undoped structure crystalline is Hexagonale

Lanthanum was discovered in the «earth» as oxide, obtained by Johan Gadolin and Anders Gustaf Ekeberg from gadolinite and euxenite. Lanthanum oxide was isolated in 1839 by Carl Gustaf Mosander. Reasonably pure metallic lanthanum was first prepared in 1923. The lanthanum is extracted from the monazite [(Ce, La, Th, Nd, Y) PO₄] and from the bastnaesite [(Ce, La, Th, Nd, Y) (CO₃) F]. Its separation from other rare earth is delicate. Lanthanum isotopes are: [5]

- Stable isotope: ¹³⁹La
- Radioactive isotope: ¹³⁸La

Properties	Physical and chemical characteristics
Symbol	La
atomic number	57
Atomic molar mass	371.37 g/mol (heptahydrate)
Fusion point	858 °C (1,576 °F; 1,131 K)
Boiling point	1,000 °C (1,830 °F; 1,270 K)

oxidation number	+3
Physical state	Solid
Chemical family	Rare earth
Crystal structure	Hexagonal
Solubility in water	957 g/L (25 °C)
Solubility	soluble in ethanol (heptahydrate)

Table(I.1): Physico-chemical properties of lanthanum. [6]

I.5.1 Lanthanum Area of Use:

- Briquet stone: made from mischmetal (a rare earth mixture containing 20% lanthanum).
- Hydrogen storage: in the LaNi_5 alloy in the form of foam.
- The Catalyst for petrol engines: LaPbMnO_3 applied to lanthanum oxide is a good catalyst
- Optical glass: the addition of lanthanum compounds, La_2O_3 oxide or, $\text{La}_2(\text{CO}_3)_3$ carbonate increases the refractive index and decreases the chromatic aberration
- Tungsten alloy: It is used in the form of cylindrical rods as an emissive electrode for TIG welding torches. Or plasma welding torches. Tungsten alloy - lanthanum oxide increases the permissible intensity, facilitates arcing, and minimizes electrode degradation during welding
- Lanthanum carbonate $\text{La}_2(\text{CO}_3)_3$ ingested in the form of offensive tablets is used as a phosphate chelator to control hyperphosphatemia in hemodialysis patients to prevent renal osteodystrophy (source: Fosrenol monograph, Shire)

Other uses: Like other rare earth, it is used for magnetic alloys, in superconducting compounds, as a component of cathode ray tube phosphors, as a “dopant” in laser crystals, as a fluorescent compound (LaPO_4 lanthanum phosphate) studied for anti-fraud markings.

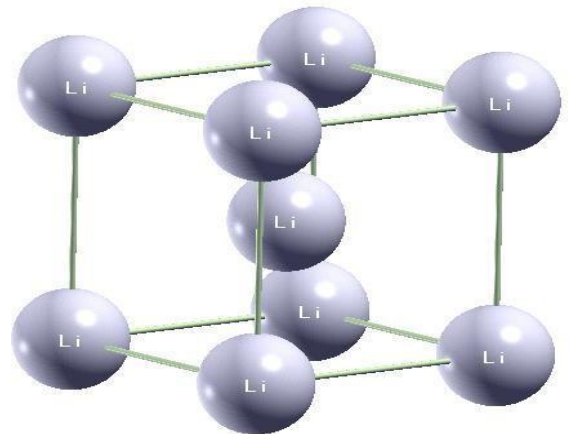
I.6 The Lithium:

Lithium is a chemical element with the symbol Li and atomic number 3. It is a soft, silver-white metal belonging to the alkali metal group of chemical elements. Under standard conditions, it is the lightest metal and the least dense solid element. Like all alkali metals, lithium is highly reactive and flammable. For this reason, it is typically stored in mineral oil. The Li₂O compound has a body-centered cubic structure Figure (I.9). The general properties of Li₂O are shown in the table below :



(a)

Figure(I.9):(a) Samples of metallic lithium



(b)

Figure (I.10): (b) Structure of the Li-compound

I.6.1Uses:

- This deliquescent colorless salt is an oxidizing agent used in the manufacture of red-colored fireworks and flares.
- The hydrated form, lithium nitrate trihydrate, has an extremely high specific heat of fusion, $287 (\pm 7) \text{ J/g}$, [3] and hence can be used for thermal energy storage at its melt temperature of 303.3 K . [7].
- Lithium Nitrate has been proposed as a medium to store heat collected from the sun for cooking. A Fresnel lens would be used to melt solid lithium nitrate, which would then function as a 'solar battery', allowing heat to be redistributed later by convection. [8]

Properties	Physicalandchemicalcharacteristic
molecular formula	Li
Atomic number	3
Molar mass	68.946g/mol
electronegativity	1.0
Volumetric mass	0.53 g.cm ⁻³ à20°C
melting point	255 °C (491 °F; 528 K)
boiling point	600 °C (1,112 °F; 873 K) (decomposes)
Atomic radius	0.145nm
Ionic radius	0.06nm
Electron configuration	1s ² 2s ¹
First ionization energy	520,1 k J m o l ⁻¹
crystal structure	Body-Centered Cube

Table(I.2) :Physico-chemical properties of Lithium.

I.7 Copper oxide Doping:

CuO Doping in general, is an encouraging pathway to optimize the properties of CuO nanostructures with metal and rare earth ions such as In. Mn. Li. Fe. Ni. Zn. La. Cr. Ce. Y....., many researchers have studied the effect of these transition metals on the physio-chemical properties of CuO thin films.

There are numerous studies on doping copper oxide with lanthanum, in which La-doped CuO nanostructured films are recommended for optoelectronic applications. some of the results yielded by these studies are set out below:

- Incorporation of La ion in CuO reduces the crystallite size and induces a number of non-radiative transition centers in CuO .

- Crystallite size of La-doped CuO nanostructures increases from 19.8 to 26.1 nm as La wt% increases from 0 to 8 wt%. Up to 8%, the optical band gap decreases from 1.61 to 1.04 eV. As a result, La-doped CuO nanostructured films are recommended for optoelectronic applications.
- Another result reveals that, The optimized 1% lanthanum (La) doped CuO electrocatalyst exhibits outstanding OER and HER activity in 1.0 M KOH electrolyte posting a potential of 1.552 V vs RHE for OER and -0.173 V vs RHE for HER at a current density of ~ 10 mA cm⁻². Therefore, the incorporation of this element into CuO nanoparticles makes it a viable high electrocatalyst.
- Researches show that doping CuO lattice with La reduces the crystallinity due to the variation of ionic radii and also leads to higher angle peak shift, they reveal the narrowing of the bandgap in doped CuO compared to undoped CuO which is due to the influence of La³⁺ impurity dopant ions on the electronic states of the crystallite, it induces the lattice distortion [9].
- The fabricated CuO and Cu_{0.99}La_{0.01}O electrode exhibited a maximum efficiency of 39 and 48 for a scan rate of 5 mV/s respectively.
- The minimal concentration of La³⁺ ion substitution within CuO NRs enhances significantly the electrical conductivity.
- Detailed examination of the photoelectrical properties of photodetectors has revealed that the photoresponsivity and directivity of Au/(CuO: La)/n-Si have been significantly enhanced compared to the photodetector without La doped CuO. Results indicated that all structural and electrical parameters strongly depended on lanthanum concentration [10].

As for copper oxide doped with Lithium, researchers have come up with a bunch of their experiment results:

- Li doped CuO nanoparticles prepared by flame spray pyrolysis and followed by spin coating for the film preparation were studied at dopant concentrations of 0.5 %, 2 %, 3.5 %, and 5 %, The photocurrent density, and photon-to-hydrogen conversion efficiency increased by a factor of five to ten when introducing Li into CuO. This is attributable to the increase in the electrical conductivity of the film by almost two orders of magnitude, i.e. from $2 \times 10^{-6} \sim 4 \times 10^{-6}$ S/cm to

$7 \times 10^{-5} \sim 3 \times 10^{-4}$ S/cm, and thus the increase in the lifetime of the photogenerated charge carriers[11].

- The crystallite size and average size found to be increased for the samples by increasing the Li doping concentrations from $x = 0$ to 14 nm for crystallite size and 35 to 79 nm for average size[12].
- A significant reduction in optical energy band gap is observed from 2.99 to 2.76 eV with an increase of Li concentration from 0 to 9%, respectively.
- The optical spectra reveal that the absorbance was decreased by the increase of Li doping[13].
- Ray analysis with elemental mapping of the Li-doped CuO thin films shows that the Li dopants are incorporated homogeneously into the CuO thin film matrix[14].

I.8 The effect of co-doping on optical and electrical properties of nanomaterials

Doping is an effective route to enhance the area of applications of a nanomaterial by modifying its optoelectronic properties by tuning the electronic band structure. However, the use of single dopant results in the presence of charged defects, which act as recombination centers and reduce the carrier lifetime, limiting the material's catalytic efficiency, Co-doping has been proposed which is defined as doping acceptor with other impurities simultaneously. Researchers mainly focused on studying the effects of co-doping on optical and electrical properties, In addition to studying the mechanisms of dopant pair interactions, especially in wide bandgap materials.

Some of the pilot results that addressed this strategy are listed below:

- Extensive studies on co-doping have shown positive effects on improving the p-type conductivity of ZnO as well as the conductivity and the stability of p-type ZnO films and nanowires [15].
- Experience confirmed that Co-doping of TiO₂ with Cr and N, reduces the band-gap and enhances the photo-activity property[16]. Besides the photo-catalyst application, the formation of intermediate bands is also desirable for the design of solar-cell materials [17]. Then, enhanced electrical conductivity was measured following Cr-N co-doping, resulting in improved performance compared with N mono-doped samples [18].

- Some research has focused on the effects of other partially compensated co-doping pairs in TiO₂. Khan *et al.* performed density functional theory (DFT) calculations and found that Mo-N codoping could reduce the band-gap to 1.5 eV, enhancing the absorption of visible light [19]
- An other experiment found that codoping ZnS with N and C greatly enhances the visible light absorption compared with undoped ZnS.

I.8.1co-doping of CuO

- A few results are reporting concerning codoping Copper oxide (CuO) nanoparticles prepared by sol-gel method. What is found as results are displayed in what follows:
- Doping CuO with Manganese (Mn), and co-doping with Neodymium (Nd) elements, it is found that the optical band gap is reduced from 1.77 to 1.71 eV This decrease is may be attributed to the fact that the impurity band merges with conduction band of CuO. Then, SEM images from have revealed that grains have a structure of clusters the collisions between molecules increase which in turn increase temperature Hall measurements reveal that the conductivity of the sample increases with temperature. The magnetic studies show that the prepared nanostructures are found to have a maximum value of saturation magnetization at 3 wt % for Mn, Nd co-doped CuO, i.e. ~0.07 emu/g [20]
- In another case, it is noted that The binary doping extends the visible light band gap of CuO to more NIR absorption. Furthermore, an excellent intrinsic ferromagnetic hysteresis loop with high saturation magnetization of ~1 emu/g and retentivity of 0.252 emu/g was found in Cu_{0.94}Fe_{0.03}Mn_{0.03}O structure.

Based on this bibliographical synthesis, Lanthanum and Lithium were chosen as a doping and co-doping of copper oxide thin films in order to study the influence of introducing these elements in CuO lattice and how extent they enhance its optical and electrical properties.

I.9 Thin Film Deposition Processes

The evolution of science has led to a diversity of thin film deposition techniques used in the preparation process. This diversity is due to the many uses of transparent trans oxides as thin layers. Physical - chemical.

I.9.1 Physical Processes

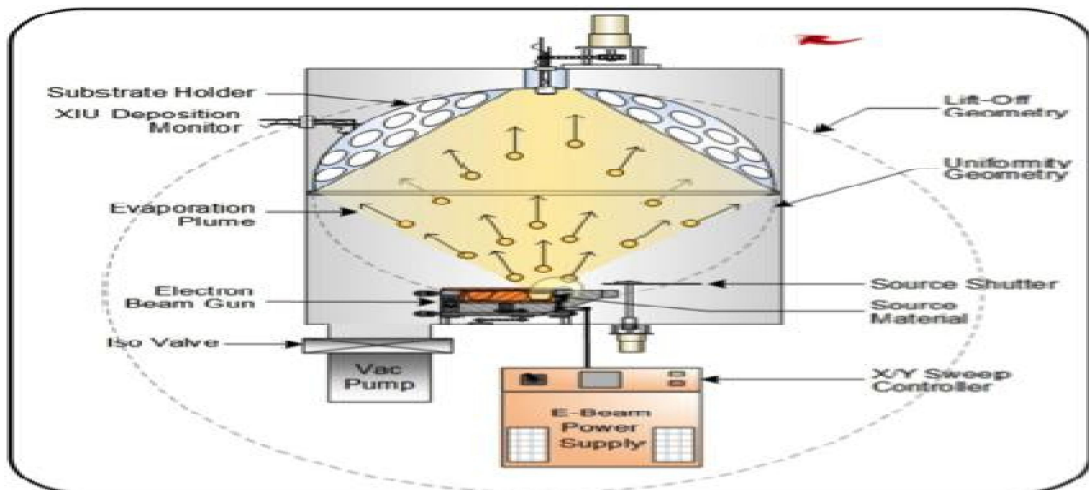
I.9.1.1 Physical vapor deposition

- **Sputtering**

A thin film deposition technique in which a part of the material to be prepared is bombarded with high-velocity positive-ion particles which, in turn, extract atoms from the material to form a stable, highly adhesive, homogeneous thin film.

- ***Thermal evaporation***

Thermal evaporation is a process in which the material to be vaporized is heated to the melting point at very low pressure. The proportion of the vapor cloud within the high vacuum chamber increases, condenses and travels to the lower surface, leading to the evaporation of the material that forms a vapor stream and drains into the substrate to form a thin film.



Figure(I.11): Diagram of E-Beam Evaporation Process.

I.9.2 Chemical Process

I.9.2.1. Chemical Evapore Déposition

- **Sol-gel**

Gel solution is the method used in our current research. This technique is the most common of the chemical methods for preparing thin membranes. The basic principle is to convert the solution into gel by means of a set of chemical reactions at a given temperature for gel deposition.

- **Chemical Spray Pyrolysis Method**

Thermolysis is the process of spraying solution at a hot surface and at a certain temperature where the components interact to form chemical compounds. The

chemical reaction occurs at the surface of the pillar. The basic principle of the thermolysis technique is the thermolysis of salts.

I.10 Sol-gel method

The sol-gel technique (corresponding to the abbreviation «solution-gelification») is an ideal method for making ceramic materials, powders, fibres and films thin, and is particularly well suited for making coatings such as thin layers of oxides . This great diversity, both on the materials side and on the format, has made this process very attractive in technological fields such as optics, electronics, biomaterials, sensors (detection), the separation supports

(chromatography). It also has the advantage of using a soft chemistry and being able to lead to very pure or doped materials depending on the intended application. A sol is a stable dispersion of colloidal particles (1 -1000 nm) within a liquid. These colloids are animated by a Brownian motion that keeps them in suspension and is mainly subjected to the interaction forces of van der Waals and electrostatics, A gel corresponds to an interconnected. three-dimensional network within which the solvent is trapped in pores. If the network is consisting of colloidal particles, we speak of «colloidal gel» whereas if it consists of macromolecules, we speak of «polymeric gel.

I.10.1 The different stages of the Sol-Gel procedures

The principle of the Sol-Gel pathway is to obtain inorganic materials in the form of high-quality optical films from an organic solution. The production of a Sol-Gel film is carried out in three steps [21]:

- The first is the development of a metallic alcoxide solution.
- The second is the deposition of the solution, in the form of a thin layer on a substrate.
- The final step is the thermal treatment of the gelled layer to remove the organic compounds and densify the film.

I.10.2 Main system states during the soil-gel transition

The first state is that of hydrolyzed and/or condensed soils (a): liquid solution of metallic alcoxides and partially dissolved in a solvent.

The addition of water (1) causes the appearance of hydrolysis and reactions of polymerization. Oligomers and polymers are formed in solution (b). The viscosity of the solution increases until a t_{gel} gel is obtained (time required to obtain the gel after adding water to the conditions considered) (c).

The word gel has meaning only at the macroscopic level, or it appears as one solid, although still containing a large amount of interstitial liquid.

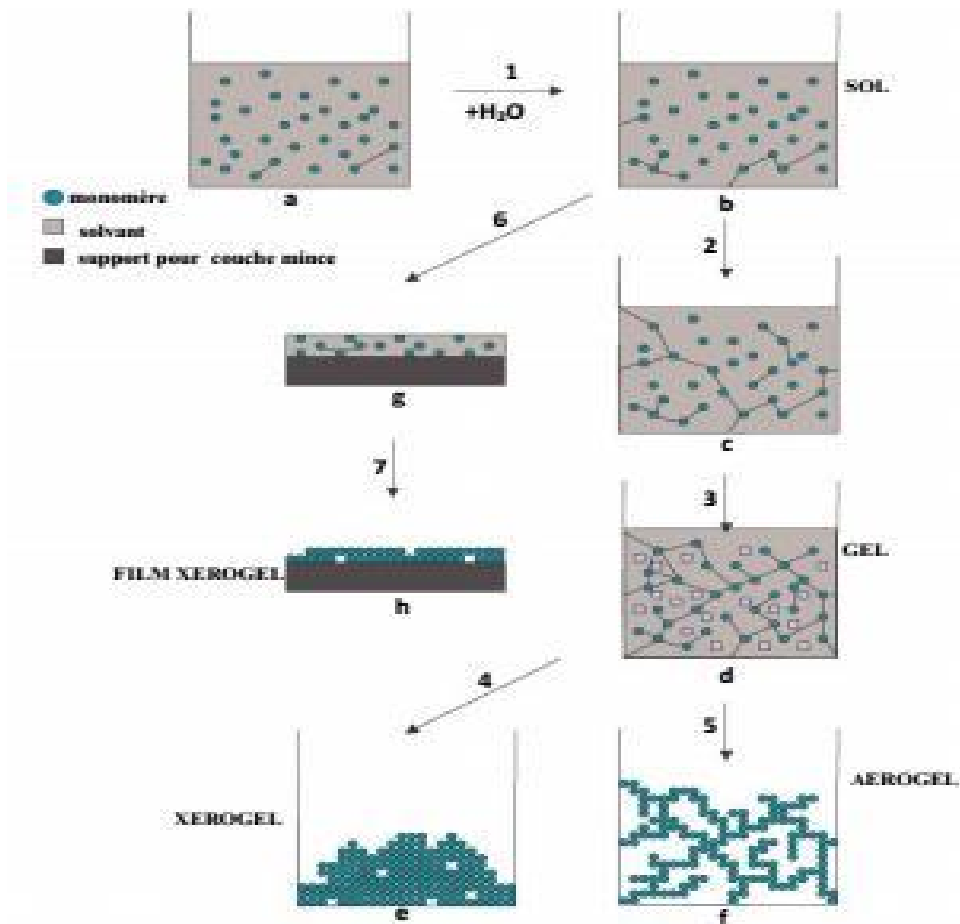
At the molecular level nothing changes, the mesh of the gel is very loose just after the freezing point, and species not linked to frost can still diffuse and react (polymerization, depolymerisation and grafting to the network).

Then the gel ages (3), by successive grafts its mesh becomes denser, the molecules and especially macromolecules diffuse much more difficult. This period can last several t_{gel} (d). Syneresis (expulsion of the solvent) can sometimes be observed.

The gel can be dried under mild conditions (4). It hardens by compacting: it is a xerogel (e) (later application to form dense glasses and ceramics).

The solvent can be evaporated under supercritical conditions (5) (high and constant evaporation rate) to form a very small gel: it is an aerogel. (f).

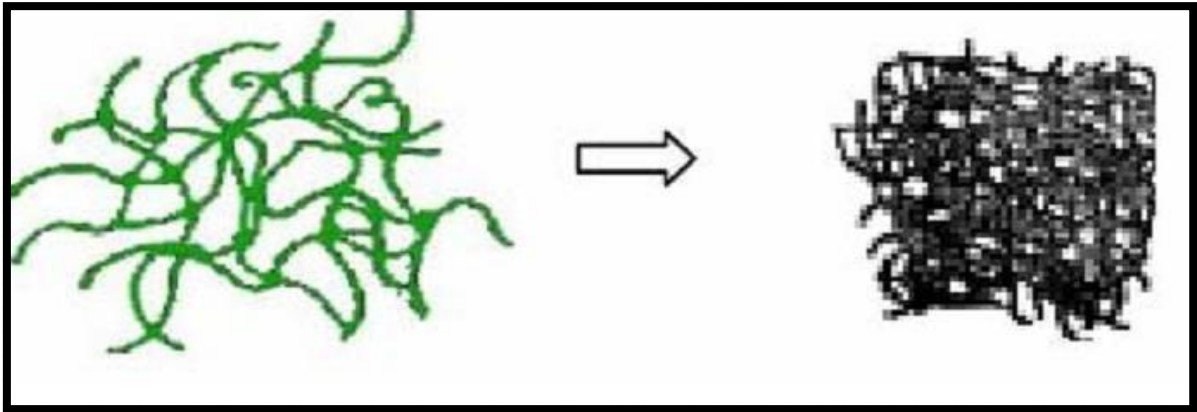
When one is still only at the stage of the soil, it is possible to spread the soil on a surface (6,7) to form thin-film xenrogels (spin-coating and deep-coating techniques) (h)



Figure(I.12):Main steps in a soil-gel synthesis of a material.

Parameters influencing reaction kinetics:

- Temperature: The chemical kinetics of the different reactions involved in the formation of nanoparticles and the assembly of nanoparticles into a gel network are accelerated by temperature, if the temperature is too low, gelation may take weeks or months. If the temperature is too high, the reactions that join nanoparticles together into the gel network occurs so quickly that clumps form instead and solid precipitates out of the liquid.
- Solvent: As molecules assemble together (polymerize) into nanoparticles, the solvent needs to be able to keep the nanoparticles dissolved so that they don't precipitate out of the liquid. Also, the solvent can play a role in helping nanoparticles connect together. As a result, the solvent makes a big difference in ensuring a gel network can form.
- Time: Depending on the type of gel being made, different steps in the gel formation process work differently over different time scales. In general, slower is better for sol-gel. If a gel is allowed to form slowly, it usually has a much more



uniform structure. This often means a stronger gel and, in the case of potentially transparent gels like silica, results in a clearer gel that Rayleigh scatters less (appears less blue). Speeding reactions up too much causes precipitates to form instead of gel network, and can make a gel cloudy and weak or simply not

Figure(I.13): The formation of the polymeric gel.

A low level of hydrolysis (basic pH) favours nucleation and leads to the formation of a colloidal solution. In the case of basic catalysis, pore size is controllable (unlike acid catalysis). The gel formed is called “colloidal gel” and has a broad pore (cluster) structure [22].

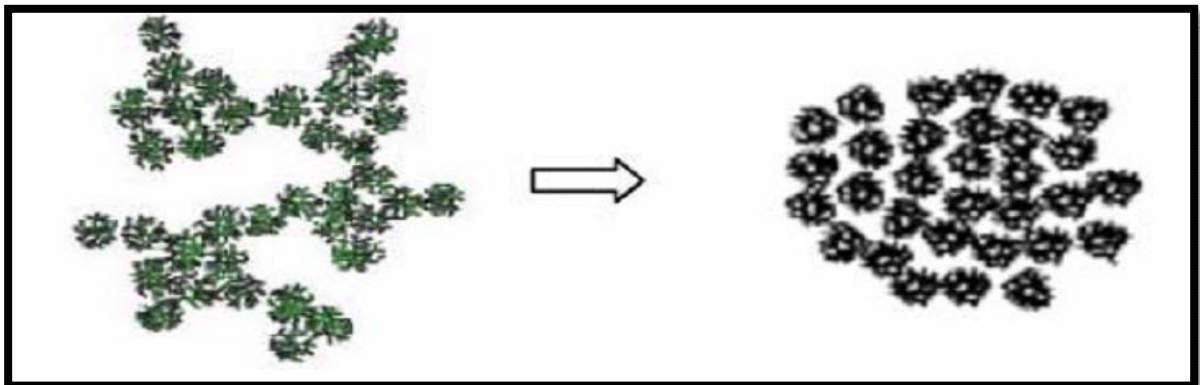


Figure (I.14): The formation of the colloidal gel.

I.10.3 The main techniques for depositing thin films by sol-gel

Several techniques can be used for the deposition of thin films on a given substrate: the "spin-coating", the "drain-coating" and "dip-coating". Each having their own characteristics, the choice of method of deposition depends on the characteristics of

the substrate such that its geometry or size. The two methods presented below are the most commonly used [23].

I.10.3.1 Dip-coating

The dip-coating technique can be described as a film deposition process where the substrate to coated is immersed in a liquid and then withdrawn with a well defined speed under controlled temperature and atmospheric conditions.

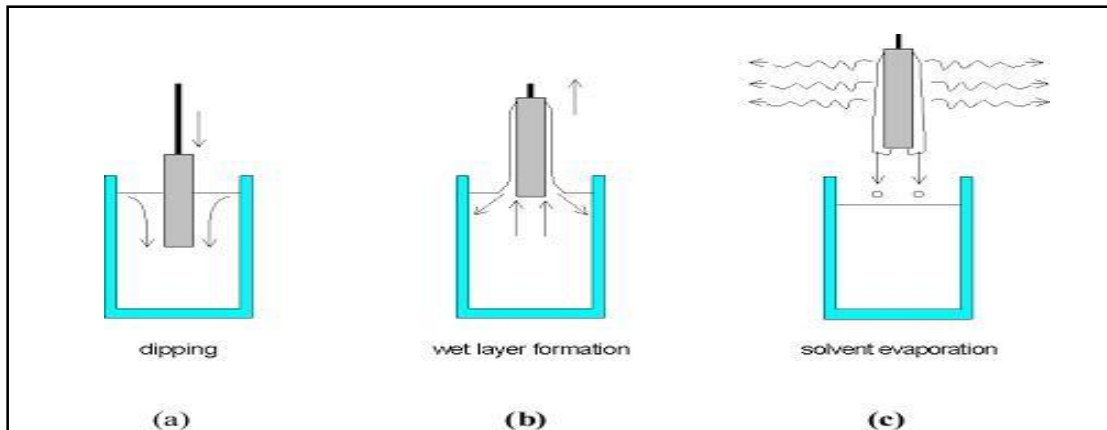


Figure (I.15): Stages of the dip-coating process: a) dipping of the substrate into the coating solution; b) wet layer formation by withdrawing the substrate; c) gelation of the layer by solvent evaporation [24].



Figure(I.16):Dip coater.

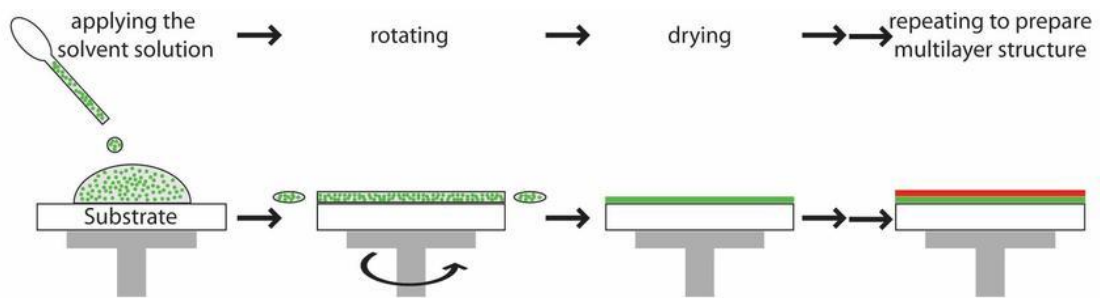
I.10.3.2 Spin-coating:(Centrifugation)

This method involves depositing a small puddle of a fluid resin onto the center of a substrate. Then spinning the substrate at high speed. This technique has the advantage of being easily implemented, for moderate investments. It gives excellent

results on planar substrates with dimensions of the order of cm². This deposition method can be divided into four phases, shown schematically in **figure II.17**:

- 1) The deposition of the solution.
- 2) The start of rotation: the acceleration step causes the flow of liquid outwardly of the substrate.
- 3) Rotating at a constant speed allows the ejection of excess liquid in the form of droplets and the reduction of the thickness of the film uniformly.
- 4) Evaporation of the more volatile solvent which increases the reduction of the thickness of the deposited film.

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



Figure(I.17): The four steps of spin coating.



Specifications:

Actuator	Brushless DC motor
Spinning speed	10 - 8000 rpm
Maximum substrate size	100 mm diameter
Power input	230V, 50Hz
Read out	20 X 4 line LCD
Acceleration	0 - 2000 rpm/sec
Spinning speed Accuracy	< 5%.
Programmable parameter	Speed, acceleration, dwell time and number of steps
Maximum number of steps	5
System memory	5 programs (non - volatile)

Figure(I.18):Spin coater.

I.10.4 Drying and annealing thin layers (heat treatment)

the deposition and formation of gels is followed by two other operations: drying and annealing. These two operations are necessary to obtain thin layers of good quality,

change the structural properties of the materials used; therefore, a in-depth study of these two heat treatments was carried out in order to obtain the best possible structures.

- **The drying** of the deposited layer is a very important step in the realization of quality materials; it corresponds to the evaporation of residual solvents by diffusion to through pores. Drying is done at low temperature.
- **Annealing** or heat treatment is separated from the drying phase; this phase is essential in the formation of the material. Annealing has two main functions: the elimination of the organic species present in the starting solution (organic groups of the Alkyl type (-OR-)) and the crystallization and densification of the material. Annealing is typically performed at temperatures between 300°C and 700°C.

Usually, the dry gel is given a calcination treatment to turn it into a crystalline material. The following reactions usually occur: desorption of solvent and water physically absorbed from the walls of micropores (100–200°C), decomposition of residual organic groups into carbon dioxide (300–500°C), collapse of small pores (400–500°C), collapse of larger pores (700–900°C), and continued polycondensation (100–700°C). The phenomena of sintering and densification are produced through different mechanisms such as condensation by evaporation, surface diffusion, grain limit, and mass diffusion.(Guadalupe Valverde Aguilar* Department of Nanotechnology and Functional Materials, CICATA Unidad Legaria, Instituto Politécnico Nacional, Mexico,DOI: 10.5772/intechopen.82487, From the Edited Volume IntechOpen,Sol-Gel Method Design and Synthesis of New Materials with Interesting Physical, Chemical and Biological Properties,Edited by Guadalupe Valverde Aguilar)

I.10.5 Advantages and disadvantages of sol-gel method

The main advantages are:

- ❖ Simplicity of the process and speed of execution.
- ❖ Low energy cost.
- ❖ Simultaneously coating both sides of the substrate in a single operation (dip-coating) and the ability to form multilayer.

- ❖ Possibility of making thin layers of mineral oxides at low temperature on heat sensitive supports
- ❖ Possibility of making organo hybrid materials as thin or monolithic layers with specific properties.
- ❖ Doping facilitated in large quantities
- ❖ Selecting appropriate conditions can prepare various new materials

The advantage of the Sol Gel method is that it is quite simple to use, allowing materials to be processed directly in various forms: thin layers, fibres, fine powders and solid materials, with high purity and better homogeneity.

The main disadvantages are:

- ❖ cost of very high alcoxide precursors.,Delicate process control and long process times.
- ❖ thin thickness of the layers, so one must perform several
- ❖ The major drawback is the low thickness of the layers, so one must perform several steps of depositing and drying to obtain a thickness of several hundred nanometers, this increases the risk of cracking as the first deposited layers undergo all successive drying which increases the risk of short circuit when the electrical tests [25].

I.11 Applications of the sol-gel technique

The materials derived from the sol-gel technology are found in four main. industrial activities namely:

- Chemical applications that take up the syntheses of powders, catalysts, membranes.
- Optical applications that include ophthalmic coatings,optical fiber synthesis.
- Biochemical applications that include drug formulation, development of new treatments, cosmetic formulations, artificial bone tissue, dentistry... These applications, although few in the market, are promised to an important development. However, they will require the strictest production constraints (GMP in the pharmaceutical sector).
- Structure” applications for glass, ceramics,insulation, refractory or composite materials, fibres, abrasives and coatings. These materials include

chapter I :Bibliographical Study on TCO Thin Films and Deposit technique]

electronic applications for the synthesis of dielectric, ferromagnetic and electrochromic coatings [26]

**Chapter II: Elaboration
and Characterization of
CuO Thin Films**

II.1 Generality on thin film

Molecular atomic layer deposition depends on the use of heterogeneous or heterogeneous organic or mineral compounds. It is a bipedal characteristic of the caudal layer, and its thickness is expressed in micrometers to nanometers, the latter of which can be used in many applications that have achieved extraordinary and striking developments:

Thicker coatings are used for corrosion-protective, wear-resistant or hardened surfaces. They require localized property measurements to be able to understand and engineer the next level of performance.

II.2 Mechanism of Thin Films Growth

In order for the thin layer to be formed and classified, there are basic growth patterns that need to be followed in order to successfully obtain the thin layer growth process.

II.2.1 Nucleation

The nucleus is the production of a small mass through the absorption process and the migrations of atoms to the substrate, and it is considered to be a stage of maturity (growth) of the film in a single two-dimensional layer pattern.

II.2.2 Island structure

Over time, the growth of the nucleus and the formation of larger islands, which are often small three-dimensional crystals, are formed and matured by direct collision from the steam phase and their production increases under the following conditions :

- At high substrate temperature.
- At a low boiling point of film material.
- At low deposition rate.
- At weak binding energy between film material and substrate.
- At a high surface energy of the film material.
- At a low surface energy of the substrate.

II.2.3 Coalescence

These islands develop and develop certain features after the confluence of islands that form large masses by propagation and become spherical.

II.2.4 Channel and Holes

And after these carrots form channels, but the latter may have mass defects, such as holes or gaps, where these spaces are directly proportional to the volume of crystals formed in the canals, where the contraction of these spaces leads to a decrease in volume, and from which we can say that they are free channels.

II.2.5 Continuous film

This continuous film phase is the last stage of film growth in which gaps are filled entirely by secondary nucleus, growth and integration, and in this way a continuous and perfect film is obtained.

II.3 Spin coating technique

Spin coating is a procedure used to deposit uniform thin films to flat substrates. Usually a small amount of coating material is applied on the center of the substrate, which is either spinning at low speed or not spinning at all. The substrate is then rotated at high speed in order to spread the coating material by centrifugal force.

A machine used for spin coating is called a Spin coater.

II.3.1 Preparation of the substrate

a- Choice of the substrate:

The CuO layers studied are deposited on glass substrates. This substrates which have a length of 2.5cm and a width of 2.5cm, cut by a diamond-tipped pen. In this our work, Our choice of this kind of substrates was based on a set of criteria:

- The thermal compatibility with CuO (the thermal dilation coefficients which minimize the stress in the interface film/substrate:thermal expansion coefficient is compatible with that of the deposited material which serves to limit. stress effects during annealing [63].(Mémoire AMEL GUETTAF -maser2-2017)
- the chemical composition of the glass substrates does not lead to contamination of our thin films by diffusion of chemical species during annealing .

- the index of the substrate must be lower than that of the thin layer.

II.3.1.1 Important guidance and steps during the experiment:

- ✓ must be ascertained, the solution must adhere to the substrate. Because, Adhesion is influenced by mechanical consolidation during gelling.
- ✓ In an ideal case, all measurements should be made on the same substrate to ensure that a good correlation can be established between the results, but this is often not possible [13]. (mémoire : zeribi fatma / *Elaboration et caractérisation des couches minces d'oxyde de Titane (TiO₂) à différentes nombres des couches par voie Sol-Gel (spin coating)*)
- ✓ The quality of the sample deposit depends on the cleanliness and surface condition of the substrate. The cleaning of substrates is a very important step that takes place in a clean place, we will see the detailed method for cleaning the substrates in the next paragraph.

b- Cleaning of the substrate

cleaning substrates is a very important step because this latter determines the adhesion and homogeneity qualities of the deposited layers. The process used for cleaning glass substrate is described by the following steps: Washing with soap solution to clean any dust or attachments.

- Rinsing with distilled water to remove soap.
- The substrates are placed in the Acetone for 10 minutes .
- Cleaning in a water distilled bath.
- Drying using a drier thus all traces of greases and impurities stuck to the substrate's surface, are removed.



Figure(II.1): The substrates and a diamond-tipped pen.

II.3.2 products used in the experiment

II.3.2.1The solids elements

a-Properties cupric acetate (monohydrate): the precursor

Molecular Formula	$C_4H_6CO_4 + H_2O$
Atomic molar mass	199.65 g/mol
Fusion point	115° C
Boiling point	decomposition
Volumetric mass	1.88 g/cm ³
Physical state	solid
Solubility in water	72 g.L ⁻¹
Solubility in ethanol	Poorly soluble



Figure(II.2): Cupric acetate.

b-Properties of Lanthanum Chloride (dopant)

Molecular Formula	$LaCl_3$
Atomic molar mass	371.371g/mol (heptahydrate)
Fusion point	858°C
Boiling point	1.000°C
Density	3.84 g/cm ³
Physical eta	Solid
Solubility in water	957 g/L (25°C)
Soluble in ethanol	Soluble in ethanol
(heptahydrate)	(heptahydrate)



Figure(II.3):Lanthanum chloride

c-Properties of lithium Nitrate (co-dopant)

Molucelar formula	LiNO₃
Atomic molar mass	68.946 g/mol
Fusion point	255 °C (491°F ,528 K)
Boiling point	600°C(1.112°F,873 K) (decomposes)
Volumetric mass	2.36 g/cm³
Physical state	solid
Solubility in water	52.2 g/100 ml (28°C)
Solubility in ethanol	Soluble in ethanol (heptahydrate)



Figure(II.4): Lithium Nitrate

II.3.2.2 Liquid elements:

a.the catalyst:

Molecular Formula	C₂H₇NO
Molar mass	61.08 g/mol
Melting point	170 °c
Boiling point	10 °c
Density	1.012g/cm³
Physical state	Liquid(viscours fluid)

b. **The solvent:**In the present work, we used **ethanol** as an organic solvent. Its characteristics are recorded in the following Table:

Molecular Formula	C₂H₅OH
--------------------------	-------------------------------------



Atomic molar mass	46.07g/mol
Melting point	78.37°C
Boiling point	
Density	0.789g/cm³à 20°C
Physical state	transparent liquid
Solubility in water	miscible
Soluble in ethanol	

Figure(II.5) :Ethanol

II.3.3 -Preparation of the solution

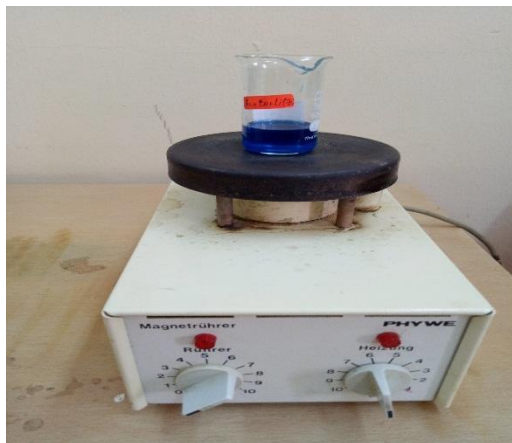
Monohydrated copper acetate(0,2 M) was dissolved in15ml of ethanol with some drops of (MEA) at a temperature of 70°C for 2 hours under agitation by a magnetic stirrer. Until obtained a clear and homogeneous bluish solution, and then left it for 24 hours. Till we get a solution of undoped Copper acetate.different co-doping percentages of Lanthanum and lithium were prepared using Lanthanum trichloride as a source of CuO doping in percentage 1% and lithium nitrate as a source of CuO co-doping with lithium in percentages 1%.3%.5%.7%. 15 ml of pure Ethanol (C₂H₅OH) was used as a solvent.



Figure(II.6): Lithium powder oxide solution



Figure(II.7): undoped copper oxide solution



Figure(II.8): Lanthanum Powder(La)

Figure(II.9): La-doped CuO solution

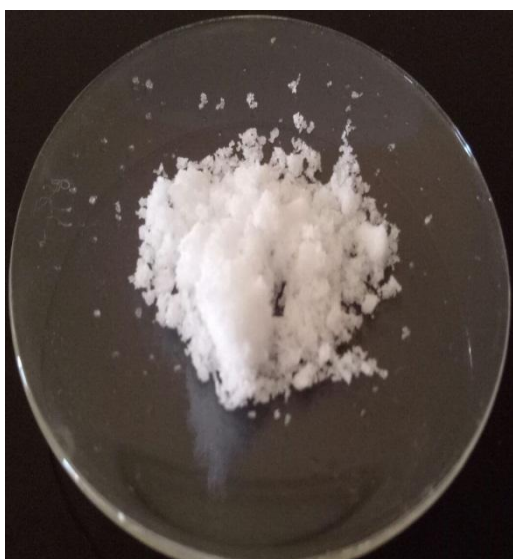


Figure (II.10): Lithium Powder (Li)

Figure(II.11): Li doped CuO solution

II.3.4 Depositing of thin films

The prepared solutions are undoped CuO(0%), CuO + La(1%), CuO + La(1%) Li(1%), CuO + La(1%) Li(3%), CuO + La(1%) Li(5%), CuO + La(1%) Li(7%).

After 24 hours of solution rest: comes the step of deposition and thermal treatment:

a-Deposition step

The obtained solutions mentioned previously

Were dropped on glass substrate using a syringe because it makes it easier to apply to spread the solution evenly by centrifugal force.

b-Thermal treatment

Drying of thin layers: After each coating, the coated film was dried at 200 °C for 10 min in a furnace since the boiling points of the solvents ethanol and MEA are 78.37 °C and 170 °C, respectively, and the thermal decomposition temperature of copper acetate is 237 °C to evaporate residual solvents at the substrate surface and the initiation of formation and crystallization of the CuO film. Both deposition and drying are repeated six times (So we get 6 layers) on the substrates. The experimental conditions of the spin coater apparatus were fixed as follows conditions :

- Rotation speed (t/min): 3000
- Deposit time (s): 30 min

Annealing thin layers: Drying alone is not enough to obtain the desired degree of material to be manufactured. After the deposition and drying of the sixth layer, we thin films into a resistance furnace to be annealed at 500 °C for 1 hour, with a view to the final densification of the obtained films

II.4 Experimental techniques for characterizing thin film layers

The optimization of the preparation conditions is the main task in order to get device quality films. This has to be carried out on the basis of detailed structural, compositional, morphological, optical and electrical properties of the films obtained at different growth conditions. In the following sections the techniques used for the film characterizations are discussed briefly.

We used different techniques to characterize the layers:

- ✓ Optical properties: Measurement of transmittance and optical absorption, Raman and Photoluminescence of films.
- ✓ Electrical properties: Measurement of Photocuring layers.
- ✓ Morphological and structural characterization: X-ray diffraction (DRX), Scanning electron microscope (SEM), X-ray spectrometer (EDX), Atomic force microscope (AFM)

II.4.1 Optical characterization

Optical methods make it possible to characterize a large number of parameters.

They have the advantage over electrical methods, being non-destructive and not to require the realization, always delicate, of ohmic contacts. They require only a transparent substrate in the wavelength range to be explored.

II.4.1.1 UV-Visible Spectroscopy

UV-Visible spectroscopy is a non-destructive optical analysis method that is based on the transition from a fundamental state to an excited state of an electron of an atom or of a molecule by excitation by an electromagnetic wave. The spectrophotometer principle consists of a source consisting of two lamps that allow a continuum of emission over the entire UV-Visible wavelength range. A mobile monochromator makes it possible to select wavelengths and thus to make a scan of the spectral range. The photon beam at the selected wavelength is reflected by a mirror that synchronizes the motion of the monochromator, then the beam passes through the sample and reference. Finally, an amplifier makes it possible to compare the transmitted intensity with the emission intensity [27].

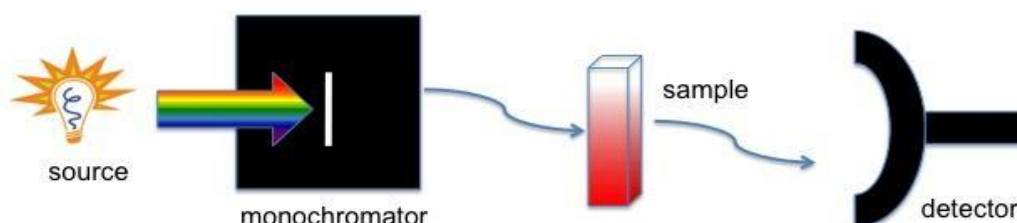
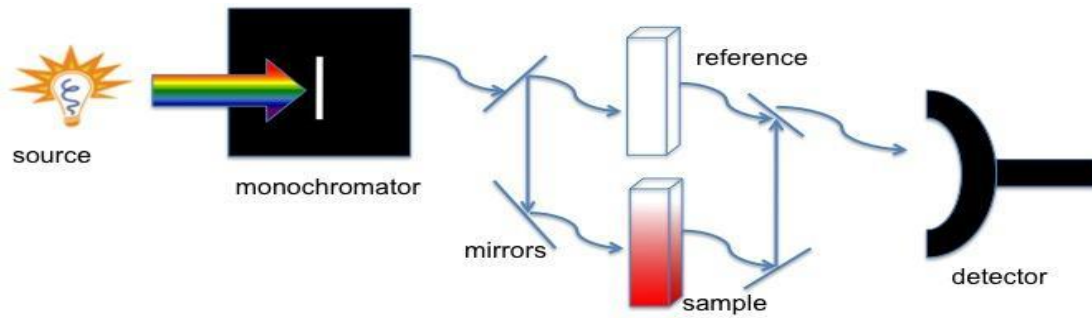
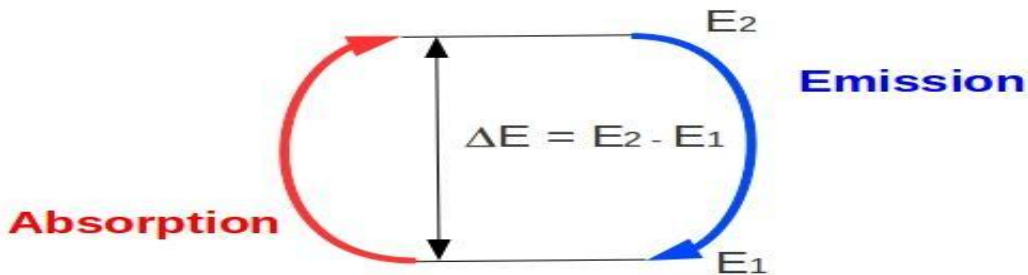


Figure (II.12) : The principle of UV-Visible transmitted spectroscopy with out reference



Figure(II.13) :The principle of UV-Visible spectroscopy with reference



Figure(II.14) :The transition of electrons

- **Retrieval of information**

The ratio of the transmitted light intensity I to the incident light intensity I_0 , when light is passed through an absorbing film, is given by Beer-Lambert equation:

$$I = I_0 \exp(-\alpha d)$$

Where α is the absorption coefficient and d the thickness of the film.

a-The absorption coefficient

In the spectral field where the light is absorbed, and by knowing the film's thickness, we can determine the absorption coefficient for each value of transmittance T in (%) which corresponds to energy by the law of Beer-Lambert:

$$T(\%) = I / I_0 \cdot (100) \quad (\text{the law of Beer-Lambert})$$

$$\alpha = (1/d) \ln(100/T(\%))$$

- The absorption coefficient α is related to the extinction coefficient k by the equation:

$$\alpha = \frac{4\pi k}{\lambda}$$

Where: λ is the wavelength of the light [28].

- **UV-Vis-NIR Spectrometer :**

The experimental setup in principle is very simple. A high intensity lamp (or change of lamps

in different spectral regions) giving radiation from UV to NIR region is required. A monochromator selects different wavelengths, which fall on the sample. Depending upon its properties, the sample reflects or absorbs certain wavelengths and transmits the rest. The transmitted (or reflected) intensity at different wavelengths are detected by a photodetector and given as an input to a recorder or computer [29].

The transmission spectrometer used is Perkin Elmer LAMBDA 25 UV/VIS Spectrometer with double beam one for their reference (glass) the other with the sample (glass-film), the spectral range extends from wavelength $\lambda = 300 \text{ nm}$ to 1200 nm .

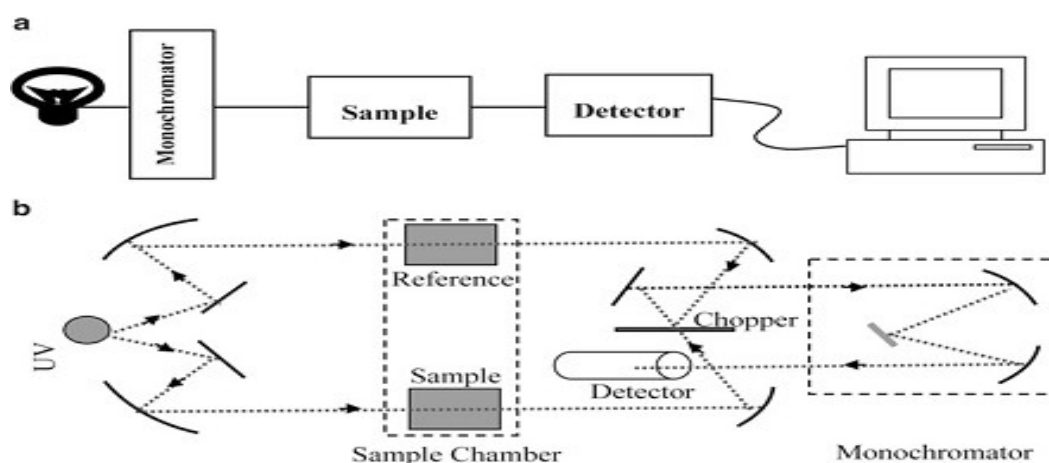


Figure (II.15): (a) Schematic of UV-Vis spectrometer. (b) Schematic of dispersive spectrometer [30].

B-Optical Gap determination

The fundamental absorption is related to the band-to-band transitions in a polycrystalline semiconductor, i.e., to the excitation of an electron from the valence band to the conduction band. Therefore, the fundamental absorption can be used to determine the energy gap of the semiconductor.

The absorption coefficient is related to the optical band gap via Tauc's equation [26]:

$$(\alpha h\nu)^n = A(h\nu - E_g)$$

Where :

h : Planck's constant,

v : the photon frequency

n: following a direct or indirect gap transition (optical type of transition)

A : constant

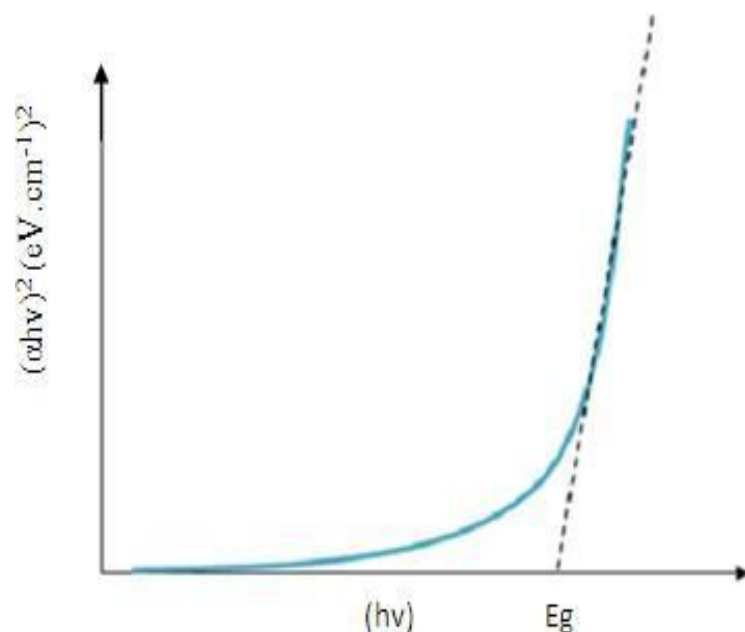
E_g : the band gap of the film.

So for a direct gap such as CuO, which is the case with our oxides, α is expressed as a function E_g according to the following equation :

$$(\alpha h\nu)^2 = A(h\nu - E_g)$$

Thus, if we trace $(\alpha h\nu)^2$ as a function of the energy of a photon $E = h\nu$ and extrapolate the linear part of α^2 to the x-axis (i.e., $\alpha^2 = 0$), we obtain the value of E_g (Figure II.15)

The method for its extraction consists in first calculating the absorption coefficient α in cm^{-1} . For a direct transition semiconductor, the method then consists in drawing the curve $(\alpha h\nu)^2 = f(h\nu)$ where $h\nu$ is the energy of the photons in eV ((with $h\nu \text{ (eV)} = hc / \lambda = 12400 / \lambda \text{ (Å)}$)), Extrapolation of the linear part of the curve with the x-axis (energies) gives the forbidden band value.



Figure(II.16): illustration of band gap determination

b- determination of Urbach energy

The empirical parameter E_{00} , often referred to as the “Urbach tails” has the dimension of energy and is frequently used to determine the film quality (measures the degree of disorder in amorphous semiconductors) [31]. E_u is usually used to describe the width of the localized states in the band gap (but not their positions). Pankove has shown that the value of E_u is related to the impurity concentration [32]. However, Redfield has shown that all defects (point, line, and

planar defects) lead to local electric fields that cause band tailing. Thus, the Urbach energy can be considered a parameter that includes all possible defects [33].

In this work, the Urbach tail is used as a parameter for assessing the amount of disorder in CuO films.

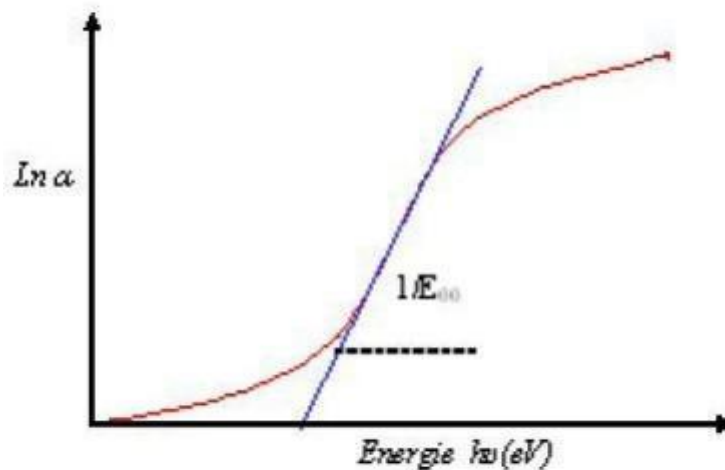
$$\alpha = \alpha_0 \exp(h\nu / E_{00})$$

α_0 : est constant.

E_u : l'énergie d'Urbach (ou tout simplement E_{00}).

By drawing $\ln(\alpha)$ versus $h\nu$ we can determine E_u value as the reciprocal of the linear part's slope (Figure II.18):

$$\ln \alpha = \ln \alpha_0 + (h\nu / E_{00})$$



Figure(II.17): illustration of Urbach energy determination

II.4.2 Electrical Characterization

Electrical resistivity (ρ) is the most commonly deduced value from ohmic measurements. It represents the inverse of conductivity (ζ).

To measure electrical resistivity, several devices have been developed. We are interested here in the so-called four-point method. The term tip here means that the contact at the level of the thin layer is carried out in a punctual way by means of a tip-shaped electrode usually in gold. Two measuring geometries can exist: aligned points and square arranged points. In the configuration of the 4 Aligned points, the two external points are used to bring the I-current while the two internal points are used to

measure the U-potential difference. These electrodes are equidistant and have a distance a (Figure II.19).

When the distance a between the terminals is much greater than the film thickness thin, (d a) (the thickness is negligible compared to other dimensions), the lateral dimensions can be considered infinite. In this case, a two-dimensional model of the conduction is considered "a cylindrical propagation of the field lines in the thin layer" and gives [34]:

With:

ρ : the resistivity of the layer

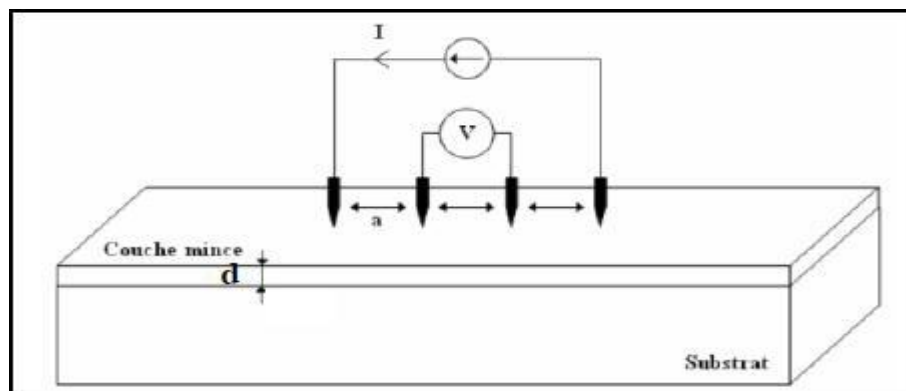
d : the thickness.

K :identifiable transactions by : $K = \frac{\ln 2}{\pi}$

the report $\frac{\rho}{d}$ characterizing the layer notes R_s and it is expressed as Ω , a ready coefficient K, R_s is the ratio of voltage U to current I.

Based on the above considerations, we have the formula to deduce the resistivity of the four-point measure by knowing the thickness:

$$\rho = \left(\frac{\pi U}{\ln 2 I} \right) \cdot d = R_s \cdot d$$



Figure(II.18): Schéma d'un dispositif quatre pointes alignées [34]

Chapter III: Results and Discussion

III.1 Introduction

This chapter aims to display, discuss and interpret the different results obtained in the present work namely the results of optical and electrical characterization according to the previous researches.

III.2 Characterization of the prepared films

III.2.1 Thin films' thickness Measuring

Films' thicknesses were measured using the program Hebal Optics on the computer to calculate the thicknesses of CuO thin films co-doped La and Li. The results of calculating are shown in the table (III.1).

The Samples	Thickness (nm)
Undoped copper acetate	291
AC + La (1%)	279.5
AC + La + Li (1%)	282
AC + La + Li (3%)	286
AC + La + Li (5%)	287
AC + La + Li (7%)	294

Table(III.1): Thickness of CuO thin films co-doped with La+Li (%) by sol gel technique.

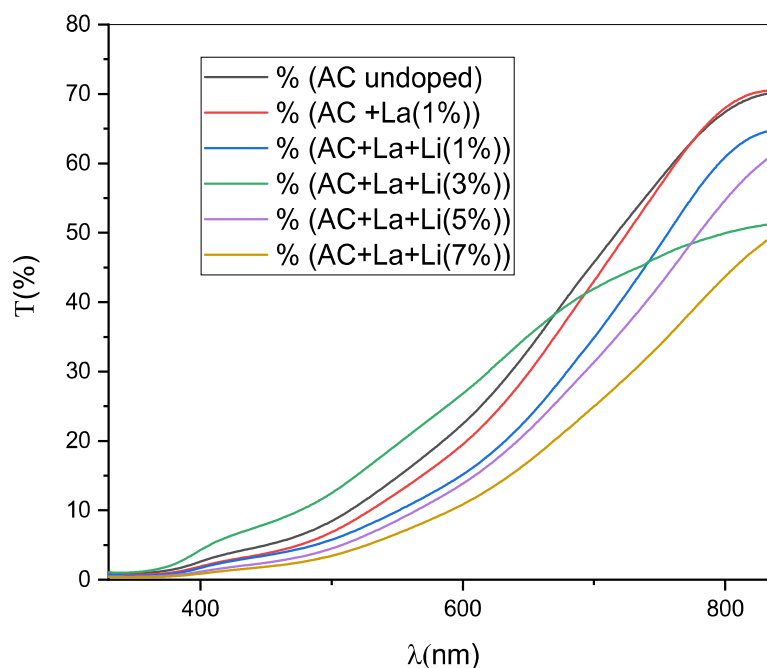
- **Optical properties:**

The optical measurements were carried out using Perkin Elmer Lambda 25 UV-Visible. Wave length spectral ranges between 300 nm and 1100 nm. In this section we will display, discuss and interpret the results related to the Transmittance and absorbance spectra of the thin films as well as those related to the films' optical

constants such as optical gap, Urbach's energy, absorption coefficient, reflection R, the extinction coefficient K, and the refractive index n.

III.2.2 Effect of the dopant rates on the transmittance spectra

Figure(III.1) exhibits the optical transmission T curves as a function of wavelength of undoped and CuO doped thin films.



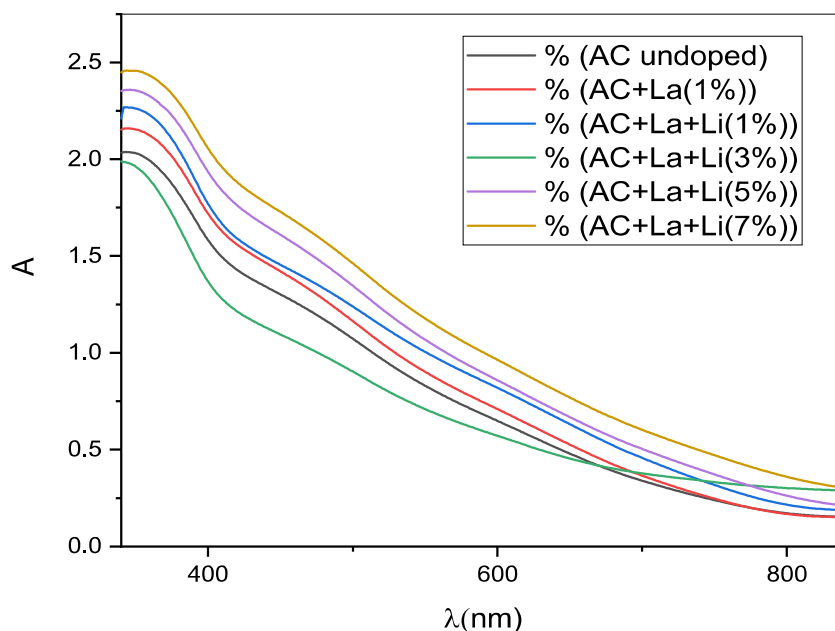
Figure(III.1): Transmittance spectra of CuO thin films

it is clear that The curves of transmittance increases by increasing the wavelength for all thin films, we note a low values of transmittance in the ultraviolet wavelength region of the spectrum This can be explained by an increase in photovoltaic absorption resulting from an increase in the number of electronic transfers between the equivalence range and the conduction range.

On the other hand, we can observe that the average transmittance of CuO: La, Li decrease with the increase in the Li-codoping percentage, this decrease in transmittance film average could be explained by the increase in film thickness which is in agreement with the beer-Lambert law.

III.2.3 Effect of the concentration of the co-dopants on the Absorbance

the absorbance spectra of the different samples is shown in figure (III.2).



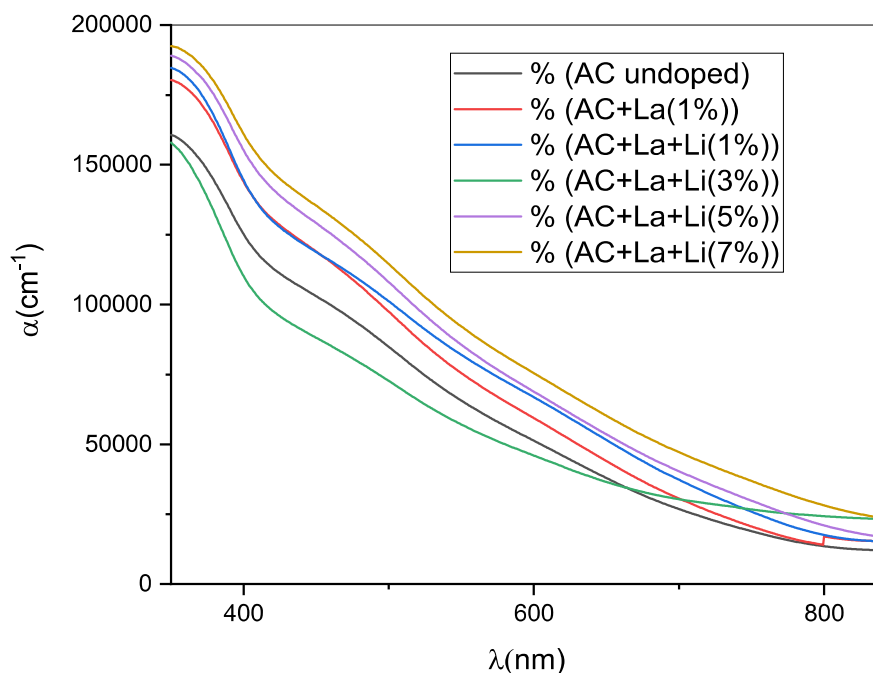
Figure(III.2): Adsorption spectra of undoped copper oxide thin films and co-doped with La and Li

the absorption values are gradually reduced with the increase of wavelength but they increase with the increase of co-doping percentages which return to the increase in carrier concentration.

as it displays in figure (III.2), all the samples exhibit a high absorption of incident photons toward lower wavelength, this region is used to determine the gap energy.

III.2.4 Effect of the concentration of co-dopant on the absorption coefficient

using the absorption coefficient relationship mentioned in the second chapter, the absorption coefficient as a function of photon energy is drawn and presented in figure (III.3).

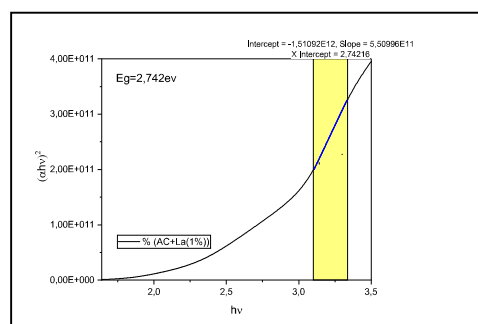
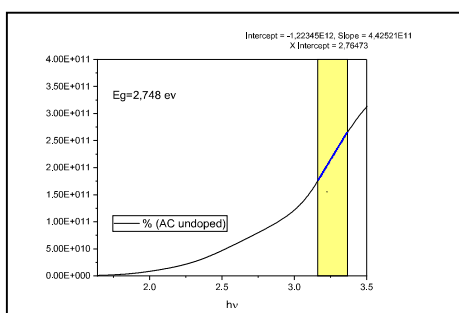


Figure(III.3): The absorption coefficient curve for $h\nu$ of undoped and co-doped copper oxide films

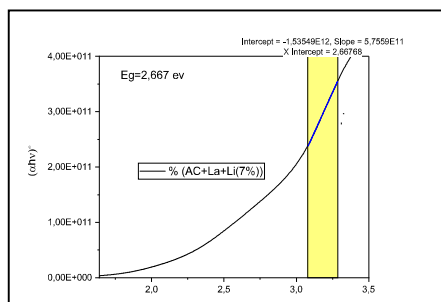
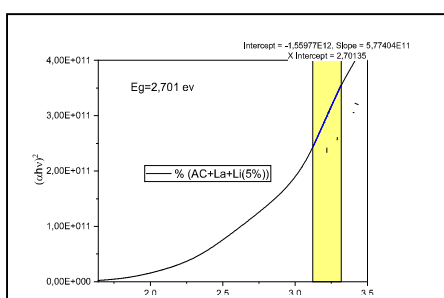
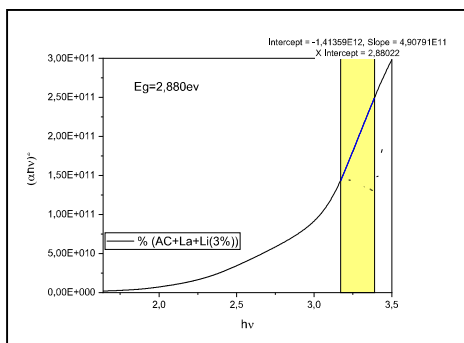
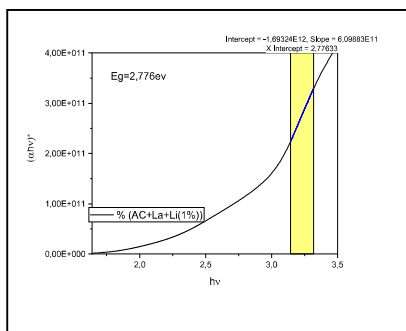
As it is depicted in figure (III.3), the absorption coefficient increases by increasing wavelength. La 1% Li3% shows a low absorption coefficient in related to the undoped and the other co -doped films.

III.2.5 Optical gap

The values of bandgap depicted in table (III.2) and presented in figure (III.4) gives a clear idea of visual absorption. It can be calculated by a relation (Tauc) that depends on the variables $(Ah\nu)^2$ as a function of $(h\nu)$.

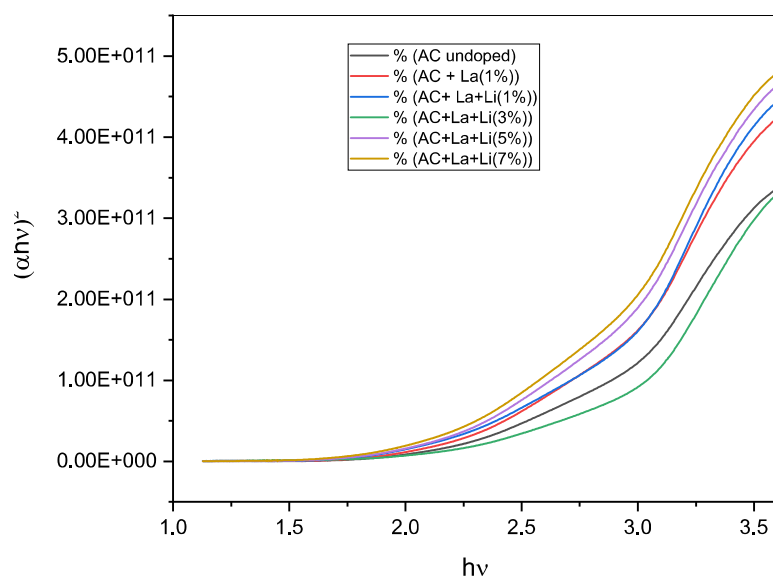


Chapitre III :Results and Discussion



The samples	Eg(ev)
AC undoped	2.764
AC+La (1%)	2.742
AC+La+Li (1%)	2.776
AC+La+Li (3%)	2.880
AC+La+Li(5%)	2.701
AC+La+Li (7%)	2.667

Table(III.2): Energy gap value of copper oxide thin films co-doped with La and Li.



Figure(III.4) : The curve of changes $(Ahv)^2$ as function of (hv) for copper oxide thin films co- dopant with La and Li.

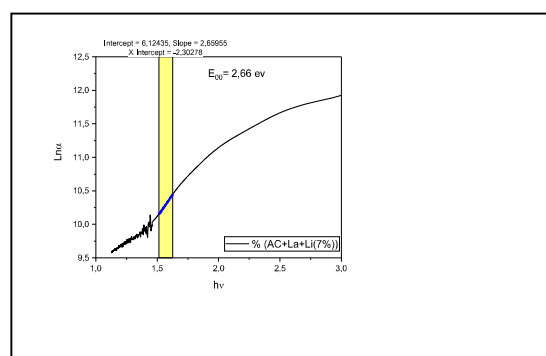
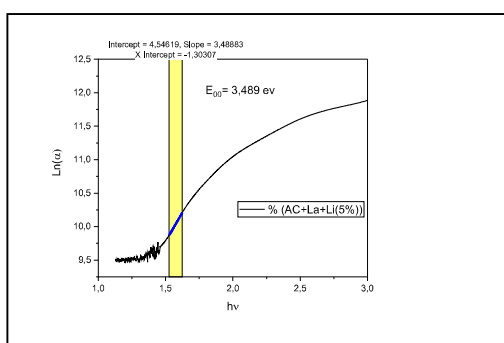
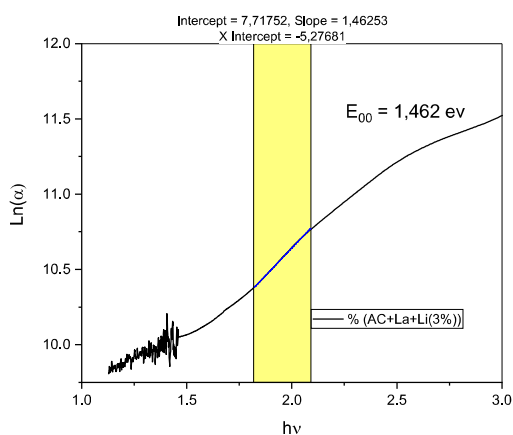
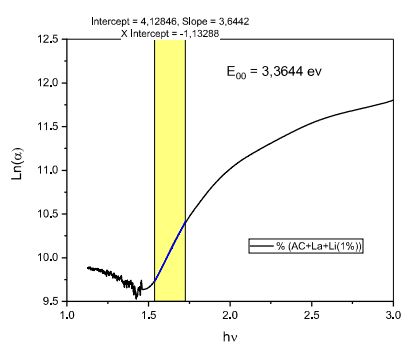
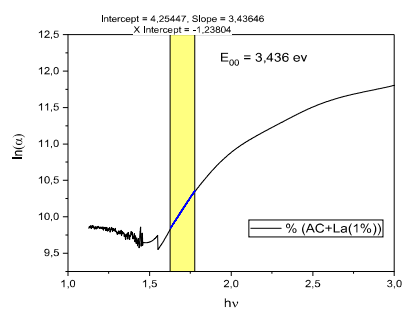
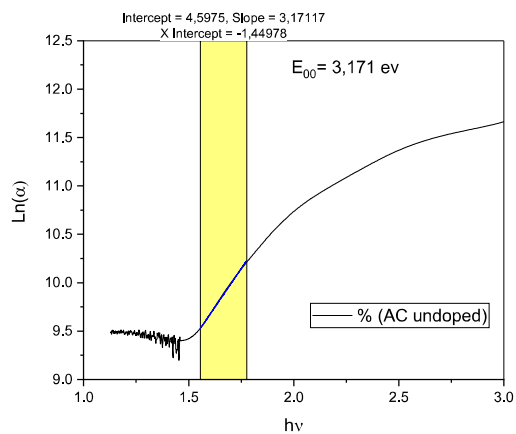
The energy gap values obtained in different co-dopant retes decreases from the undoped level to La 1% (from 2.764 ev to 2.742 ev). The introducing of La 1% has the effect of reducing the value of the band energy of the undoped film unlike the low rates of Li (1%-3%) which has an opposite effect. Whereas, high rates of Li (5%-7%) reduce more the gap energy till 2.66 ev in related to the undoped film. the decrease of the energy gap can be explain that La dopant brings new local levels under transport package and these levels are ready to receive electrons and generating tails in the energy divide works.

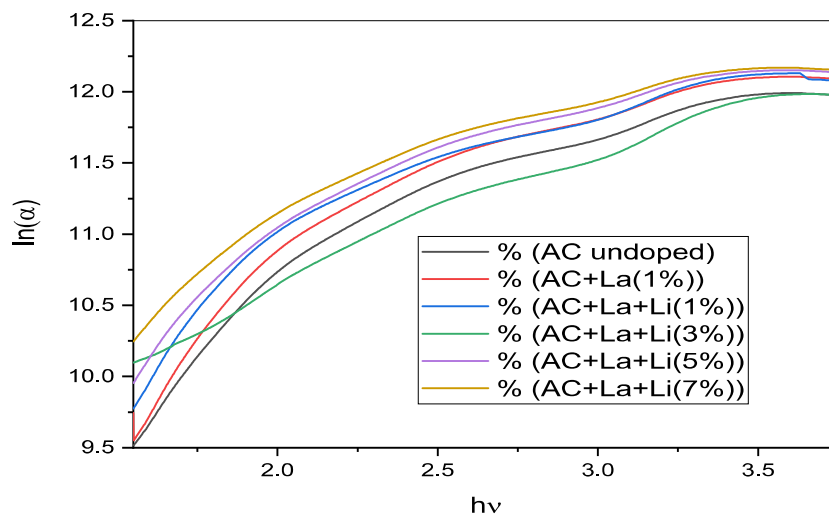
For co-doped with Li there is a change in the profile of E_g ; in two ratios 1% and 3% of Li dopant We've noticed an increase in gap energy from 2.74 to 2.88 ev and then it decreases to 2.66 in the level of co-dopage La1%Li7% .

III.2.6 The Disorder (Urbach energy)

The same thing as the optical gap, using the method indicated in the second chapter, $\ln(\alpha)$ as function of hv is drawn for all level of co-doping,as shown in figure (III-5).

Chapitre III :Results and Discussion



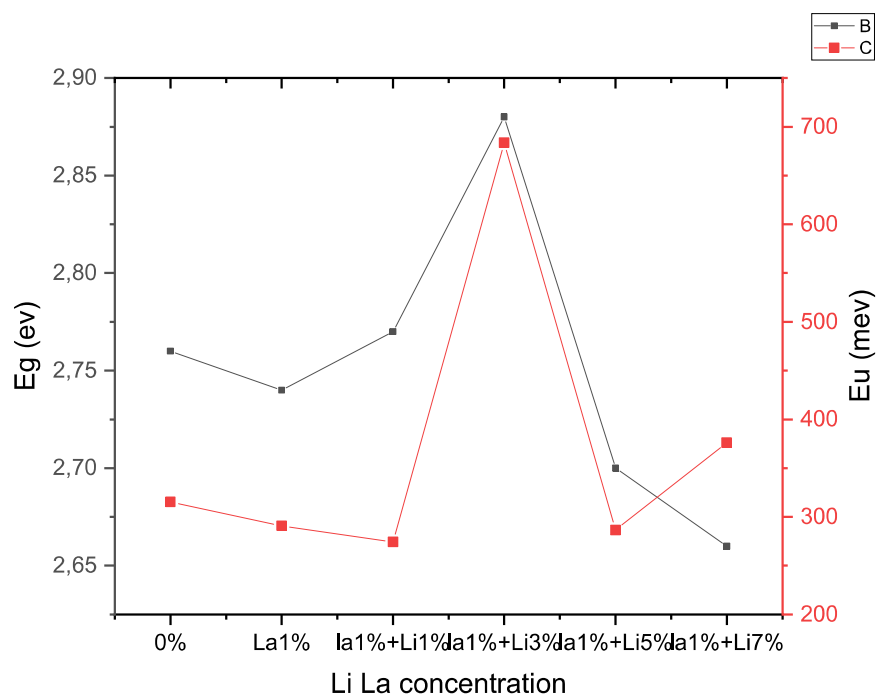


Figure(III.5):Ln(α) as a function of ($h\nu$) for copper oxide thin films co-doped with La and Li

The samples	$E_{00}(\text{mev})$
AC undoped	315.34 meV
AC+La (1%)	290.9 meV
AC+La+Li (1%)	274.4 meV
AC+La+Li (3%)	683.7meV
AC+La+Li(5%)	286.6 meV
AC+La+Li (7%)	375.98 meV

Table(III.3):Eurbach value of copper oxide thin films co-doped with La and Li.

The next figure shows the variation of both the optical gap and the energy of Urbach for different co-doping ratios (CuO:La,Li) :



Figure(III.6): Band energy and Urbach energy as function of co-doping ratios (CuO : La,Li).

III.2.7 The reflection

Reflection spectrum is calculated from absorption and transmission spectrum according to the following equation [3]:

$$T + A + R = 1 \quad \longrightarrow \quad R = 1 - T - A$$

Figure(III.7) represents the change of the refractive parameter as a function of the photon energy for the copper oxide thin films (CuO):

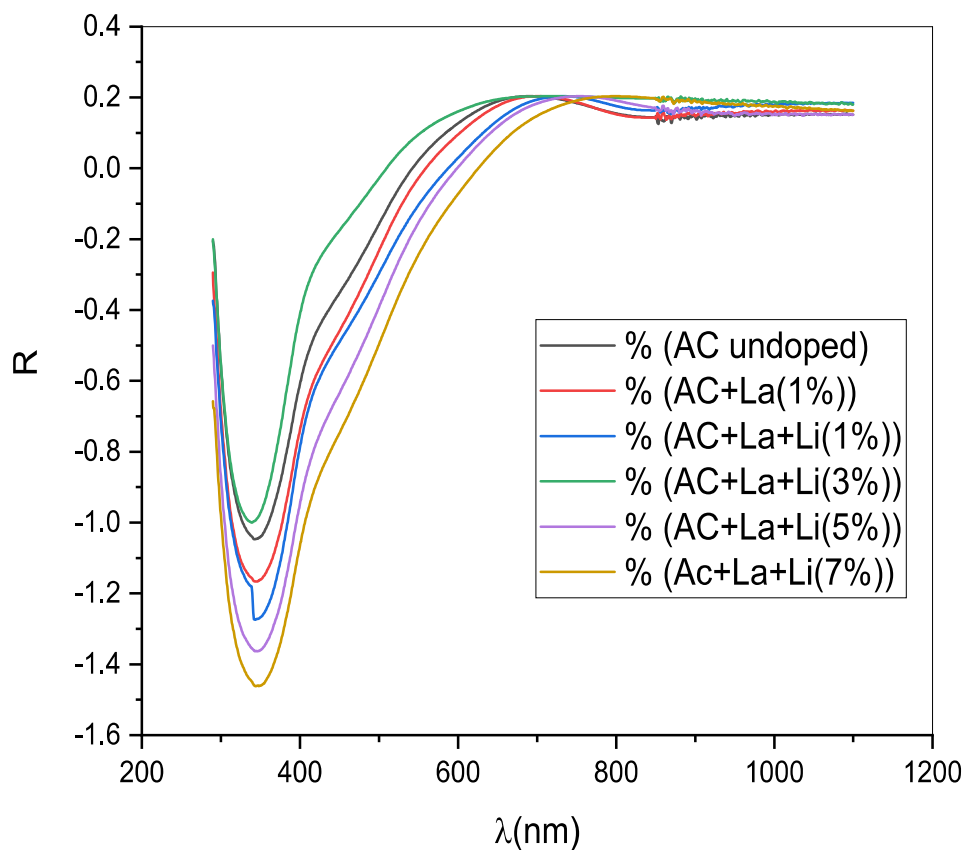


Figure (III.7): Optical reflection spectrum of La,Li co-doped CuO films as a function of wavelength.

We note that the refractive coefficient curve behavior of undoped and co-doped CuO thin films is increasing as photon energy increases, this is due to the increased absorption factor resulting from electronic transfers.

III.2.8 The extinction coefficient K

The extinction coefficient of undoped and co-doped copper oxide with La and Li, was calculated according to the relation mentioned before. Figure (III- 8) shows the change of the extinction factor as a function of photon energy for undoped and co-doped copper oxide thin films.

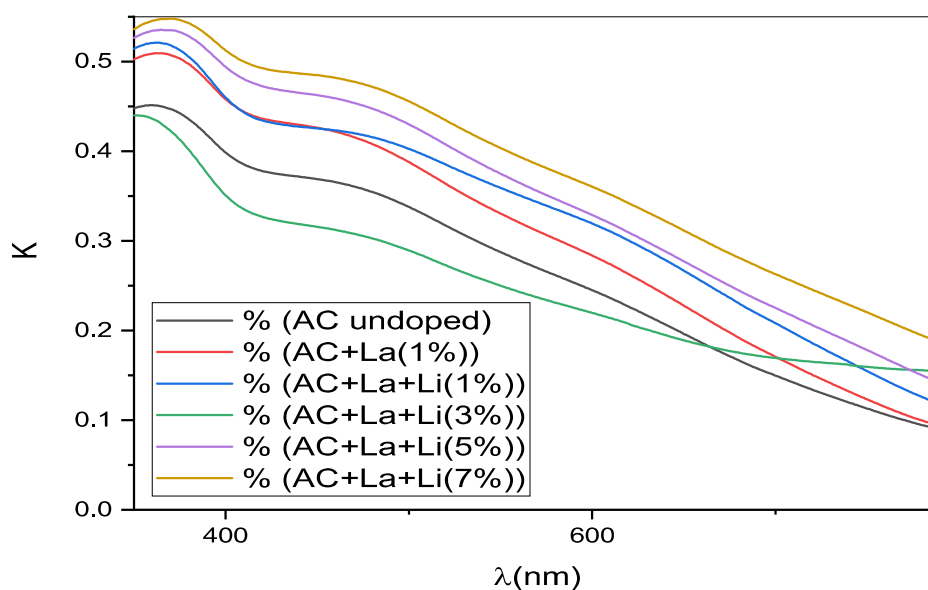


Figure (III- 8): shows the change of the extinction factor as a function of photon energy for undoped and co-doped copper oxide thin films.

as it is shown in figure(III.8) ,the extinction coefficient curves of undoped and co-doped copper oxide thin films is slightly lower at high wavelengths and then it rise up rapidly and abruptly in the range of short wavelengths.This behavior has a relation with how fast the free carriers can move.

III.2.9 The refractive index n

The refractive index characterizes the attenuation of the propagation speed of the light wave as it passes through the material.

Figure(III.9) represents the variation of the refractive coefficient as a function of the wavelength of the elaborated samples:

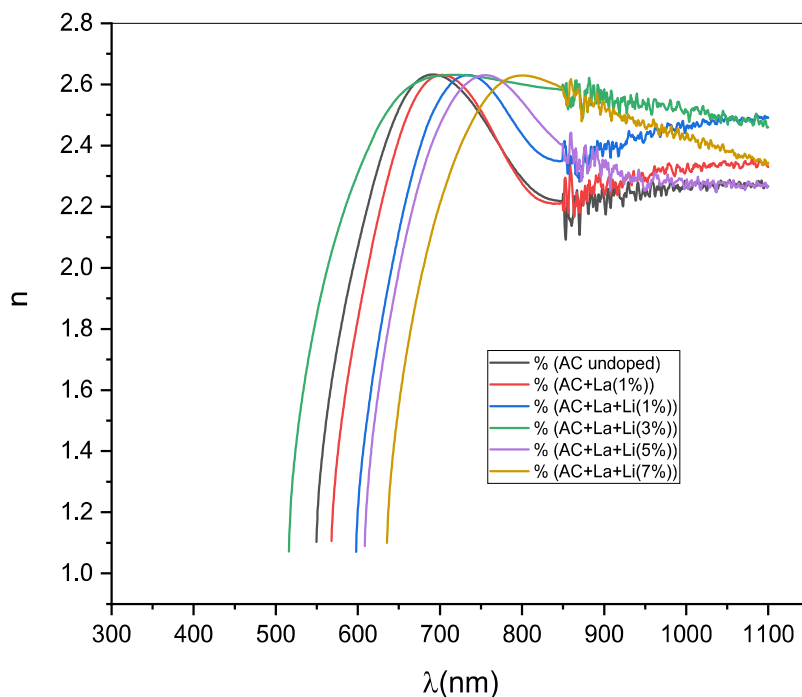


Figure (III.9): the refractive index of La and Li co-doped CuO films.

As it is depicted in the value of the refractive index for La and Li doped CuO films, varies in the visible range between 1.05 and 2.6.

- **Electrical properties**

III.2.10 Determination of the electrical resistivity

the measurements of the electrical resistivity of the elaborate films were carried out using the four-point probe method.

The samples	The resistivity (Ω .cm)
undoped Copper acetate (AC)	12.7077372
AC + La (1%)	0.0506454
AC + La + Li(1%)	0.03385269
AC+La+Li(3%)	0.01671298

AC + La + Li(5%)	0.01508128
AC + La + Li(7%)	0.01425047

Table (III.4):The results of electrical resistivity by tge four point method.

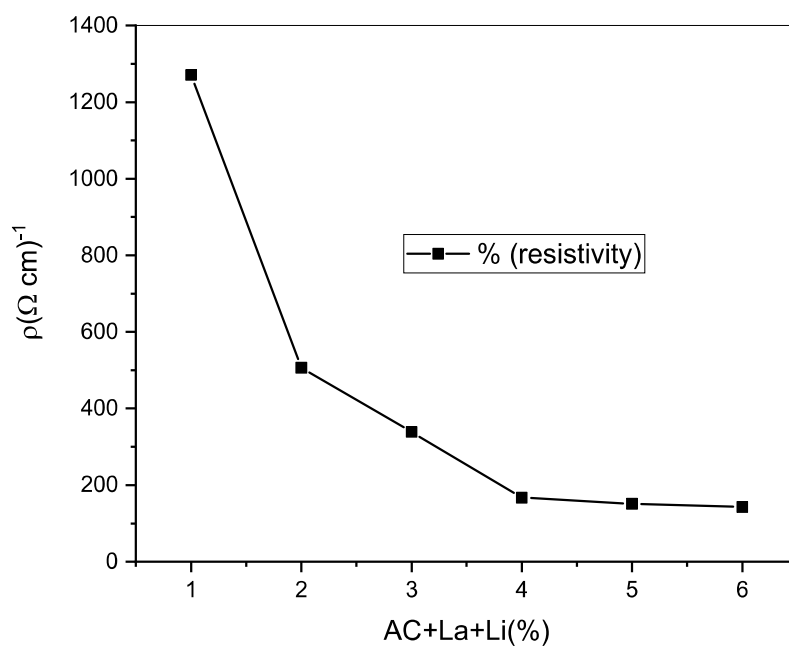


Figure (III.10): variation of resistivity as a function of co-dopant of CuO with La and Li.

As figure(III.10):shown, the resistivity decrease from 12.707 $\Omega \cdot \text{cm}$ to 0.014 $\Omega \cdot \text{cm}$ with the increase in the co-dopant rates, This can be attributed to an increase in electron mobility which in turn increases the electrical conductivity of the thin films which impove their electrical properties.

Conclusion

Conclusion

This work aims to elaborate and characterize the thin films of undoped copper oxide co-dopant with Lanthanum and Lithium with different concentration and study their impact on the optical and electrical properties.

For this purpose a series of six samples have been prepared and deposited on glass substrates.

optical and electrical characterization was carried out using respectively UV-VIS spectroscopy and Four-point technique for determining the electrical resistivity.

The obtained results have shown that the average transparency in the visible range was found around 60 %, while the absorption is found increasing with the increasing rate of the co-doping. The optical gap E_g was found to range between 2.66 in the doping case of La1%Li7% and 2.88 eV in the case of La1%Li3%. The minimum resistivity was recorded at the high level of co-doping (La1%Li7%) corresponds to the maximum carrier concentration. We conclude that co-doping CuO thin films, with La and Li, changes its characteristic carriers.

At the end of this study and according to what we have learned from the experience of co-doping CuO with La and Li elements, we propose the following perspectives :

- Repeating the experience of each level of co-doping more than one time
- Investigating the impact of a high level of co-doping of CuO thin films with La and Li
- Performing other characterizations than optical and electrical measurements
- Studying the effect of more than one parameters on co-doped CuO properties, such as the temperature of the substrate, Deposition Time, Co-dopant with other elements.

Reference

References :

- [1] L.Bergerot, « Etude de l'élaboration d'oxyde transparent conducteur de type-p en couchesminces pour des applications a l'électronique transparente ou au photovoltaïque », Matériaux ,Université de Grenoble Alpes,Français , 2015.
- [2] A.Gul, « ZnO and CuO Nanostructures: Low Temperature Growth, Characterization, their Optoelectronic and Sensing Applications», Linköping University, SE-601 74 Norrköping, Sweden, 2012.
- [3] M. LamriZeggar , «Cupric Oxide thin films deposition for gas sensor application», Doctorat thesis, frères Mentouri Constantine 1 university, Algeria, 2016.
- [4]H. Sihem, « Élaboration d'un nanomatériau mésoporeux de type NANORODS à base de dioxyde de titane (TiO₂), et sa mise en œuvre dans un procédé d'élimination photocatalytique des polluants organiques (PCP, MO, CV) », Mémoire de Magister, université de Constantine 2009.
- [5] R.David . Lide, « CRC Handbook of Chemistry and Physics », Copyright Taylor and Francis Group LLC 2009.
- [6] C. Colle , C.Mourlon ,P.Herrer,Fiche radio nucléide : Cérium 144 et environnement, IRSN,http://www.irsn.fr/FR/Larecherche/publications-documentation/fichesradionucleides/Documents/environnement/Tellure_Te123m_v1.pdf,p 2 ,2003
- [7]J Patrick Shamberger, R.Timothy ,«Thermophysical Properties of Lithium Nitrate Trihydrate from (253 to 353) K»,Journal of Chemical & Engineering Data. 57 (5): 1404–11. doi:10.1021/je3000469,2012.
- [8] M.Kenisarin,K,Mahkamov,(2016).«Salt hydrates as latent heat storage materials:Thermophysical properties and costs», Solar Energy Materials and Solar Cells, 145 (3): 255–86. doi:10.1016/j.solmat.29.10.2015.
- [9] Artical,January 2018 Materials Research Express5(2)
- [10] Y,R.Serif ,M .CAGLAR,«Surfaces and interfaces»,14 octobre 2020.
- [11] C.Chiang,Y.Shin,S.Ehrman,journal of the Electrochemical,2011,iopscience.iop.org.
- [12] P.Chand, A.Gaur,A.Kumar,U.K.Gaur.Applied surface science , 2014.

References]

- [13] K.Zarkazar,documentary Collage of science ,University of Bablon,Iraq.
- [14] P.Chand, A.Gaur,Uk.Gaur,Applied surface science ,2014.
- [15] W. Zhu, X. Qiu, V. Iancu, X. Chen, H. Pan, W. Wang,N. M. Dimitrijevic, T. Rajh. Meyer, M. P. Paranthaman, G. M. Stocks, H. H. Weitering, B. Gu, G.Eres, and Z. Zhang,«Band gap narrowing of titanium oxide semiconductors by noncompensated anion-codoping for enhanced visible-light photoactivity», *Phys.Rev. Lett*,103(22), 226401, 2009.
- [16] A. Luque and A. Martí,« Increasing the efficiency of ideal solar cells by photon induced transitions at intermediate levels», *Phys. Rev. Lett*,78(26), 5014 ,1997.
- [17] Z. Bi, M. P. Paranthaman, B. Guo, R. R. Unocic, C.A. Meyer, X. Bridges, Sun, and S. Dai,*J. Mater. Chem.*, High performance «Cr, N-codoped mesoporous TiO₂ microspheres for lithium-ion batteries»,*A* 2(6), 1818 ,2014.
- [18]M. Khan, J. Xu, N. Chen, and W. Cao,*J. AlloysCompd*,«First principle calculations of the electronic and optical properties of pure and (Mo, N) co-doped anatase TiO₂»,513, 539 2012.
- [19] M. Muruganandham and Y. Kusumoto, «Synthesis of N,C codoped hierarchical porous microsphere ZnS as a visible light-responsive photocatalyst», *J. Phys. Chem*,C113(36), 16144 2009.
- [20]A.Albert,R.manoharana,R.Chandramohana,R.David,S.prabub,V.Valanarasub,A.GaneshcM ohdShkirc,S.Kathalingamd,AlFaifyc,Journal of Molecular Structure ,Volume 1171, 5 November 2018, Pages 388-39.
- [21] S. MabroukYakout,Elsevier B.V,<https://doi.org/10.1016/j.optmat.2020.110769>, All rights reserved.«Optical Materials», Volume 112.
- [22]Ye.Zhizhen,He.Haiping, LiJiang ,«Nano Energy»,Volume 52, October 2018, Pages 527-540.
- [23] L.F. Francis,« Sol-Gel methods for oxide coatings», *Intermet and Ceram. Coat*,2.31.1999.
- [24]F.F «,«Elaboration et caractérisation des couches minces d'oxyde d'indium obtenue par procédé Sol-Gel: l'effet de température du recuit»,Université Mohamed Khider de Biskra,26juin 2018.

References]

- [25] A. Saadi, «*Rotational speed and solvent effect on the structural and optical properties of ZnO thin films prepared by SOL-GEL (Spin coating) method*», Master Dissertation ,University Mohamed Khider , Biskra, Algeria, 2014.
- [26] E. Marenga, «*Sol-Gel Synthesis of functional nanocomposites based on inorganic oxides*», PhD Thesis, University of Naples Federico II, 2008.
- [27] A. Saadi, « *Rotational speed and solvent effect on the structural and optical properties of ZnO thin films prepared by SOL-GEL (Spin coating) method*», Master Dissertation ,University Mohamed Khider , Biskra, Algeria, 2014.
- [28] M. C. Benachour, «*Elaboration et caractérisation des couches minces de TiO₂ dopées à l'erbium, à différentes températures et épaisseurs* », mémoire de magister, université de Constantine 2011.
- [29] M. Mostefa, « *Elaboration de films minces d'oxydes semi-conducteurs par voie sol gel*», thèse de doctorat, univ de Biskra, 2014.
- [30] Y. Anouar, « *L'effet de la concentration de la solution sur les propriétés des couches minces de ZnO élaborées par la méthode sol gel (spin coating)* », mémoire master, univ Mohamed khider-Biskra, 2015.
- [31] D. Raoufi, T. Raoufi, Applied Surface Science, 255 (2009) 5812–5817.
- [32] K. Sulabha Kulkarni, Capital Publishing Company, 3rd edition, pp176, 2015.
- [33] J. Tauc, R. Gorigorovici and A. Vancu, «*Physica Status Solid*», A15.1966.
- [34] J. A. Olley, «*Solid State Communications*», 13(9)(1973)1437-1440.

Abstract

In this work we have prepared thin films of copper oxide CuO co-doping with Lanthanum 1% and Lithium which was taken at the following concentrations (1%,3%,5%,7%) using sol gel spin coating method on to glass substrates. We have studied the effects this co-doping on the optical and electrical properties of these thin films. The prepared samples were characterized by UV-VISIBLE spectroscopy for optical properties and the four-point method for the electrical measurements. The experimental results indicated that the average transmission of the films in the visible range is 70% and the gap ranges between 2.66 eV and 2.88 eV. In addition, Urbach energy dropped from 315.34 to 290.9 meV when we add the lanthanum and it changes when lithium is added. The electrical measures showed that the films have low electrical resistivity from 12.7077 ($\Omega\cdot\text{cm}$) in the case of undoped CuO films to 0.0142 ($\Omega\cdot\text{cm}$) in the case of CuO co-doped with La1%Li7% which reflects the enhancement of electrical properties due to the co-doping with La and Li.

Key words : thin films, copper oxide , Lanthanum , Lithium , co-dopant, sol gel (spin coating).

Résumé :

Dans ce travail, nous avons préparé des couches minces d'oxyde de cuivre CuO co-dopage avec de Lanthane 1% et Lithium qui a été pris aux concentrations suivantes (1%,3%,5%,7%) en utilisant la méthode de sol gel spin coating sur les substrats de verre. Nous avons étudié les effets de ce co-dopage sur les propriétés optiques et électriques de ces couches. Les échantillons préparés ont été caractérisés par spectroscopie UV-Visible pour les propriétés optiques et la méthode de quatre points pour les mesures électriques. Les résultats expérimentaux ont indiqué que la transmittance moyenne des couches dans le gamme visible est de 70% et gap optique varie entre 2.66 eV et 2.88 eV. En outre, L'énergie d'Urbach est passée de 315.34 à 290.9 meV lorsque nous ajoutons le Lanthane et elle change lorsque de Lithium est

ajouté. Les mesures électrique ont montré que les couches ont une faible résistivité électrique de 12.7077 ($\Omega.cm$) dans le cas des couches CuO non dopés à 0.0142 ($\Omega.cm$) dans le cas de CuO co-dopé avec La1% Li 7% ce qui reflète l'amélioration des propriétés électriques due au co-dopage avec La et Li .

Mots clés : couches minces , oxide de cuivre, Lanthane, Lithiume, co-dopage , sol-gel (spin coating).

الملخص:

في هذا العمل، قمنا بتحضير شرائح رقيقة من أكسيد النحاس مزدوجة التطعيم باللانثيوم بنسبة 1% والليثيوم الذي اخذ بالنسب التالية (1%, 3%, 5%, 7%) باستخدام طريقة الطلاء المغزلي لمحلول هلامي على ركيزة زجاجية. قمنا بدراسة تأثير هذا التطعيم المزدوج على الخصائص البصرية والكهربائية لهذه الشرائح. تميزت العينات المحضرة بالتحليل الطيفي للأشعة فوق البنفسجية المرئية من اجل الخصائص البصرية و طريقة المسابر الأربعة من اجل القياسات الكهربائية. اشارت النتائج التجريبية الى ان متوسط النفاذية في الأفلام في المدى المرئي هو 70% ونطاق الفجوة بين 2.66 الى 2.88 إلكترون فولط. بالإضافة الى ذلك, انخفضت طاقة ديرباخ من 315.34 الى 290.9 ملي إلكترون فولط عندما اضفنا اللانثيوم وتغيرت عندما اضيف الليثيوم. القياسات الكهربائية أظهرت ان الشرائح لديها مقاومة كهربائية منخفضة حيث كانت 12.7077 (اوم.سنتيمتر) في حالة أكسيد النحاس الغير مطعم الى 0.0142 (اوم.سنتيمتر) في حالة أكسيد النحاس المزدوج التطعيم الذي يعكس تعزيز (La(1%)Li(7%) الخصائص الكهربائية بسبب مشاركة المطعومات.

الكلمات المفتاحية: الشرائح الرقيقة , اسيتات النحاس , اللانثيوم, الليثيوم , التطعيم المزدوج, المحلول الهلامي (الطلاء المغزلي