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Physical Properties of Sol Gel Copper Oxide (CuO) Thin Films; Sol concentration effect

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Table of Contents

Table of Contents

General Introduction

General Introduction

The spectacular progress achieved in nanoscience has allowed the development of several applications of nanomaterials in various fields. In particular, semiconductor nanostructures represent systems of great importance in the fields of nanotechnology and biology. These semiconductor nanostructures have in fact remarkable properties, different from those of the bulk material. The quantum size effect changes the absorption and emission properties of the nanomaterials.

Metal oxides are an important class of materials: from both scientific and technological point of view. They found huge interesting applications in different technological fields [1-7]. Metal Oxide semiconductors are gaining interest as new materials that may challenge the supremacy of silicon and they are known for many years ago due to the industrial interest on their unique properties.

The physicochemical properties of metal oxide thin films are closely related to preparation processes and operating conditions. Indeed, it is possible to obtain thin films having an amorphous or crystalline structure. Thereafter, films structural, electrical and optical properties can be tailored by varying the condition and the deposition process. Therefore, control of film properties is principales parameters of metal oxide films preparation to be used in wide applications such as: fabrication of microelectronic circuits, sensors, piezoelectric devices, fuel cells, coatings against corrosion, and as catalysts.

Copper have two oxidation states 1+ and 2+, while under special circumstances some compounds of trivalent are also reported. It was shown that this trivalent copper survives not more than few seconds. Consequently, cuprous oxide (Cu_2O) and cupric oxide (CuO) are the two stable forms of copper oxide [8]. However, only cupric oxide (CuO) phase is reported as a gas-sensitive material, as an absorber layer in solar cells and exhibits a number of interesting properties such as high temperature superconductivity, electron correlation effects, and spin dynamics. This led to a rapid research expansion in theoretical studies, fabrication, characterization and applications of CuO based devices in the latter half of the 20th century [6-7, 9].

Several methods for elaboration of nanomaterials in general and metal oxides thin films in particular, have developed among which, we can mention the classical methods such as PVD (Physical Vapor Deposition) and CVD (Chemical Vapor Deposition), but these techniques require sophisticated and expensive equipment; very high vacuum, high temperature.... etc. Among these techniques, sol–gel [10] can be used in various fields and in the production of different materials, but it is in the realization of thin film that it finds its main application. This technique is employed increasingly for the fabrication of materials with a better homogeneity and higher purity. In comparison to other techniques, sol gel method has its own advantages, such as simplicity, low temperature, lower cost, large area substrate coating, easier composition control and easier doping incorporation.

The objective of this work of memory is the elaboration of copper oxide (CuO) thin films by sol-gel spin coating technique, on glass substrates, then the structural, optical and electrical characterization of the samples obtained. We have studied the influence of the precursor concentration on the different properties of the thin films.

In addition to an introduction and a general conclusion, this work has three separate chapters:

In the first chapter we will present some basic concepts about nanomaterials, their arrangement, thin films, and their methods of elaboration, and applications of nanotechnologies. Then we discussed the concept of semiconductors followed by metal oxides. We then determine the physical properties of CuO and the main fields of its applications .

In second chapter, our attention was focused on the protocol of elaboration of CuO thin films by sol gel spin coating technique, thus the determination of the different deposition parameters, different structural and optical characterization techniques are used, as X-ray deffractometry (XRD), photoluminescence (PL), and transmittance.

In the last chapter, we gather and discuss the experimental results concerning the optical and structural properties of the CuO thin films.

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Chapter I

Metal oxides nanomaterials

I.1. Introduction

Recently copper oxide has found numerous applications in the field of nanotechnology where nanostructured copper oxides based materials have been used in electronics, catalysts and in transparent conducting films. This chapter covers a general description of nanotechnology together with synthesis approaches and their challenges are presented. In the rest of this chapter we are presented a brief survey on structural, optical and electrical properties of CuO thin films and their most important applications in various technological areas.

I.2. Motivation for Nanotechnology

Nanotechnology is a completely new branch of science and engineering that hit the market a few years ago. Nanotechnology is a revolution where even a 0.1 nm variation in particle size plays a significant role. Fundamentally, nanoscale implies a range from 1 to 100 nm. Nanotechnology can be best explained as the development, synthesis, characterization, and application of materials and devices by tailoring their shape and size at the nanoscale [1].

There is some confusion among newcomers about the difference between nanoscience and nanotechnology. To make it understandable, one can state that nanoscience deals with the arrangement of atoms and understanding their fundamental properties at the nanoscale, whereas nanotechnology is the controlling of matter at atomic scale while synthesizing a new material with different exotic properties. Nanotechnology is already receiving attention across all branches of engineering as it is an interdisciplinary area of research. The general population isn’t aware of its presence in daily life but it is emerging in medicine, energy and the environment, defense and security, electronics and materials. This emerging technology is also a breakthrough in the domain of highly powerful computers and communication devices. Research in this field mainly depends on two concepts: positional assembly and self-replication

Nanotechnology is the study of phenomena and fine-tuning of materials at atomic level, where a significantly different property is obtained compared to a larger scale. Very recently, individuals and groups have been working on different aspects of nanotechnology such as renewable energy harvesting and converting it into useful electrical energy. [2] Thermal, nuclear, wind, hydrolytic, and solar energy scavenging have ushered in a new area of research, “nanopiezotronics,” whose fundamental principle utilizes the coupled piezoelectric and semiconducting properties of nanowires and nanorods for fabricating electronic devices or systems such as field-effect transistors and diodes. The physics of nanopiezotronics is based on the principle of a nanogenerator that converts mechanical energy into electric energy. As the structures that are responsible for the generation of electric current have a dimension at nanoscale, the term nanogenerator is most suitable[3].

A little history

The earliest systematic discussion of nanotechnology is considered to be a speech given by Richard Feynman (American physicist and Nobel laureate, 1918-1988) in 1959 at the California Institute of Technology entitled: "There's Plenty of Room at the Bottom." In this speech Feynman discussed the importance "of manipulating and controlling things on a small scale" and how they could "tell us much of great interest about the strange phenomena that occur in complex situations." He described how physical phenomena change their manifestation depending on scale.

The term 'nanotechnology' was used first by the Japanese scientists Norio Taniguchi (1912-1999) in a 1974 paper on production technology that creates objects and features on the order of a nanometer. The American engineer K. Eric Drexler (b. 1955) is credited with the development of molecular nanotechnology, leading to nanosystems machinery manufacturing.

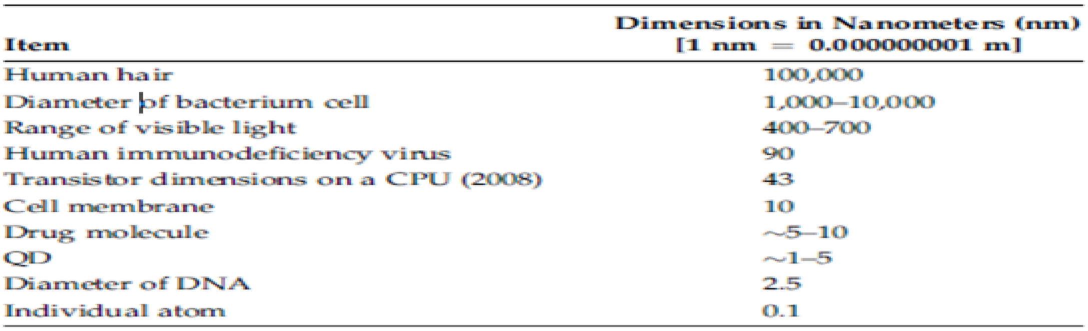
Today, the nanotechnologies include all studies and processes for the fabrication and manipulation of structures, devices and systems at the nanometer (nm) scale.

I.3. what does nano mean?

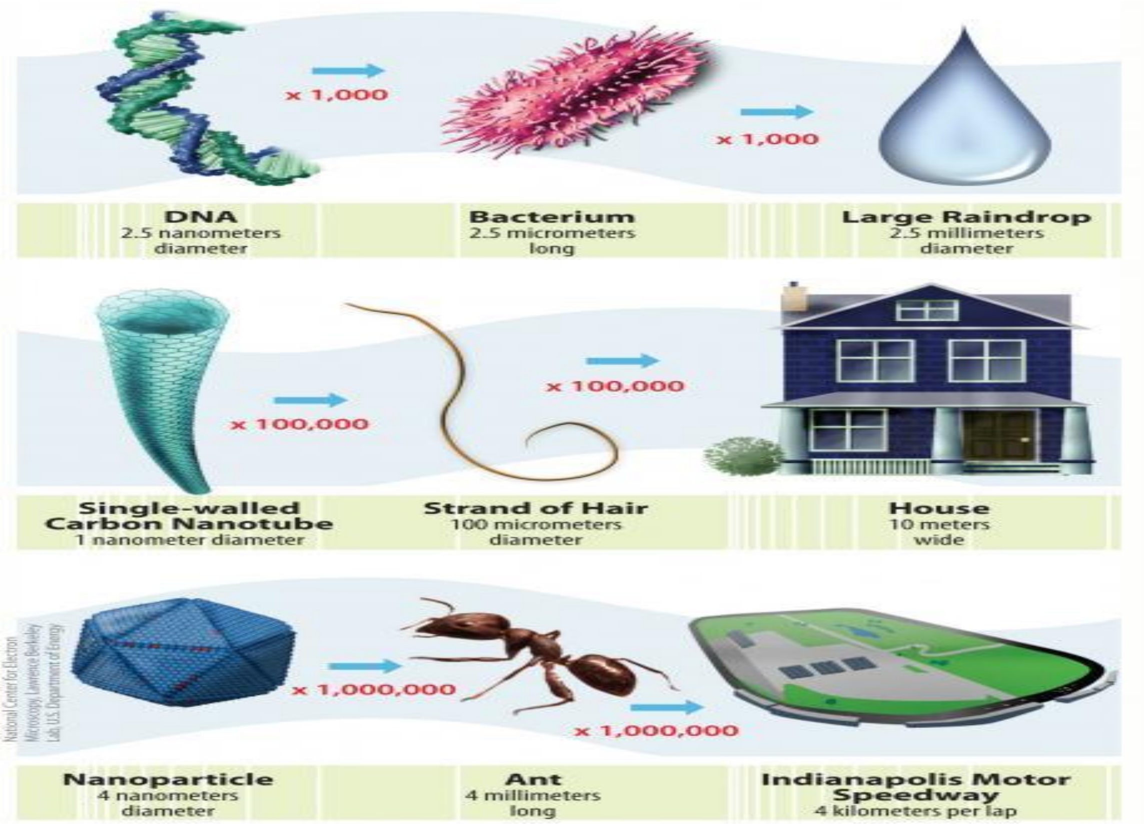
The prefix “nano” is derived from the ancient Greek “nanos”, meaning "dwarf”. Today, “nano” is used as a prefix that means one nanometer is equivalent to one thousandth of a micrometer, one millionth of a millimeter, and one billionth of a meter Coupling the word “nano” with the unit “meter” brings the term “nanometer”, which indicates a unit of spatial measurement that is one billionth of a meter. With this in mind, nanotechnology shall be defined as the science, engineering, and technology conducted at the scale that range between 1 and 100 nanometers.

Nanotechnology is the design, manufacture and application of functional structures, devices and basic understanding between physical properties, phenomena and physical dimensions. Nanotechnology deals with materials or structures in the nanometer scale. Why are we so fascinated with downsizing materials to a nanoscale? The fundamental physical, chemical, and biological properties of materials are surprisingly altered as their constituent grains are decreased to a nanometer scale owing to their size, shape, surface chemistry, and topology.

Table 1. Some objects, with a characteristic length dimension for each



Item	Dimensions in Nanometers (nm) [1 nm = 0.000000001 m]
Human hair	100,000
Diameter of bacterium cell	1,000–10,000
Range of visible light	400–700
Human immunodeficiency virus	90
Transistor dimensions on a CPU (2008)	43
Cell membrane	10
Drug molecule	~5–10
QD	~1–5
Diameter of DNA	2.5
Individual atom	0.1



National Center for Electron Microscopy, Lawrence Berkeley Lab, U.S. Department of Energy

Figure I.1. Size of the nanoscale

I.4. Nanomaterials

The scientific story of nanomaterials began much early. One of the first scientific reports is the colloidal gold particles synthesized by Michael Faraday as early as 1857**.** Nanomaterials are cornerstones of nanoscience and nanotechnology. Nanostructure science and technology is a broad and interdisciplinary area of research and development activity that has been growing explosively worldwide in the past few years. It has the potential for revolutionizing the ways in which materials and products are created and the range and nature of functionalities that can be accessed.

Nanoscale materials are defined as a set of substances where at least one dimension is less than approximately 100 nanometers. Nanomaterials are of interest because at this scale unique optical, magnetic, electrical, and other properties emerge. These emergent properties have the potential for great impacts in electronics, medicine, and other fields [2]

I.4. Classification of nanomaterials

Classification of nanomaterials is based on the number of dimensions, which are not confined to the nanoscale range (<100 nm).

1. Nanomaterials of zero (0) dimenssion: The most common representation of these substances is nanoparticles.

2. Nanomaterials of one (1) dimenssion: materials include nanotubes, nanorods, and nanowires.

3. Nanomaterials of two (2) dimensions: nanomaterials exhibit plate-like shapes.include nanofilms, , and nanocoatings.

4. Nanomaterials of three (3) dimenssions: Materials possess a nanocrystalline structure or involve the presence of features at the nanoscale. nanomaterials can contain dispersions of nanoparticles, bundlesof nanowires, and nanotubes as well as multinanolayers.

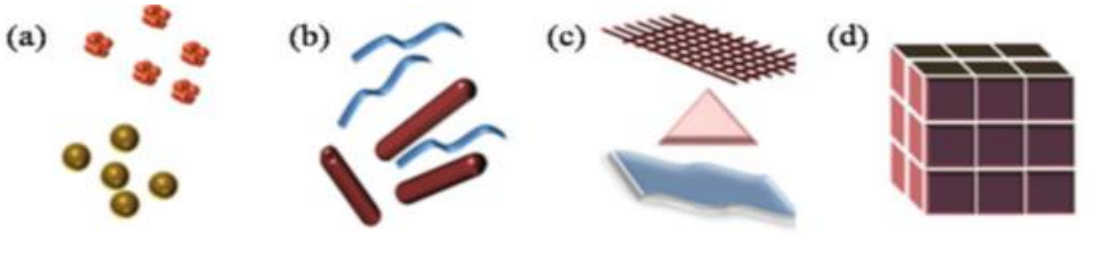


Figure 2. Classification of Nanomaterials (a) 0D spheres and clusters, (b) 1D nanofibers, wires, and rods, (c) 2D films, plates, and networks, (d) 3D nanomaterials.

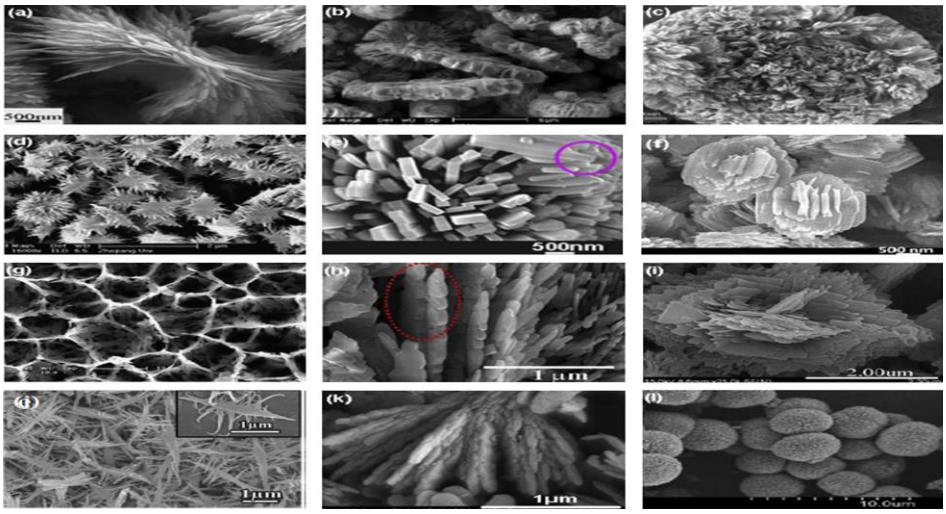


Figure 3. Typical SEM images of various CuO nanostructures [4]

I.5.Manufacture of nanomaterials

To manufacture the nano-objects two methods exist :

I.5.1. A “bottom-up” method:

This method allows the assembly or the positioning of atom or molecules in a precise way thus allowing the manufacture of materials whose structure is perfectly controlled. This method uses mainly physical and chemical processes.

I.5.2. A so-called “top down” method:

This method involves miniaturizing the current systems. The structures are thus gradually under dimensioned until reaching nanometric proportions. This method uses mainly mechanical processes.

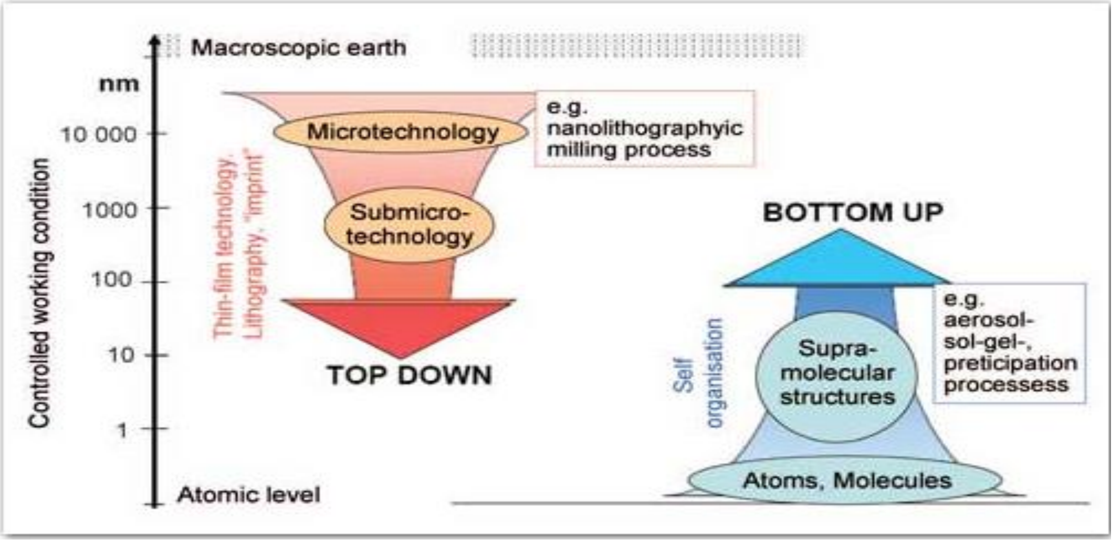


Figure 4. Methods of nano-objects production: top-down and bottom-up.

I.6.Effect of nanometric dimensions

Nanotechnology brings about the reduction of the size of bulk materials, inducing size-dependent effects arising from:

a) A significant increase of the surface to volume ratio involving a huge increase of the interfacial area and of the fraction of the species at the surface.
b) A change of the physico-chemical properties of the species at the surface and in the nanoparticle interior in comparison with that in the bulk material.
c) Changes in the arrangement (lattice structure, interatomic distances) of the species in the nanoparticle and the concentration of defects.

d) Confinement and quantum-size effects (The quantum size effect changes the absorption and emission properties of the nanomaterials).

I.7. Applications of nanotechnology

Nanotechnology is a rapidly growing technology with considerable potential applications and benefits. Among the numerous applications of nanotechnology:

In medicine

One application of nanotechnology in medicine currently being developed involves employing nanoparticles to deliver drugs, heat, light or other substances to specific types of cells (such as cancer cells). Particles are engineered so that they are attracted to diseased cells, which allows direct treatment of those cells. This technique reduces damage to healthy cells in the body and allows for earlier detection of disease.

In electronic

Improving display screens on electronics devices. This involves reducing power consumption while decreasing the weight and thickness of the screens. Increasing the density of memory chips. Researchers are developing a type of memory chip with a projected density of one terabyte of memory per square inch or greater. Developing a lead-free solder reliable enough for space missions and other high stress environments using copper nanoparticles.

Fuell cell

How can nanotechnology improve fuel cells? Catalysts are used with fuels such as hydrogen or methanol to produce hydrogen ions. Platinum, is the catalyst typically used in this process. Companies are using nanoparticles of platinum to reduce the amount of platinum needed, or using nanoparticles of other materials to replace platinum entirely and thereby lower costs**.** Fuel cells contain membranes that allow hydrogen ions to pass through the cell but do not allow other atoms or ions, such as oxygen, to pass through. Companies are using nanotechnology to create more efficient membranes; this will allow them to build lighter weight and longer lasting fuel cells. Fuel cells that can replace batteries in electric cars are also under development. Hydrogen is the fuel most researchers propose for use in fuel cell powered cars.

Cleaner water

Nanotechnology is being used to develop solutions to three very different problems in water quality. One challenge is the removal of industrial wastes, such as a cleaning solvent called TCE, from groundwater. Nanoparticles can be used to convert the contaminating chemical through a chemical reaction to make it harmless. Studies have shown that this method can be used successfully to reach contaminates dispersed in underground ponds and at much lower cost than methods which require pumping the water out of the ground for treatment.

Chemical Sensors

Nanotechnology can enable sensors to detect very small amounts of chemical vapors. Various types of detecting elements, such as carbon nanotubes, zinc oxide nanowires or palladium nanoparticles can be used in nanotechnology-based sensors. Because of the small size of nanotubes, nanowires, or nanoparticles, a few gas molecules are sufficient to change the electrical properties of the sensing elements. This allows the detection of a very low concentration of chemical vapors.

Household

The most unmistakable utilization of nanotechnology in the family unit is cleaning toward oneself or "simple to-clean" surfaces on pottery or glasses. Nanoceramic particles have enhanced the smoothness and hotness safety of normal family supplies.

Textiles

The utilization of engineered nanofibers as of now makes garments water- and stain-repellent or wrinkle-free. Materials with a nanotechnological completion can be washed less much of the time and at lower temperatures. Nanotechnology has been utilized to incorporate small carbon particles film and ensure full-surface assurance from electrostatic charges for the wearer.

In physics

Conductivity measeurment of a signale molucule. Conductivity through small jonction with few defects. Observation of magnetic of spin polarized currents are possible.

Fabrication of laser and waveguides, optical switches , modulators and photoic crystals.

I.8. Thin films materials

I.8.1. Introduction

Thin film technology is simultaneously one of the oldest arts and one of the newest sciences. Involvement with thin films dates to the metal ages of antiquity. Consider the ancient craft of gold beating, which has been practiced continuously for at least four millenia. Gold's great malleability enables it to be hammered into leaf of extraordinary thinness while its beauty and resistance to chemical degradation have earmarked its use for durable ornamentation and protection purposes. The Egyptians appear to have been the earliest practitioners of the art of gold beating and gilding. Many magnificent examples of statuary, royal crowns, and coffin cases that have survived intact attest to the level of skill achieved [5].

I.7.2. Definition of thin films

Thin films are a substance deposited in another substance called a substrate. The layer is reduced to one of the dimensions (thickness) of this deposite, which ranges from nanometers fractions. This semi-second dimension gives the first characteristic of thin films, and more importantly, reversing materials in bulk film characteristics are generally affected by the conditions of preparation : Deposition method and criteria, substrate type….

I.7.3. Thin films deposition methods

The progress in thin films science and technology accelerated following the development of vacuum technology for the vapor phase synthesis of layers with controlled and reproducible properties. Thin film applications rely strongly on the electrical, optical and physical properties of the materials chosen. These properties depend on the deposition methods and processes to fabricate the films. Thus, there is a relationship between film growth dynamics and specific film property, which in turn depends on deposition method.

The methods of preparation can be classified in two categories:

- ✓ Physical methods
- ✓ Chemical methods

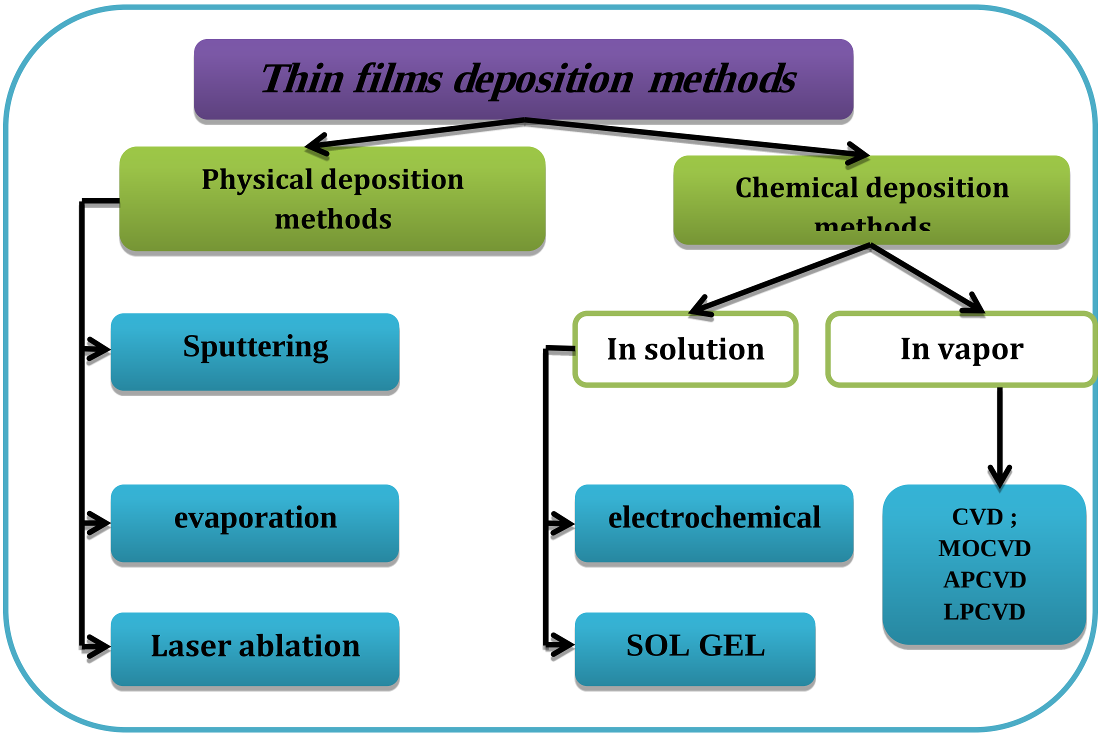


Figure I.5. Thin films deposition

I.8.3.1. physical vapor deposition (PVD)

In PVD processes, atoms or small clusters of atoms are removed from a source (solid or liquid). These atoms are traveling in a vacuum chamber reaching a substrate to form a thin film. The rate of deposition depends mainly on system pressure, source-substrate distance and substrate temperature. Generally, PVD deposition processes contain at least four steps namely [6]

a) A source of film material is first provided; **b)** Then the material is transported to the substrate with a uniform arrival rate under proper vacuum environment; **c)** The deposition takes place and as time goes on; **d)** A thin layer is formed on the substrate

I.8.3.1.1. Sputtering

In this method, the substrate is placed in a chamber containing a gas (usually Argon) at low pressure, in which an electric discharge is caused. This discharge has the role of ionizing the gas atoms. The ions thus obtained are accelerated by a potential difference and come to bombard a cathode made of the material to be deposited (target) [7]. Under the impact of accelerated ions, atoms are torn off the cathode and deposited on the substrate. In some cases, a gas is introduced into the chamber in addition to argon, which will react chemically with the atomized atoms to form the material that it is desired to obtain. Then, we have a reactive cathode sputtering. This method makes it possible to have low resistivity deposits and good stoichiometry layers having a visible transmission [8].

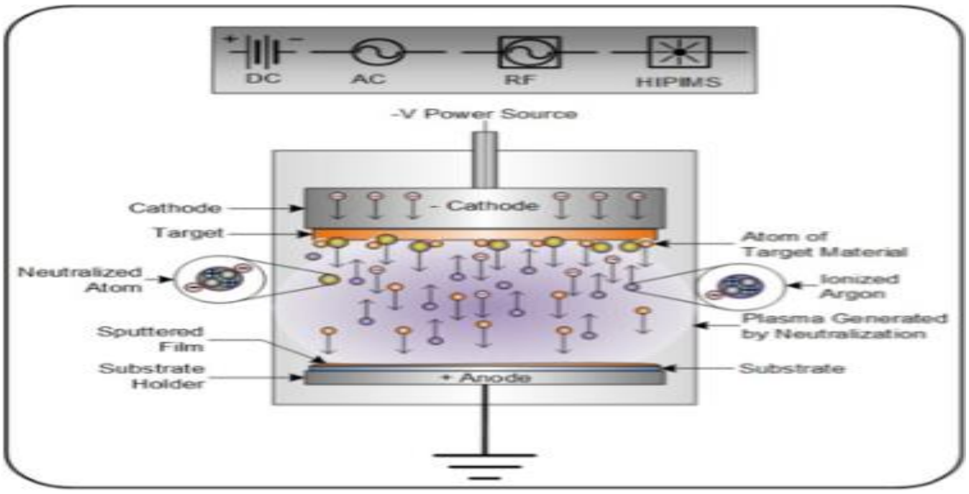


Figure.I.6. Sputtering method

I.8.3.1.2. Evaporation

The vapors of the material to be deposited are obtained by heating it by various means: Joule effect, induction (coupling of a high frequency generator), electron gun, laser beam or electric arc. Evaporation is carried out under a high vacuum (pressure of the order of 10^{-3} to 10^{-4} Pa) [9].

As the vapor flow is localized and directional, it is often necessary to subject the substrate to a rotational or translational movement with respect to the evaporation source, so as to achieve homogeneous deposition and uniform thickness. The best results are obtained on surfaces practically perpendicular to the vapor flow [10].

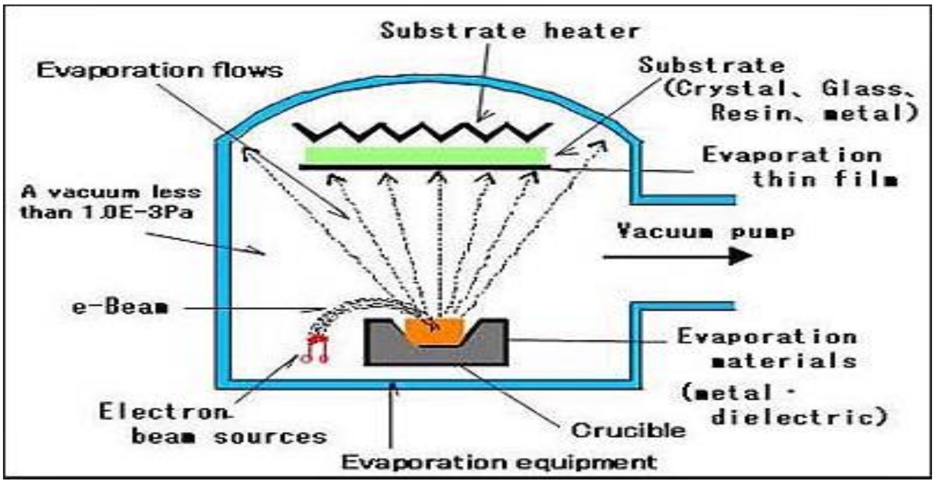


Figure I.7. Evaporation method

I.8.3.2. Chemical vapor deposition (CVD)

Chemical vapor deposition (CVD) is the process of chemically reacting a volatile compound of a material to be deposited, with other gases, to produce a nonvolatile solid that deposits atomistically on a suitably placed substrate. It differs from physical vapor deposition (PVD).Because CVD processes do not require vacuum or unusual levels of electric power, they were practiced commercially prior to PVD. Among the reasons for the growing adoption of CVD methods is the ability to produce a large variety of films and coatings of metals, semiconductors, and inorganic as well as organic compounds in either a crystalline or vitreous form, possessing desirable properties. Furthermore, the ability to controllably create films of widely varying stoichiometry makes CVD unique among deposition techniques. The fundamental sequential steps that occur in every CVD process are sketched in Figure I.8.

a) Convective and diffusive transport of reactants from the gas inlets to the reaction zone; **b)** Chemical reactions in the gas phase to produce new reactive species and by-products; **c)** Transport of the initial reactants and their products to the substrate surface; **d)** Adsorption (chemical and physical) and diffusion of these species on the substrate surface; **e)** Heterogeneous reactions catalyzed by the surface leading to film formation;**f)** Desorption of the volatile by-products of surface reactions;**g)** Convective and diffusive transport of the reaction by-products away from the reaction zone.

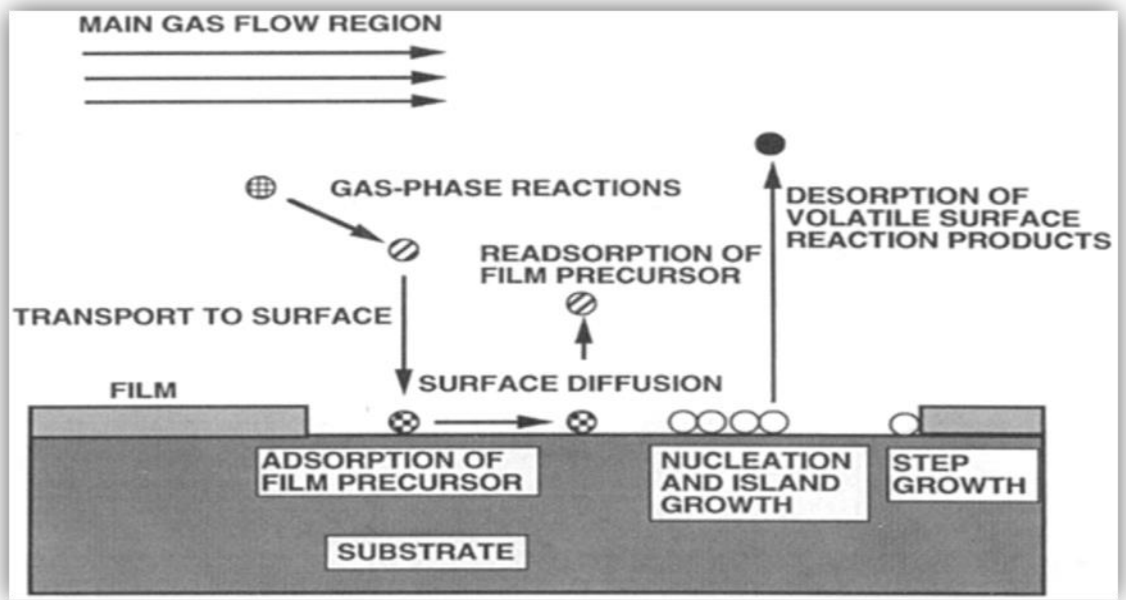


Figure I.8. Sequence of gas transport and reaction processes contributing to CVD film growth

I.7.3.3. Sol-gel

The sol-gel technique is a process for the elaboration of materials allowing the synthesis of glasses, ceramics and organo-mineral hybrid compounds, from precursors in solution. It makes to produce thin layers consisting of stacks of nanoparticles of metal oxides. This process is carried out under so-called mild chemistry conditions, at significantly lower temperatures than those of conventional synthetic routes. These conditions also offer the possibility of combining organic and mineral species to form new families of organo-mineral hybrid compounds with novel properties.

Sol–gel processes, as the name suggests, involve a solution that is transformed into a gel and then deposited on a surface. The starting material is a metal alkoxide dissolved in a suitable solvent, often ethanol. The addition of a little water hydrolyzes the material so that it forms a polymeric material, usually helped by making the solution slightly acidic. The resulting material is a loose gel with liquid filled pores that can be applied to a surface by dipping or spinning.

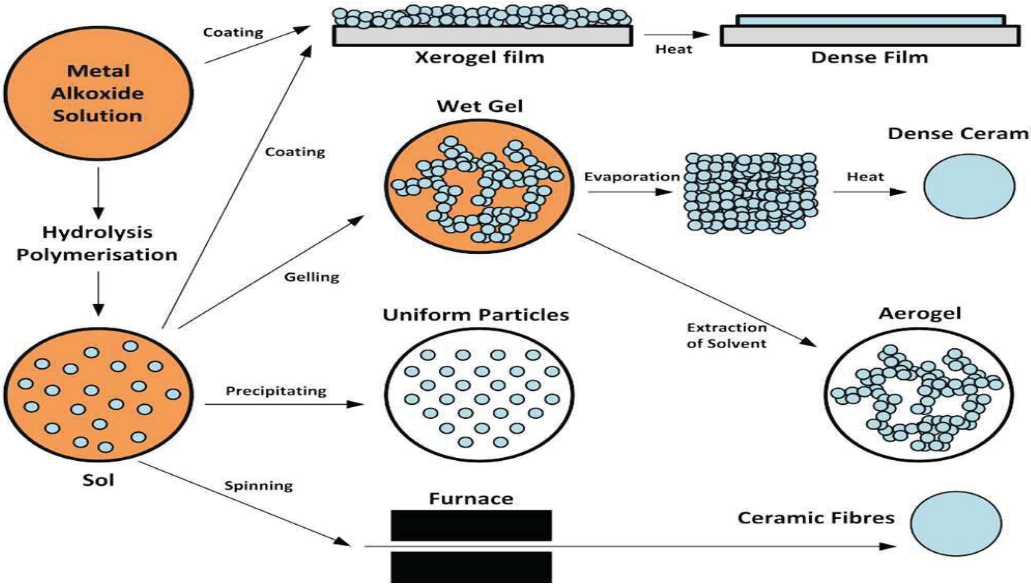


Figure I.9. Sol-Gel method

I.7.4. Growth modes of thin films

Thin film formation involves basic processes of nucleation and growth. Concerning thin film nucleation on substrate surface, there are three primary growth modes that they occur at the earliest stages of film formation. They can be distinguished based on bonding strength between depositing species and the substrate surface atoms. These 2D growth mechanisms are including [11]:

- Two-dimensional layer-by-layer (Frank-Van der Merwe) mode. This growth mode valids when the deposited atoms have a greater bonding strength and are applied for the homoepitaxial growth.

- Island growth mechanism (Volmer-Weber) mode is applied when the smallest stable clusters nucleate on the substrate and grow in three dimensions to form islands on the surface. This type of growth mode happens when atoms or molecules in the depositing films are more strongly bound to each other than to the substrate atoms.

- Mixed layer-island (Stranski- Krastanov) mode is an intermediate mixture of the preceding two modes. In this mechanism, first one or more layers are formed followed by the growth of 3D islands. Figure 9 shows the schematic illustration of these three thin film growth modes in terms of substrate surface coverage.

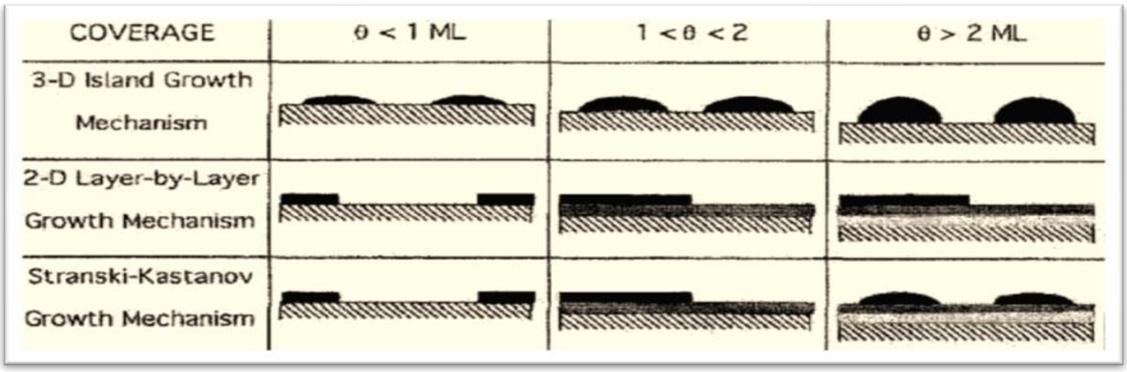


Figure I.10. Simplified schematic view of three growth modes of thin film.

I.7.5. Applications of Thin Films

Although the study of thin film phenomena dates back well over a century, it is really only over the last four decades that they have been used to a significant extent in practical situations. Many thin film devices have been developed which have found themselves looking for an application or, perhaps more importantly market. In general these devices have resulted from research into the physical properties of thin films. The rising cost of conventional energy on the one hand, and the limitation of their resources on the other hand, make photovoltaic energy more and more a solution among the promising energy options with advantages like abundance, the absence of any pollution and the availability in greater or lesser quantities in all points of the terrestrial globe. Currently, there is renewed interest in solar energy facilities, especially for remote site applications.

The conversion of light into electricity:

The term "photovoltaic" often abbreviated as "PV", was formed from the words "photo" a Greek word meaning light and "Volta" the name of the Italian physicist Alessandro Volta who invented the electrochemical cell in 1800. L photovoltaic effect is the direct conversion of solar energy into electricity.

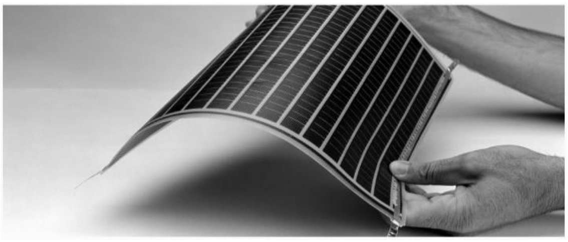


Figure I.11. Photovoltaic solar panels

In optic, the thin films used as anti-reflection coating for lenses and mirrors…etc

In chemistry as corrosion protection….etc

In magnetism as hard disk and Random Access Memory…..etc

In the medical fields as neurological sensors…etc.

In electronics as piezoelectric sensors, transistors, diodes and integrated circuits…etc

I.8. Semiconductors

I.8.1 Definition of semiconductor

The semiconductor is a material in the solid or liquid state that conducts electricity at room temperature but less easily than a conductive metal. At low temperatures, pure semiconductors behave like insulators; at high temperatures or in the presence of light or impurities the conductivity of semiconductors increases sharply and can even become comparable to that of metals [12].

I.8.2. Band Gap

In solid materials, interactions between atoms “smear” the valence shell into a band of energy levels called the valence band. Valence electrons are confined to that band. When an electron acquires enough additional energy, it can leave the valence shell, become a free electron, and exist in what is known as the conduction band. The difference in energy between the valence band and the conduction band is called an energy gap or band gap. This is the amount of energy that a valence electron must have in order to jump from the valence band to the conduction band. Once in the conduction band, the electron is free to move throughout the material and is not tied to any given atom. Figure I.12 shows energy diagrams for insulators, semiconductors, and conductors.

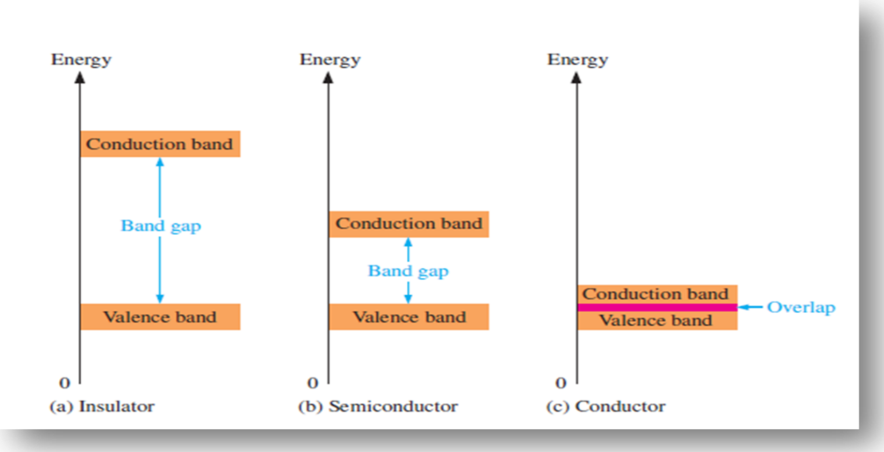


Figure I.12. Energy diagrams for the three types of materials

I.8.3.Types of Semiconductors

Semiconductors can be classified as: Intrinsic Semiconductor and extrinsic Semiconductor. Extrinsic Semiconductors are further classified as: a **n**-type Semiconductors and **p**-type Semiconductors.

In **p-type semiconductors**, holes are the majority carriers and electrons are the minority carriers. In **N-type semiconductors** electrons are the majority carriers and the holes are the minority carriers.

I.8.4. PN Junction

When a n-type silicon comes into contact with a p-type silicon they form what is known as a junction (figure I.13). The current can only pass in one direction. In fact, if we look at it in terms of energy, the electrons from the “n” side do not have the same energy as those from the “p” side; these latter electrons take part in the bonding process and are strongly bonded in the crystalline lattice. The “n” electrons, which are free, are now more energetic. What happened to their contact? What happens when we try to join two liquid bodies of two different levels? What happens is that there is a flow of one into the other. But here, the liquid is electrically charged, and the passage of the electrons from the “n” crystal to the “p” crystal leads to the appearance of a difference in potential which balances the system. This is equal to the energy difference in volts of the banded-electron linked to the free electron states as is the case for silicon. If we directly polarize the atom, where the negative pole is on the “n”, then the current will flow. As a consequence, the “n” and “p” parts of a crystal automatically isolate themselves, which is a property used in semi-conductor components[13].

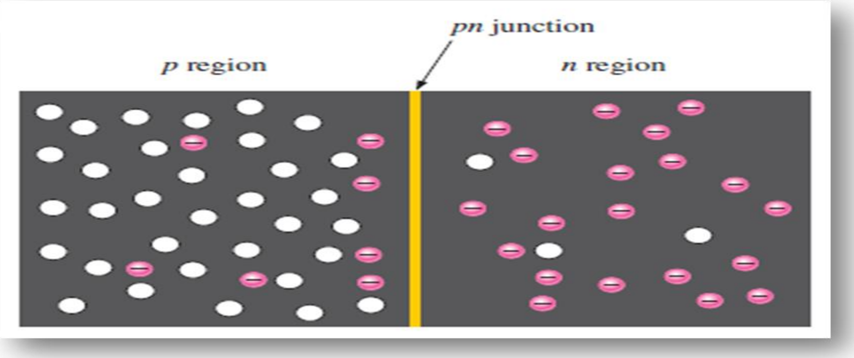


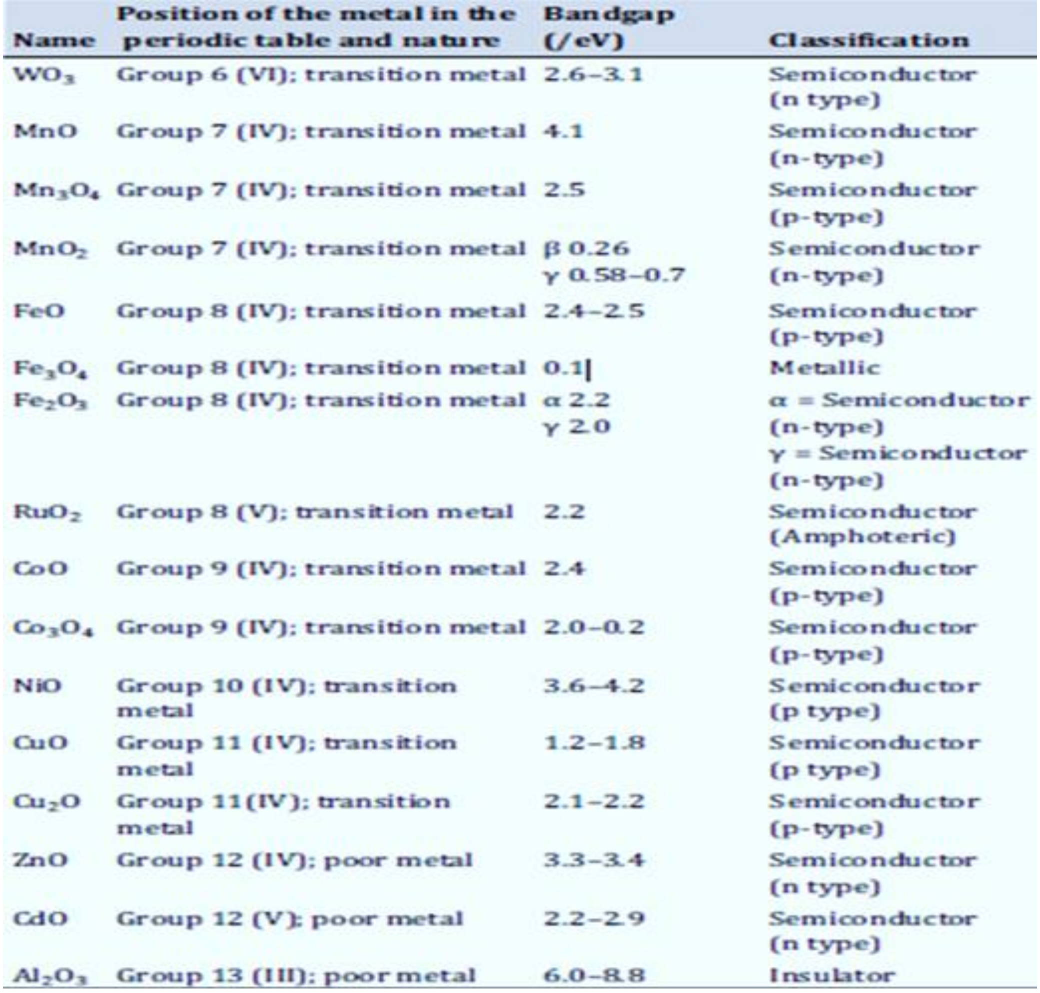
Figure I.13. PN junction

I.9. Metal Oxide

A metal oxide in general is a body consisting of metal atoms and oxygen. We can classify metal oxides, either according to the nature of the conduction by electrons or holes, or according to whether the metal oxides are simple or complex.

Metal oxides play a very important role in many areas of chemistry, physics and materials science. Metal oxides exhibit metallic, semiconducting, or insulating character due to the electronic structure difference. Normally, oxides formed by metals residing at the left or right of the periodic table are generally insulating in nature (e.g., MgO, CaO, Al_2O_3, SiO_2), whereas those formed by the metals residing at the middle of the periodic table are semiconductors or metallic in nature (e.g., ZnO, NiO, TiO_2, CuO, Fe_2O_3, Cr_2O_3). A chart pointing out the nature of various metal oxides in terms of conductivity property is provided in Table I.1

Table I.1. Provide chart pointing out the nature of various metal oxides in terms of conductivity property.



Name	Position of the metal in the periodic table and nature	Bandgap (/eV)	Classification
WO_3	Group 6 (VI); transition metal	2.6–3.1	Semiconductor (n type)
MnO	Group 7 (IV); transition metal	4.1	Semiconductor (n-type)
Mn_3O_4	Group 7 (IV); transition metal	2.5	Semiconductor (p-type)
MnO_2	Group 7 (IV); transition metal	β 0.26 γ 0.58–0.7	Semiconductor (n-type)
FeO	Group 8 (IV); transition metal	2.4–2.5	Semiconductor (p-type)
Fe_3O_4	Group 8 (IV); transition metal	0.1	Metallic
Fe_2O_3	Group 8 (IV); transition metal	α 2.2 γ 2.0	α = Semiconductor (n-type) γ = Semiconductor (n-type)
RuO_2	Group 8 (V); transition metal	2.2	Semiconductor (Amphoteric)
CoO	Group 9 (IV); transition metal	2.4	Semiconductor (p-type)
Co_3O_4	Group 9 (IV); transition metal	2.0–0.2	Semiconductor (p-type)
NiO	Group 10 (IV); transition metal	3.6–4.2	Semiconductor (p type)
CuO	Group 11 (IV); transition metal	1.2–1.8	Semiconductor (p type)
Cu_2O	Group 11(IV); transition metal	2.1–2.2	Semiconductor (p-type)
ZnO	Group 12 (IV); poor metal	3.3–3.4	Semiconductor (n type)
CdO	Group 12 (V); poor metal	2.2–2.9	Semiconductor (n type)
Al_2O_3	Group 13 (III); poor metal	6.0–8.8	Insulator

I.9.1. Metal Oxide semiconductors

Metal oxide semiconductor has been widely studied due to it varied properties and applications. Metal oxide semiconductor films have received considerable attention in recent years due to their optical and electrical properties. Some of them are good candidates for transparent conductive oxide films. Oxide semiconductors are preferential in photo-electrochemistry because of their exceptional stability against photo-corrosion on optical excitation in the bandgap [14], furthermore, because of large bandgap (>3 eV) of this type of materials [15]. Undoped and doped oxide thin films have a wide range of applications as an important semiconductor material such as solar cells and electrical, piezoelectric or luminescent devices and also as gas sensors and chemical sensors. It is well known that chemical doping greatly influences the electronic and optical properties of oxide thin films.

I.9.2. Transparent conductive oxides (TCO)

There is a family of oxides, which in addition to being transparent can become conductors (of type n) if they have an excess of electrons in their network. This excess of electrons can be created either by defects of structure inducing an imbalance in the stoichiometry of the oxide, either by appropriate [16].

These oxides are called conductive transparent oxides (TCO). These TCOs have a high gap and are in fact degenerate semiconductors, that is to say that their Fermi level is very close to the conduction band (BC), or even within this band , for heavily doped TCOs. This means that the BC is already full of electrons at room temperature, thus making the TCO conductive. In addition, the high TCO gap (~ 3-4 eV) prevents them from absorbing photons with energy below this gap, and therefore makes them transparent to visible light. These TCOs are widely used materials, because many applications look for this combination of optical transparency with electrical conductivity, and have cited some applications such as: Flat screens, Anti-freeze windows, Heat reflective windows (buildings, ovens, etc..), Electrochromic mirrors and windows, Touch control screens, Electromagnetic protection, Dissipation of electrostatic charges and Solar cells.

I.10. Copper Oxides

I.10.1. Choice of copper oxide

Among all metal oxides, copper oxides have attracted more attention because of their unique properties. Cuprous oxide (Cu_2O) and cupric oxide (CuO) are two important copper oxide compounds because of their stability. They present an interesting variety of properties that can be fully exploited in solar cells, magnetic storage systems, gas sensors and catalysts [17-21].

I.10.2. Properties of copper oxides

I.10.2.1. Cuprite (Cuprous) oxide Cu_2O

I.10.2.1.1. Crystallographic structure

Monovalent Copper Oxide or Cuprite crystallizes in space group Pn3m Oxygen ions define a centered cubic lattice in which cuprous ions occupy the center of half of the cubes of a/2 edges (Figure I.14). The structural characteristics of Cu_2O are reported in the table I.2.

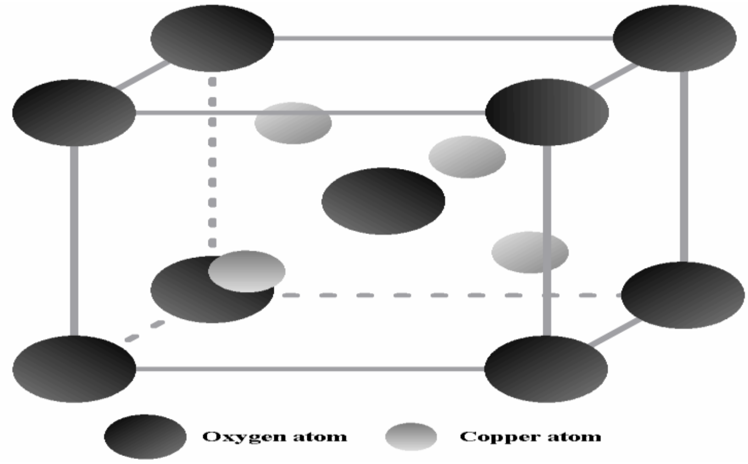


Figure I.14. Crystal structure of Cu_2O

I.10.2.1.2. Electrical properties

The properties of cuprite and especially its electrical properties have been extensively studied. This oxide, solid or in thin films, is a p-type semiconductor with a direct band gap Eg of the order of 2 eV. This mode of conduction has been attributed to the presence, at room temperature, of copper vacancies [22].

Table I.2. Physical properties of cuprite Cu_2O

Density	**6.10g/cm3**
Molar mass	**143.092g/mol**
Lattice parameter	**4.27Å**
Fusion point	**1235°C**
Relative dielectric constant	**7.5**
Length of the Cu -O connection	**1.85 Å**
Length of the O-O bond	**3.68 Å**
Length of the Cu - Cu bond	**3.02 Å**
Width of the forbidden band (Eg)	**2.09eV**

I.10.2.2. Cupric (tenorite) oxide CuO

I.10.2.2.1. Crystallographic structure

CuO or tenorite oxide is distinguished from the transition metal monoxides 3d by its monoclinic structure. It is a black ionic solid having as fusion temperature 1134°C. In this structure, copper is at the center of square planes defined by oxygen anions (Figure I.15). Tenorite crystallizes in the C2/c space group with lattices parameters defined in Table I.3.

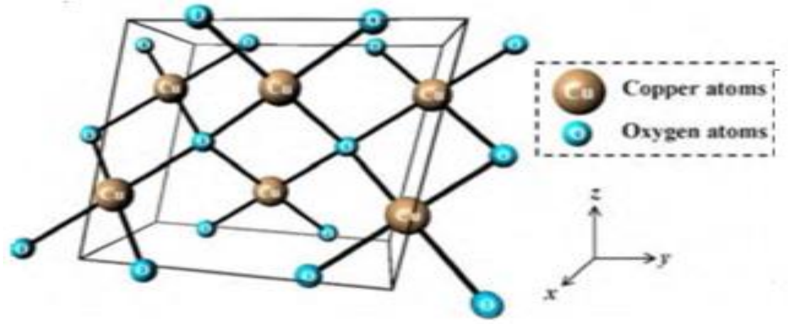


Figure I.15. Schematic representation of the crystallographic structure of CuO: the gray spheres represent the Cu^{2+} ions and the red spheres the O^{2-} ions.

I.10.2.2.2. Electrical; Electronic and transport properties

Copper oxide CuO is also a p-type semiconductor with smallest band gap at the center of Brillouin zone Γ. The figure I.16 shows the electronic structure of CuO in the monoclinic structure. The calculation using Density Function Theory (DFT) in located density approximation found a band gap values of 1.251 eV which is in agreement with the experimentally measurements reported at ambient temperature indicating a band gap values in the range 1.2 to 1.9 eV [22]. CuO generally shows low conductivity. Large variations in the resistivity values have been reported as well as a strong dependence of the resistivity according to the method of elaboration, which have been attributed to either non-stoichiometry or grain boundary conduction. However, the conductivity evolution exhibits an original behavior that can be used as a key component for semiconductor glasses or even semiconductor-based gas sensors. The possible reasons for this behavior are: the small amount of impurity in the compound and its temperature stability in a low oxygen partial pressure atmosphere.

The important properties of CuO is that it is capable of absorbing a large number of oxygen in volume and on the surface, this excessive oxygen on the surface or in the volume gives the semiconductor "p" and the oxidation catalytic properties of Cu_2O, when CuO is irradiated by visible light in aqueous media, these excessive oxygen species are free making it a unique material for photocatalytic. In the following table we quote some physical properties of CuO.

Table I.3. Physical properties of cupric CuO

Density	6.32g/cm^3
Lattice parameters	a=4.69Å , b=3.42Å ,c=5.13Å β=99.54°
Fusion point	1134°C
Relative dielectric constant	12
Contact lengthCu-O	1.95 Å
The length of the O-O connection	2.62 Å
The length of the copper connection	2.3 Å
Width of the forbidden band (Eg)	1.2 – 1.9 eV

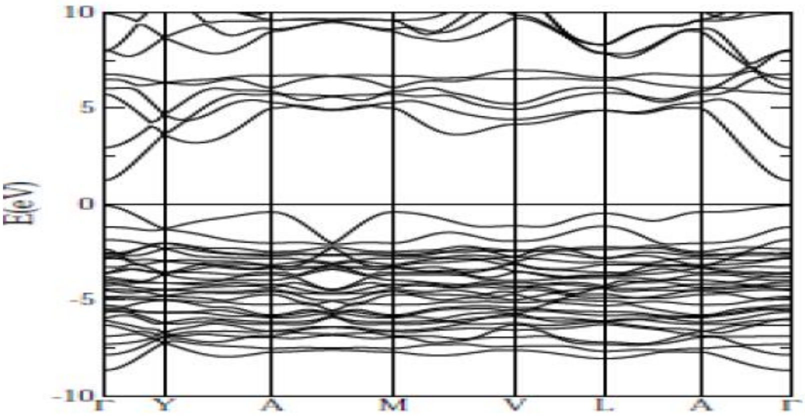


Figure I.16. Band structure of CuO calculated using the DFT+U method [23]

I.10.2.2.3.Optical properties

Thin films of CuO have a transparency between 0 and 80% in the visible region and a refractive index varies in the range of 1.5 to 3.5. Native point defects are intrinsic in semiconductors, they play an important role in the electronic properties of semiconductors. The formation energies of these defects are also calculated for three different types of native point defects: vacancies (V_{Cu}, V_O), antisite (Cu_O, O_{Cu}) and interstitial (Cu_i, O_i) defects. The optical properties of CuO vary according to various factors such as: grain size, substrate temperature, thickness, doping concentration, strain strain, structural parameters, defects and disorder, as well as deposit techniques and conditions [24].

Under the action of a high-energy light beam or electron bombardment, copper oxide emits photons. This phenomenon corresponds to luminescence. Depending on the conditions of elaboration, different luminescence bands were observed. The UV and visible luminescence are due to the near-band-edge (NBE) emission or inter band emission and to the different defect states

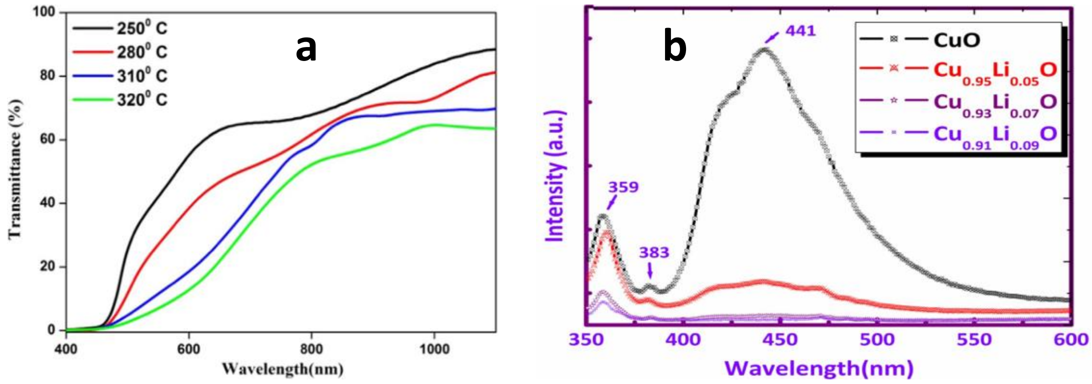


Figure I.17. Transmittance (a) [25] and photoluminescence (b) [26] of CuO thin films

I.10.3. Applications of CuO thin films

CuO is a promising material for various applications due to the abundance of its components in nature, low-cost production, good thermal stability, and electrochemical properties. This combined property enables CuO thin films to be a serious candidate for several applications namely: high-temperature superconductors, solar cells, gas sensors, magnetic storage media, varistors, catalysis, antimicrobial activity, photoelectrochemical cell and batteries [17-21, 27]

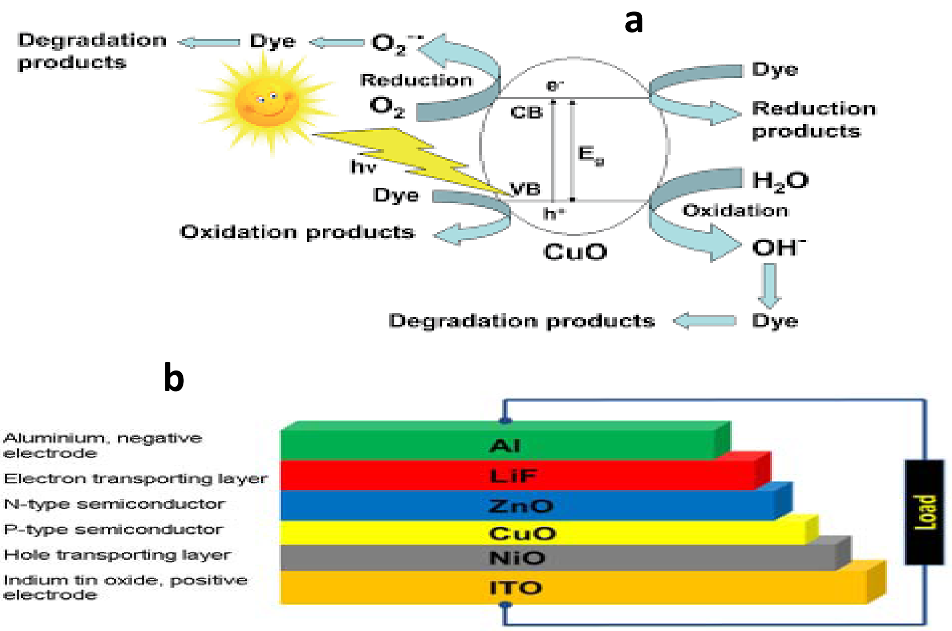


Figure I.18. Some applications of CuO; photocatalysis [28], solar cell [29]

I.11. Deposition of copper oxide (CuO) thin films by Sol-Gel technique

The development of a high quality thin layer of copper oxide (CuO) is a very important and delicate step; several techniques have been used for the production of CuO thin films. Among these techniques, the sol-gel technique with the multiple advantages that they offer indeed. They lead to products of high purity and make it possible to control the composition of the final material at the molecular level. They also allow a control of the doping and the thickness of the coating, it can be very low thus offering a lower use of the product, a low toxicity emission and therefore a minimum of production cost. The main steps in the preparation of thin films by the sol-gel process are: preparation of the precursor solution, deposition of the prepared sol on a substrate by the chosen technique, heat treatment of the xerogel. The manufacture of CuO thin films is influenced by several factors:

-Nature and concentration of precursors

- Type of solvent and the additives

-Aging time of the solution

-Nature of the substrate

-Substrate coating method and its speeds

-Drying and annealing of thin films

Precursor:

Table I.4. regrouped the different precursors used to develop of CuO thin films

Copper Nitrate	$Cu(NO_3)_2$
Copper Chloride dihydrate	$(CuCl_2).2H_2O$
Copper sulfate pentahydrate	$CuSO4,5H_2O$
Copper acetate	$[Cu(CH_3COO)_2]$
Copper acetatedihydrate	$[Zn (CH_3COO)_2.2H_2O]$

Solvent

The most commonly used solvents are alcohols, dipolar and amphoteric solvents with a dielectric constant which is chain length dependent. Some of which are mentioned in this table.

Table I.5: Characteristics of some most popular alcohols as solvents

Alcohol	Formula	Dielectric constant at 20 °C	Boiling point (°C)
Methanol	CH3OH	32.35	64.7
Ethanol	CH3CH2OH	25.00	78.3
1-Propanol	CH3CH2CH2OH	20.81; 20.10 (at 25 °c)	97.2
2-Propanol	CH3CH OH CH3	18.62	82.2
1-Butanol	CH3CH2CH2CH2OH	17.80	117.7
2-Butanol	CH3CH2CH OH CH3	15.80 (at 25°c)	99.5
2-Methoxyethanol	CH3OCH2 CH2OH	16.90	124.6

Additives

Additives allow playing several roles. They act as basic or an acid. The additives play the role of stabilizing the hydrolysis and condensation of alkoxides and avoid rapid precipitation**,** For example, copper chloride dihydrate has limited solubility in alcohols such as ethanol and 2-propanol in the absence of other agents such as monoethanolamine or heating [30].

I.12. Conclusion:

In this chapter we have presented concepts about nanotechnology and nanomaterials (their design, manufacture) as we have introduced some of their applications. We have shown copper oxide in the form of thin films and some of its interesting properties including: optical, electrical, electronic ... and some of its applications and how to prepare it in a sol Gel method.

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Chapter II

Sol-Gel Technique

Elaboration of CuO thin films

And

Experimental techniques for characterization

II.1. Introduction

Developing a good quality material and mastering its structural, optical and electrical properties is a major challenge. A good mastery of the experimental processes makes it possible to modify the physical properties of the material according to the need imposed by the type of application [1]. In this chapter, we will describe the sol gel fabrication thin films method as well as the deposition parameters and necessary steps for the elaboration copper oxide thin films (preparation of the various solutions, the substrates, deposition of the thin films, and finally annealing). We will expose some thin films characterization techniques such as X-ray diffraction (XRD) to study the structural properties of samples, photoluminescence and UV-Vis spectroscopy to study optical properties.

II.2. Sol-Gel technique

II.2.1. Definition

The term sol-gel corresponds to the abbreviation "solution-gelation". Briefly, a "sol" is a colloidal suspension of oligomers whose diameter is only a few nanometers. Subsequently, this "sol" can be evolved through chemical reactions into an infinite viscosity network called "gel". The basic principle of the sol-gel process is as follows: a solution based on precursors in the liquid phase is converted into a solid by a set of chemical reactions (hydrolysis and condensation), most often at room temperature, hence the term "soft" chemistry. The sol-gel method allows the elaboration of a large variety of oxides in different configurations (monoliths, thin films, fibers, powders). This great diversity, both in terms of materials and formatting, has made this process very attractive in technological fields such as optics [2-3], electronics[4], biomaterials[5], sensors(detection), separation media (chromatography). It has, moreover, the advantage of using a soft chemistry and being able to lead to very pure or doped materials according to the intended application.

II.2. 2.Physico-chemical principles

The starting solution is usually a precursor, a solvent (usually an alcohol), sometimes a catalyst (acidic or basic) and water. Each compound is dosed very precisely because the properties of the gel depend on it. The nature of the desired material imposes the precursor. The choice of the solvent and the catalyst is then dictated by the chemical properties of the precursor. The latter being the principal component of the solution [6]

II.2.3. Precursors

The precursors most often used in the sol-gel process are the metal alkoxides of the general formulas $M(OR)n$ where M denotes a metal of valence n and R is an alkyl chain of type $(CnH_{2n} + 1)$. They can be of very high purity and have high solubility in a wide variety of organic solvents. The synthesis, the reaction behavior and the physical properties of the alkoxides have been widely studied [7-8], which is why it will be recalled only the main characteristics necessary for the understanding of the reactions of the alkoxides in solution.

II.2.4. Reaction mechanisms

The presentation of the various steps of formation of the oxide will then make it possible to understand the role of each constituent of the elaborated solutions. The sol gel process is based on two reactions: hydrolysis and condensation [9].

II.2.4.1. Hydrolysis reaction

In order for the alkoxides to condense at room temperature, the hydrolysis of the -OR groups must begin the reaction process. This step is necessary to give rise to hydroxyl groups –OH

$$M\text{-}(OR)n + H_2O \rightarrow HO\text{-}M\text{-}(OR)n\text{-}1 + R\text{-}OH \ldots\ldots\ldots\ldots\text{ (II.1)}$$

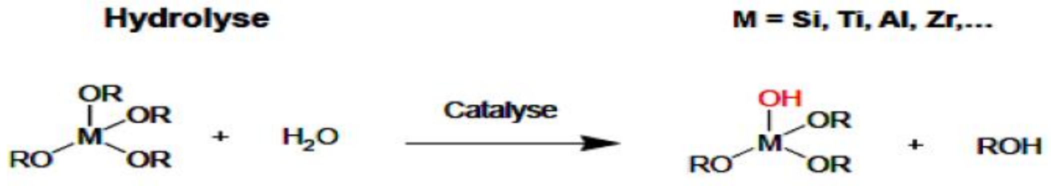

Figure II.1. Schematization of the hydrolysis process

Hydrolysis is a nucleophilic substitution of a -OH ligand for a -OR ligand. It is accompanied by water consumption and alcohol release. During this step, the functionality of the precursor with respect to the polycondensation is created.

II.2.4.2. Condensation reaction

The -OH groups generated during the hydrolysis are good nucleophiles and go during the condensation, resulting in the creation of M-O-M bridges:

Alcoxolation: $(OR)_{n-1}\text{-}M\text{-}OH + RO\text{-}M\text{-}(OR)_{n-1} \rightarrow (OR)_{n-1}\text{-}\ M\text{-}O\text{-}M\text{-}(OR)_{n-1} + R\text{-}OH..\text{(II.2)}$

Oxolation: $(OR)_{n-1}\text{-}M\text{-}OH + HO\text{-}M\text{-}(OR)_{n-1} \rightarrow (OR)_{n-1}\text{-}\ M\text{-}O\text{-}M\text{-}(OR)_{n-1} + H_2O\ldots\ldots\text{ (II.3)}$

Like hydrolysis, condensation changes the coordination of the metal, but does not increase its coordination. When these two reactions are complete, a gel is obtained. The transformation of the solution into a solid polymeric cluster is then generally called the sol-gel transition.

II.2. 5. Sol-gel transition

The scheme generally adopted for gelation is that of growing polymer chains which agglomerate by condensation and form clusters during the progress of the hydrolysis and condensation reactions, polymeric clumps, the size of which increases with time, are created. When one of these clusters reaches an infinite size (that is to say in a practical way the size of the container), the viscosity also becomes infinite: it is the sol-gel transition point. From this moment, the infinite cluster called "gel fraction" continues to grow by incorporating the smaller polymeric groups. When all the bonds have been used, the gel is formed. From a macroscopic point of view, the transition can be followed by the mechanical behavior of the solution. It then results in the divergence of the viscosity of the solution and a growth of the elastic constant in the gel phase G (or coulomb modulus) [6]. The evolution of the viscosity of a sol and that of its Coulomb modulus are thus presented schematically in figure II.2, as a function of time: at the complete formation of the gel, the viscosity becomes infinite, whereas the elastic constant tends towards its maximum value. The solid cluster formed from the base solution can then be seen as an interleaving of the polymeric chains forming a disordered solid structure. This structure still contains trapped liquid masses [10]. Their eliminations are done by evaporation. Like all chemical reactions, the sol-gel transition is sensitive to its environment, such as temperature or humidity, which can, depending on its nature, modify the kinetics of the reactions.

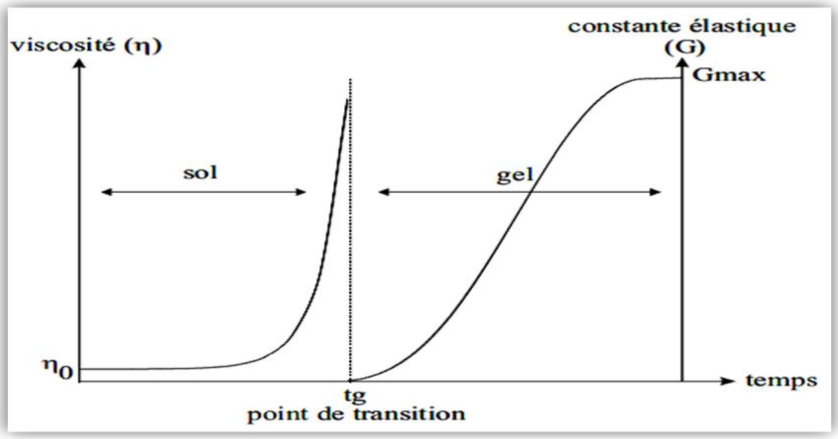

Figure II.2. Evolution of the viscosity of the solution and the elastic constant of the gel. The point *tg* corresponds to the time at the end of which the transition sol gel is reached

II.2.6. Parameters influencing the kinetics of the reactions

In the case of alkoxide precursors, the sol-gel transition is not reversible. The final structure of the gel is set up at the time of the reactions, and therefore, already determines its properties to come. Only a few characteristics can be modified during the following stages (deposition, drying, annealing). The relative kinetics of hydrolysis and condensation, responsible for the growth of the polymeric clusters that generate the network, will impose the characteristics of the gel obtained. These reaction rates, and consequently the viscosity, depend on several parameters which must therefore be taken into account when choosing a production process:

II.2.6.1. Temperature

This is the first parameter to consider, which is involved in any chemical reaction. In our case, it has an influence on the rates of hydrolysis and condensation from the preparation of the sol, and then during aging or storage. Obviously, the higher it is, the faster the reactions.

II.2.6.2. Choice of the alkoxide and its concentration:

This choice is made according to the reactivity of the alkoxide, and the type of sample that one wants to elaborate. As for the concentration in the sol, it is especially important during condensation; in fact, the weaker it is, the more the molecules capable of binding are distant from each other, which delays the reactions [11].

II.2.6.3. Solvent

The alkoxides are not miscible in water, it is therefore necessary to mix the precursors, water and optionally the catalyst, in a common solvent. It is then preferable to use the alcohol corresponding to the -OR ligand of the alkoxide, in order to avoid possible reactions between the various components that may modify the kinetics of reactions. So the starting sol is usually an alcoholic solution [12].

II.2.6.4.Sol pH (choice of catalyst)

Given the mechanisms involved in gelation, it seems obvious that pH will play an important role in the evolution of reactions; in fact, the H_3O^+ and OH^- ions do not have the same influence on the two types of reaction: the H_3O^+ cation, attracted by oxygen, facilitates the substitution of the OR groups by OH^- (hydrolysis), while the OH^-anion, attracted by the electronegative metal M, favors the formation of M-O-M (condensation) bonding. In summary, it can be said that an acidic medium promotes hydrolysis, while a basic medium accelerates condensation [13-14]. Catalysis thus acts directly on the shape of the material developed. This factor will also significantly affect the porosity of the final material, which will partially condition the physical properties.

II.2. 7. Deposition of thin films by sol-gel

The sol-gel route makes it possible to produce films having a thickness of between a few nm and a few µm. Several techniques have been developed for the deposition of thin films on a given substrate. The choice of the technique depends on the characteristics of the substrate such as its geometry or its size as well as the geometric properties that one wants to give to the layer such as the thickness [15]. We will review the most commonly used.

II.2.7.1. Centrifugation or spin coating:

This method consists in depositing by centrifugation a solution on a substrate [16]. This technique has the advantage of being easily implemented, for moderate investments. It gives excellent results on flat substrates whose dimensions are of the order of cm^2. This deposit method can be decomposed into four phases, schematized in Figure II.3.

a) The deposit of the solution

b) The beginning of the rotation: the acceleration phase causes the flow of the liquid towards the outside of the substrate

c) Constant speed rotation allows the ejection of the excess liquid and the reduction of the thickness of the film uniformly

d) The evaporation of the most volatile solvents which accentuates the decrease in the thickness of the deposited film.

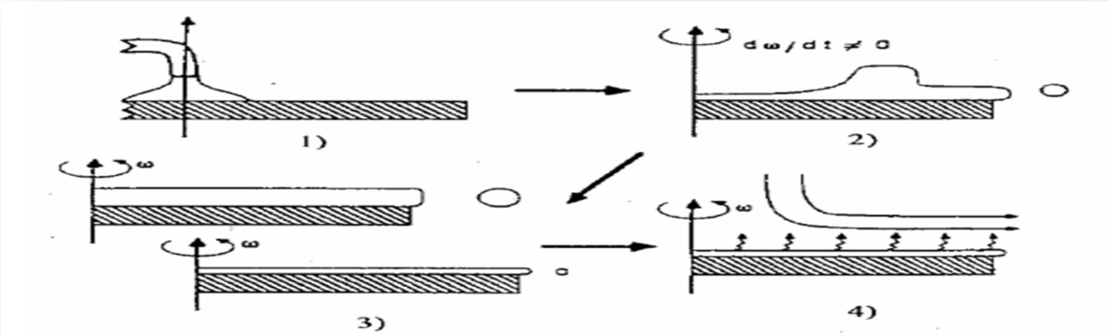

Figure II.3. Deposition of thin films by centrifugation: the four deposition steps (ω represents the speed of rotation of the substrate)

By controlling the rotation parameters, it is possible to calculate the thickness of the deposited film: Meyerhofer has published a model taking into account the parameters coming into play during deposition the thickness is then given by the following relation [17]:

$$h = c.\left(\frac{3\eta e}{2\rho\omega^2}\right)^{\frac{1}{3}} \quad \text{……………………………..……….. (II.4)}$$

With:

c: constant

e: Evaporation rate

η: The viscosity of the solution Kg.$m^{-1}.s^{-1}$.

ω: Rotational speed s^{-1}(rad)

ρ: the density of the solution Kg. m^{-3}

It is then possible for a solution whose viscosity is given, to control the thickness of the films by fixing the speed of rotation.

II.2.7.2. Dip – Coating

The simplest means of depositing a material thinly onto a surface to use a random adsorption process, with the coating material in solution. This approach is very effective and generally provides homogeneous, smooth, thin films. It is possible to control the film thickness and internal layer structure by altering the concentration of material in solution, the immersion time, and by using multiple dipping cycles [18-19].

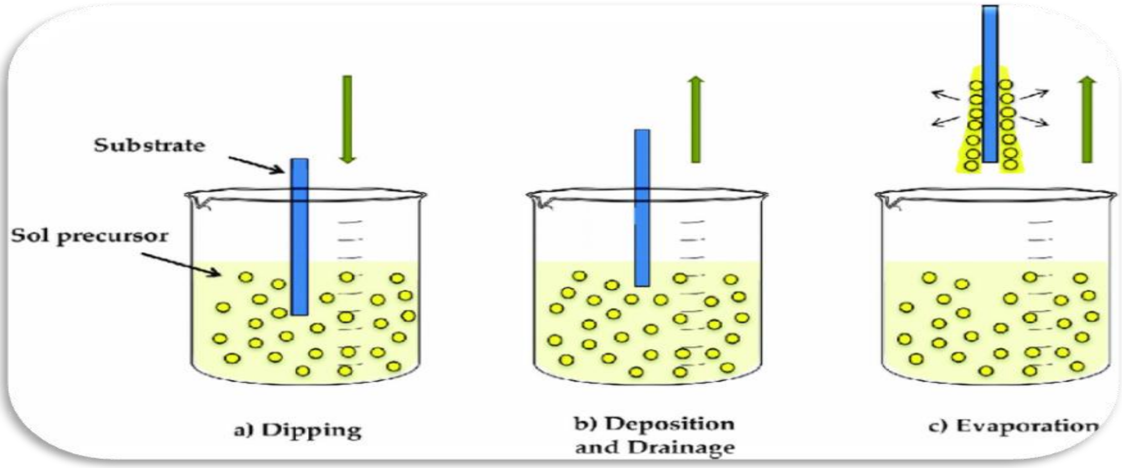

Figure II.4. The different stages of the dip-coating technique.

The thickness of the deposited film, denoted h, is given by Landau and Levich law:

$$h=c\frac{(\eta U)^{2/3}}{\gamma lv\sqrt{\rho g}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(II.5)}$$

Where

c: a constant, it is equal to 0.8 for a liquid considered as Newtonian

η: Viscosity of the sol in Kg.m^{-1}.s^{-1} ; U: The drawing speed in m.s^{-1}

ρ: Density of the solution in Kg.m^{-3} ; g: Gravity constant in N.Kg^{-1}

γlv: Surface tension (vapor-liquid)

II.2.8. Thin film treatment

The drying of the deposited layer is a very important step in the production of quality materials, it corresponds to the evaporation of the residual solvents by diffusion through the pores. Drying is done at low temperature [20]

The annealing is separated from the drying phase, this phase is essential in the formation of the material. The annealing has two main functions: The elimination of the organic species present in the starting solution (organic groups of alkyl type (-OR-)) and the crystallization and densification of the material (figureII.5). It is carried out at temperatures between 300 ° C and 700 ° C [21].

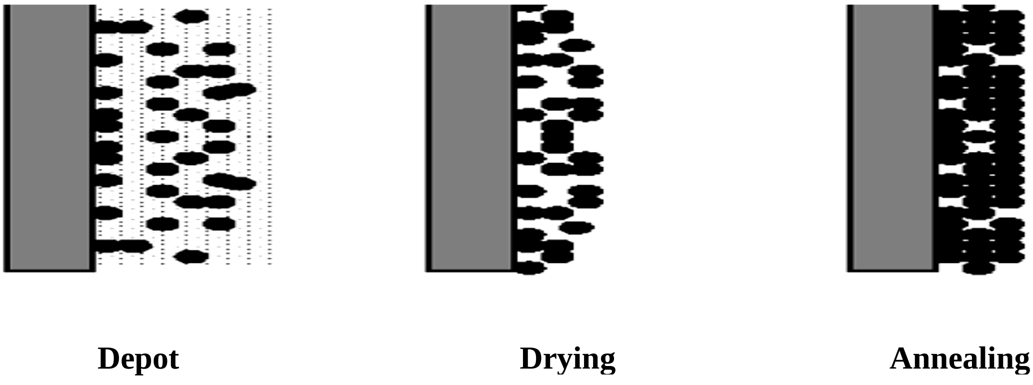

Figure II.5. Influence of drying and annealing on the porosity of thin films.

II.2.9. The main advantages of Sol-Gel technique are:

a) Possibility of producing thin layers of mineral oxides at low temperatures on heat-sensitive substrates.

b) Possibility of producing organo-mineral hybrid materials (true nanocomposites in which mineral and organic species are mixed at the molecular scale) in the form of thin or monolithic layers with specific properties.

c) Deposition of thin layers on both sides of the substrate in a single operation.

d) Realization of multi-component deposits in a single operation. facilitated doping in large quantities.

e) The Sol Gel method has the advantage of being simple enough to implement allows to directly developing the materials in various forms: thin layers, fibers, fine powders and massive materials, with high purity and better homogeneity.

II.2.10. The main disadvantages of Sol-Gel technique are:

a) Very high alkoxide precursor cost.

b) Delicate process control and long process times.

c) Handling a significant amount of solvents.

d) Low thickness of the layers, so one must perform several coating.

Deposition and drying steps to obtain a thickness of several hundred nanometers, which increases the risk of cracking because the first deposited layers all undergo successive drying which increases the risk of short circuit during electrical tests.

II.3. Elaboration of copper oxide thin films by technique the Sol-Gel spin-caoting

II.3.1. Different preparation steps:

The spin-coating sol-gel method has been used. As we have seen in this chapter, to develop thin films of copper oxide, this technique makes it possible to obtain films of high purity and homogeneity with varied compositions. Figure II.6 shows schematically the preparation steps of copper oxide thin films by sol-gel-spin coating process. This technique includes several steps:

a) Chemical preparation of the solution to obtain the liquid (Sol).
b) Preparation of substrates.
c) Deposition of solution on the substrate.
d) Annealed thin films to result in the desired crystallized and densified material.

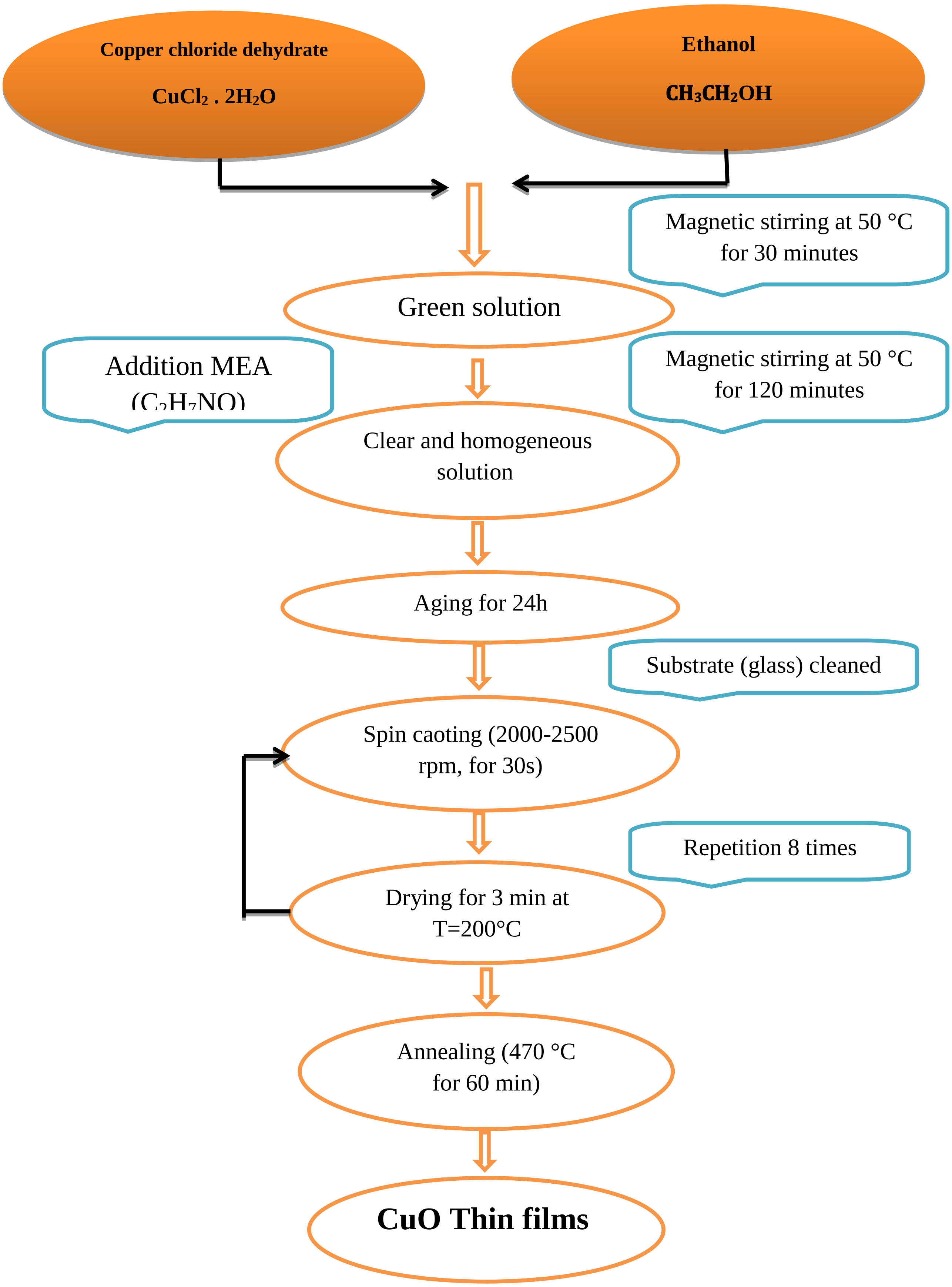

Figure II.6. Preparation steps of copper oxide thin films by sol-gel-spin

II.3.2. Chemical elements involved in the formation of solutions:

In order to prepare the solutions, we use several chemical components where we remind some of their chemical and physical properties:

a) Copper chloride dehydrate: this compound was used as a precursor:

Table II.1. Some physical and chemical properties of copper chloride dehydrate.

Chemical formula	$CuCl_2 .2H_2O$
Form	Solid
Color	light blue
Melting Point	598 °C
Molar mass	170.48g\mol
Density at 20 ° C	2.53g/cm^3
Solubility in water at 20 ° C	757g/l

b) Monoethanolamine (MEA): as a stabilizer or additive.

Table II.2. Some physical and chemical properties of monoethanolamine.

Chemical Formula	$NH_2CH_2CH_2OH$
Form	Liquid
Color	Colorless to yellow
Molar mass	61.08g/mol
Density at 20 ° C	1.01g/cm^3
Boiling point	170C°

c) Ethanol: alcohol as a solvent.

Table II.3. Some physical and chemical properties of ethanol.

Chemical Formula	CH_3CH_2OH
Form	Liquid
Color	Colorless
Molar mass	46.08g/mol
Density at 20 ° C	0.789g/Cm3
Boiling point	78.3°C

II.3.3. Preparation of solutions

In our work, to study the effect of the molar concentration (molarity) and to determine the optimal concentration to synthesize high quality CuO thin films, we prepared three solutions with different molarity: 0.2, 0.4, 0.6 mol/L. The precursor solution (sol) leading to the deposition of CuO thin films was obtained by dissolving copper chloride dehydrate ($CuCl_2.2H_2O$) in solvent (Ethanol) with magnetic stirring at 50 ° C and after 30 minutes a volume of monoethanolamine (MEA) was added in a molar ratio (n (MEA) \ n(chloride) = 1), in order to dissolve possible precipitates of work hydroxide, the volume total of the solution is Vt = 15 ml. The solution is then brought to magnetic stirring at 50 °C for 2 hour, the solution of which becomes clear, homogeneous and light green. Finally the solution is aging for 24 hours. In the following table the different proportions of the reagents used.

Table II.4. Different proportions of the reagents

	Number of moles of precursors in 15m	Mass (g) of precursors in 15ml	Volume of solvent Ethanol (ml)	Volume of Stabilizer (MEA) (ml)	Molarity of the final solution (mol/L)	Volume of the final solution (ml)
Copper chloride dehydrate CuO	**0.003**	**0.5114**	**14.80**	**0.18142**	**0.2**	**15**
	0.006	**1.0228**	**14.23**	**0.36285**	**0.4**	**15**
	0.009	**1.5343**	**13.84**	**0.54427**	**0.6**	**15**

II.3.4. Preparation

II.3.4.1. Choice of substrates

The substrates used in the context of this work are glass slides, It is an amorphous material widely used in the optical field but also in the field of high technology, its uses are varied giving rise to a very important production. The quality of the deposit of the samples depends on the cleanliness and the surface condition of the substrate. Cleaning is therefore an important step: you must remove all traces of grease and dust and check that the surface of the substrate does not show to the naked eye, scratches or flatness defects. These conditions are essential for the good adhesion of the deposit on the substrates, and its uniformity (constant thickness).

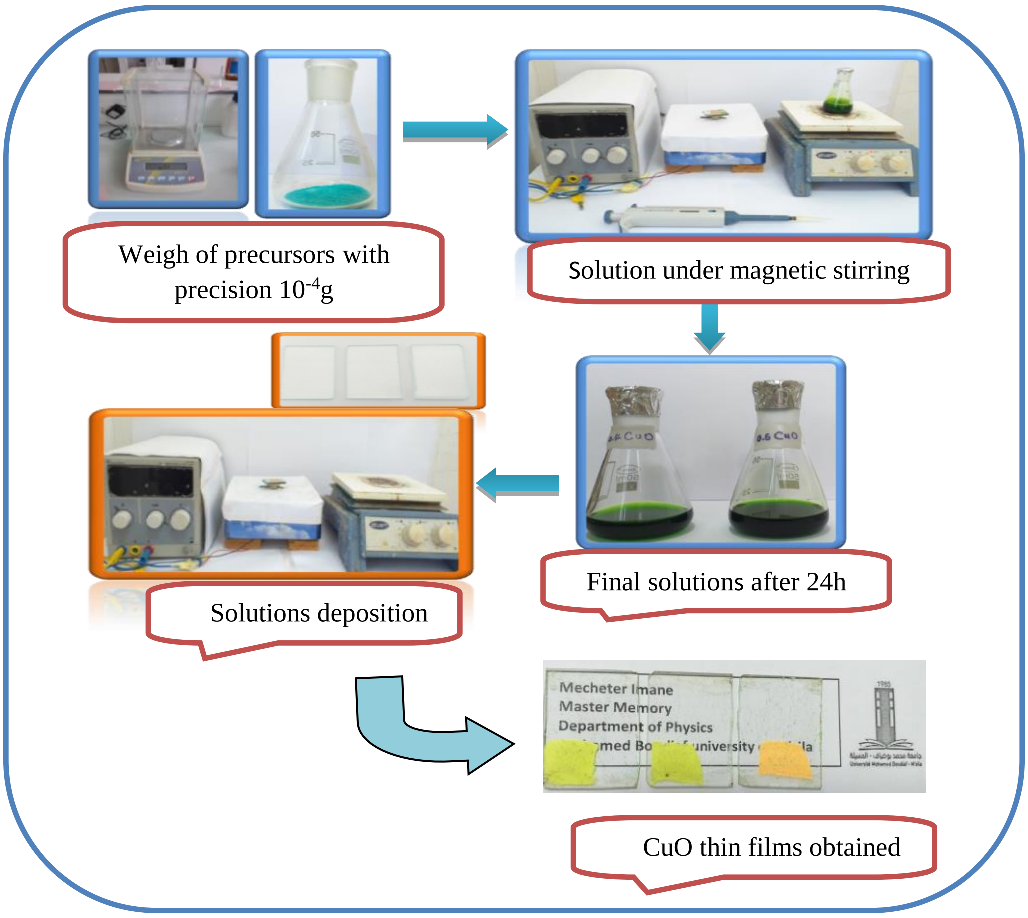

Figure II.7. Experimental setup used: preparation of solutions and deposition

II.3.4.2. Cleaning the substrates

The procedure for cleaning the substrates is as follows: Cleaning in a beaker filled with eluted HCl and then rinsed with distilled water. The substrates are then kept away from dust.

II.3.5. Deposition of CuO thin films by spin coating technique

The deposition procedure comes immediately after the preparation of the substrates and solutions. The spin-coating technique consists of simply depositing the aged solutions (a few drops using a micropipette) on the surface of the substrate fixed on a rotational support of controlled speed (2000-2500 rpm during 30s). This step allows the solution to spread (evenly) over the entire surface of the substrate thanks to the centrifugal force. After each deposition, the layers were dried at 200 ° C for 4 min, and the deposition-drying process was repeated 8 times for each solution.

II.3.6. Annealing of CuO thin films

The heat treatment performed after the elaboration of the thin layers makes it possible to eliminate the residues of the precursors used in the starting solution. The heat treatment also makes it possible to densify the material and to crystallize it in the desired phase. In our work the annealing of the films was carried out in an oven at 470 ° C for 60 minutes .

II.4. Experimental Techniques for thin films characterization

We characterized our thin films by different techniques.

II.4.1.Structural characterization

II.4.1.1. X-Ray Diffraction (XRD) Principe:

The crystalline structure of the thin films was analyzed by X-ray diffraction (XRD). This method, mainly applicable to crystallized materials (in powders, monocrystalline or polycrystalline), aims to specify the structure of materials, to measure lattices parameters, the crystallites size, and the orientation statistic of crystallites. It must also make it possible to examine the state of constraint. A polycrystalline material is composed of a multitude of grains (crystallized domains considered as single crystals), themselves consisting of stacks of crystalline planes. These planes are defined by their Miller indices (hkl), characterizing the orientation of the lattice with respect to the elementary crystal lattice, and by their interticular distance d_{hkl}. This distance can be measured by X-ray diffraction using Bragg's law.

$$2d_{hkl}\sin\theta = n\lambda\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots..(II.6)$$

d_{hkl}: Interreticular distance, that is, the distance separating two consecutive index planes (hkl).

θ: Incidence angle of X-rays on the surface of the studied material. Also called a half deflection angle in geometry called θ-2θ or symmetrical diffraction

n:Order of reflection.

λ: Wavelength of the X-ray beam of the same order of magnitude as the Interreticular distance

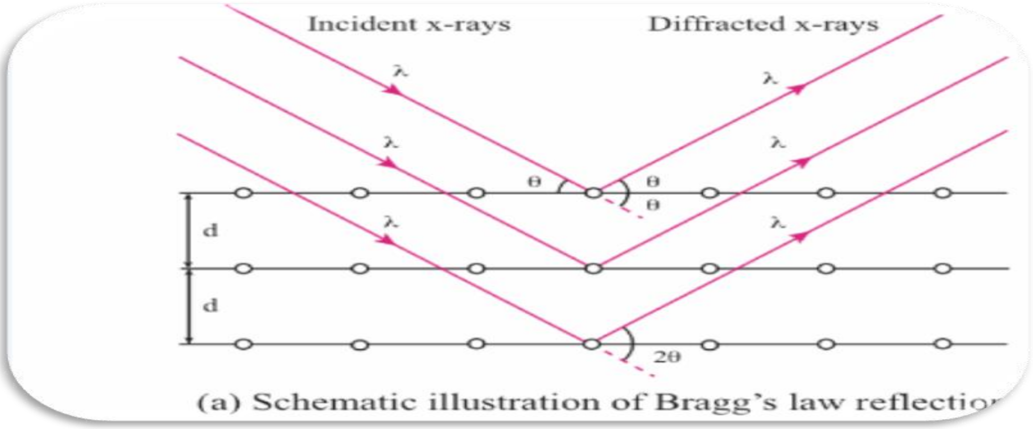

Figure II.8. Principle of X-ray diffraction

Diffractometer used

X-ray diffraction experiments were performed on a « X'Pert PRO MPD X-ray diffractomètrer ». X-radiation is produced by an anticathode of copper don wavelength is λ (Cu) = 1.5418 Å

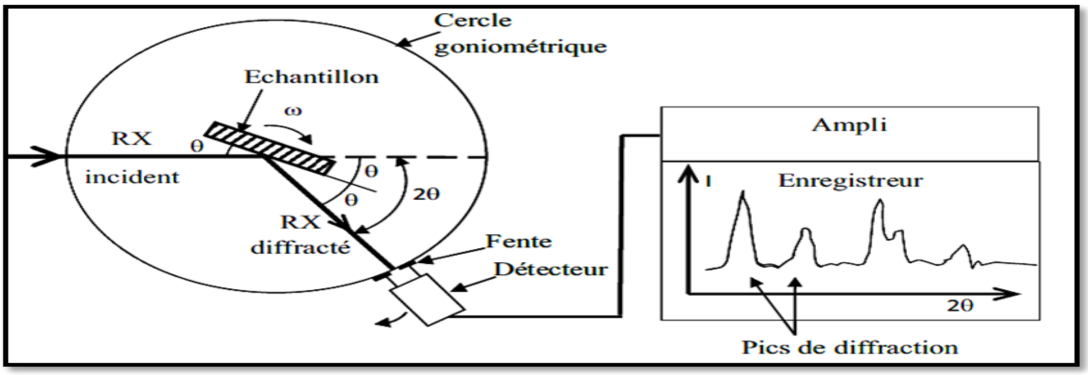

Figure II.9. Operating diagram of an X-ray diffractometer

II.4.2. Optical characterizations

II.4.2.1. Photoluminescence Spectroscopy

Photoluminescence (PL) is the unconstrained outflow of light from a material under optical excitation. PL examinations can be utilized to describe an assortment of material parameters. PL spectroscopy gives electrical (instead of mechanical) portrayal and it is a specific and to a great degree delicate test of discrete electronic states. The power of the PL signal gives data on the nature of surfaces and interfaces. PL examination is nondestructive. Also, time-determined PL can be quick, making it helpful for describing the fastest procedures in a material. The central restriction of PL investigation is its dependence on radiative occasions. Materials with poor radiative effectiveness, for example, low - quality circuitous band crevice semiconductors. Figure II.10 shows the schematic diagram and the major components of the instrument that is used to measure photoluminescence.

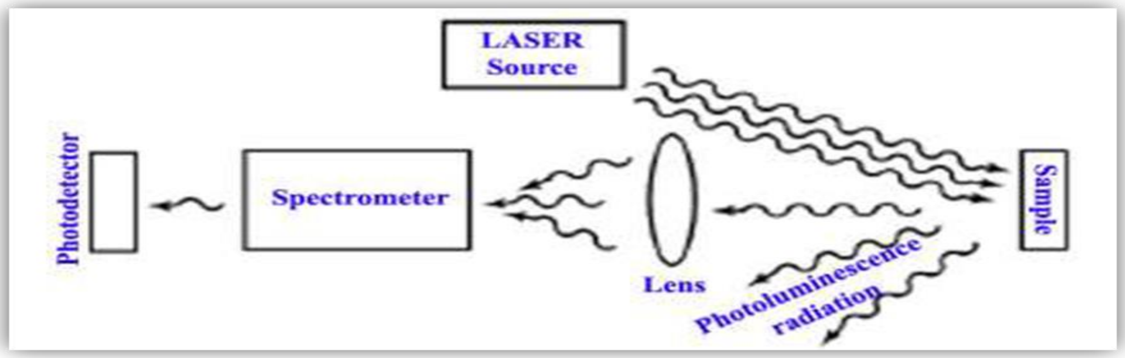

Figure II.10. A schematic diagram of PL Spectrophotometer

Principle

Its principle consists of exciting the electrons of a material studied with a generally monochromatic radiation, and the light emitted by the latter is analyzed in response. By absorbing a particle of radiation, the electrons of the material pass from a lower energy state to a higher energy state, and then they reemit photons by de-energizing to return to a stable energy state. In our study, we used a spectroscopy Perkin Elmer LS 50 B with two excitation wavelengths 350 and 500nm.

II.4.2.2. UV-Visible spectrophotometer

Ultraviolet-visible spectroscopy (UV-Vis) is used to measure the absorption spectrum of light by the sample in the ultraviolet and visible (UV / Vis) range, where the energy absorbed causes disturbances in the electronic structure of atoms, ions or molecules. One or more electrons absorb this energy to jump from a low energy level to a higher energy level. This technique tells us about some optical properties of the material such as the estimation of the optical absorption threshold, the absorption coefficient, the optical gap and the refractive index. The optical transmittance spectra of the films involved in our work were carried out at room temperature by a UV-Visible UV-Visible UV 3101 PC spectrometer type Shimadzu, whose spectral range extends over a range of 350 nm to 800 nm. The UV-visible spectrophotometer consists of three main parts: the radiation source, the sample holder and the reference, and the measurement system.

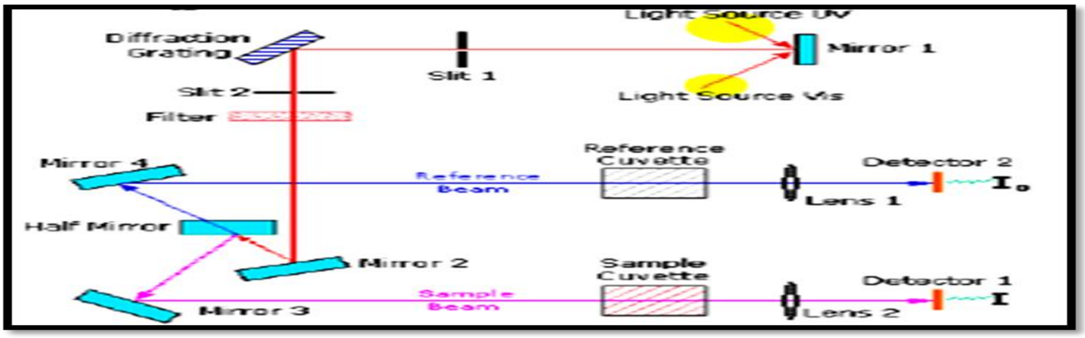

Figure II.11. Schematic representation of the UV-Visible spectrophotometer

II.5. Conclusion

In this chapter we have presented the steps of preparation of CuO thin films with different concentrations by the sol-gel spin-caoting technique and the different characterization techniques; X-ray diffraction for structural properties and photoluminescence and transmittance spectroscopy for optical properties.

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Chapter III

Results and discussion

III.1. Introduction

We have successfully synthesized CuO oxide semiconductor nanostructure thin films on glass substrates by sol gel spin coating technique without obtaining other phases. The thin films obtained have been characterized by different techniques. X-ray diffraction for the study of structure, crystallite size, deformation and defects. Optical transmission in the UV-visible and photoluminescence for the determination of fundamental optical properties such as different emissions and optical gap. These characterizations are important because they directly condition the applications of elaborate samples. This chapter concerns the study of the experimental results of the CuO nanostructures thin films obtained. We will discuss the different results and the influence of the concentration of precursor on the structural and optical properties of nanostructure thin films.

III.2. Structural properties

The film thicknesses were measured using Stylus Profilometer (model: D 500). In this work thickness of all thin films (8 layers) about (420 nm).

XRD analysis was carried out to investigate the structural properties of CuO nanostructures thin films deposited on glass substrates with various precursor concentrations. The observed XRD pattern for CuO nanostructures thin films in the scan range of 30˚ to 70˚ are shown in Figure III.1

XRD pattern of CuO contained the diffraction peaks at 2θ = ~32°, ~35°, ~38°, ~46°~48°, ~ 53°,~ 58°, 61°, 66° and ~ 68° which are assigned to reflection planes of (110), (002), (200), (-112), (-202), (020), (202), (-113), (-311) and (220) show the monoclinic ténorite structure of CuO (JCPDS card number 002 -1041).

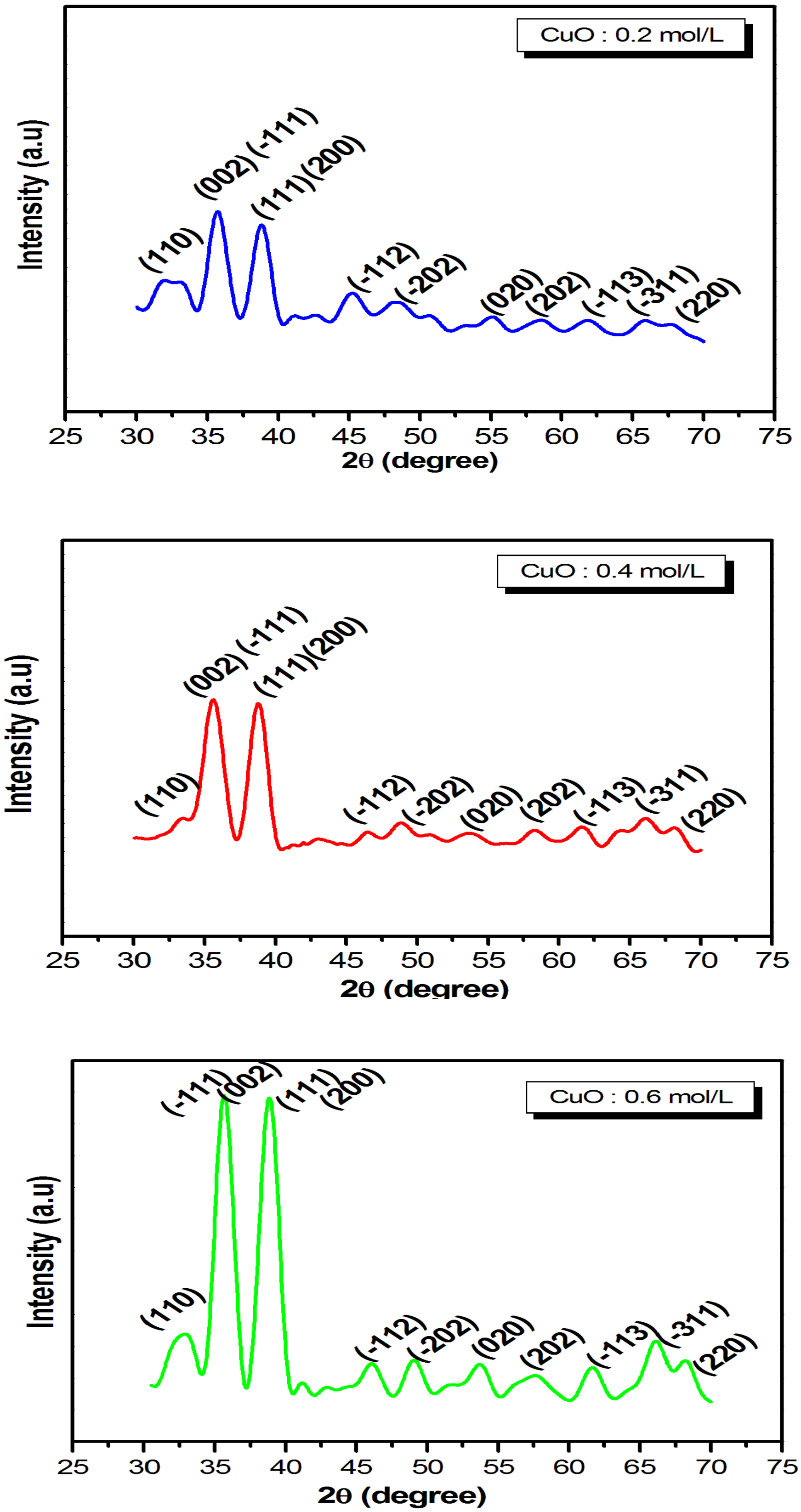


Figure III.1. XRD patterns of CuO nanostructures thin films deposited at different precursor concentrations (0.2, 0.4 and 0.6 mol/L)

The existence of more than one peak shows that oxide films are a polycrystalline. The absence of hydroxide phase Cu $(OH)_2$ or any other impurity phases except CuO indicates the excellent purity of the CuO nanostructures. The CuO nanostructures thin films with good crystal quality are suitable for differents applications devices.

The diffraction peaks of CuO cupric oxide nanostructure thin films are intense and the intensity of peaks greatly increases with increasing precursor concentration, which can be attributed to the increased and improved crystallinity of the CuO monoclinic phase [1-2]. The observed broadening in XRD diffraction peaks as evident from the Figure 1 shows that the CuO nanostructures are in the nanometer range.

The crystallite size D for the films and the microstrain ε due to crystal imperfection and distortion was calculated by using following relations [3]:

$$D = \frac{K\lambda}{\beta cos\theta}$$

$$\varepsilon = \frac{\beta}{4tg\theta}$$

The dislocation density (σ), which gives the amount of defects in the crystal and the number N of crystallites by unit are estimated using the equations [1,4]:

$$\sigma = \frac{1}{D^2}$$

$$N = \frac{1}{D^3}$$

where $\lambda = 1.54Å$ is the wavelength of X-rays, K is a constant equal to 0.90, β is full Width at Half Maximum of diffraction peak measured in radians and θ is the Bragg angle.

The differents structural parameters of CuO nanostructures thin films are summarized in table 1, 2, 3

Table 1. Summary of the structural parameters of CuO (0.2 mol/L) nanostructures thin films extracted from X-ray diffraction analysis.

predominant Peaks Pos. [°2θ]	hkl	d-spacing(Å)	FWHM (rad)	Crystallites Size D (nm)	Micro Strain ε	Number of crystallites N $(10^3\,nm^{-3})$	Dislocation density σ $(10^2 lines.nm^{-2})$
35,71	(002) (-111)	2,511	0,021	6,6	0,49	3.47	2.3
38,76	(111) (200)	2,320	0,020	6,66	0,50	2.47	2.3

Table 2. Summary of the structural parameters of CuO (0.4 mol/L) nanostructures thin films extracted from X-ray diffraction analysis.

predominant Peaks Pos. [°2θ]	hkl	d-spacing(Å)	FWHM (rad)	Crystallites Size D (nm)	Micro Strain ε	Number of crystallites N $(10^3\,nm^{-3})$	Dislocation density σ $(10^2 lines.nm^{-2})$
35.60	(002) (-111)	2.518	0.023	6.026	0.54	4.56	2.7
38.85	(111) (200)	2.315	0.022	6.3	0.51	3.99	2.5

Table 3. Summary of the structural parameters of CuO (0.6 mol/L) nanostructures thin films extracted from X-ray diffraction analysis.

predominant Peaks Pos. [°2θ]	hkl	d-spacing(Å)	FWHM (rad)	Crystallites Size D (nm)	Micro Strain ε	Number of crystallites N $(10^3\,nm^{-3})$	Dislocation density σ $(10^2 lines.nm^{-2})$
35.60	(002) (-111)	2.518	0.022	6.3	0.523	3.99	2.51
38.85	(111) (200)	2.315	0.023	6.02	0.54	4.5	2.76

The average crystallite size calculated and it was about 6 nm revealed a very fine nanocrystalline structure. Most reports [5-6] are available where D was found greater than 8 nm. Baturay et al [4] revealed that small values of crystallites because of the improvement in crystallinity of CuO films.

It can be said that crystallites are less strained and dislocations in CuO thin film formed with precursor concentration of 0.2 mol/L. indicates the decrease in lattice imperfections and formation of high-quality films

The texture is a term designating a preferential orientation of the crystallites of a polycrystalline material. Depending on various factors, the crystallites can be oriented, not completely random, but preferably in one or more particular direction. The texture coefficient measures the relative degree of preferred orientation of specific (hkl) plane. This coefficient is calculated through the XRD spectrum according to the following formula [7]:

$$TC_{hkl} = \frac{I_{hkl}}{I_{0_{hkl}}}\left(\frac{1}{n}\sum_{i=1}^{i=n}\frac{I_{hkl}}{I_{0_{hkl}}}\right)^{-1} \text{……………………..(III.1)}$$

n is the number of diffraction peaks. I_0 is the standard intensity of the plane (hkl) taken from the JCPDS data. I is the measured intensity of (hkl) plane observed in XRD patterns. TC = 1 gives a random orientation of crystallites. The TC values greater than one (TC >1) indicates the abundance of the crystallites in a given (hkl) plane. For the TC (hkl) values that lie between zero and one indicate the lack of crystallite orientation in this direction [1].

Figure III.2 shows TC_{hkl} values corresponding to reflections planes for CuO thin films with different precursor concentrations. As shown in figure III.2 revealed the TC(hkl) values, it can be seen clearly that (002) (2θ = ~35°) and (200) (2θ = ~38°) planes are the preferential ones. At low precursor concentration, the TC of (002) plane is higher than the TC of (200) plane, because the abundance of crystallites in that direction.

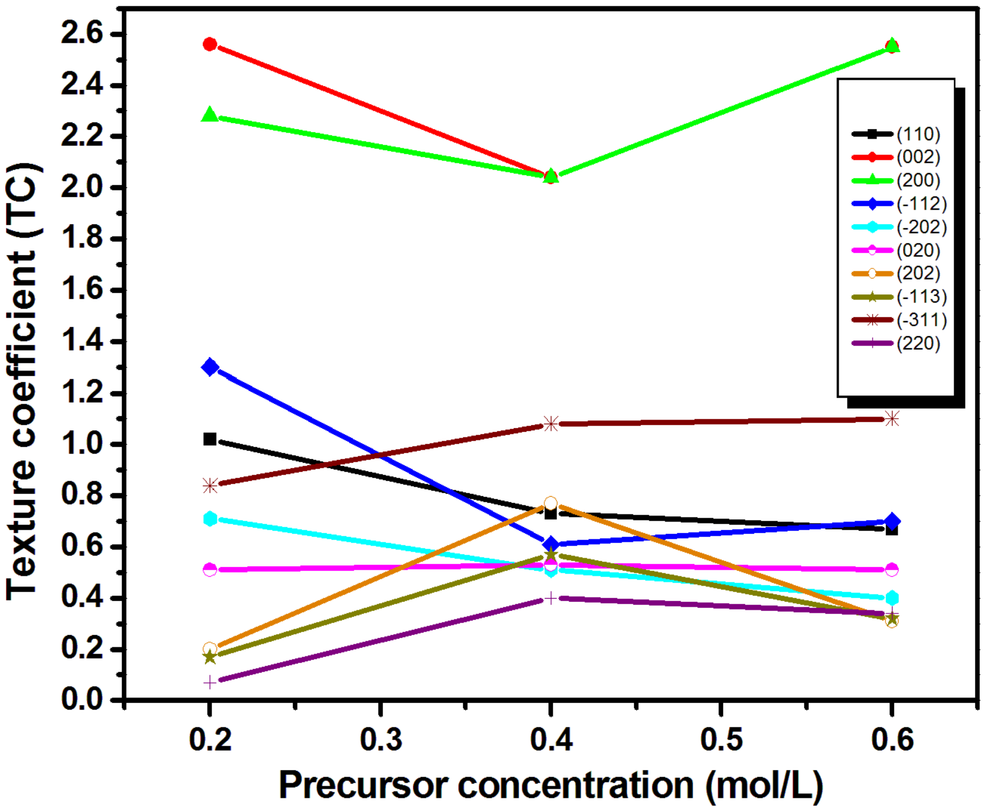


Figure III.2. Variation of texture coefficient TC of different planes (hkl) of CuO with precursor concentrations

The lattice parameter (a ≠ b ≠ c, α = γ = 90°, β= 99,5° for CuO monoclinic tenorite structure) were calculated from the predominant XRD peaks of monoclinic phase CuO by using the following relation [8]:

$$\frac{1}{d^2} = \frac{1}{sin^2\beta}\left[\frac{h^2}{a^2} + \frac{k^2 sin^2\beta}{b^2} + \frac{l^2}{c^2} - \frac{2hl\,cos\beta}{ac}\right] \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(III.2)}$$

$$2dsin\theta = n\lambda \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(III.3)}$$

For CuO monoclinic tenorite structure

$$c = \frac{2d_{002}}{sin\beta}$$

$$a = \frac{2d_{200}}{sin\beta}$$

$$b = 2d_{020}$$

The values of the lattice parameters for CuO phase in thin films are represented in figure III. 3

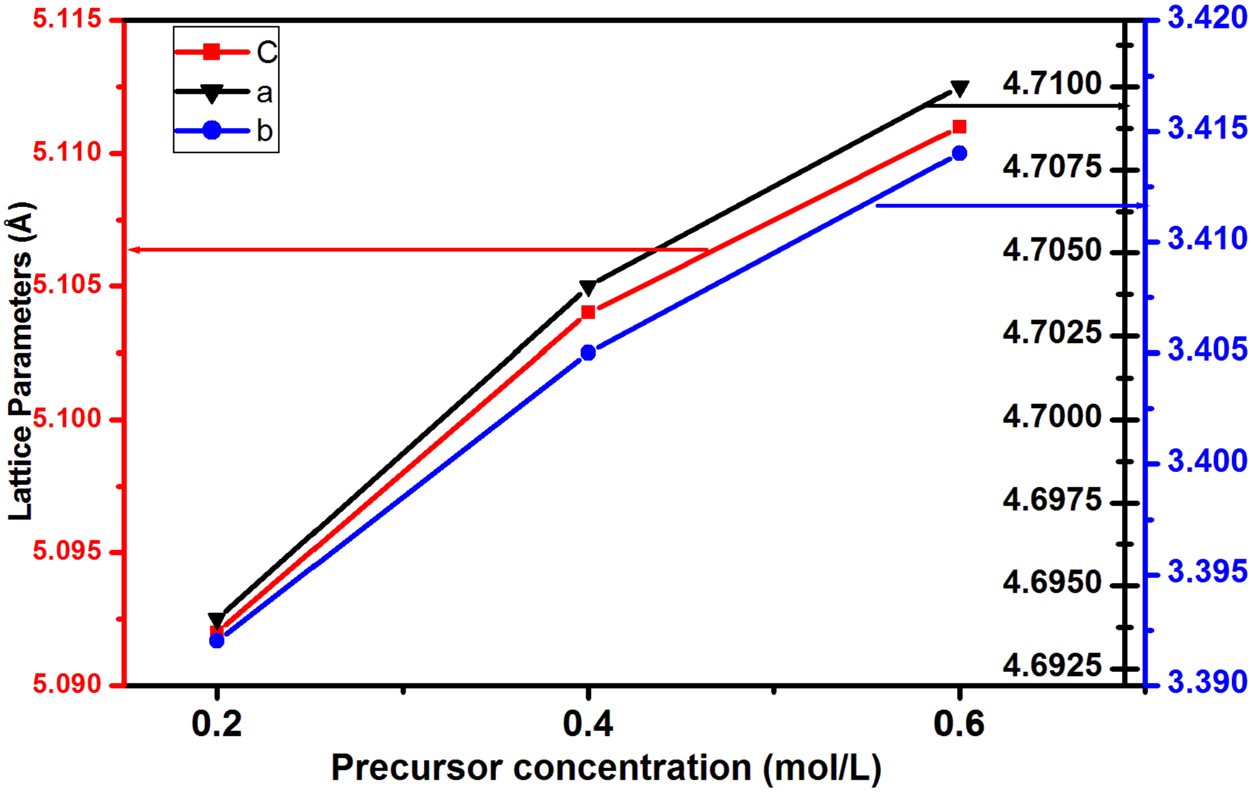


Figure III.3. Variation of values of the lattice parameters for CuO with precursor concentrations

Figure III.3 shows that there is not much difference between the standard and calculated values of the lattice constants.

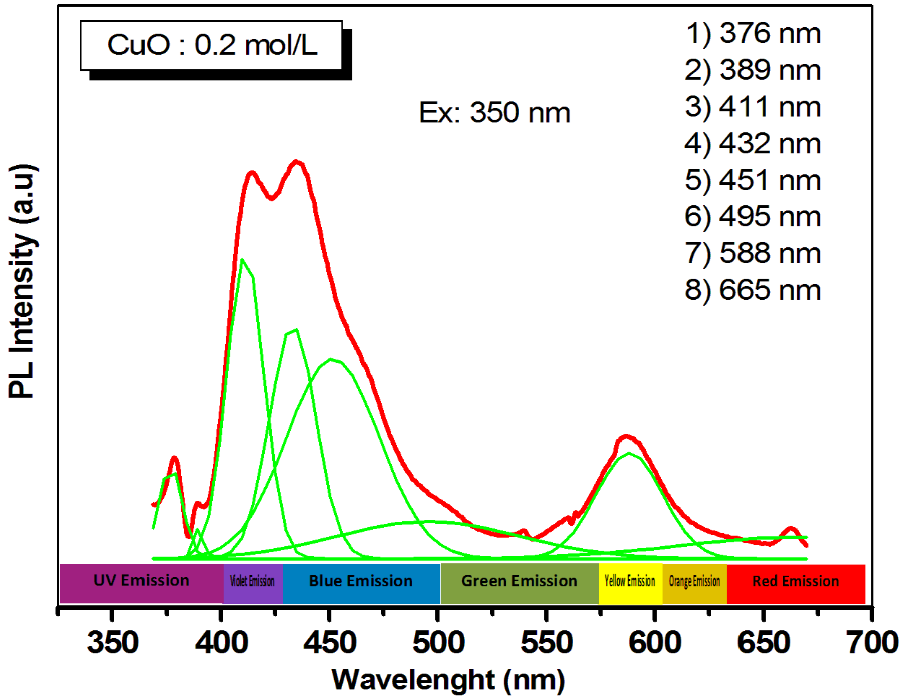
Compared with CuO thin film at low precursor concentration, the lattice parameters **a**, **b** and **c** slightly increased with concentration, this can be explained by the abundance of Cu atoms, atomic diffusion, and the decrease of crystalline defects such as vacancies.

III.3. Optical properties

III.3.1. Photoluminescence

Photoluminescence spectroscopy is a convenient characterization technique because it is nondestructive, contact less and results from simple spectral data collection. The PL can be used to study different types defects by identification of various recombination levels. Generally, the PL of Copper Oxide (CuO) exhibited more emission peaks in the visible and UV regions, which is attributed to exciton recombination and different defect states such as copper vacancy (V_{Cu}), oxygen vacancy (V_o), Cu interstitial (I_{Cu}), oxygen interstitial (I_{Cu}), Cu_O (antisite Cu atom in the oxygen sublattice) and O_{Cu} (antisite O atom in the copper sublattice) [9-10]. These defects, results in radiative recombination transitions between either valence or conduction band and defect levels or between defect and defect levels. The intensity gives a measure of the relative rates of radiative and non-radiative recombination processes. More information can be gotten from the photoluminescence study of CuO films, but the reported results on photoluminescence of the CuO thin films are few to date and did not give a reasonable explanation about the luminescence behavior due to the complex band structure of CuO. Luminescence properties of CuO are strongly dependent on sizes and shapes of nanocrystals. Finally, considering these parameters in the design of CuO-based photo-electronic devices is important.

Figure III.4 and III.5 show the luminescence spectra at the excitation wavelength of 350 nm and 500nm for CuO nanostructures thin films with deconvoluted peaks obtained by Gaussian fitting.



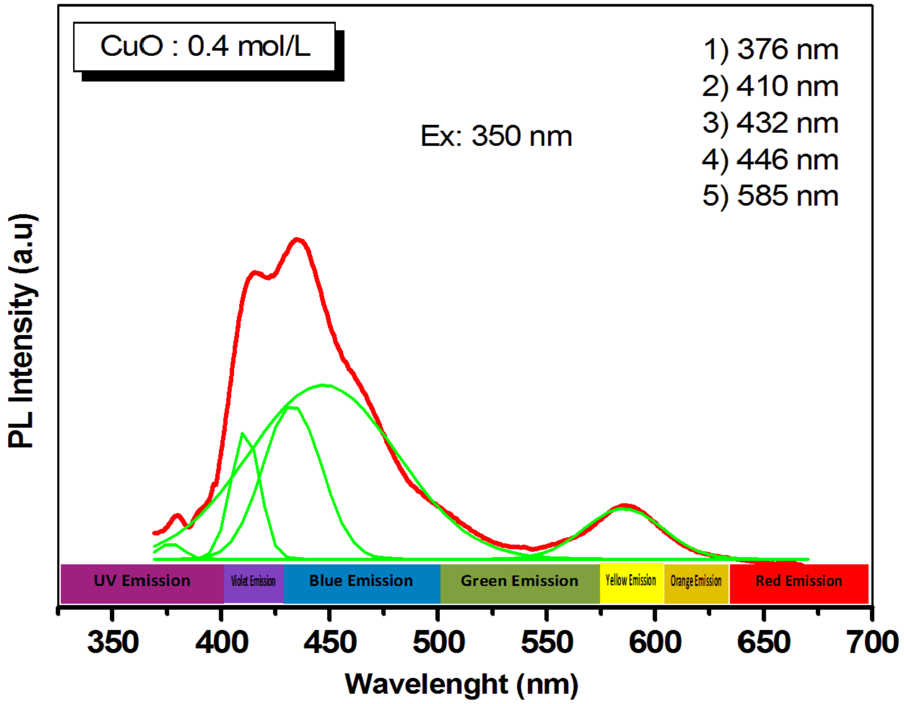


Figure III.4. Room temperature PL spectra of CuO nanostructures thin films with 350 nm of excitation with deconvoluted peaks obtained by Gaussian fitting.

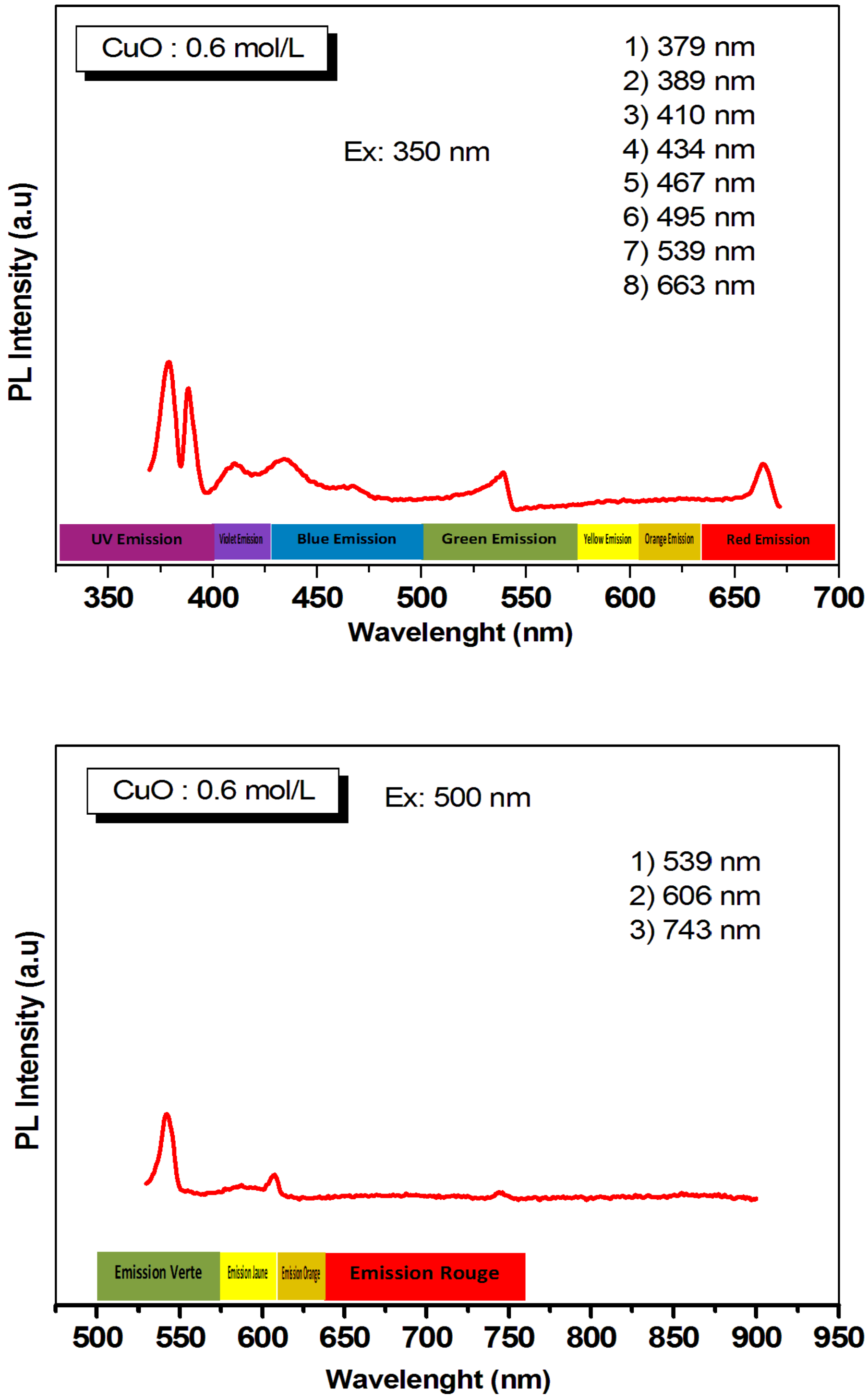


Figure III.5. Room temperature PL spectra of CuO nanostructures thin films with 350 nm and 500 nm of excitation

The emission spectrum of the excitation at 350 nm gives different peaks as depicted in figures. The peaks376 and 389 nm are attributed to the near-band-edge (NBE) UV emission or inter band emission. The origin of UV emission in CuO is due to the recombination of electron–hole pair in free-excitons. These peaks correspond to the band gap energy of CuO nanostructures. Chand et al [11] deemed that the UV emissions centered at 359 and 383 nm were the band edge emissions of CuO. Vimala Devi et al [12] reported that the emission bands detected at 324–397 nm are attributed to the radiative annihilation of excitons in CuO.

Gobbiner et al [13] demonstrated that the peaks at 3.92eV and at 4.52eV could be attributed to near band edge emission or inter band emission, originate due to electron-hole pair (excitonic) recombination in CuO.

Bhuvaneshwari et al [14] reported that he peak appearing between 370 – 385 nm is attributed to the excitonic transitions in CuO. Wang et al [7] reported that the recombination of electron-hole pair in free-excitons results in the UV emission peak at 341 nm and a dominant emission peak at 390 nm is attributed to the near band-edge emission of CuO nanostructures.

The peak at 410 nm with violet emission is due to the transition from sub-band of the conduction band to oxygen interstitial [13]

The observed emissions in blue region 432- 495nm are attributed to the oxygen vacancies [12]. Sharma et al [10] reported that the emission at 468 nm and 488 nm are assigned to energy levels of defect sites, e.g. V_{Cu} (copper vacancies), Cu_i (copper interstitial) and Vo (oxygen vacancy) in CuO nanoparticles. Chand et al [11] reported that the PL peak at 441 nm corresponds to blue emission in the visible region. The origin of visible emission in copper oxide nanomaterials is generally attributed to the oxygen vacancies. Grobiner et al [13] reported that the blue emissions peaks at 442 and 460nm are attributed to radiative recombination of electrons from acceptor level of oxygen interstitials to donor levels of copper interstitials. Bhuvaneshwari et al [14] reported that the broader peak in the range 410-425 nm may be accounted for by the transitional oxygen vacancies and interstitial oxygen. Wang et al [15] reported that in the PL spectrum of pure CuO, a small hump of luminescence blue band at 489 nm is caused by transition vacancy of oxygen and interstitial oxygen.

The peak at 539 nm in CuO : 0.6mol/L linked to the green emission region is due to singly ionized oxygen vacancies [12]. Grobiner et al [13] reported that the peak at 541nm corresponds to green emission of CuO thin film and is attributed to electronic transition from singly ionized oxygen vacancies and photo-excited electrons. Toufik et al [9] reported that the luminescence peak at 539 might correspond to singly ionized oxygen vacancies, resulting in green emission of CuO. This type of oxygen vacancy contributes to recombination of photogenerated holes with a single ionized electron in the valence band of the electronic band structure of CuO.

The peak ~ 588nm (606nm for excitation at 500 nm) corresponding to yellow emission from CuO is acclaimed to doubly ionized oxygen vacancies [12]. The red peak emission at 665nm (743nm for excitation at 500 nm) appear due to the transition of electrons from the conduction band to an acceptor level and the transition of electrons from a donor level to the valance band or an acceptor level in copper oxide [9].

It can be clearly seen from figures that the luminescence intensity of defects decreases and some is almost completely quenched with red shift and increases the luminescence intensity of UV emissions with increasing CuO concentration, this may be due the crystal quality is usually improved with concentration of precursor, which confirm the XRD results.

In our study, schematic electronic level diagram proposed for CuO thin films is presented in Figure III.6**,** which includes the differentes transitions.

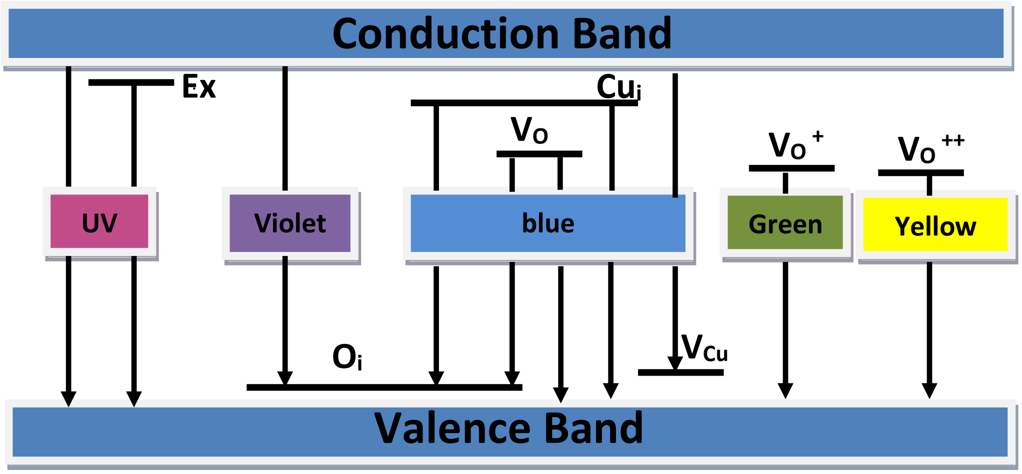


Figure III.6. Schematic electronic level diagram proposed for CuO thin films

III.3.2. optical transmittance

The optical transmittance spectra of CuO thin films deposited at different precursor concentrations in the wavelength range 350–800 nm at room temperature are shown in Figure III.7. It was observed that the average transmittance of all films is between 50 to 70 % in the visible region, this may be explained by the size and grain boundary scattering effect [16].

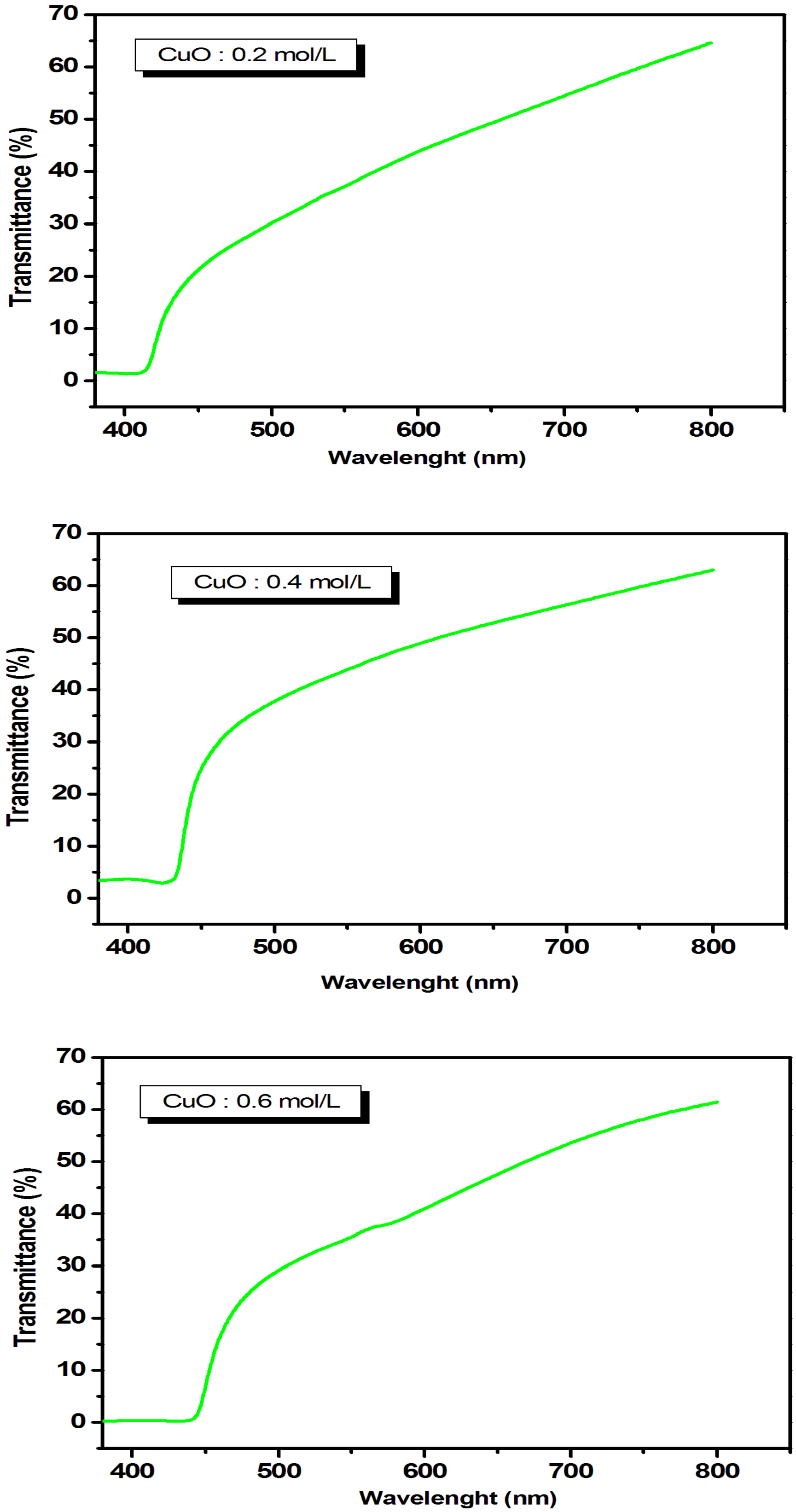


Figure III.7. Optical transmittance spectra of CuO thin films deposited at different precursor concentrations

A sharp absorption edge has been observed for all films in the region between 400 and 450 nm. This attributed to the absorption of light by copper oxide (CuO) thin films [1]. These materials have a high absorbance in the visible wavelength and gap energy.

The band gap (*E*g) was estimated from the following equation:[6]

$$(\alpha h\upsilon)^2 = A(h\upsilon - Eg)\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(III.4)$$

Where $h\nu$ is the photo energy and α is the absorption coefficient of the films, which was calculated from the equation:

$$\alpha = (-1/d)\ln T\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(III.5)$$

Where T is the transmittance and d is the film thickness.

The band gap was determined by extrapolating the linear region of $(\alpha h\nu)^2$ versus the photo energy. The variation of $(\alpha h\nu)^2$ versus the photon energy ($h\nu$) of CuO thin films and the variation of band gap with different precursor concentrations is shown in Figure III.8 and Figure III.9 respectively.

Compared with the value of band gap of CuO bulk (1.2eV), The blue-shift behavior of absorption edge (band gap) of our nanostructures thin films and as evident from the PL spectrum is ascribed to the quantum confinement result with reduce in the size of the nanostructures (6 nm) [6].

It is clear that the band gap energy of CuO decreases with increasing precursor concentration, which can be attributed to improved crystallinity of the CuO thin films, which is confirmed by XRD results. Similar results have been reported by other works [1].

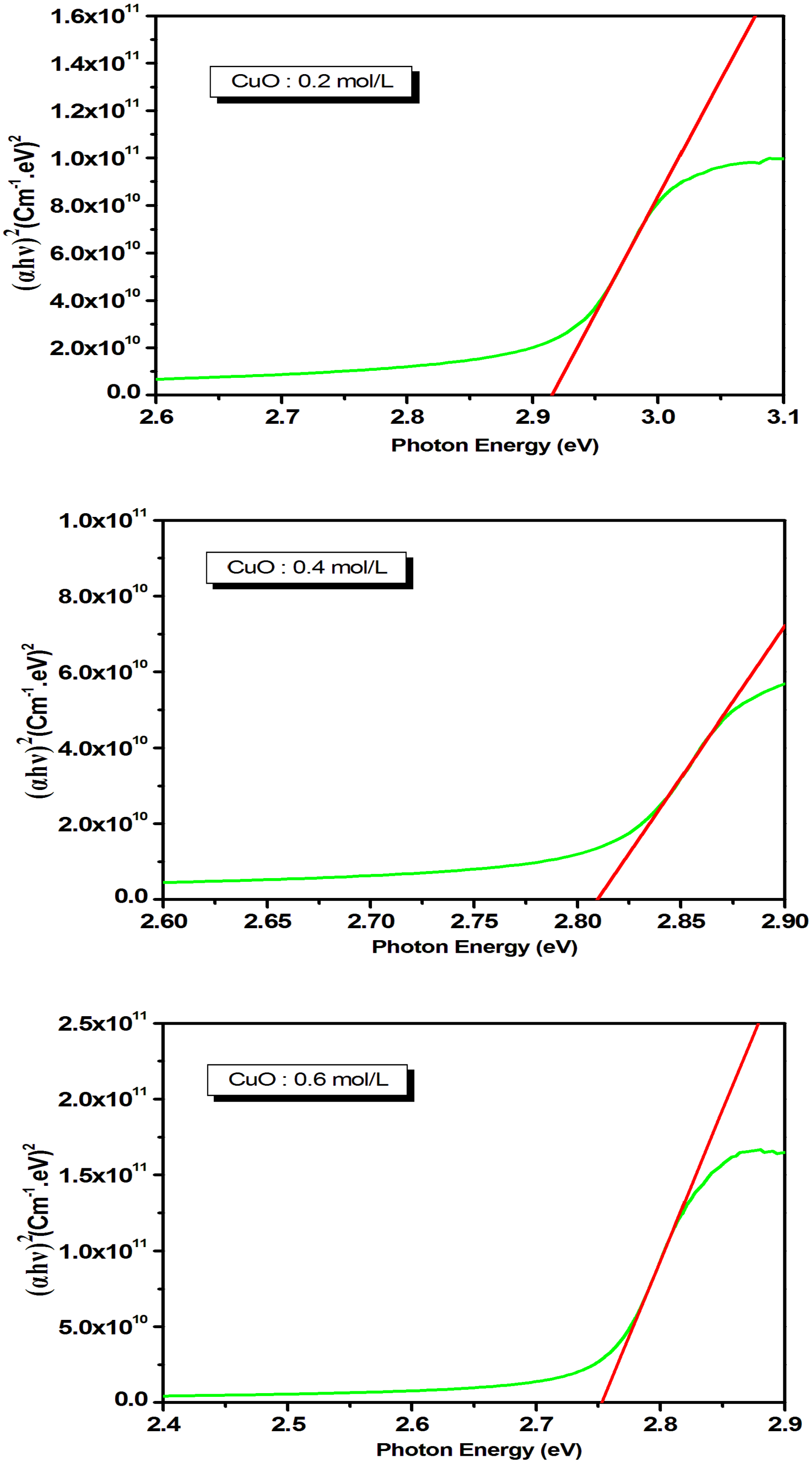


Figure III.8. The plots of $(\alpha h\nu)^2$ versus photon energy ($h\nu$) of CuO thin films deposited with different precursor concentrations

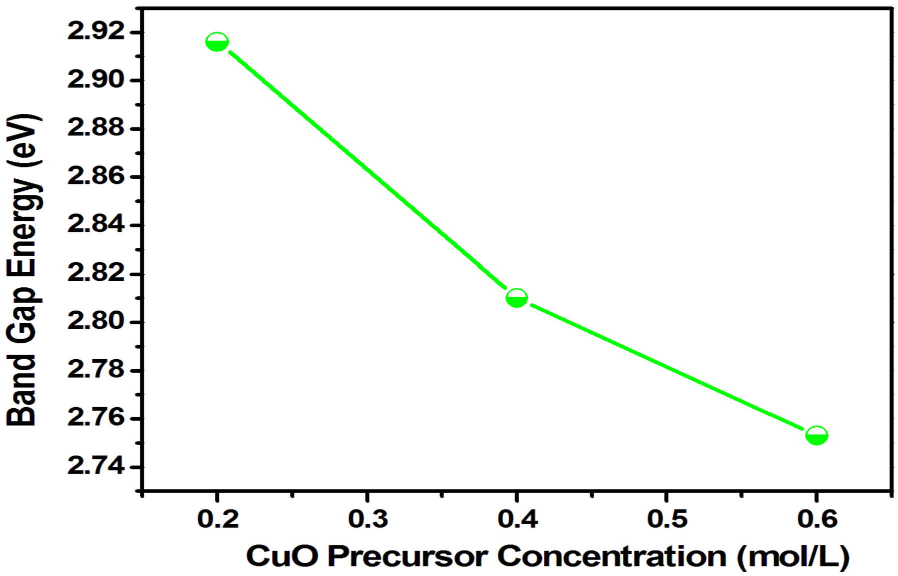


Figure III.9. Band Gap of CuO thin films versus precursor concentrations

We remarqued that the photon energy of the ultra violet emission in PL spectra of CuO thin films is significantly higher than the value of the bandgap. The similar phenomena have also occurred in other studies [17]. Chand et al. [11] deposited Li-doped CuO thin films by pulsed laser deposition. They all included three luminescent centers, namely, ultraviolet emissions at 359 and 383 nm and blue emission at 441 nm. The bandgap of the Li-doped CuO thin films was reduced from 2.99 to 2.76 eV with increasing Li doping concentration. They deemed that the UV emissions centered at 359 and 383 nm were the band edge emissions of CuO. Al-Ghamdi et al. [18] prepared three CuO thin films by magnetron sputtering grown on glass substrates with different thicknesses. In their work, PL specta of films excited with ultraviolet light of wavelength λext = 350 nm, showed a UV emission of 387 nm (3.20 eV), whereas the bandgap of the three films was 1.73, 1.88 and 2.2 eV.

III.3. Conclusion

In summary, high quality Copper Oxide CuO nanostructures thin films with different precursor concentrations were successfully synthesized on glass substrates by sol–gel spin coating technique. The influence of the precursor concentrations on the structural and optical properties of CuO thin films was investigated. X-ray diffraction shows us, the high crystallinity of all films with preferential orientation and crystallite size is 6 nm. The intensity of peaks greatly increases and the lattice parameters **a**, **b** and **c** slightly increased with increasing precursor concentration. Photoluminescence of all films showed emissions in the ultraviolet (UV) and several visible emissions such as violet, blue, green, yellow and red, correspond to near-edge band (NBE) of CuO and the different defects in copper oxide. the luminescence intensity of defects decreases and some is almost completely quenched with red shift and increases the luminescence intensity of UV emissions with increasing CuO concentration, this may be due the crystal quality is usually improved with concentration of precursor. The average transmittance of all films is between 50 to 70 % in the visible region. A sharp absorption edge has been observed for all films in the region between 400 and 450 nm. This attributed to the absorption of light by copper oxide (CuO) thin films. Compared with the value of band gap of CuO bulk (1.2eV), a blue-shift behavior of absorption edge (band gap) of our nanostructures were observed. The band gap decreases with precursor concentrations, which can be attributed to improved crystallinity of the CuO thin films.

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General Conclusion

General Conclusion

High quality Copper Oxide CuO nanostructures thin films were deposited on glass substrates by sol–gel spin coating technique with different precursor concentrations. Copper chloride dihydrate, ethanol and monoethanolamine (MEA) were used as precursor, solvent and stabilizer, respectively. We optimized different deposition conditions for elaborate a CuO films with good quality which can be used in several applications such as: solar cells and photocatalysis. The influence of the precursor concentrations on the structural and optical properties of CuO thin films was also investigated.

In order to obtain a maximum of information on our samples several characterizations were carried out: Structural characterization: X-ray diffraction (XRD); Optical properties: measure of transmittance, optical absorption and photoluminescence of films.

X-ray diffraction shows, the high crystallinity of all films with preferential orientation and crystallite size is 6 nm. The intensity of peaks greatly increases and the lattice parameters **a**, **b** and **c** slightly increased with increasing precursor concentration.

Photoluminescence of all films showed emissions in the ultraviolet (UV) and several visible emissions such as violet, blue, green, yellow and red correspond to near-edge band (NBE) of CuO and the different defects in copper oxide.

The average transmittance of all films is between 50 to 70 % in the visible region. A sharp absorption edge has been observed for all films in the region between 400 and 450 nm. This attributed to the absorption of light by copper oxide (CuO) thin films. The band gap was determined to be 2.7-2.9 eV (decreased with precursor concentration) that is significantly greater than the band gap of CuO bulk.

These CuO thin films have a high quality of structural and optical properties suitable for different applications such as solar cells, photocatalysis and gaz sensor.

الخواص الفيزيائية للأفلام الرقيقة لأكسيد النحاس (*CuO*)؛ تأثير تركيز المحلول

ملخص

في هذه الدراسة ، تم تصنيع الأفلام الرقيقة النانوية لأكسيد النحاس (CuO) بتركيزات مختلفة من السوالف (0.2 ، 0.4 ، 0.6 مول / لتر) على ركائز زجاجية بواسطة تقنية السائل الهلامي مع تقنية التدوير. تم استخدام ثنائي كلوريد النحاس والإيثانول ومونوإيثانولامين (MEA) كسوالف ومذيبات ومثبت، على التوالي. تم دراسة الخصائص البنيوية والضوئية لأغشية CuO من خلال تقنيات حيود الاشعة X ومطيافية الاشعة فوق البنفسجية و المرئية UV-Vis وتقنية تحليل مطيافية اللمعان الضوئي PL . تظهر حيود الأشعة السينية أن التبلور عالي لجميع الأفلام ذات اتجاه نمو تفضيلي وحجم الحبيبات بلغ 6 نانومتر. أظهر مطيافية اللمعان الضوئي لجميع الأفلام انبعاثات الأشعة فوق البنفسجية (UV) والعديد من الانبعاثات المرئية مثل البنفسجي والأزرق والأخضر والأصفر والأحمر تتوافق مع نطاق شبه الحافة لطاقة الفجوة (NBE) لأكسيد النحاس CuO والعيوب المختلفة في أكسيد النحاس. يتراوح معدل النفاذية لجميع الأفلام بين 50 إلى 70٪ في المنطقة المرئية. لوحظ وجود حافة امتصاص حادة لجميع الأفلام في المنطقة بين 400 و 450 نانومتر. ويعزى ذلك إلى امتصاص الضوء بواسطة الأفلام الرقيقة من أكسيد النحاس . و يوافق عتبة الامتصاص الموافق للانتقال بين نطاق التكافؤ و نطاق التوصيل (CuO) تم تحديد طاقة الفجوة في النطاق 2.7-2.9 eV (انخفضت مع تركيز السوالف) التي هي أكبر بكثير من طاقة الفجوة لأكسيد النحاس CuO ذو الابعاد الكبيرة .يمكن استخدام أفلام CuO المحضرة ذات النوعية الجيدة في العديد من التطبيقات مثل: الخلايا الشمسية والحفز الضوئي.

الكلمات الرئيسية: طريقة السائل الهلامي مع تقنية التدوير، الأفلام الرقيقة CuO ، الخصائص البنيوية، الخصائص الضوئية، النفاذية، اللمعان الضوئي.

Physical Properties of Sol Gel Copper Oxide (CuO) Thin Films; sol concentration effect

Abstract

In this study, copper oxide (CuO) nanostructured thin films with different precursor concentrations (0.2, 0.4, 0.6 mol/L) were synthesized on glass substrates by the sol–gel spin coating technique. Copper chloride dihydrate, ethanol and monoethanolamine (MEA) were used as precursor, solvent and stabilizer, respectively. Structural, optical and luminescence properties of the CuO films were investigated by XRD, UV-Vis spectrometry and PL spectroscopy techniques. X-ray diffraction shows, the high crystallinity of all films with preferential orientation and crystallite size is 6 nm. Photoluminescence of all films showed emissions in the ultraviolet (UV) and several visible emissions such as violet, blue, green, yellow and red correspond to near-edge band (NBE) of CuO and the different defects in copper oxide. The average transmittance of all films is between 50 to 70 % in the visible region. A sharp absorption edge has been observed for all films in the region between 400 and 450 nm. This attributed to the absorption of light by copper oxide (CuO) thin films. The band gap was determined to be 2.7-2.9 eV (decreased with precursor concentration) that is significantly greater than the band gap of CuO bulk. Elaborated CuO films with good quality can be used in several applications such as: solar cells and photocatalysis.

Keywords: Sol gel-Spin Coating method; CuO Thin films Structural properties; Optical properties; Transmittance; Photoluminescence.