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Elaboration and characterization of tin oxide thin films deposited by spray pyrolysis

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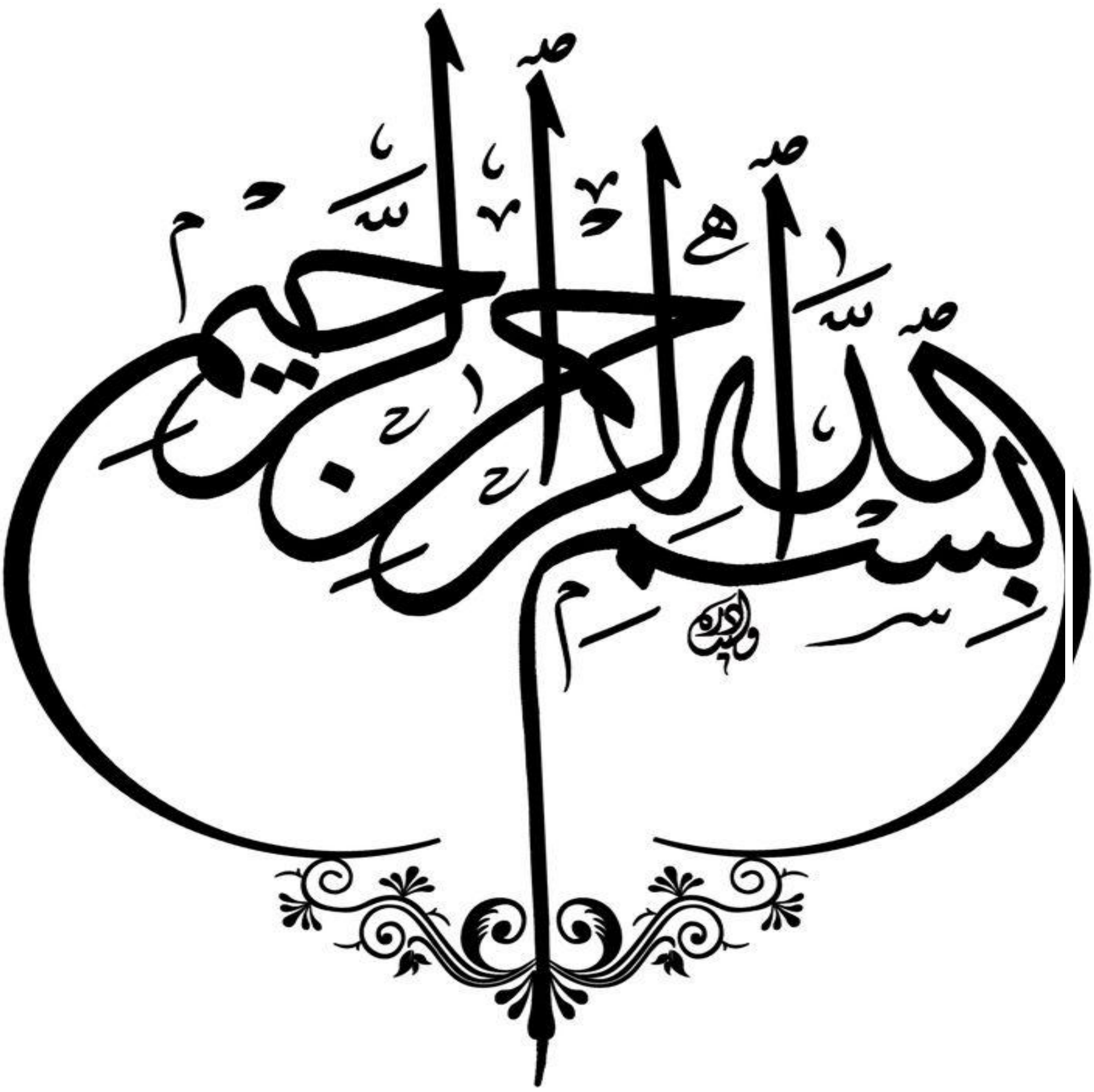

«يَرْفَعِ اللَّهُ الَّذِينَ آمَنُوا مِنكُمْ وَالَّذِينَ أُوتُوا الْعِلْمَ دَرَجَات»

المجادلة – الآية 11

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Dedication

To my parents

the reason of what I become today

thank you for your support and continuous care.

To my brothers

I am very grateful to have both of you.

To you Samiha thank you for your support and nice companying during this year.

Nour

Dedication

To my parents

for their love and sacrifice throughout my life.

Their encouragement had inspired me from the day I learned how to read and write until what I have become now.

To my sibling Wiame, Hana and Saif

Whose affection, love and encouragement especially thank for my nephew Mirna

To my friends Fatima, Yousra and Mouna

for their endless love

To you Nour

how lucky I am to have a golden friend like you and to share a precious moments with you.

Samiha

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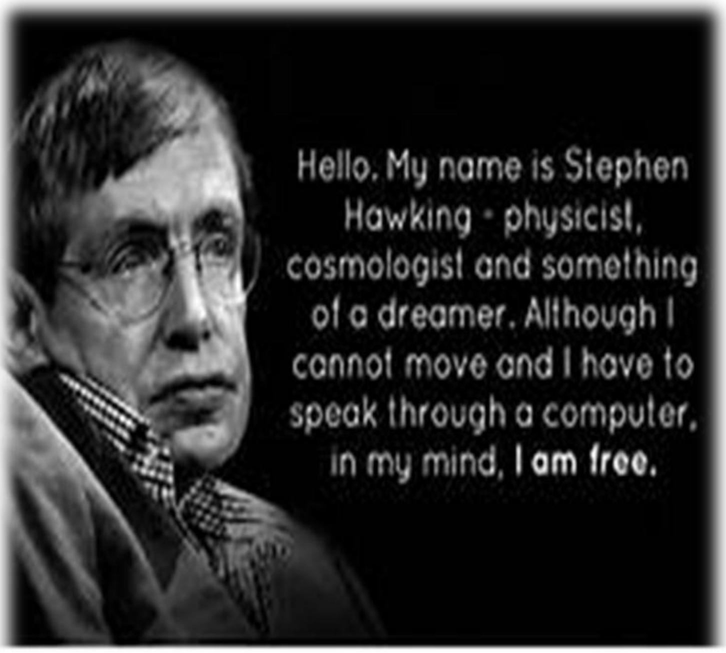
symbol	signification	Unit
M	Mass molar	g / mol
C	Solution concentration	mol / l
m	Mass	g
V	Volume	l
Ø	Diameter	m
T	Temperature	^{o}C
α	Absorption coefficient	cm^{-1}
n	Refractive index	
k	Extinction coefficient	
E_g	Energy of optical band gap	eV
T	Optical transmittance	%
I	Intensity of light	Lx
t	Film thickness	nm
λ	Wavelength of incident photon	nm
φ_S	Spray flow rate	ml / h
$h\upsilon$	Energy of incident photon	eV
E_{Urb}	Urbach energy	eV
I	Electrical current	A
V	Voltage	V
ρ_s	Surface resistivity	Ω / sqr
σ	Electrical conductivity	$\Omega^{-1}.cm^{-1}$
d	Distance	m

LIST OF ABBREVIATION

SnO_2	Tin Dioxide
PLD	Pulsed-Laser Deposition
MBE	Molecular Beam Epitaxy
RHEED	Reflection High-Energy-Electron Diffraction
DC	Direct Current
RF	Radio Frequency
CVD	Chemical Vapor Deposition
PECVD	Plasma Enhanced Chemical Vapor Deposition
MOCVD	Metal-Organic Chemical Vapor Deposition
LPCVD	Low Pressure Chemical Vapor Deposition
Sol-gel	Solution-Gelling
TMOs	Transition Metal Oxides
TCOs	Transparent Conducting Oxides
$SnCl_2.2H_2O$	Tin (II) Chloride Dihydrate
$SnCl_4.5H_2O$	Tin Tetrachloride Pentahydrate
TCD	Tin (II) Chloride Dihydrate
V_{TCD}	Volume Of Tin (II) Chloride Dihydrate
UV-Vis-NIR	Ultraviolet-Visible-Near Infrared

GENERAL INTRODUCTION



Hello. My name is Stephen Hawking - physicist, cosmologist and something of a dreamer. Although I cannot move and I have to speak through a computer, in my mind, **I am free.**

GENERAL INTRODUCTION

Every solid object has a surface; this surface is the discontinuity in the properties of the bulk materials and has been the target of modifications (artistic decoration and/or functional improvement) since the earliest times of humankind [1].

Transparent conducting oxides (TCOs) constitute a unique class of materials, which combine two physicals properties together: high optical transparency and high electrical conductivity. TCOs films like SnO_2, ZnO have attracted the attention of many research workers due to their wide range of applications, such as solar cells, gas sensors,.... etc [2].

Tin dioxide (SnO_2) is one of the semiconducting oxides, which had a considerable attention due to its amazing properties, it has unique optical, electrical, transparent, conductive properties. Tin oxide has wide band gap an n-type semiconductor of tetragonal structure and can resist high temperature [3]. It has been widely used for various applications such as gas sensor, transistors, lithium batteries, solar cells...etc [3].

SnO_2 films can be prepared by different techniques such as sputtering, chemical vapor deposition, thermal evaporation, sol-gel method, ion beam assisted deposition and spray pyrolysis technique [3,4].

The Spray pyrolysis is one of the most cost-effective methods to prepare SnO_2 films due to its ability to deposit large uniform area with low fabrication cost, simplicity and low deposition temperature [3,5].

The purpose of this work is the elaboration of thin films onto glass substrates heated at 300°C, by ultrasonic spray pyrolysis technique, from precursor solution of tin chloride (II) dihydrate ($SnCl_2.2H_2O$) using two different solvent types, and the study of the effect of the solution concentration and solvent type on the properties of SnO_2 thin films, The deposit was made at the level of laboratory of material and structure of electromechanically systems and their reliability (LMSSEF: *Laboratoire des Matériaux et Structure des Systèmes électromecaniques et leur Fiabilité*) of Larbi Ben M'Hidi University in Om El Bouaghi.

These films are characterized by UV-Visible-NIR double beam spectrophotometer and four-point probe technique to determine their optical and electrical properties, respectively.

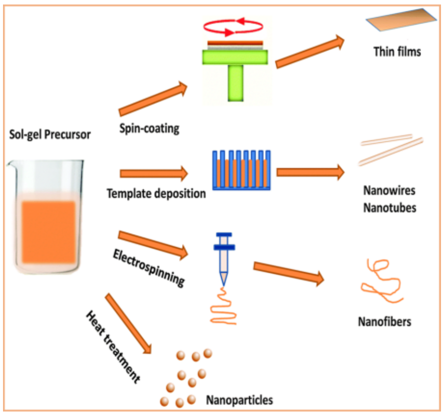
Our work is organized into three chapters as follows:

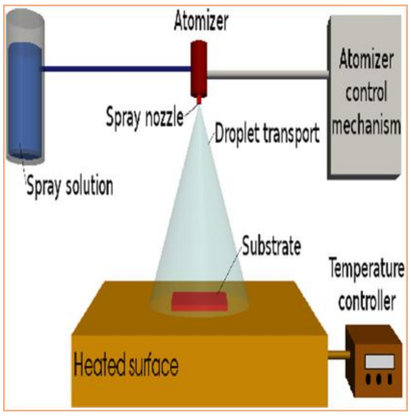
In the first chapter, we present overview on thin film, the definition of metal oxides, the essential properties of tin oxide (structural, optical, and electrical) and the field of its applications. More that the deposition techniques used to develop TCOs films, such as spray pyrolysis, which is very attractive for making functionally graded films.

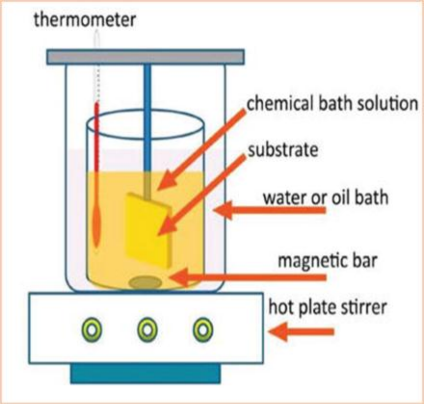
In the second chapter is devoted to the elaboration of tin oxide thin films as well as the various experimental techniques to characterize our coatings.

In the third chapter, we present the discussions of the experimental results obtained of tin oxide thin films.

At the end, we conclude our work with general conclusion that summarizes the different steps and results achieved in this work.

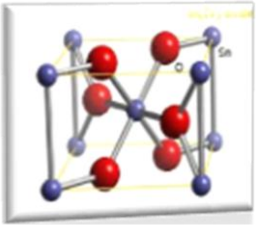


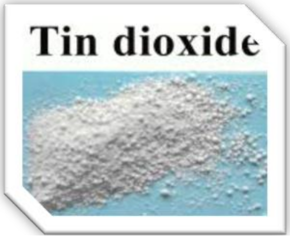




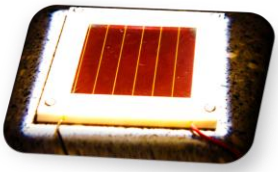
Chapter I

Generalities about tin dioxide thin films





Tin
dioxide
thin film



Chapter I: Generalities about tin dioxide thin films

I.1. Overview on thin film

I.1.1 Thin film definition

Thin film is a layer of material ranging from fractions of a nanometer (monolayer) to several micrometers in thickness. This small distance between the two surfaces limits (almost two-dimensional) causes a perturbation of the majority of physical properties [6].

The atoms of thin film grow on a substrate surface arranged predictably in their almost correct crystallographic position [6].

Thin films are especially appropriate for applications in microelectronics and integrated optics. However the physical properties of the films differ from the properties of the bulk material. Thin film is defined as a low-dimensional material created by condensing one-by-one atomic/ molecular/ ionic [1].

The thin film of the same material, of the same thickness may have different physical properties depending on whether it is placed on an amorphous insulting substrate such as glass [7].

I.1.2. Mechanism of thin films formation

The formation of thin films is one of the aspects of such development where the restriction as dimensional growth rules out the existence of two-dimensional thin films. This has vast range of applications in different areas. Thin films can be prepared from variety of materials such as metals, semiconductors, insulators or dielectric and many more materials with different kind of preparation techniques. For the deposition of thin films various preparation methods have been developed. New methods are also being evolved to improve the quality of thin films deposit with maximum reproducible properties and minimum variation in their compositions. The required thin film properties and versatility can be obtained by using proper thin film preparation method. In the thin film deposition process, following basic steps are to be considered [2].

- The initial materials used for the deposition is prepared in the atomic, molecular or finest particulate form before the deposition.
- The finest form of materials is transported on the substrate in the form of vapor stream, the solid, or the spray.
- Deposition of the material on the substrate and the film growth by nucleation-growth process.

I.1.3. Classification of thin film deposition technique

Thin film materials are the key elements of continued technological advances made in the fields of optoelectronic, photonic, and magnetic devices. The processing of materials into thin films allows easy integration into various types of devices. The properties of material significantly differ when analyzed in the form of thin films [2].

The vast varieties of thin film materials use in their deposition processing and fabrication techniques. The process of thin film deposition occurs by multiple techniques with its requirement of being single or multicomponent, alloy/oxide/compound coating on substrate of different shapes and size. Depending on the nature of way used for the thin films deposition the technique can be broadly classified as [2]:

- Physical deposition techniques.
- Chemical deposition techniques.

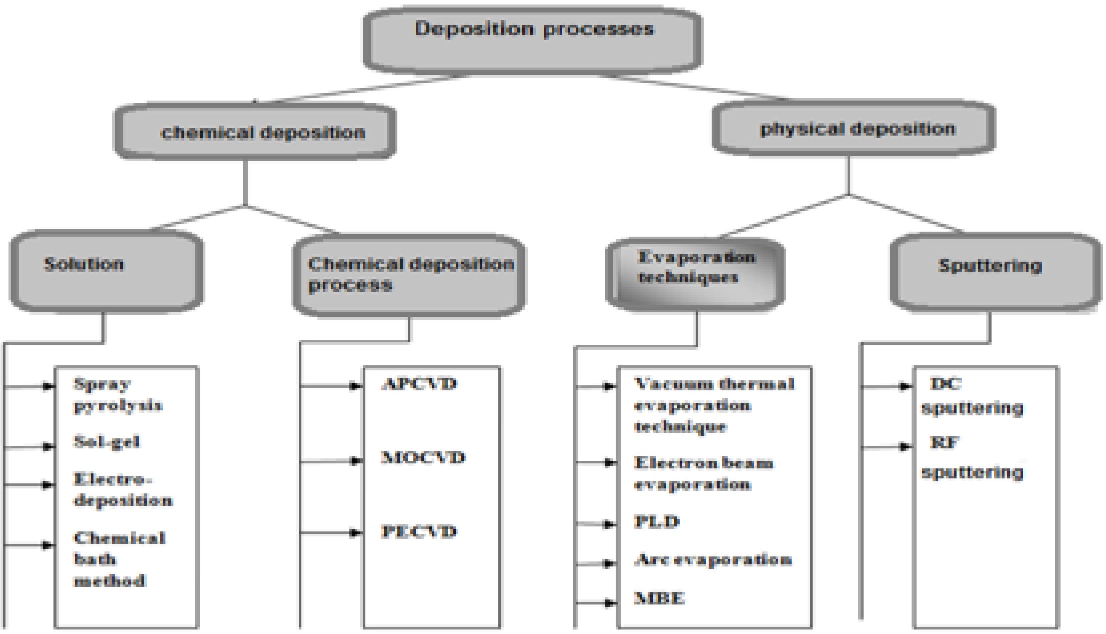


Figure I.1. Flowchart illustrates the physical and chemical deposition process wide spread thin film techniques [8].

I.1.3.1. Physical deposition technique

The physical deposition techniques are those in which the material required for deposition is made available in the atomic, molecular or particulate form before deposition. This is usually done at sufficiently high temperature. The condensation of vapor on substrate material kept at relatively low temperature yields [2]. Physical deposition can be further subdivided in:

I.1.3.1.1. Evaporation techniques

Evaporation methods are considered as the common deposition of materials in the form of thin-layer films. The general mechanism of these methods is obtained by changing the phase of the material from solid phase to vapor phase and converting again to solid phase on the specific substrate. It takes place under vacuum or controlled atmospheric condition [9].

a. Vacuum thermal evaporation technique

Vacuum evaporation technique is the simplest technique used to prepare amorphous thin films especially chalcogenide films such as CdSSe, MnS, Ge-Te-Ga, in addition, the tin dioxide can be prepared by annealing under oxygen flux tin layers obtained under vacuum evaporation process [10,11].

The technique of thermal evaporation is strongly dependent on two parameters: thermally vaporized material and applying a potential difference to the substrate under medium or higher vacuum level ranging from 10^{-5} to10^{-9} mbar. Figure I.2 shows the schematic diagram of thermal evaporation system with substrate holder on a planetary rotation system and directly above the evaporating source [9].

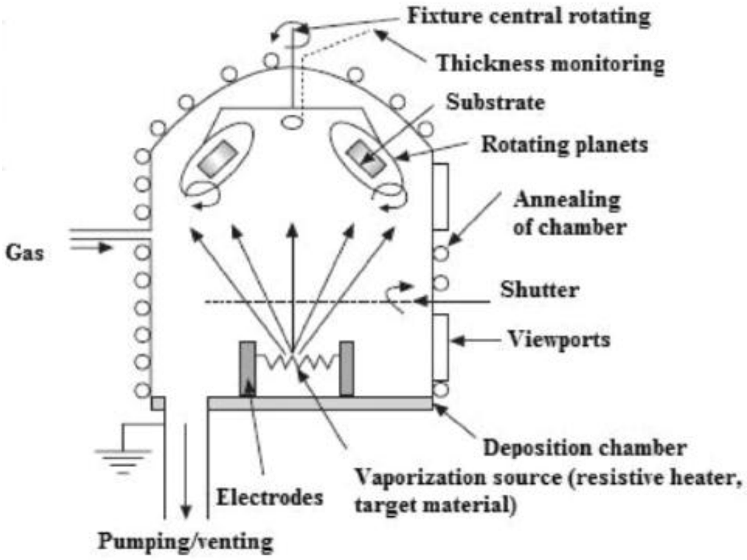


Figure I.2. Schematic of vacuum thermal evaporation technique [9].

b. Electron beam evaporation

This type of evaporation is another method of physical deposition where the intensive beam of electrons is generated from a filament and steered through both electric and magnetic fields to hit the target and vaporize it under vacuum environment as shown in Figure I.3. Thin films prepared by electron beam evaporation are of good quality and purity [9].

Large categories of materials can be prepared by electron beam evaporation technique such as amorphous and crystalline semiconductors, metals, oxides, and molecular materials [11].

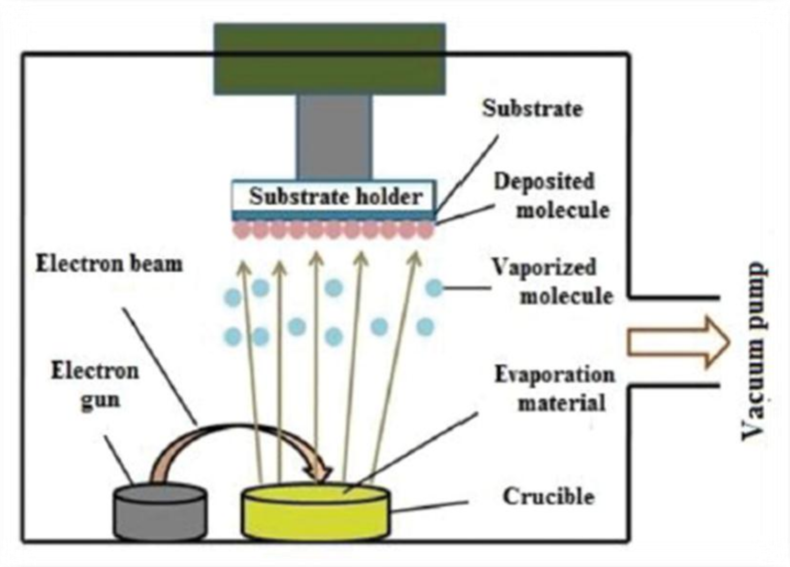


Figure I.3. Schematic diagram of electron beam evaporation [9].

c. Laser beam evaporation (pulsed-laser deposition)

Pulsed-laser deposition (PLD) is another physical deposition technique to deposit the thin film-coating system [12]. During the thin-film deposition process, the laser beam is used to ablate the material for depositing the thin films inside a vacuum chamber as shown in Figure I.4 [9].

Different kinds of laser sources are being used to ablate the target. The most common sources are KrF (248 nm), XeCl (308 nm), and Nd-YAG laser (1064 nm) [13]. When the laser beam strikes the target material, it produces the plume, which could deposit on the various substrates. The created plume may contain neural- and ground-state atoms and ionized species.

In the case of metal oxide thin films, oxygen is used to deposit the oxides of metals. The coating of thin films through PLD follows three modes: Frank–van der Merwe, Stranski–Krastanov, and Volmer–Weber. PLD has some advantages over other physical deposition systems because of its fast deposition time and its compatibility to oxygen and other inert gases [9,14].

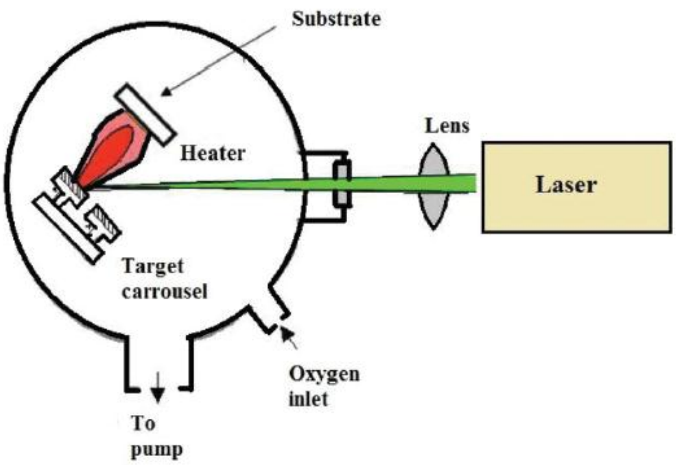


Figure I.4. Schematic of pulsed-laser deposition [9].

d. Arc evaporation

Arc evaporation is a technique whereby an arc is used for coating. The arc evaporation process begins with the striking of a high current, low voltage arc on the surface of a cathode that gives rise to a small highly energetic emitting area known as a cathode spot. The temperature at the cathode spot is extremely high (around 15000°C), which results in a high velocity (10 km/s) jet of vaporized cathode material.,. This behavior causes the apparent motion of the arc. If a reactive gas is introduced during the evaporation process, dissociation, ionization, and excitation can occur during interaction with the ion flux, and a compound film will be deposited. A magnetic field moves the cathode spot to ensure that it does not stay too long at one place, since it will cause ejection of a large amount of macro-particles or droplets, which are poorly adhered in the coated film. Sometimes filters are used to remove any droplet from the coating flux. Arc melting is a similar process, whereby no evaporation occurs but, because of the heat, melting of the metals creates the required alloy [15,16].

e. Molecular Beam Epitaxy

Molecular beam epitaxy (MBE) is a technique used to produce ultrathin films as high quality epitaxial layers with very sharp interfaces and good control of thickness, doping, and composition. Deposition usually takes place under high or ultrahigh vacuum conditions. Because of the high degree of control possible with MBE and the possibility of growing compound semiconductors, it is a valuable tool in the development of sophisticated electronic and optoelectronic devices [16,17].

The MBE process can be considered a refined form of evaporation. Ultrapure target materials are placed in effusion cells and heated to their sublimation points. Molecular beams there by produced are then directed toward substrate, in the vicinity of which they may react chemically with each other or other gaseous species introduced into the vacuum chamber and then condense as a layer on the substrate. FigureI.5 shows the schematic of a typical MBE apparatus. Each fabricated layer has a definite crystallographic relationship with the substrate. The substrate is usually heated and often rotated continuously to improve uniformity of deposition. A reflection high-energy-electron diffraction (RHEED) gun is used for in situ monitoring [16,17].

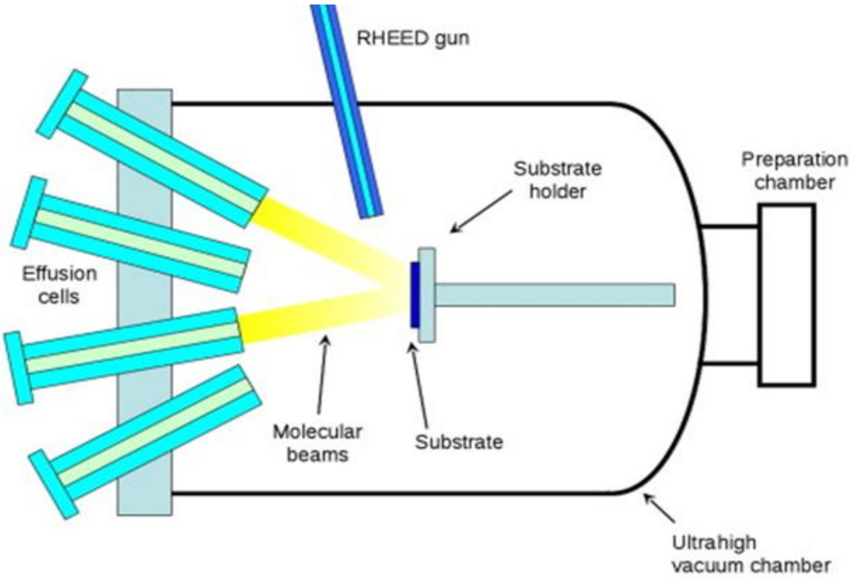


Figure I.5. Schematic of a typical system for molecular beam epitaxy (MBE) [17].

I.1.3.1.2. Sputtering technique

Sputtering technique is mostly used for depositing metal and oxide films by controlling the crystalline structure and surface roughness. The simple form of the sputtering system consists of an evacuated chamber containing metallic anode and cathode in order to obtain a glow discharge in the residual gas in the chamber. Also, an applied voltage in the order of several KeV with pressure more than 0.01 mbar is sufficient for film deposition. The sputtering process depends on the bombardment of the ions released from the discharge to the molecules in the cathode leading to the liberation of the molecules from the cathode with higher kinetic energy [9]. The atomic weight of the bombarding ions should be nearly to that of the target material in order to maximize the momentum transfer. These molecules move in straight lines and strike on the anode or on the substrate to form a dense thin film. The diagram of the sputtering system is shown in Figure I.6 [9].

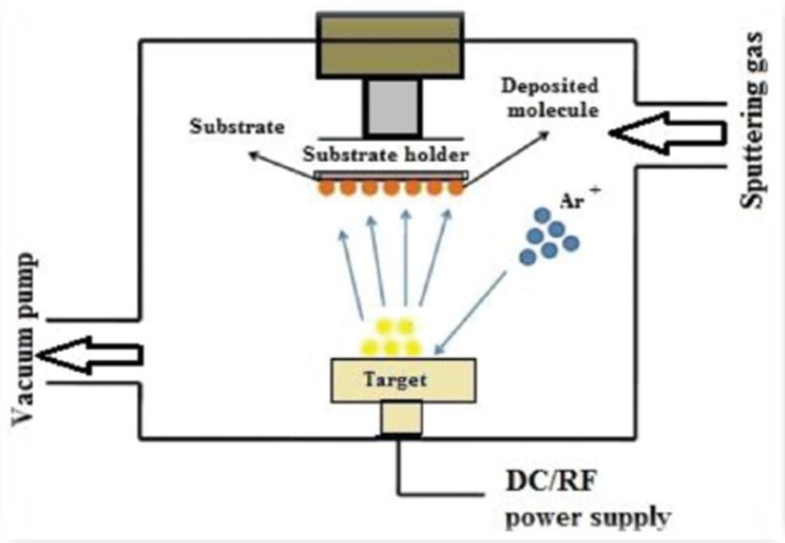


Figure I.6. Sputtering system diagram [9].

There are two common types of sputtering process: direct current (DC) and radio frequency (RF) sputtering. The first one depends on DC power, which is generally used with electrically conductive target materials. It is easy to control with low-cost option. The sputtering uses RF power for most dielectric materials. A common example for sputtered films is aluminum nitride films. These films were prepared by both DC-sputtering and RF-sputtering technique, and their structure and optical properties were compared [18, 19].

I.1.3.2. Chemical deposition methods

There are many different chemical methods for preparing thin films, which illustrate in Figure I.1 [8]. But by their nature, many of these are restricted to one or perhaps a few different materials, related to a specific chemical reaction or series of reactions [6].

Although the production of thin films via physical methods as previously described gives good quality and functionalizes properties, it is highly expensive and perhaps requires a large amount of material target. Since the need to produce good-quality thin films with low economical cost is necessary, chemical deposition techniques are widely used globally [9].

I.1.3.2.1. Chemical Vapor Deposition

Chemical vapor deposition (CVD) is a versatile technique used for depositing gas phase reactants (precursors) onto a solid substrate creating thin films. CVD can be used to deposit on to large areas, i.e. microelectronics.

This technique offers the potential for good film uniformity and composition control with excellent step coverage. The technique is able to deposit films that are highly dense and pure as well as being uniform with good adhesion. CVD also has the capability to control crystal structure and film morphology by changing the temperature and deposition rate [20].

Chemical vapor deposition is the formation of solid material (metal, insulator or semiconductor) from the reaction of source gases (or vaporized liquids) [20].

a. Plasma Enhanced Chemical Vapor Deposition (PECVD)

The main advantage of this technique is that the plasma decomposition allows film deposition to take place at much lower temperatures than those employed in atmospheric CVD using decomposition reactions [6]. The diagram of the PECVD is shown in Figure I.7.

The initial application of PECVD was in microelectronics, namely electrical insulation films, conductive films, semiconductors, and capacitors [20].

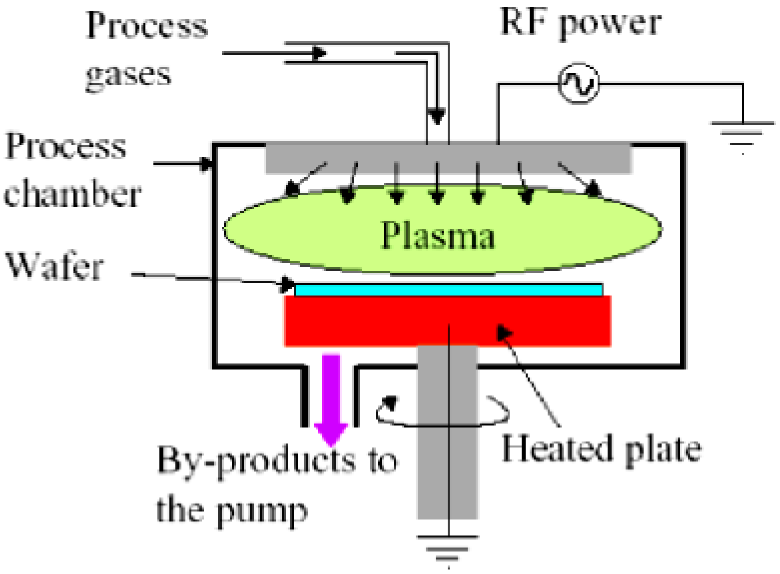


Figure I.7. PECVD system diagram [21].

b. Metal-Organic Chemical Vapor Deposition (MOCVD)

The technique is essentially the same as CVD, except that at least one of the precursors is a volatile metalorganic compound, such as a metal alkyl. The formation of the required compound takes place by pyrolysis of the metalorganic compound with another (inorganic or organic) gaseous precursor. The diagram of the MOCVD is shown in Figure I.8.

The main advantage of MOCVD is the relatively high volatility of the organic compounds at moderate temperatures, and the fact that, since all these are in the vapor phase, precise control of gas flow rates and partial pressures are possible [6].

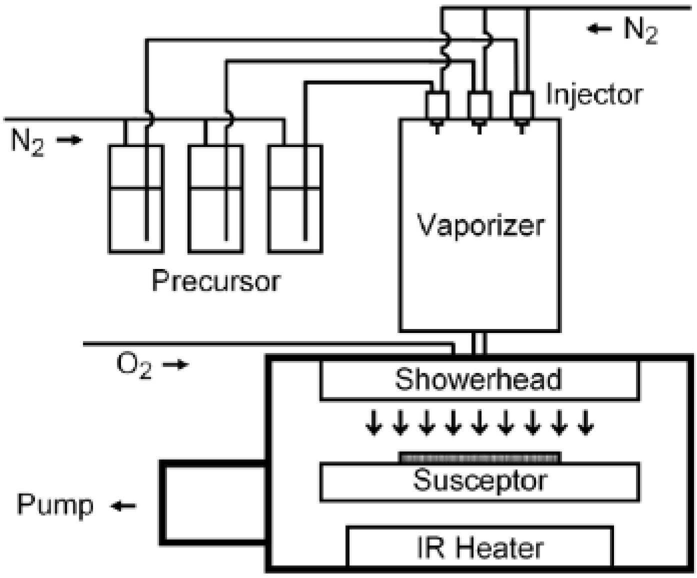


Figure I.8. MOCVD System diagram [21].

c. Low-Pressure Chemical Vapor Deposition (LPCVD)

The growth of thin films by Low Pressure Chemical Vapor Deposition (LPCVD) is one of the most important techniques for deposition of thin films in modern technology [22]. The reasons of a broad application of the LPCVD method are in the possibility of deposition of different elements and compounds at relatively low temperatures in amorphous and crystalline phase with high degree of uniformity and purity. A simple handling, high reliability of operations, fast deposition, homogeneity of deposited layers and high reproducibility are the basic characteristics the LPCVD method (Figure I.9) [23].

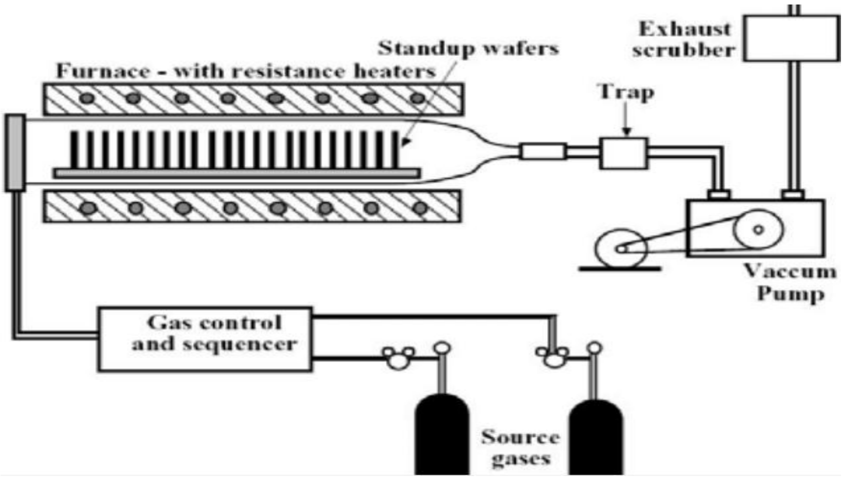


Figure I.9. Schematic description of system [23].

I.1.3.2.2. Chemical deposition in solution

a. Sol–Gel Method

The sol–gel process is regarded as being a cost-effective and simple technique to synthesize primarily oxide ceramics [6].

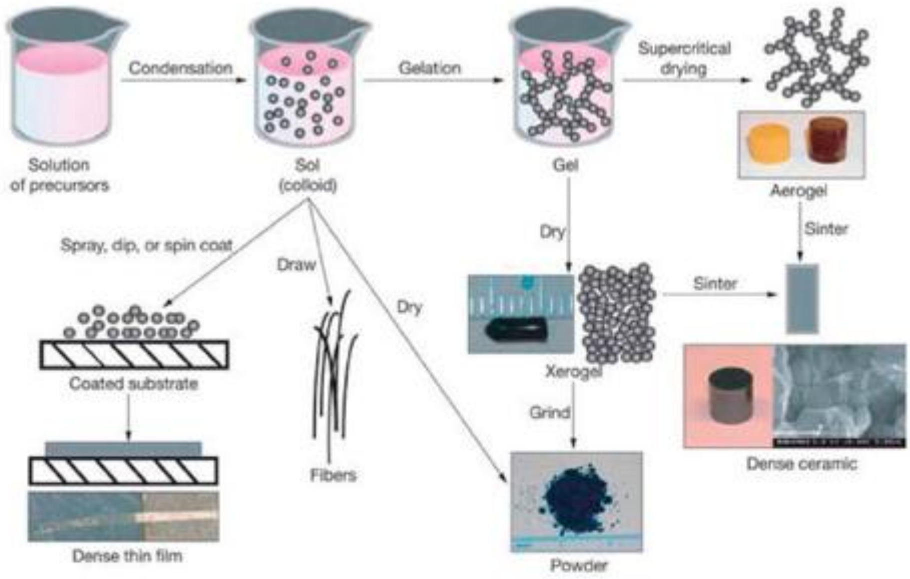


Figure I.10. Sol-gel method diagram [9].

The sol-gel technique is broadly used for the synthesis of oxide materials. Sol-gel process is one of the famous wet-chemical methods. It works under lower-temperature processing and gives better homogeneity for multicomponent materials. The word "'sol"' means the formation of a colloidal suspension and 'gel' means the conversion of 'sol' to viscous gels or solid materials. Two routes are used to prepare transition metal oxides (TMOs) as follows [9]:

- ❖ Preparing of inorganic precursors via inorganic salts in aqueous solution.
- ❖ Preparing of metal alkoxide precursors via metal alkoxides in no aqueous solvents.

b. Chemical bath deposition technique

Chemical bath deposition method is also known as solution growth technique or controlled precipitations. It is the oldest method to deposit films on a substrate. The deposition can be performed at lower temperatures. It is based on the formation of a solid phase from a solution.

In the chemical bath deposition procedure, the substrate is immersed in a solution containing the precursor. This method depends upon parameters such as bath temperature, pH of the solution, the molarity, and time. Figure I.11 represents the simple chemical bath deposition method [9].

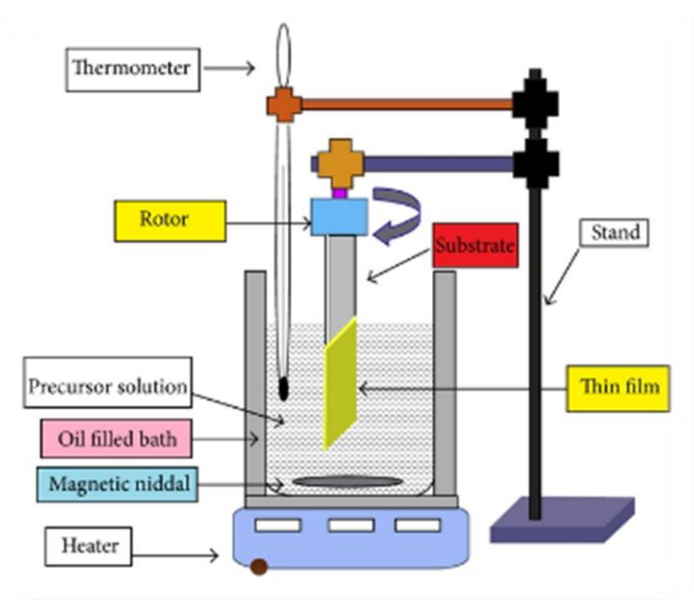


Figure I.11. Chemical bath deposition technique [9].

c. Electrodeposition

This technique involves passing a high electric current through a solution containing the material such that a film of a material, usually a metal or an oxide, is deposited on one of the electrodes immersed in the solution [6]. e.g The electrodeposition of tin oxide thin film from nitric acid solution [24].

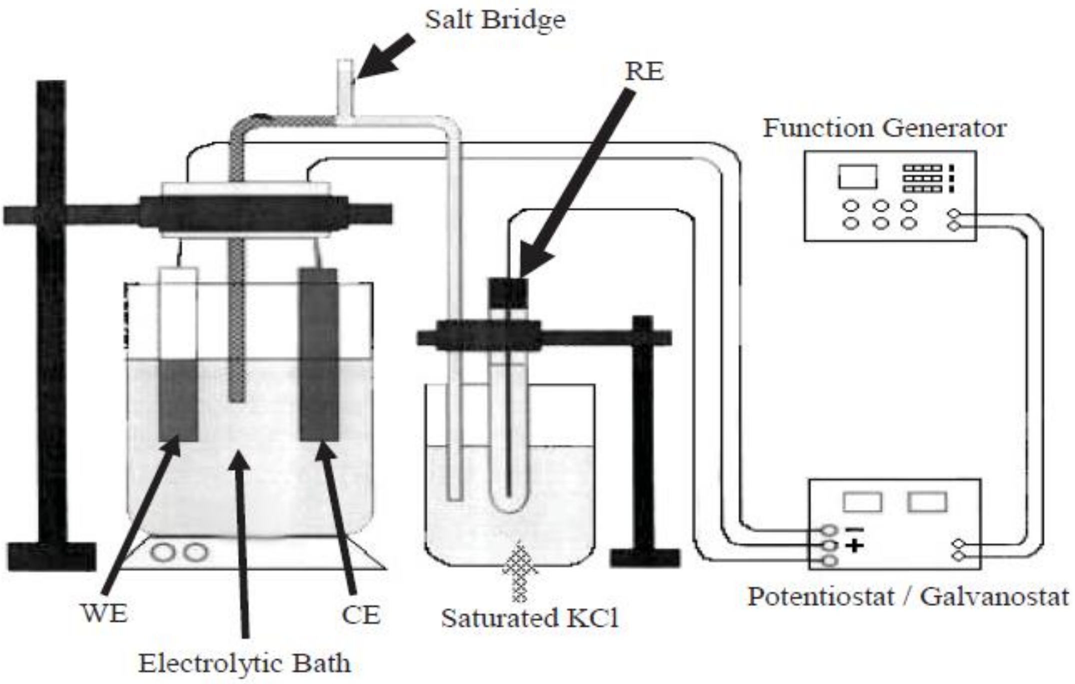


Figure I.12. Electrodeposition scheme to deposit thin films [25].

d. Spray pyrolysis technique

The thin films used in this study were carried out by spray pyrolysis. This technique is an intermediate between pneumatic spraying, chemical deposition in vapor phase, appears to be very simple and relatively cost-effective particularly with respect to the cost of equipment [26].

❖ Definition

Spray pyrolysis is a process in which a thin film is deposited by spraying a solution on a heated surface, where the constituents react to form a chemical compound, the desired compound are volatile at the temperature of deposition [27].

Pyrolysis is a process by which a solid (or liquid), undergoes under the effect of heat [28]. Thermal decomposition leads to the formation of new molecules. This allows to receive products with a different, often more superior character than original residue. Thanks to this feature, pyrolysis becomes increasingly important process for today industry as it allows bringing far greater value to common materials and wasting [29].

❖ General principle of the spray process

The process is particularly useful for deposition of oxides and has long been a production method for applying a transparent electrical conductor of SnO_x to glass for example SnO_2 thin films deposited by spray pyrolysis technique [30].

The description of film formation by the spray pyrolysis technique can be summarized as following [31]:

- The droplet resides on the surface as the solvent evaporates, leaving behind a solid that may further react in the dry state.
- The solvent evaporates before the droplet reaches the surface and the dry solid imping on the surface, where decomposition occurs.
- The solvent vaporize as the droplet approaches the substrate, there to undergo a heterogeneous reaction.

The entire reaction takes place in the vapor state. A conventional thermal process is illustrated in Figure I.13.

Pyrolysis or thermal decomposition of a gaseous compound entails passing a vapor over a heated substrate, which causes decomposition and the condensation of a stable solid [6].

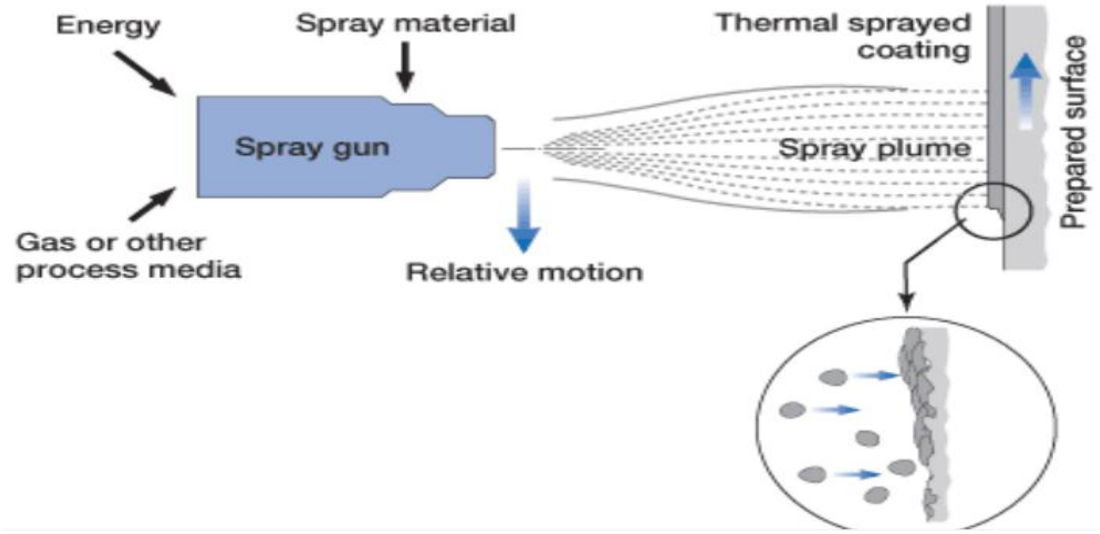


Figure I.13. Thermal spray process principle [32].

I.2. Metal oxides

Metal oxides are a chemical compound formed between metals, specifically cations and oxygen. These compounds require a minimum of two elements, as compounds do, and always contain at least one oxygen, though there can be more than one. These formations tend to be solid, basic and denser than their non-metallic oxide counterparts. Metal oxides typically contain an anion of oxygen in the oxidation state of -2. A great example is iron oxide, more commonly known as rust [33].

There are two main families of metal oxides, the first of which concerns p-type (hole conduction), they are known to be relatively unstable because of their tendency to exchange oxygen from their lattice easily with air. However, p-type is used for some application such as high temperature oxygen sensors [33]. The second family includes n-types (electron conduction). They fill the majority of gas sensor applications, as they are more stable [6].

Table I.1. List of some metal oxides [6].

n-type metal oxide	p-type metal oxide
SnO_2	NiO
ZnO	PdO
TiO_2	TeO_2

I.3. Properties and applications of SnO_2

I.3.1. Properties of tin dioxide

Tin dioxide thin film is one of the important transparent conducting oxides and applied in various fields such as in solar cells, optoelectronic devices, heat mirror, gas sensors…, due to its electrical and optical transparency in visible light spectrum [27].

I.3.1.1. Structural properties of tin dioxide

Tin oxide is a wide band gap semiconductor (energy band gap 3.6 eV), and it has only the tin atom that occupies the center of a surrounding core composed of six oxygen atoms placed approximately at the corners of a quasi regular octahedron (Figure I.14**).** In the case of oxygen atoms, three tin atoms surround each of them, forming an almost equilateral triangle. The lattice parameters are a = b = 4.737 Å and c = 3.186 Å [34,35].

Tin dioxide has a single phase at room pressure called cassiterite and adopts a rutile quadratic lattice. Each tin ion Sn^{+4} is in the middle of an almost regular octahedron formed by six oxygen ions O^{-2} [34]. Figure I.14 shows the rutile structure of SnO_2 which contains tin atoms at the corners and center of the unit cell.

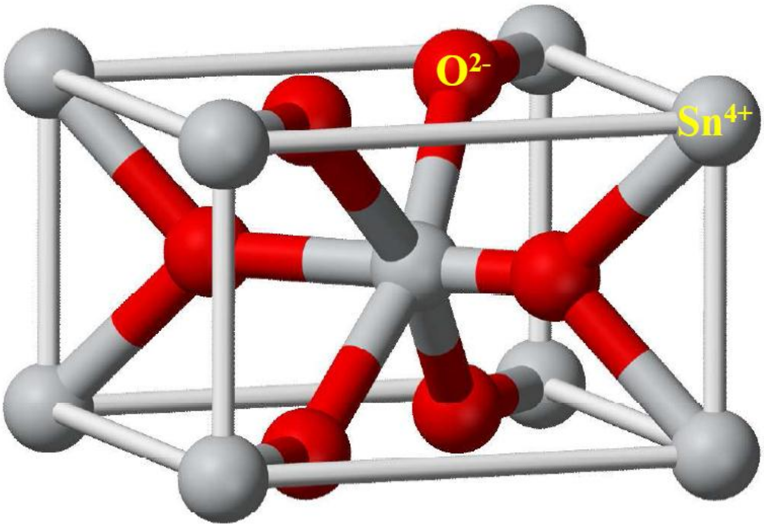


Figure I.14. The rutile structure of SnO_2 [34].

Table I.2. Structural properties of SnO_2 [1,34].

properties	**SnO_2**
Crystalline structure	Tetragonal
Mesh volume(Å^3)	71.49
binding length Sn-O(Å)	2.3
Elemental mesh parameters	a = b = 4.737 Å and c = 3.186 Å

I.3.1.2. Optical properties of tin oxide

The optical properties of SnO_2 depend on the electromagnetic wave interaction with the semiconductor electrons. An intergenerational electromagnetic wave with this material will be completely absorbed by it, if the energy associated with the equation I.1 is able of transferring electrons from the valence band to the conduction band, thus to be at least equal to the gap.

$$E = h\upsilon = \frac{hc}{\lambda} \qquad \text{I.1}$$

Then, if we want the material to be transparent in the full extent of the visible range (400nm-800nm), well transparency throughout the spectrum of visible will therefore be ensured by a value of gap at least equal to 3.6 eV [7]. SnO_2 has high transparency in the visible wavelength range [36].

- **Gap of SnO_2**

Tin oxide (SnO_2) is a semiconductor n-type with wide energy band gap (*E*g= 3.6-4.2 eV) and a direct band gap [7,28,31,35-37]. The undoped SnO_2 has low electrical resistance and high optical transparency in the visible range of the electromagnetic spectrum. These properties make tin oxide suitable for many applications, particularly as an electrode material in solar cell, light emitting diodes, transparent electromagnetic shielding materials, etc [27].

Table I.3.optical properties of SnO_2 [1,36,38].

properties	SnO_2
Transmission in the visible range	85%
Refractive index	1.8-2
Optical band gap	3.6–4.2 eV

I.3.1.3. Electrical properties of tin oxide

Tin dioxide (SnO_2) close to perfectly stoichiometry condition, have low free carrier concentration and high resistivity, which is similar to insulation. However, nonstoichiometric forms of these oxide films have high free carrier concentration. In other words, during crystal growth, there is an oxygen vacancy in the structure and therefore the formula for thin film form of this material is SnO_{2-X}, where x is the deviation from stoichiometry. Indeed, the electrical conduction in this material results from existence of defects in the crystal, generally, either oxygen vacancies or interstitial atoms, which may act as donor [1].

The tin oxide is a semiconductor with a large band gap. Knowing the electronic band structure of SnO_2 is necessary to understand its electro-optique properties. The electronic configurations of Sn and O knowing that their atomic numbers will be respectively 50 and 8 are the following [6]:

The band structure is characterized by:

- A valence band consisting of molecular orbital's involving mainly the atomic orbital 2p of the oxygen atoms:

$$O^{2-} : 1s^2\ 2s^2\ 2p^6.$$

- A conduction band consisting of molecular orbital's derived from the overlapping of the atomic orbitals 5s and 5p of tin atoms

Sn^{4+}: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^6\ 4d^{10}$.

- Because of its specific character (large band), the electrons in this band can acquire a high mobility.

Table I.4.electrical properties of SnO_2 [1,6].

properties	SnO_2
Optical band gap nature	direct
Conductivity type	n
Free carrier concentration (cm^{-3})	10^{18}-10^{20}

I.3.2. Applications of tin oxide thin film

Tin oxide has attracted a great interest in scientific community as tin possesses a dual valency, with tin preferably attaining an oxidation state of 2+ or 4+. This dual valency facilitates a variation of the surface oxygen composition resulting in different structure-function properties. SnO_2 is the most abundant form of tin oxide and is one of the technological significances in various applications [39].

Tin oxide was mainly studied as an n-type semiconductor material with a wideband gap of 3.6 eV. SnO_2 with a rutile structure was widely applied in catalysis, gas sensors, rechargeable Li-ion batteries, transparent conducting electrodes, and other optical electronic devices. In particular, tin dioxide was studied as catalyst and support for the catalyst in several organic reactions. The acidity of a metal oxide mainly depends on the percentage ionic character of the metal‐ oxygen bond and the oxidation state of the metal. A metal oxide with a low percentage ionic character and high oxidation state possesses more acidity. Among different metal oxides, SnO_2 with a lower percentage ionic character and a higher oxidation state of 4+ (for Sn) showed high acidity which can catalyze certain reactions owing to its interesting properties like acid-base and red- ox, SnO_2 is found to be an active and versatile catalytic material [39].

Chapter II

Elaboration of tin dioxide thin films

Chapter II: Elaboration of tin oxide thin films

This chapter has two parts. The first part describes the ultrasonic spray pyrolysis technique and description the steps of preparation of the tin oxide thin films while in the second part we will present the optical and electrical characterization methods for our films.

Part one: Ultrasonic spray pyrolysis technique

II.1. Choice of ultrasonic spray pyrolysis technique

A variety of techniques has been used to deposit tin oxide thin films. These include spray pyrolysis ultrasonic, spray pyrolysis chemical vapor deposition, activated reactive evaporation, ion-beam assisted deposition, sputtering, and sol–gel methods [40]. Among these techniques, spray pyrolysis have proved to be [5,41,42]:

- Spray pyrolysis is particularly attractive for metal oxide thin films elaboration.
- Simple technique, reproducible and inexpensive, as well as suitable for large area applications.
- The simple experimental arrangement makes easy access to observe the deposition process and adjustment during the experiment.
- High growth rate and mass production capability for large area coatings make them useful for industrial as well as solar cell applications.
- In addition, spray pyrolysis opens up the possibility to control the film morphology and particle size in the nm range hence, high quality thin films.
- Spray pyrolysis is a versatile technique for deposition of metal oxides.

Up to now, many researchers have prepared SnO_2 using chemical spray pyrolysis. One of the major problems of this technique is controlling the evaporation of generated droplets [41].

II.2. Thermal effects of the substrate on droplets

According to figure II.1, several processes can occur depending on the range of used temperature [5,43]:

- **In process A**: the droplet splashes on the substrate, vaporizes and leaves a dry precipitate in which decomposition occurs.
- **In process B**: the solvent evaporates before the droplet reaches the surface and the precipitate impinges upon the surface where decomposition occurs.

- **In process C**: the solvent vaporizes as the droplet approaches the substrate then the solid melts vaporizes and the vapor diffuses to the substrate to undergo a heterogeneous reaction there, this is true CVD.
- **In process D**: At the highest temperatures, the chemical reaction takes place in the vapor phase.

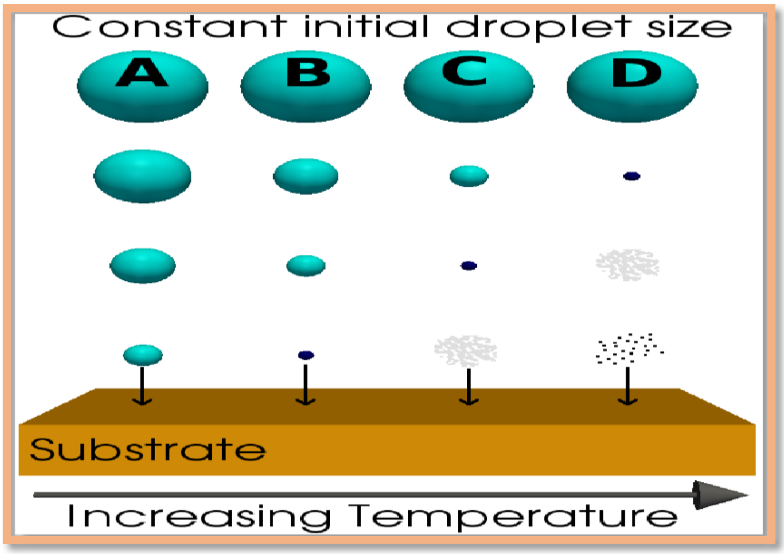


Figure II.1. Thermal effects of the substrate on droplets [44].

As the droplet traverses the ambient, there are four forces simultaneously acting on it, describing its path. Those forces are gravitational, electrical, thermophoretic, and the Stokes force [43].

II.3. Experimental process

SnO_2 Thin films were deposited by the CSP technique from aqueous solutions containing tin (II) chloride dihydrate ($SnCl_2.2H_2O$) (99·8%, Aldrich) was dissolved in a wide variety of precursor solutions (distilled water, methanol) at different molarities.

II.4. Preparation of substrate

The substrates were microscope glass slides measuring almost 1.2 mm in thickness and 2.54 cm by 2.54 cm in dimensions prepared as Figure II.2 is shown.

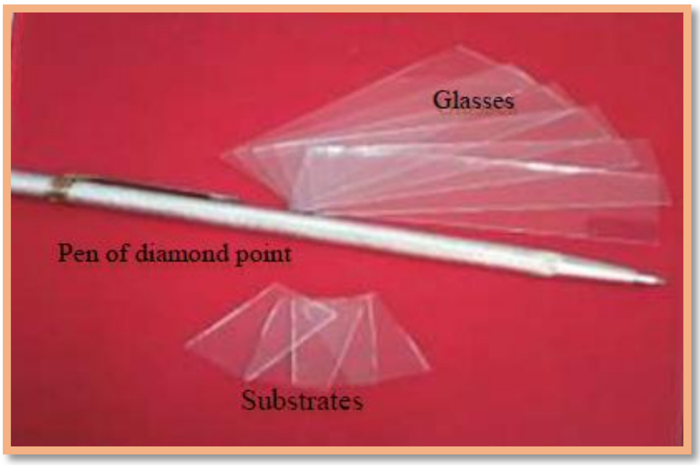


Figure II.2. Glasses substrates and diamond pen.

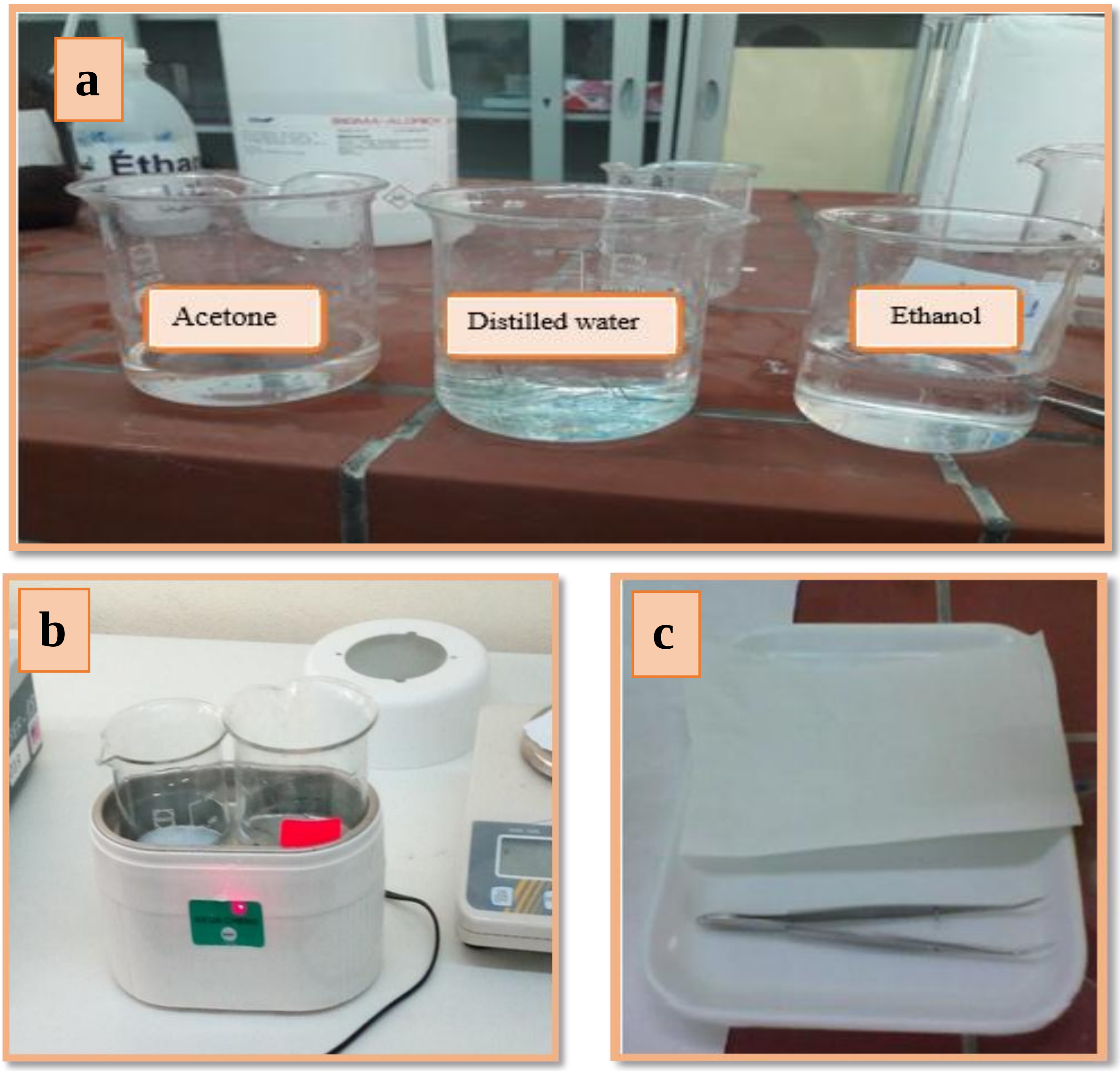


Figure II.3. Substrate’s cleaning process.

The films formed are of nanoparticle regime, so the substrate used should be completely dirt free as follow [45]:

- The glass slides are cleaned using distilled water.
- Soaking in acetone to remove greases.
- Immersing in distilled water in a beaker and sonicated to remove the traces of acetone.
- Soaking in ethanol to remove organic matter.
- Cleaning with distilled water to get the ethanol off.
- Finally, using Joseph paper to dry substrates slides (Figure II.3.c).

The glass slides were ultrasonically cleaned in each bath for about five minutes (Figure I.3.b).

II.5. Preparation of solutions

There are several precursors to obtain thin films of tin oxide such as tin tetrachloride pentahydrate ($SnCl_4.5H_2O$), tin dichloride dihydrate ($SnCl_2.2H_2O$) [4].

In our work, we have chosen tin dichloride dihydrate solute once in distilled water, other in methanol as spraying solution. To obtain a solution (V_{TCD}) of ($SnCl_2.2H_2O$) with the mass molar (M=225.63 g/mol) and molarity (C_1=0.1 mol/l) as follow:

- Measure a mass of tin dichloride dihydrate $m_{TCD} = C_1.M.V_{TCD} = (0.678\pm0.02)$g using a balance (**KERN442-432N**).
- The previous mass was dissolved at volume (V=30 ml).
- The solution was stirred with ultrasonic stirrer for about fifteen minutes.

The other solutions have different molarities (C_2=0.08mol/l, C_3=0.06mol/l, C_4=0.04mol/l and C_5=0.02mol/l) are prepared using dilution from the main solution, the molarities are obtained according the next relation:

$$C_1V_1 = C_nV_n \qquad \text{II.1}$$

Tin dioxide is soluble in both distilled water and methanol but methanol is most preferred because of their low surface tension, and viscosity facilitates the formation of small spray droplets while its low boiling point enables it to be efficiently removed from the deposition chamber in the vapor phase [41].

Figure II.4. Preparation of spraying solutions: **a:** TCD **b:** mass of TCD **c$_1$:** ($SnCl_2.2H_2O$) +Distilled water **c$_2$:** ($SnCl_2.2H_2O$) +Methanol.

II.6. Ultrasonic spray pyrolysis's equipment

At laboratory of material and structure of electromechanically systems and their reliability (LMSSEF: *Laboratoire des Matériaux et Structure des Systèmes électromecaniques et leur Fiabilité*) of the University of Larbi Ben M'Hidi in Om El Bouaghi, we have developed tin oxide thin films using ultrasonic spray pyrolysis technique.

Figure II.5. Complete experimental devices of the ultrasonic spray pyrolysis technique.

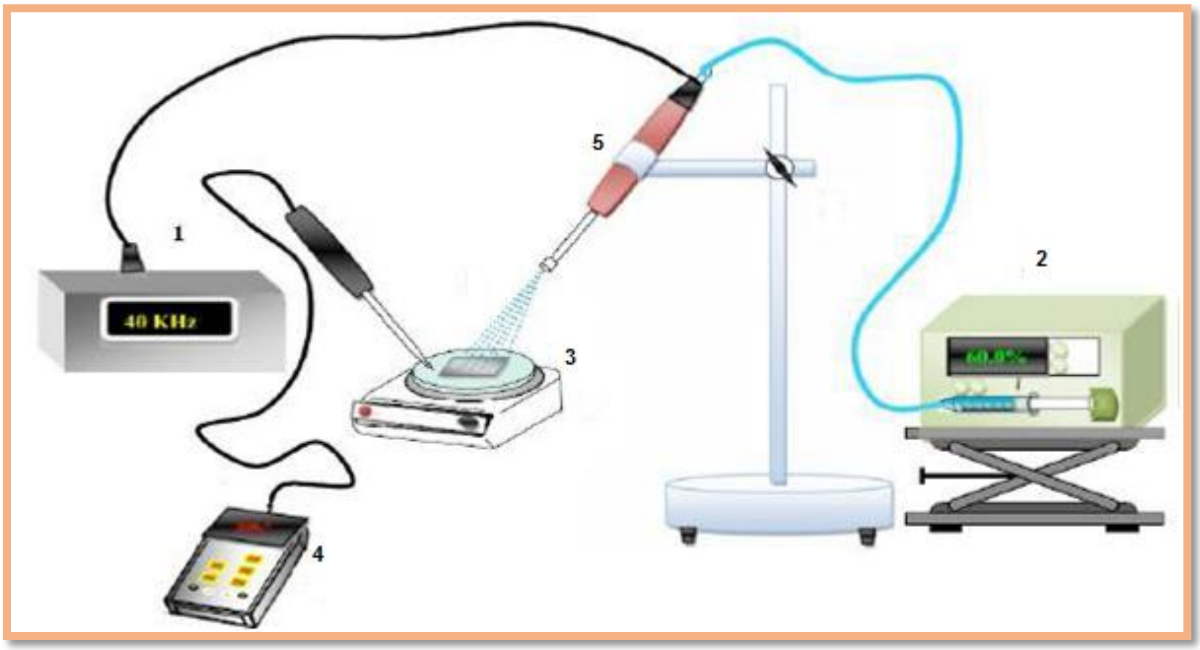


Figure II.6. The schematic experimental set up of the spray pyrolysis system [44].

The schematic experimental set up of the spray pyrolysis system, which is built in LMSSEF lab, is shown in figureII.6. It consists of:

1. **Ultrasonic generator (40 KHz) with an atomizer**: allows decomposing the solution at the atomizer to very fine droplets (Ø ~40 µm), the atomizer is placed on a support height adjustable to control the nozzle spray distance.
2. **Syringe pump** Model PHOENIX D-CP (GF-FOURES) to control the precursor solution flow rate.
3. **Substrate heater**: it is substrate holder (Ø =25 cm) heated by joule effect, the latter is connected to a digital thermometer. The used temperature in our experiment (300-320)°C.
4. **Digital thermometer (TD 121; Pt100)**: is a device to measure the temperature. It is based on the fact that the electrical resistance of platinum varies according to the temperature (T=-199…+850°C). In this work the platinum tip is connected to the heater.
5. **Syringe contains the solution.**

II.7. Choice of deposition substrate

The choice of glass as deposition substrate was adopted due for the next reasons [44,46]:

- The good agreement of thermal expansion coefficient between glass (α_{glass}=8.5x10^{-6} K^{-1}) and SnO_2 (α_{SnO_2}=4x10^{-6} k^{-1}) to minimize the stress interface film/substrate.
- Electrical insulation and dimensional stability.
- For economic reason.
- Their transparency, which adapts well for the optical characterization of films in visible.
- Glass can improve the layers (better adhesion, good structure, and better piezoelectric activity).

II.8. Preparation of thin films

After the preparation substrates and solutions, the procedure for deposition the samples all come in following steps:

- The prepared precursor solution of tin (II) chloride dihydrate $SnCl_2.2H_2O$ with different molarities (0.02M, 0.04M, 0.06M, 0.08M, and 0.01M) using two different solvents (distilled water and methanol) are placed at the spray gun to be sprayed, through a glass nozzle of over a hot glass substrate. By means of air as a carrier gas to reach a substrate in the form of very fine droplets. Prior to deposition the glass substrates (25.4× 25.4×1) mm^3 was kept at ambient temperature to avoid thermal shock.

- The substrates are gradually heated to the chosen deposition temperature (300°C) by an electrical heater.
- The nozzle was kept at a distance of 5 cm from the substrate during deposition.
- The spray rate φ_S of 60 ml/h was maintained using ultrasonic generator (40 KHz).

After deposition process was completed (for 5 min), the films were kept on the heater at a deposition temperature for a while in order to provide sufficient time and temperature for recrystallization. This resulted in formation of well adherent, transparent and uniform thin films. The SnO_2 formulation can be represented as [3]:

$$SnCl_2 + 2H_2O \rightarrow SnO_2 + Cl_2^{\square} + 2H_2^{\square} \qquad \text{II.2}$$

Process parameters for the spray deposition of SnO_2 thin films are presented in table II.1.

Table II.1. Process parameters for the spray deposition of SnO_2 thin films.

Solvent	- **Distilled water** - **methanol**
($SnO_2.2H_2O$) **solution concentration**	0.1M, 0.08M,0.06M,0.04M,0.02M
Substrate temperature (°C)	300
Nozzle-substrate distance (cm)	5
Spray rate (ml/h)	60
Deposition time (min)	5

Part two: Characterization techniques of thin films

II.1. Optical characterization and measurement

II.1.1. Ultraviolet-visible spectroscopy

Ultraviolet-visible spectroscopy is a non –destructive optical characterization technique based on the transition of electron from fundamental state to an excited state due to excitation by an electromagnetic wave. This technique allows working on small amounts of materials deposited in thin films or in suspension [47]. It refers to absorption spectroscopy or reflectance spectroscopy in the ultraviolet visible spectral region. The absorption or reflectance in the visible range directly affects the perceived color of the chemicals involved; it measures the intensity of light passing through a sample *(I)* and compares it to the intensity of light before it passes through the sample *(I_0)*. The ratio (I/I_0) is called the transmittance and it is usually expressed as a percentage (T %) [48].

This technique can provides information on the optical properties besides what it mentioned previously such as optical absorption coefficient (α), the estimation of optical gap E_g, and optical refractive index (*n*,*k*). It can also in certain cases give information about the thickness of studied sample [49].

To obtain the optical properties of our samples we used a double beam recording spectrophotometer type **(V-630)** one passes through the reference (air) and the other through the sample (glass+layer) so the output intensities amplified. Figure II.7 shows the principle of UV-Vis- NIR spectrophotometry.

We were able to obtain spectra representing the variation of optical transmittance *T (%)* according to the wavelength in the UV-Visible-NIR range (190 nm- 1100 nm).

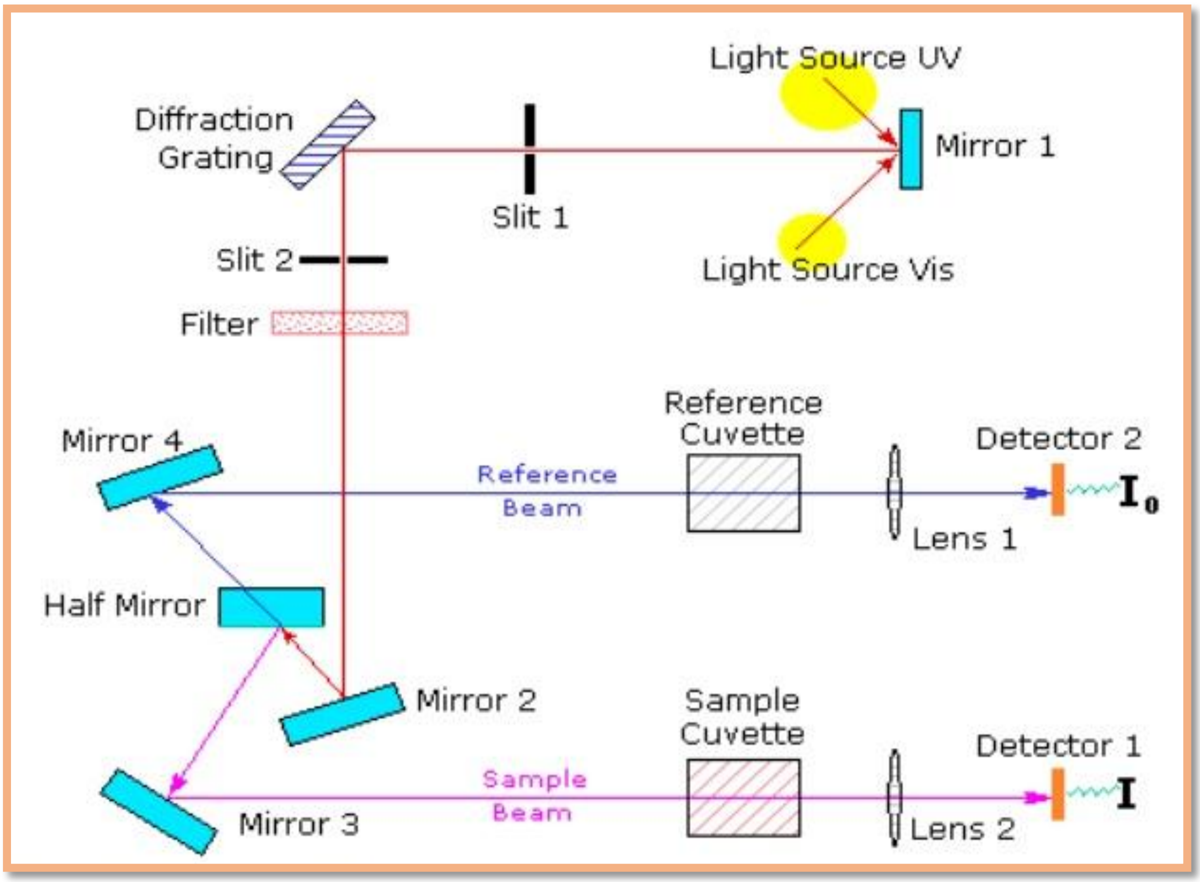


Figure II.7. Schematic spectrometer of UV-Vis [21].

Figure II.8. Experimental device for UV-Vis-NIR spectroscopy.

II.1.1.1. Film thickness

We used two methods to measure the thicknesses of our samples.

a. Envelop method

Thickness of deposited samples prepared at different molarities was calculated using modified Swanepoel envelop method (an envelope was drawn using the maximum and minimum of each curve) and also used value of refractive index n_s of glass substrate was (n_s=1.52). The Figure II.9 shows an example how to determine the thickness. To measure the film thickness we used the next equation [50, 51]:

$$t = \frac{\lambda_1 \lambda_2}{2(\lambda_1 n_2 - \lambda_2 n_1)} \qquad \text{II.3}$$

Where λ_1 and λ_2 are the wavelengths at which two successive maxima or minima occur. n_1, n_2 are the corresponding refractive indices [48]:

$$n = \left[N + \left(N^2 - n_s{}^2 \right)^{1/2} \right]^{1/2} \qquad \text{II.4}$$

Moreover, N obtained by this relation [52]:

$$N = 2n_s \frac{T_M - T_m}{T_M T_m} + \frac{n_s^2 + 1}{2} \qquad \text{II.5}$$

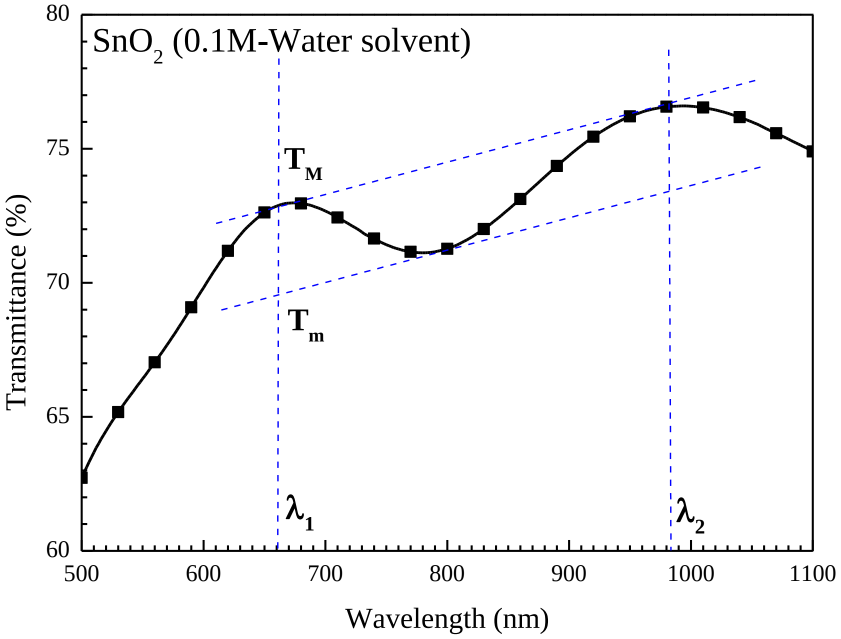


Figure II.9. Determination of interference fringes for find the refractive index and film thickness.

b. Least squares methods

The least squares method is a statistical procedure to find the best fit for a set data points by minimizing the sum of the offsets or residuals of points from plotted curve. Least squares regression is used to predict the behavior of dependent variables [39].

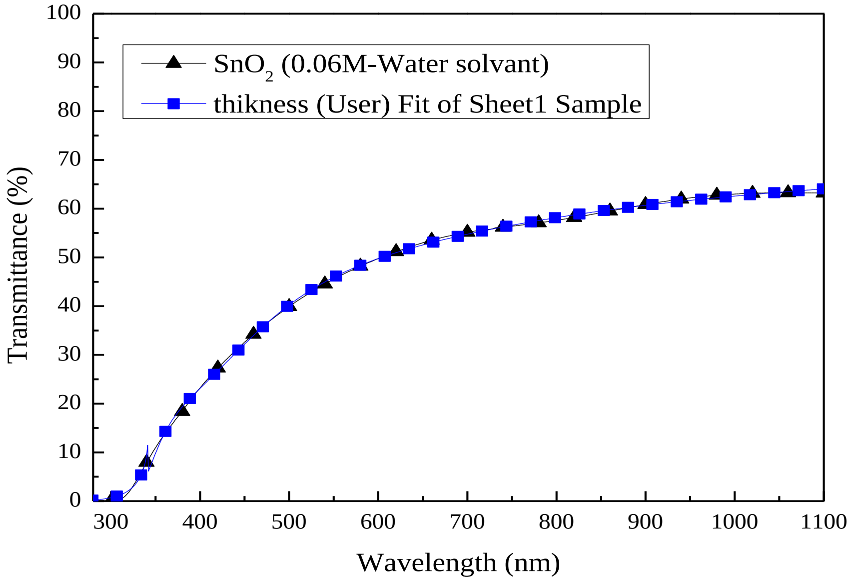


Figure II.10. Fitting the measured transmittance spectra to Swanepoel model.

We determine the thickness of thin films of tin oxide from the spectrum of transmittance, using Fit software that allows to vary a number of parameters, such as thickness , and use the least squares method to adjust a simulated transmittance curve to that measured. Some values are derived from the fit of the transmittance curve using the Origin pro software.

II.1.1.2. Determination of absorption coefficient

In the spectrum domain where light is absorbed and knowing the film thickness (*t*), the absorption coefficient of the film can be determined as a function of the wavelength according to Beer-Lambert law:

$$T = e^{-\alpha t} \tag{II.6}$$

Where:

$$\alpha = \frac{1}{t}\ln\left(\frac{100}{T}\right) \tag{II.7}$$

II.1.1.3. Determination of optical band gap

The measurement of the optical band gap of materials is important in the nanomaterial semiconductor, and solar industries. This note demonstrates how the optical band gap of a material can be determined from its UV-Visible absorption spectrum.

The term “band gap” refers to the energy difference between the top of the valence band to the bottom of the conduction band, electrons are able to jump from one band to another. In order for an electron to jump from a valence band to a conduction band, it requires a specific minimum amount of energy for the transition called the band gap energy [53].

The optical energy band gap (E_g) for the allowed transition between the conduction and valence bands can be found from the Tauc equation II.8:

$$(\alpha h\upsilon)^n = A(h\upsilon - E_g) \tag{II.8}$$

Where:

h υ: Energy of incident photon (eV).

A: Constant dependent on electron-hole mobility.

E_g: Energy of the optical gap (eV).

$n = 2$ or $n = \frac{1}{2}$ following respectively direct or indirect gap transition.

E_g can be estimated by extrapolating to the $h\nu$- axis the linear part of the $(\alpha h\nu)^2$ curve. A diagram illustrating the band gap is shown in Figure II.11.

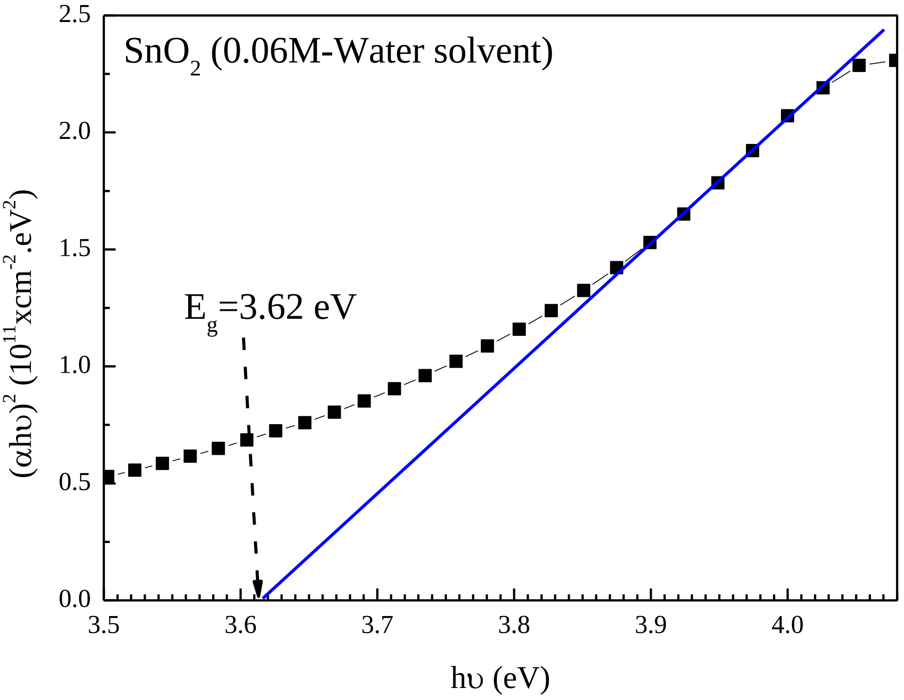


Figure II.11. Determination of optical band gap.

II.1.1.4. Determination of Urbach Energy

Urbach energy is an important parameter, which characterizes the material disorder, according to the Urbach law [54]:

$$\alpha = \alpha_0 \exp\left(\frac{h\upsilon}{E_{Urb}}\right) \qquad \text{II.9}$$

Where:

α_0: Constant.

E_{Urb}: Urbach energy.

By plotting (ln α) as function of $h\nu$ we can determine the value of E_{Urb} [54].

$$\ln\alpha = \left(\frac{1}{E_{Urb}}\right)h\upsilon + \ln\alpha_0 \qquad \text{II.10}$$

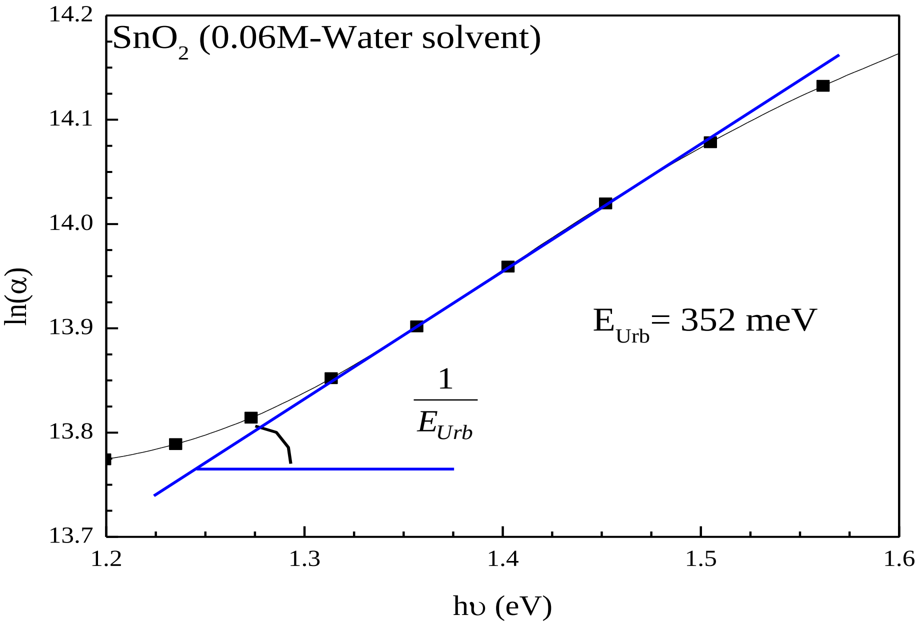


Figure II.12. Determination of Urbach energy.

II.2. Electrical properties

The four-point probes method is a simple and fast method, which measures the electrical conductivity of thin films. Its principal is using four tips (probes), equidistant in direct contact with the surface either of the sample, placed linearly, or as a square. The principle of measurement is simple, just inject a current (I) at the two external tips and measure the voltage (V) at the two internal tips (figure I.13) [55].

The electrical properties of thin films are one of their most important physical features, and differ from those of the corresponding bulk material for various reasons. Electrical properties cover a particularly wide field [56].

Electrical characterization of thin films at room temperature (~18°C). The measurement was taken in linear geometry using **Keithley 2400 Source Meter**. The four contact terminals of Keithley 2400 Source Meter were placed on the surface of thin film as shown in figure II.14.

The values of sourced current and measured voltages were used in determining sample surface resistivity using equation bellow [55,56]:

$$\rho_S = \beta\left(\frac{V}{I}\right) \qquad \text{II.11}$$

Where

β Is a geometry factor and in the case of semi-infinite thin film, $\beta=4.53$, which is just $\pi/\ln 2$ [55].

Then, the electrical conductivity σ is related to thin films thickness t according to the next equation [55]:

$$\sigma = \frac{1}{\rho_s t} \tag{II.12}$$

In order to know the electrical surface resistivity ρ_s and electrical conductivity σ of tin oxide thin films, we used a four point device type **Mandel** in the LMSSEF laboratory of Larbi ben M'Hidi University at Oum Bouaghi, the probe consists of four contacts aligned linearly and the distance between the four terminals (s=1mm). A variable current I is applied between the two external terminals and the voltage V is measured between the two internal probes using **keitheley** 2400, which makes it possible to measure low voltages.

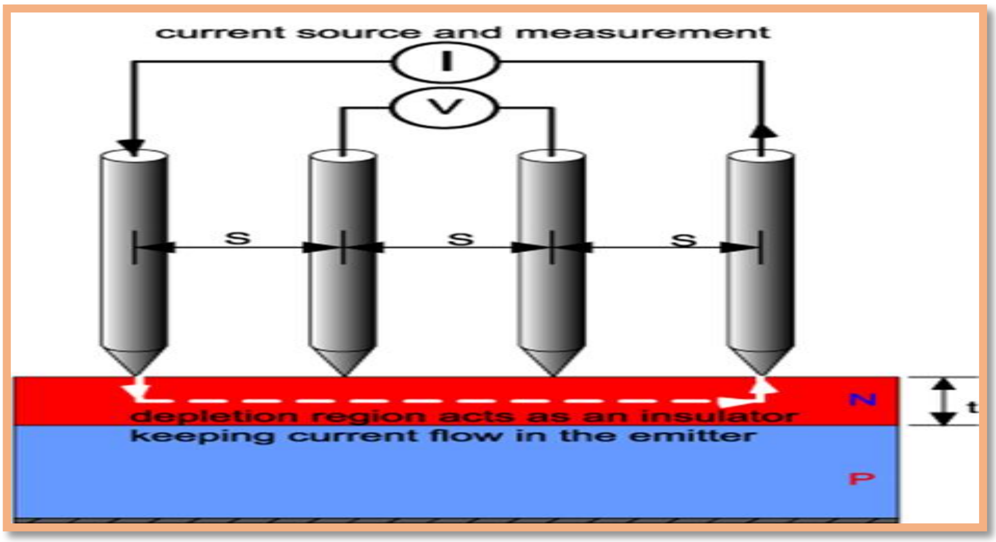


Figure II.13. Diagram representing the principle of the four-point method [1].

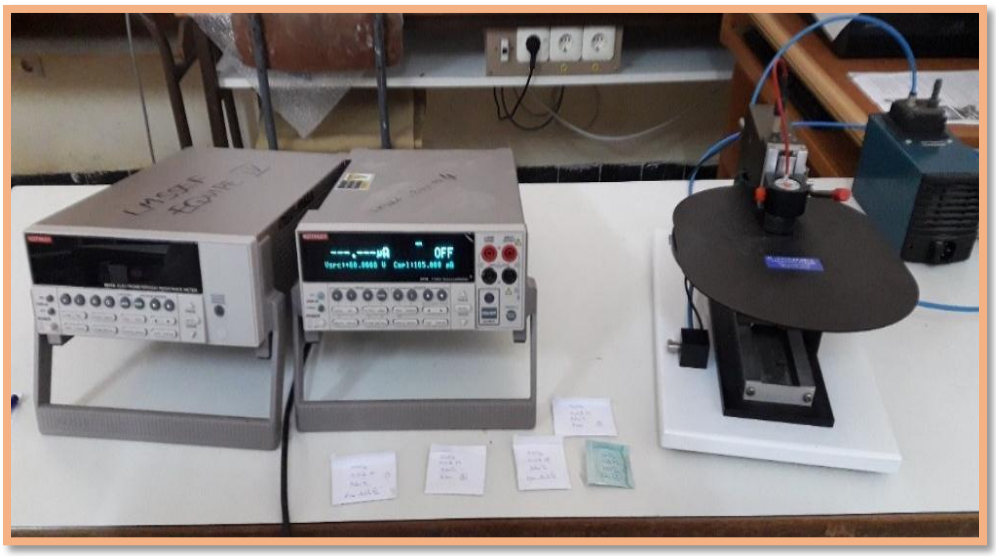


Figure II.14. Four-point probe + keitheley 2400 Source Meter.

Chapter III

Results and discussion

Chapter III: Results and discussion

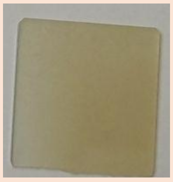
The purpose of this chapter is to present and interpret the experimental results of our work on the elaboration and characterization of tin oxide thin films deposited on glass substrates by ultrasonic spray pyrolysis technique, from tin (II) chloride dihydrate at different precursor solution concentrations (0.02, 0.04, 0.06, 0.08 and 0.1 mol/l) with constant deposition conditions.

We present the effect of the solution concentration and solvent type on the properties of the obtained films. These films are characterized by UV-Vis-NIR spectrophotometer for the determination of the fundamental optical properties (optical gap, Urbach energy and refractive index) and the average thickness of each deposited layer. To determine the electrical properties, we used the four-point probes method for the determination of electrical conductivity of our samples. Note that these characterization techniques were developed in chapter II.

III.1. Photos of tin oxide thin films

Table III.1 shows the photographs of tin oxide thin films deposited on glass substrates at different concentrations of solution (0.02, 0.04, 0.06, 0.08 and 0.1 mol/l) using two different solvent types (distilled water and methanol).

Table III.1. Photos of SnO_2 thin films deposited on glass substrates.

	Bare substrate	**C_1=0.02M**	**C_2=0.04M**	**C_3=0.06M**	**C_4=0.08M**	**C_5=0.1M**
Distilled water solvent						
Methanol solvent						

We have observed that the deposited samples at different solution concentrations of 0.02 to 0.1 mol/l using distilled water then methanol have a graded orange color of light to dark orange. This may be due to the increase on the amount of material deposited with increasing molarity.

III.2. Effect of solvent type and solution concentration on the thickness and film growth kinetics of tin oxide

We estimated the average thickness of our films from the variation of the optical transmittance according to the wavelength of the incident photon in the UV-Vis-NIR domain using the Swanepoel method by the program Origin 8.5.1 which gives highly convergent values.

Figure III.1 shows the variation of the thickness of our thin film as a function of the solution concentration using two different solvent types.

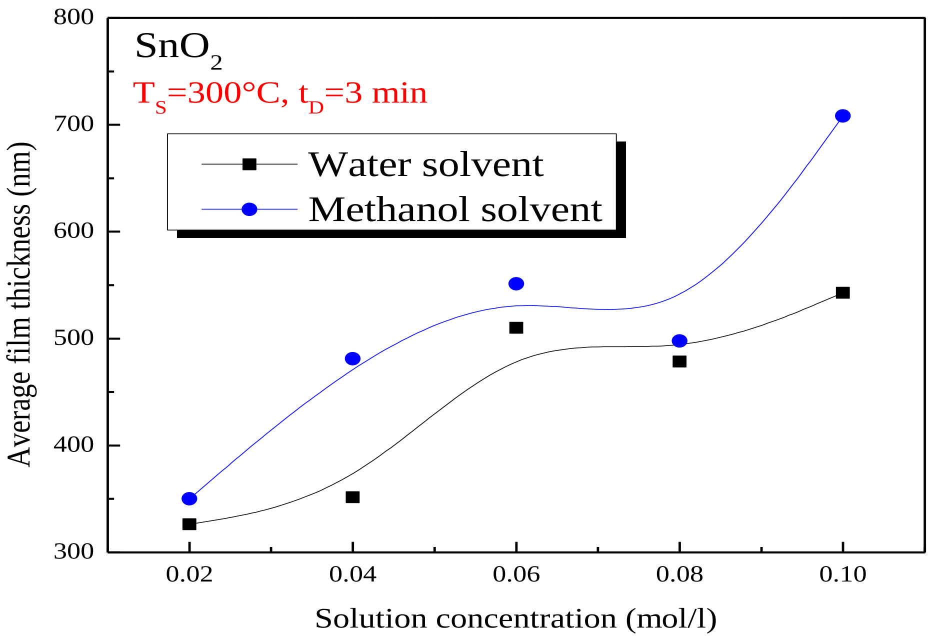


Figure III.1. Variation of average film thickness with solution concentration.

We can see a proportion between increasing of thickness of tin oxide thin films deposited by ultrasonic spray pyrolysis as increasing in solution concentration, it is noted that the thickness values are between 330 and 540 nm for distilled water precursor and between 350 and 700 nm for methanol precursor.

We can interpret the increasing of thickness by the increase in the amount of material deposited (it means there is more material that contributes to the formation of the films) [7,58].

Concerning the observed difference between the thickness values using distilled water and methanol it may be due to the solvent evaporation temperature and the reaction velocity of the alcohol solution compared to the aqueous solution, which results in disorganized crystal structure and the presence of porosity in the film that using methanol as a solvent [59,60].

III.3. Optical characterizations

III.3.1. Effect of solvent type and solution concentration on the optical transmittance of tin oxide

Figure III.2 represents typical spectra of the variation in optical transmittance as a function of the wavelength of the incident photon in the UV-Vis-NIR, recorded in the range from 300 to 1100 nm obtained of tin oxide sample prepared onto glass substrate by the ultrasonic spray pyrolysis technique, with different precursor solution concentrations of tin (II) chloride dihydrate using distilled water Figure III.2 (a), and methanol Figure III.2 (b) as a solvent with the precise experimental conditions (T_S=300°C, t_D=5 min, and d= 5cm).

Two fields of optical transmittance can be distinguished according to the wavelength:

- ❖ A region of strong absorption and low optical transmittance, which corresponds to the fundamental absorption due to the inter-band electronic transition, is seen in the higher photon energy region (ultraviolet region “$\lambda < 350$nm”).
- ❖ A region of strong transparency is located between 350 and 1100nm. The value of the transmission is about 60-80 % for distilled water and about 50-70% for methanol. In this wavelength range which corresponds to the visible and near-infrared region, we have clearly observed interference fringes in some spectra of samples that deposited by using both of solvents.

The observed interference fringes may be due to the multiple reflections on the two interfaces of the film. This indicates that the films prepared with these conditions are smooth and uniform [61].

As can also be seen there is a displacement of the absorption threshold towards the long wavelengths by the change of the solution precursor concentration and solvent type, which indicates the presence of crystalline defects in the deposited material [62].

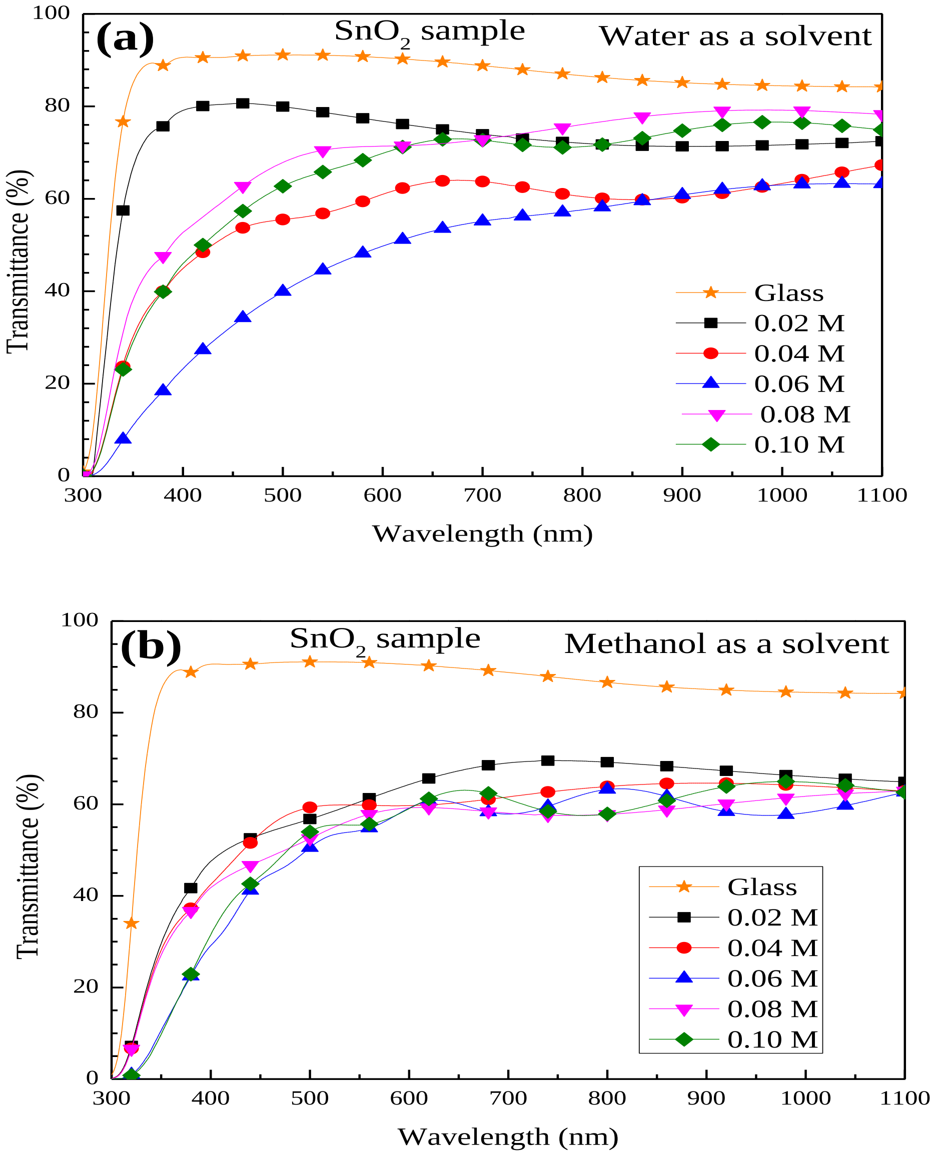


Figure III.2. Optical transmittance spectra of SnO_2 samples films at different solution concentrations using two different solvent types **(a)**: distilled water and **(b)**: methanol.

Figure III.2 shows that transmittance tendency decreases by the increasing of solution concentration and also by replacing the distilled water by methanol.

The decrease in optical transmittance may be due to the increase in the thickness of the thin films and its surface roughness and also the change of our samples color [63].

III.3.2. Effect of solvent type and solution concentration on the optical band gap of tin oxide

The optical band gap energy's values of the tin oxide thin films were determined using the optical process.

The variation of the optical gap of films with different molarities is reported in figure III.3.

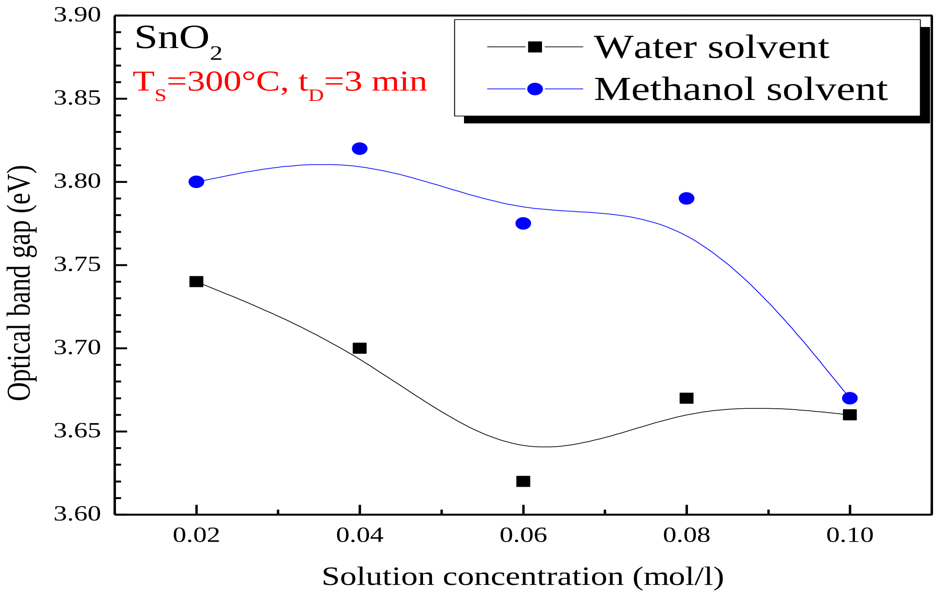


Figure III.3. Variation of optical band gap of SnO_2 with solution concentration using different solvent types.

The optical band gap is defined as the minimum energy to excite an electron from the valence band to the conduction band [30,64]. The optical band gap values in our tin oxide films are between 3.62 and 3.82 eV which is in good agreement with the interval values of tin oxide (3.6-4.2 eV) [30].

Note that the optical band gap decreases with increasing molarities by using the both solvent types, it may be due to the next reasons:

- ✓ When the number of particles is increased in the crystal structure, the particles cannot be placed into the proper lattice positions. This can leads to the formation of crystal defects. Therefore, the decrease in the band gap values for thin films can be due to the enhancement in photon scattering because of crystal defects which, on the other hand, create lattice strain [61].
- ✓ This remark also can be explained by the decrease of the grain size with the increase of the concentration of deposit [65].

Concerning the difference in the optical band gap values using distilled water and methanol, there are several works that find the optical gap is decreased by the increasing of the deposition temperature (or low boiling temperature solvents) [58-60]. Figure II.1 and Figure III.4 can give more explication.

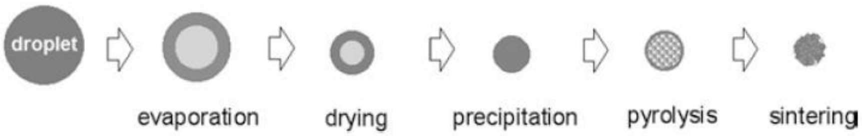


Figure III.4. Steps of powder production during the spray-pyrolysis [60].

III.3.3. Effect of solvent type and solution concentration on the Urbach energy of tin oxide

Ultrasonic spray pyrolysis is a deposition method in which film growth is achieved by pyrolytic reaction. In this situation, the atoms that arrive on the substrate can stick to the film array are not usually in an ideal position causing disorder in the structure [66].

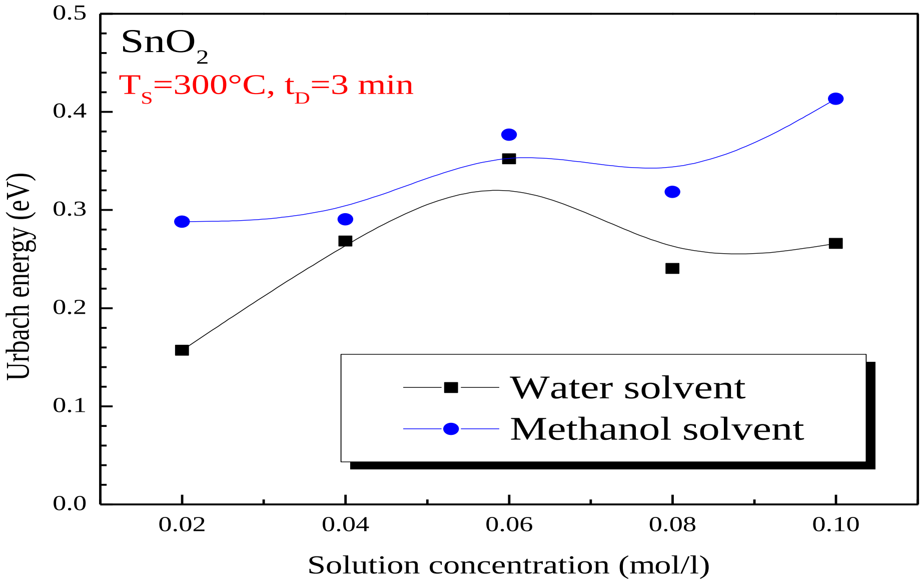
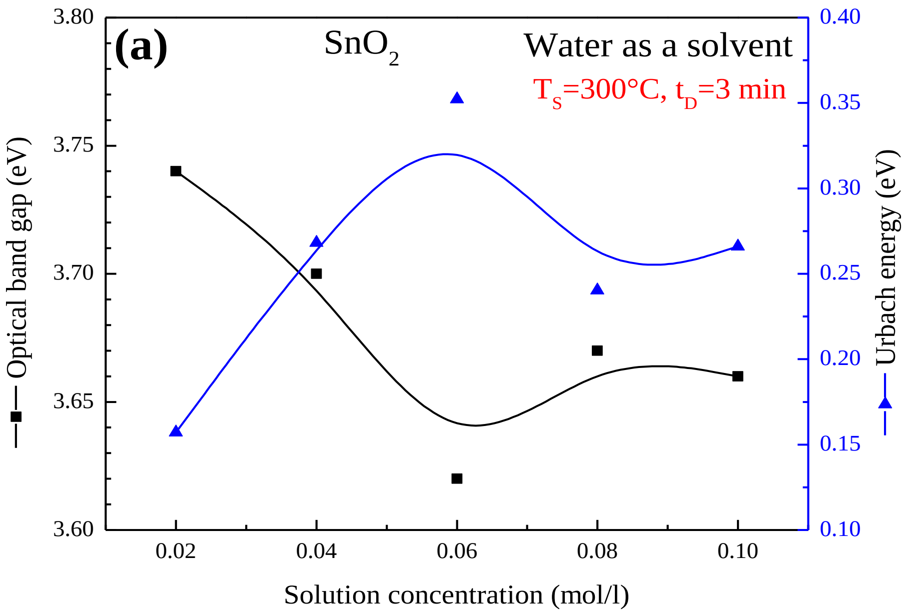


Figure III.5. Variation of Urbach energy of SnO_2 thin films with solution concentration.

In Figure III.5, we reported the variation of Urbach energy of SnO_2 films as a function of solution concentration using two different solvent types. By the increase in solution concentration from 0.02 mol/l to 0.1 mol/l by using both precursors.

The Urbach energy is increase from 0.15 eV to 0.26 eV and from 0.29 eV to 0.41 eV for using distilled water and methanol, respectively.

This increase due to the increase in the amount of atoms in the short time (augment in molarity with a stable of solution flow rate) deposited mostly in random position causing an increase in disorder of films structure [66]. Also, we can confirm the increasing Urbach energy (e.g. 0.35 eV at 0.06 mol/l for using water as a solvent) by the optical absorption threshold shift in the transmission spectra (Figure III.2) [30].



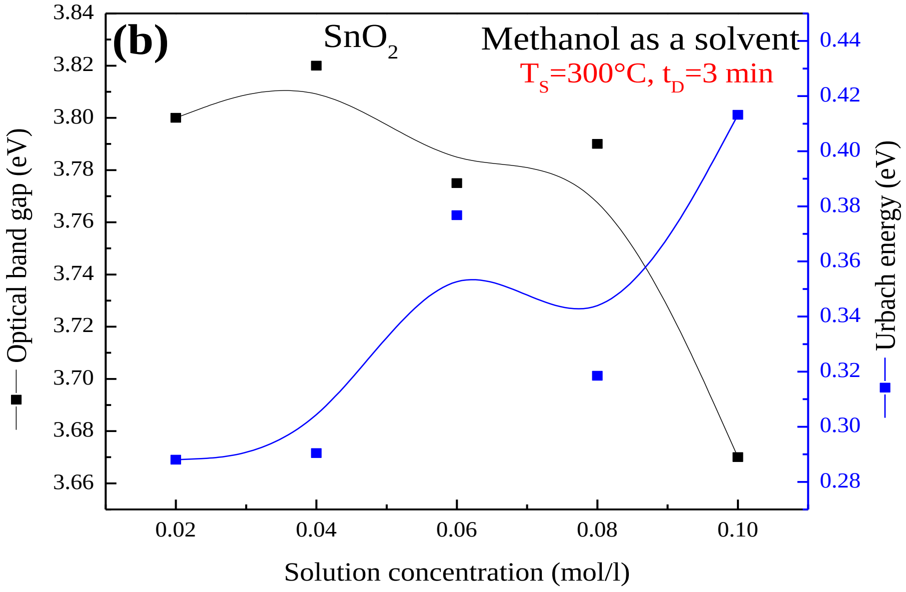


Figure III.6. Variation of E_g and E_{Urb} of SnO_2 thin films versus solution concentration using: **(a)** Distilled water and **(b)** methanol as a solvent.

We can note that the samples prepared with methanol are more disordered than distilled water based ones that may have be caused by the started of methanol evaporation (Figure III.4) and that results a disorder in crystalline structure [66]. Another way to say the ratio of deposition temperature to solvent boiling point is found to be the most important processing parameter that determines whether a crack free homogeneous and coherent film is obtained [59].

From figure III.6 (a and b), we can easily observe, like several works [58,61], the inverse relationship between the variation of optical band gap and Urbach energy as a function of solution concentration using both solvent types.

III.3.4. Effect of solvent type and solution concentration on the refractive index of tin oxide

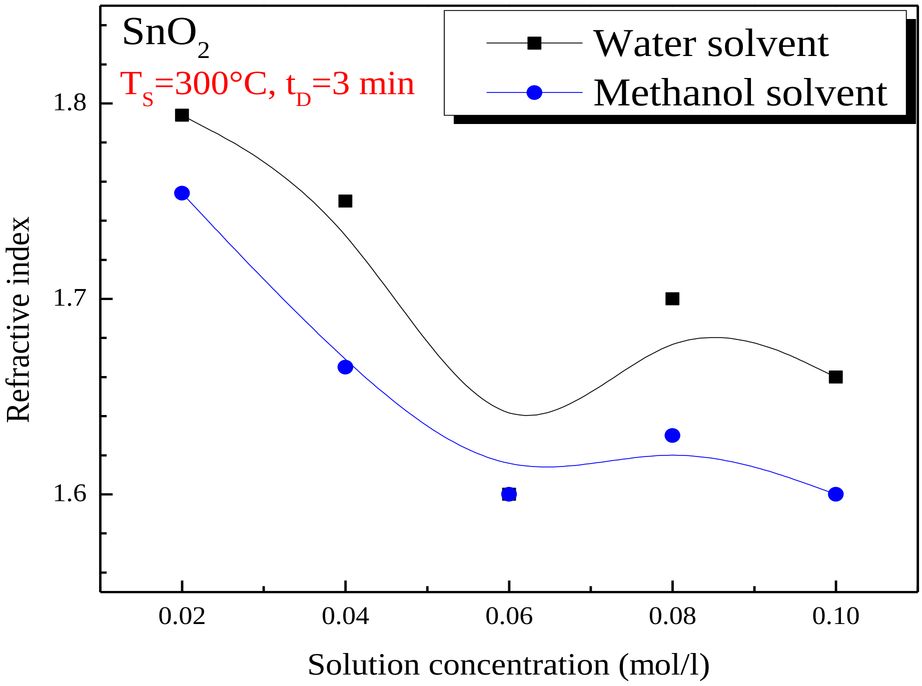
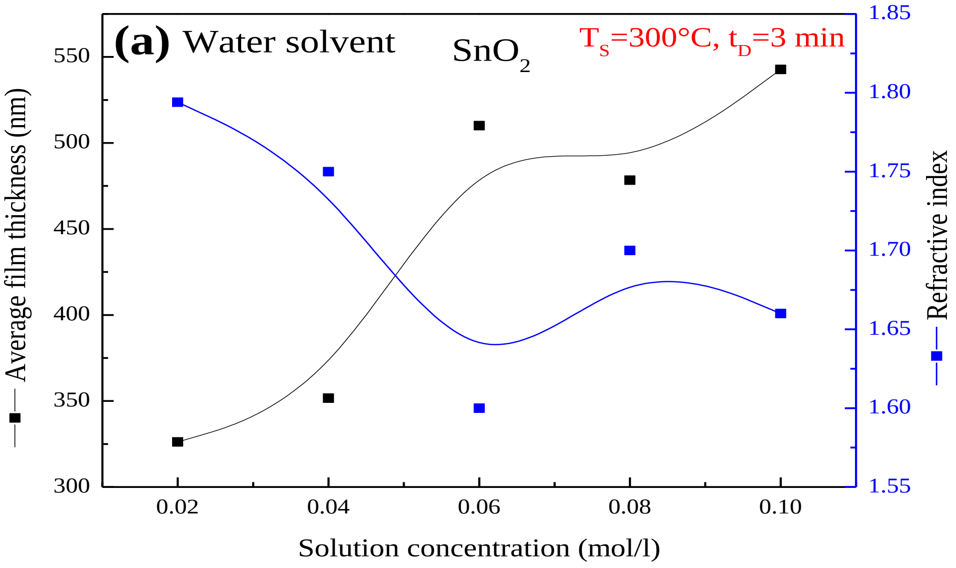


Figure III.7. Variation of refractive index of SnO$_2$ thin films with solution concentration.

Figure III.7 shows the variation of refractive index of SnO$_2$ thin films with solution concentration, using two different solvent types (distilled water and methanol). We notice that the refractive index values of our films decrease from 1.8 to 1.66 for distilled water precursor, and from 1.76 to 1.6 for methanol precursor with the increase of the concentration of solution from 0.02 to 0.1 mol/l, these values are compared with the variation range of tin oxide refractive index between 1.7 and 2.56 [67].



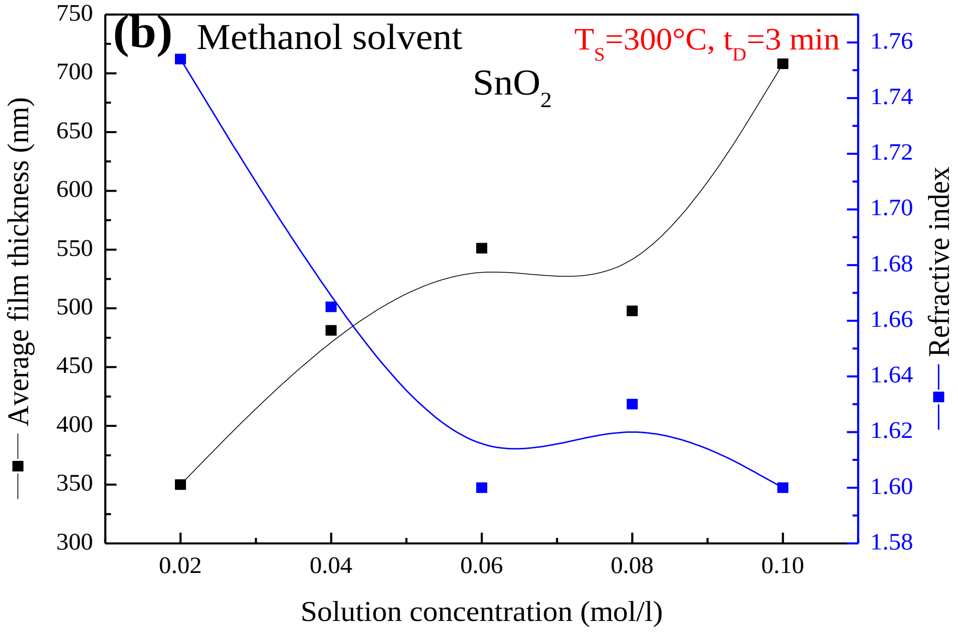


Figure III.8. Variation of *t* and *n* of SnO$_2$ thin films versus solution concentration using: **(a)** Distilled water and **(b)** Methanol as a solvent.

The decrease of the refractive index probably due to the next reason:

- As we know, the refractive index is depended on the scattering of photons in the material. Decreasing the refractive index means that photons can transfer through the material with experiencing less scattering, however a decreasing in refractive index means an increasing transmittance generally [67].

We can easily observe that the refractive index of the obtained samples using methanol solvent have less values than the ones prepared using distilled water, this can be explained by the samples prepared with methanol have more porous because films with high porosity were produced when the precursor solution used solvent low boiling temperature solvents [59,60,68].

Looking at the data presented in Figure III.8, we can see how thickness and refractive index of SnO$_2$ thin film varies with precursor's concentration. It is clear that the refractive index decreases monotonically with increasing thickness of the film. This behavior can be due to the existence of more porosity in the film [67].

III.4. Effect of solvent type and solution concentration on the electrical conductivity of tin oxide

The electrical properties of SnO_2 films were investigated by four-point probe method and it is found that all samples have n-type conduction. The surface resistivity is associated with the voltage probes, so we can obtain a fairly accurate estimation of ρ_s using the equation III.1 [61]:

$$\rho_s = \beta\left(\frac{V}{I}\right) \qquad \text{III.1}$$

In the above said configuration, a correction factor of $\beta=4.53$ was applied for the sample [61].

The surface resistivity and electrical conductivity of the films are given in Table III.2.

Table III.2. The electrical parameters values of the deposited SnO_2 thin films.

Sample molarities mol/l	ρ_s (10^5 (Ω/*sqr*))		σ (10^{-2} (Ω.cm))$^{-1}$	
	Distilled water	Methanol	Distilled water	Methanol
0.02	1.21	26.36	25.39	1.08
0.04	2.02	28.52	14.07	0.73
0.06	2.88	27.28	6.81	0.66
0.08	9.32	31.72	2.24	0.63
0.1	2.38	31.27	7.73	0.45

The increasing in molarity will increase the surface resistivity using both precursor and their values were from $0.21\text{x}10^5$ to $2.38\ \text{x}10^5$(Ω/*sqr*) and from $26.36\text{x}10^5$ to $31.27\text{x}10^5$(Ω/*sqr*) for using distilled water and methanol respectively as it was shown in table III.2.

We estimated that the electrical conductivity values of our films varies between $0.4\text{x}10^{-2}$ and 0.25 $(\Omega.\text{cm})^{-1}$. From figure III.9, the electrical conductivity values decreasing with an increase of solution concentration. As can also be seen, all deposited films using methanol with conductivity values much less than of using the distilled water as a solvent.

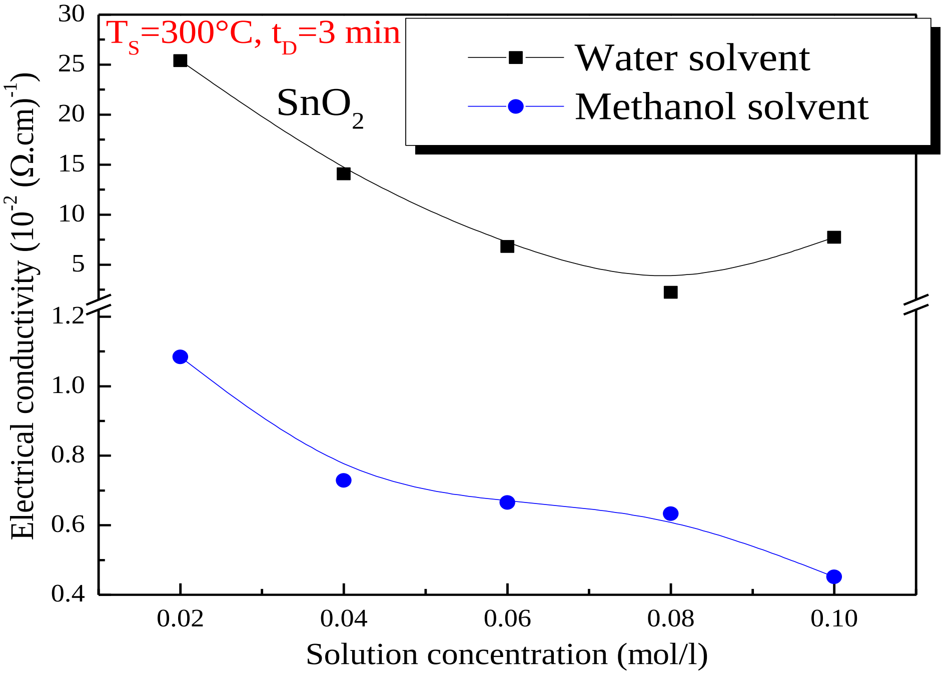


Figure III.9. Variation of electrical conductivity of SnO_2 thin films with solution concentration.

Since in the best crystal structure, there is a great mobility of charge carriers (0.25 (Ω.cm^{-1}) for using water as a solvent at 0.02mol/l).

It is well known that the electrical conductivity of semiconductors is expressed by equation III.2 [70]:

$$\sigma = n.e.\mu_n \qquad \text{III.2}$$

Where:

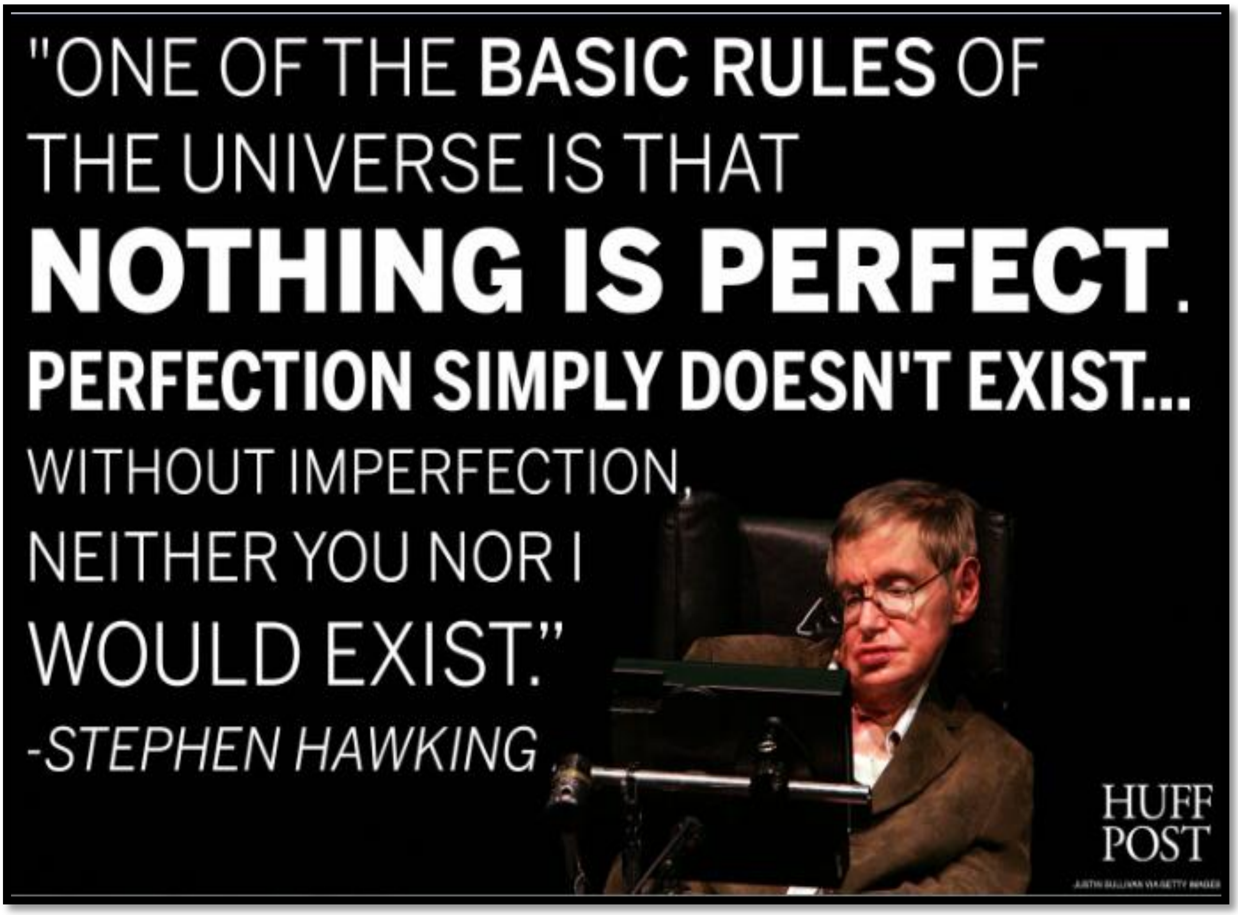
n: charge carriers concentration.

e: electronic charge.

μ_n: the mobility of charge carriers.

As the grain boundaries reduce the mobility of the carriers and since the conductivity is proportional to this parameter, this explains the low values of the conductivity of the prepared samples at high molarity.

GENERAL CONCLUSION



"ONE OF THE **BASIC RULES** OF THE UNIVERSE IS THAT **NOTHING IS PERFECT**. **PERFECTION SIMPLY DOESN'T EXIST...** WITHOUT IMPERFECTION, NEITHER YOU NOR I WOULD EXIST."

-STEPHEN HAWKING

GENERAL CONCLUSION

The aim of this study is to develop tin oxide thin films by means of ultrasonic spray pyrolysis on glass substrates and study the effect of precursor concentration and solvent type on the optical and electrical properties of these samples. This technique of making materials is very attractive, simple, easy to control, and low cost chemical technique. On the other hand, the thin films obtained are of good quality and have excellent adhesion.

Tin oxide thin films were deposited from tin (II) chloride dihydrate dissolved once in distilled water then in methanol with different molarities (0.02, 0.04, 0.06, 0.08, and 0.1 *mol/l*). Substrate temperature, nozzle-substrate distance, flow rate and spray time were maintained constant throughout the deposition process at 300°C, 5cm, 60 ml/h, and 5 min, respectively.

The obtained samples are characterized by UV-Visible-NIR spectrophotometer and four-point probe technique to determine their optical and electrical properties. The characterization of the films lead us to the following conclusions:

With the increase in the concentration of solution, we observe that UV-Visible-NIR results showed that the transmittance decrease in the visible area about 60-80% for distilled water and about 50-70% for methanol, so our samples using distilled water are more transparent than using methanol. The film thickness increases from330 to 540 nm and from 350 to 700 nm for distilled water precursor and methanol precursor respectively. We found also that our films have direct energy band gap between 3.65 and 3.75 eV using water solvent and between 3.65 and 3.8 eV using methanol solvent, thus it decreases by the increase in the concentration of solution. We observe too that Urbach energy increases with the decrease of refractive index and the electrical conductivity, these variations are interpreted by the increase in the quantity of material deposited, the increase in porosity, and the decrease in grain size, therefore the films divinely more disordered. We can conclude that when we use methanol as solvent in place of distilled water, all properties of prepared films act to increase molarities except the optical band gap.

Finally, the variation of the solution concentration and solvent type are varied the optical and electrical properties such as optical transmittance, optical gap, refractive index, electrical conductivity, and thickness, but the type of semiconductor of all deposited samples does not depend on molarity and solvent type. Tin oxide is a good candidate in several areas of applications such as catalysis, gas sensors, rechargeable Li-ion batteries, transparent conducting electrodes, and other optical electronic devices.

REFERENCES

REFERENCES

[1] K. Khlaifia, Structural and opto-electrical stydy of SnO_2 thin films elaborated by spray pyrolysis, Master thesis, Hamma Lakhder university-El-oued (2015).

[2] J.B.Chaudhari, Growth and study of optical and electrical properties of chemically deposited $CdS_{1-x}Se_x$:Ag nano composite thin films for sensor application, Doctorat Thesis, University of Rajasthan, Jaipur- India (2014).

[3] M. Selma. H.A. Fadheela, H. Oleiwe, J.H. Khulaef, Preparation and characterization of tin oxide thin films by using spray pyrolysis technique, Tech Journal 33 (2015) 529- 538.

[4] M. Marikkannan, V. Vishnukanthan, A.Vijayshankar, A novel synthesis of tin oxide thin films by the sol-gel process for optoelectronic applications, AIP Advances 5 (2015) 121-127.

[5] H.A. Hamedani, Investigation of deposition parameters in ultrasonic spray pyrolysis for fabrication of solid oxide fuel cell cathodes, Ph.D. thesis, Georgia Institute of Technology (2008).

[6] M. Mozafarifard, D. Toghraie, Numerical simulation of fractional non-fourrier heat transfert metal films under short-pluse laser, Ineternational communaications in heat and mass transfert 115 (2020) 1-9.

[7] S. Yahiaoui, L’effet de la molarité des différentes sources d’étain sur les propriétés des couches minces d’oxyde d’étain SnO_2 élaborées par Spray Ultrasonique, Magister Thesis, Mohamed Khider University – Biskra (2014).

[8] J. Thirumalai, The prominence of thin film science in technological scale, IntechOpen 24 (2017) 5-13.

[9] A. Jilani, M. Shaaban, A.H. Hammad, Advance deposition techniques for thin film and c oating, IntechOpen 33 (2017) 138-147.

[10] S. Laghrib, H.A. Adnani, D. Abdi, J.M. Pelletier, Elaboration et étude des couches minces de SnO_2 obtenu par évaporation sous vide et recuites sous oxygène, Revue des Energies Renouvelables 10 (2007) 357-366.

[11] A. Hannachi, A. Segura, H.M. Meherzi, Growth of manganese sulfide (α-MnS) thin films by thermal vacuum evaporation: Structural, morphological, optical properties, Materials Chemistry and Physics 6 (2016) 326–332.

[12] M. Lorenz, M.S.R. Rao, 25 years of pulsed laser deposition, Applied Physics 47 (2014) 1-3.

[13] A. Patel, Anesthesia for laser airway surgery benum of and hagberg Airway Management 3rd edition (2013) 828-858.

[14] H. Karl, B. Stritzker, Reflection high-energy electron diffraction oscillations modulated by laser pulse deposition $YBa_2Cu_3O_{7-X}$, Physical Reviews letters 69 (1992) 2939–2942.

[15] N. Vershinin, B. Straumaland W. Gust, Vacuum arc deposition of Mo films, Vacuum Science & Technology 14 (1996) 3252-3255.

[16] M.J. denexter, Palladium membrane technology for hydrogen production carbon capture and other applications, Johnson Matthey 60 (2016) 43-67.

[17] R.J. Martin, A. Lakhtakia, Vapor Deposition Techniques, Engineered Biomimicry 15 (2013) 383-398.

[18] C. Morosanu, V. Dumitru, E. Cimpoiasu, C. Nenu, Comparison between DC and RF Magnetron sputtered aluminum nitride films, Springer Science 38 (1997) 127–132.

[19] V. Dumitru, C. Morosanu, V. Sandu, A. Stoica, Optical and structural differences between RF and DC AlxNy magnetron sputtered films, Thin Solid Films 359 (2000) 17–20.

[20] Y. Hamedani, P. Macha, T.J. Bunning, Plasma-enhanced chemical vapor deposition: where we are and the outlook for the future, IntechOpen 10 (2016) 248-263.

[21] L. Herissi, Élaboration et caractérisation de couches minces d'oxydes métalliques destinées à des applications optoélectroniques, Doctorat Thesis, Larbi Ben M'hidi University -Oum El Bouaghi (2016).

[22] P. Padhamnath, S. Duttagupta, Optoelectrical properties of high performance low-pressure chemical vapor deposited phosphorus-doped polysilicon layers for passivating contact solar cells, Materials Chemistry and Physics 202 (2020) 79-73.

[23] M.Ivanda, H. Gebavi, D. Ristic, K. Furic, S. Music, M. Ristic, S. Zonja, P. Biljanovic, O. Gamulin, M. Balarin, M. Montagna, M. Ferarri, and G. C. Righini, Low pressure chemical Vapor Deposition of Different Silicon Nanostructure, International Journal of Termophysics 57 (2009) 1-5.

[24] K. Daideche, A. Azizi, Electrodepositition of tin oxide thin film from nitric acid solution: the role of pH, Springer Materials Science 28 (2007) 8051-8060.

[25] J. Vequizo, Electrodeposition and characterization of oxide semiconductors (SnO_2, Ga-O, and Fe-O) Thin Films, Doctorat Thesis, Nagoya Institute of Technology -Japan (2004).

[26] L. Baghrich, Elaboration et caractérisation de couches minces d'oxyde de zinc et sulfure de zinc préparées par spray ultrasonique, Doctorat Thesis, Frères Mentouri University-constantine (2015).

[27] S. Baco, A. Chik, F.M. Yassin, study on optical properties of tin oxide thin film at different annealing temperature, Science and Technology 4 (2012) 61-72.

[28] E. Stauffer, Concept of pyrolysis for fire debris analysts, Science & Justice 43(2003) 29- 40.

[29] V. Dhyani, Pyrolysis of biomass, Biomasse, Biofuels, Biochemicals 17 (2019) 217-244.

[30] K. Derrar, M. Zaabat, A. Hafdallah, N. Rouabah, b. Gasmi, I. Zerrouk, Optical and structural properties of sno_2 thin films deposited by spray pyrolysis technique: effect of solution concentration, Defect and Diffusion Forum 397 (2019) 179-186.

[31] J. Mooney, S. Radding, Spray pyrolysis processing, Annual Review of Materials Science 12 (1982) 81-101.

[32] R. Farooq, Mechanism of corrosion and erosion resistance of plasma- sprayed nanostructured coatings, IntechOpen 4 (2013) 126-132.

[33] F. Bozon-Verduaz, Nanoparticles of metal and metal oxides :some peculiar synthesis methods, size and shape control, application to catalysts preparation, Brazilian Journal of physics 39 (2009) 134-138.

[34] G.E. Patil, D.D. Kajale, V.B. Gaikwad, G.H. Jain, Spray pyrolysis deposition of nanostructured tin oxide thin films, International Scholarly Research Network 33 (2012) 1- 5.

[35] R. Sethi, A. Shabir et al, Structural optical and electrical properties of tin oxide thin films for application as a wide band gap semiconductor, Advanced Materials and Radiation Physics 3 (2015) 1-6.

[36] Z. Chen, D. Pan, Recent Advances in tin dioxide materials: some developments in thin films, nanowires, and nanorods, ACS Publications 114 (2014) 7442-7486.

[37] T.Serin, N.Serin, S.Karadeniz,H.Sari, N. Tuğluoğlu, O.Pakma ,Electrical structural and optical properties of SnO_2 thin films prepared by spray pyrolysis, Journal of Non-crystalline solids 352 (2006) 209– 215.

[38] F.A. Akgul, C. Gumus, A.O. Er, A.H. Farha, G. Akgul, Y. Ufuktep, Z. Liu, Structural and electronic properties of SnO_2, Journal of Alloys and Compounds 579 (2013) 50–56.

[39] P. Manjunathan, G.V. Shanbhag, Application of tin oxide-based materials in catalysis, Materials Science and Catalysis Division, Poornaprajna Institute of Scientific Research 408 (2020) 519-553.

[40] S. Lekshmy, SnO_2 Thin films doped indium prepared by Sol-Gel method, Sol-Gel Science and Technology 67 (2013) 29-38.

[41] G.E. Patil, D.D. Kajale, D.N. Chavan, Characterization and gas sensing performance of SnO_2 thin films prepared by spray pyrolysis, Indian Academy of Sciences 34 (2011) 1–9.

[42] M. Boshta, F.A. Mahmoud, M.H. Sayed, Characterization of sprayed SnO_2:Pd thin films for gas sensing applications, Ovonic Research 6 (2010) 93–98.

[43] T.V. Gavrilovic, M.D. Dramicanin, Nanomaterial for green energy, Micro and Nano technologies 406 (2018) 55-81.

[44] P.N. Onkundi, K.M. Munji, D.B. Bem, B. Muthoka, Effect of deposition parameters on optical and electrical properties of sno_2:al thin films prepared by spray pyrolysis technique for optoelectronic devices, International Journal of Thin Films Science and Technology 7 (2018) 25-33.

[45] S. Kaneko, Spray pyrolysis deposition for thin film formation and its application to DSC study, in 24th EU PVSEC - Hamburg (2009) 432-8003.

[46] L. Filipovic, S. Selberherr, Stress in three-dimensionally integrated sensor systems, Microelectronics Reliability 61 (2016) 3-10.

[47] A. Mujahid, F.L. Dickert, Molecularly imprinted sensors 1^{st} Edition (2012) 125-159.

[48] P.K. Manoj, B. Joseph, V.K. Vaidyan, D.S.D. Amma, Preparation and characterization of indium-doped tin oxide thin films, Ceramics International 33 (2007) 273–278.

[49] N.N. Jandow, Effects of Cu-doping on optical properties of NiO, International Letters of Chemistry, Physics and Astronomy 62 (2015) 155-162.

[50] E.R. Shaaban, I.S. Yahia, E.G. El-Metwally, Validity of swanepoel's method for calculating the optical constants of thick films, Acta Physica Polonica 121 (2012) 628–635.

[51] Ö.ERKEN, C.GÜMÜŞ, Determination of the thickness and optical constants of polycrystalline sno_2 thin film by envelope method, Journal of Science 8 (2018) 141- 151.

[52] Y.C.M. Caglar, The determination of the thickness and optical constants of the zno crystalline thin film by using envelope method, Optoelectron, Advances in Materials 8 (2006) 1410–1413.

[53] D.B. M.Hoffman., S. Martin; W. Choi, Environmental applications of semiconductor photo catalysis, Chemical Reviews 95 (1995) 69–96.

[54] S.J. khmayies, R.N. Ahmad-Bitar, A study of the optical bandgap energy and Urbach tail of spray-deposited CdS:In thin films, Material Research Technology 2 (2013) 221–227.

[55] N. Jebbari, N. Kamoun, R. Bennaceur, Effect of $SnCl_4$concentration on F:SnO_2 deposited by chemical spray pyrolysis, The proceedings of International Renewable Energy Congress -Sousse (Tunisia) 2 (2010) 276-279.

[56] P.M. Mwathe, R. Musembi, M. Munji, Effect of annealing and surface passivation on doped sno_2 thin films prepared by spray pyrolysis technique, Advances in Materials 4 (2015) 51-58.

[57] L. Herissi, Élaboration par pulvérisation pyrolytique et caractérisation de couches minces semi conductrices et transparent d'oxyde de zinc perfectionnement du système de dépôt, Magister Thesis, Larbi ben M'hidi University - Oum El Bouaghi (2008).

[58] D. Beckel, A. Dubach, A.R. Studart, L.J. Gauckler, Spray pyrolysis of $La_{0.6}$ $Sr_{0.4}$ $Co_{0.2}$ $Fe_{0.8}$ $O_{3-\delta}$ thin film cathodes, Electroceram 16 (2006) 221–228.

[59] A. K. Alves, C. P. Bergmann, F. A. Berutti, Novel synthesis and characterization of nanostructured materials, Engineering Materials 4288 (2013) 23-27.

[60] A. Allag, S. Rahmane, A. Ouahab, N. Abdelmalek, B. Gasmi, Effect of solution concentration on the structural, optical and electrical properties of SnO_2 thin films prepared by spray pyrolysis, Optik 127 (2016) 2653-2658.

[61] L. Herissi, L. Hadjeris, M.S. Aida, S. Azizi, A. Hafdallah and A. Ferdi, Ni-Doped ZnO Thin films deposited by pneumatic spray pyrolysis, Nano Hybrids and Composites 27 (2019) 21-29.

[62] A.H. Jayatissa, K. Guo, A.C. Jayasuriya, Fabrication of cuprous and cupric oxide thin films by heat treatment, Applied Surface Science 255 (2009) 9474–9479.

[63] C.M. Mahajan, M.G. Takwale, Intermittent spray pyrolytic growth of nanocrystalline and highly oriented transparent conducting ZnO thin films: Effect of solution spray rate, Journal of Alloys and Compounds 584 (2014) 128–135.

[64] L. Herissi, A. Sari, S. Bouchrit, L. Hadjeris, S. Azizi, M.S. Aida, Preparation and characterization of undoped copper oxide thin films, 1st séminaire de physique et chimie des matériaux (2018) 15-17.

[65] H. Benamra, L'effet de la température du substrat et de la molarité sur les propriétés des couches minces de sulfure de zinc déposées par spray ultrasonique, Magister Thesis, Université Mohamed kheider-Biskra-Algérie (2013).

[66] S. Kumar, T. Bhabani, P. Hota, P.V. Rajeswari, Study of optical characteristics of tin oxide thin film prepared by sol–gel method, Indian Academy of Sciences 490 (2013) 1231– 1237.

[67] H. Serrar, A. Bouabellou, Y. Bouachiba, A. Taabouche, A. Bouhank, Y. Bellal, H. Merabti. Effect of water and methanol solvents on the properties of CuO thin films deposited by spray pyrolysis, Thin Solid Films 686 (2019) 137282.

[68] F.Z. Ababsia, S. Fares, Élaboration et caractérisation des couches minces d'oxyde de nickel dopé au cuivre, Master thesis, Larbi Tébessi University -Tebessa (2018).

ABSTRACT

Elaboration and characterization of tin oxide thin films deposited by spray pyrolysis

Abstract

The aim of this work is the deposition of tin oxide thin films (SnO_2) by ultrasonic spray pyrolysis technique and study the effect of precursor concentration and solvent type on the optical and electrical properties of the prepared films, in order to obtain a good photoelectric property, which makes it an important candidate in many technological applications.

In this work, we prepared these films onto glass substrates from tin (II) chloride dihydrate dissolved in both distilled water and methanol with different molarities (0.02, 0.04, 0.06, 0.08, and 0.1 *mol/l*) under constant conditions of preparation, these films are characterized by UV-Visible-NIR spectrophotometer and four-point probe technique to determine their optical and electrical properties.

We observed that the optical and electrical properties are influenced by the variation of solution concentration and solvent type. We obtained n-type semiconductor tin oxide films and have high optical absorption in the ultraviolet domains. With the increase of solution concentration or the change of solvent type from water to methanol, the transmittance, refractive index and electrical conductivity decreases with increase in the Urbach energy and the film thickness. On the other hand, the optical band gap is decrease with molarity increasing and takes an augment values using methanol as a solvent.

Keywords: *Thin films, Tin oxide, Spray pyrolysis, Optical gap, Solvent type, Electrical conductivity.*

Elaboration et caractérisation des couches minces d’oxyde d’étain déposées par spray pyrolyse

Résumé

L’objectif de ce travail est l'élaboration des couches minces d’oxyde d’étain (SnO_2) par la technique de spray pyrolyse ultrasonique et l’étude de l’effet de la molarité et le type de solvant sur les propriétés optiques et électriques des couches préparées, afin d'obtenir une bonne propriétés photoélectriques qui en fait un candidat important dans de nombreuses applications technologiques.

Dans ce travail, nous avons préparé ces films sur des substrats en verre à partir de chlorure d’étain dihydraté dissous dans l'eau distillée et méthanol avec différente molarité (0.02, 0.04, 0.05, 0.08, et 0.1 *mol/l*) avec des conditions constantes de préparation, ces échantillons sont caractérisés par spectrophotomètre UV-Visible-NIR et la méthode des quatre pointes pour déterminer les propriétés optiques et électriques.

On observe que les propriétés optiques et électriques sont influencées par la variation de la concentration de solution et le type de solvant. On a trouvé des films de semi-conducteur d'oxyde d’étain de type n et a forte absorption optique dans le domaine ultraviolet. Avec l’augmentation de concentration de la solution ou le changement de type du solvant de l’eau au méthanol, La transmittance, l’indice de réfraction et la conductivité électrique diminuent avec l’augmentation de l’énergie d’Urbach et l’épaisseur du film. Par contre le gap optique diminue avec l’augmentation de concentration de la solution et augmente en utilisant le méthanol comme solvant.

Mots-clés : *Couches minces, Oxyde d’étain, Spray pyrolyse, Type de solvant, Gap optique, Energie d'Urbach, Conductivité électrique.*

تحضير شرائح رقيقة من أكسيد القصدير باستخدام طريقة الرش بالانحلال الحراري

ملخص

الهدف من هذا العمل هو تحضير شرائح رقيقة من أكسيد القصدير (SnO_2) باستخدام طريقة الرش بالانحلال الحراري بواسطة الأمواج فوق الصوتية و دراسة تأثير كل من المولارية و نوع المذيب على الخصائص الضوئية و الكهربائية لهذه الشرائح من اجل الحصول على خصائص كهروضوئية جيدة التي تجعل من هذه الأفلام مرشحا هاما في عديد التطبيقات التكنولوجية.

في هذا العمل قمنا بإعداد هذه الشرائح فوق حوامل الزجاج انطلاقا من محلول مائي ثم كحولي لكلورير القصدير ثنائي الهيدرات تمت اذابته في الماء المقطر ثم الميثانول بتراكيز مختلفة (0.02، 0.04، 0.06، 0.08، و 0.1 مول/ل) و بشروط ثابتة التحضير شخصت هذه العينات باستعمال مطيافية الأشعة الفوق بنفسجية-المرئية- تحت الحمراء القريبة وطريقة المسابير الأربعة لتحديد خصائصها الضوئية والكهربائية.

لاحظنا أن الخصائص الكهربائية و الضوئية للأفلام تتأثر بتغير المولارية ونوع المذيب جميع العينات التي تم الحصول عليها هي أشباه موصلات من نوع n . بزيادة تركيز المحلول و تغير نوع المذيب من الماء إلى الميثانول، تنخفض كل من الشفافية الضوئية ، معامل الانكسار و الناقلية الكهربائية بتزايد طاقة أورباخ (اللاانتظيم) و السمك من ناحية أخرى يتناقص عرض العصابة الممنوعة بزيادة المولارية و تأخذ قيم اكبر عند استعمال الميثانول كمذيب.

الكلمات المفتاحية: *الأفلام الرقيقة ،أكسيد القصدير، الرش بالانحلال الحراري،* عرض *عصابة الطاقة، طاقة* أورباخ ، *الناقلية الكهربائية.*