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THESIS of MASTER

Specialty: **Physics of materials**

Elaboration of tin dioxide thin films by spray pyrolysis using different concentrations of solution and solvent

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«يَرْفَعِ اللَّهُ الَّذِينَ آمَنُوا مِنكُمْ وَالَّذِينَ أُوتُوا الْعِلْمَ دَرَجَاتٍ»

المجادلة – الآية 11

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Dedication

Dedicate this modest work to:

My parents treasured, I ask Allah to protect and join them in highest paradise.

To my brothers khalil, Safa, Mondher, Manass and all my family

I am so grateful to have you with me.

To my friends Ichrak, Nona, Aicha, houda, Khadija, Bariza, Manel, and Samira

for their endless love.

To you Takoua my sister and my friend how lucky I am to have a golden friend like you and to share a precious moments with you

Dhikra Rahal

Dedication

I dedicate this modest work 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 family, brothers Abdou, Ilyes, Taha and kaissar and sisters Ketzi, Ferdaws, Soroor, lamia and hanin for their endless love and my nephews Aksel, Massil, Sondousse, Ghilasse and Sidra.

To my bests frindes Noona, Aicha, Ichrake and Houda I got here with their encouragemen

To my dear friends who draw the smile Khadija and Samira.

To you Dhikra How lucky I am to have a golden sister like you and to share a precious moments with you thank you for your friendship.

Takoua Zerfaoui

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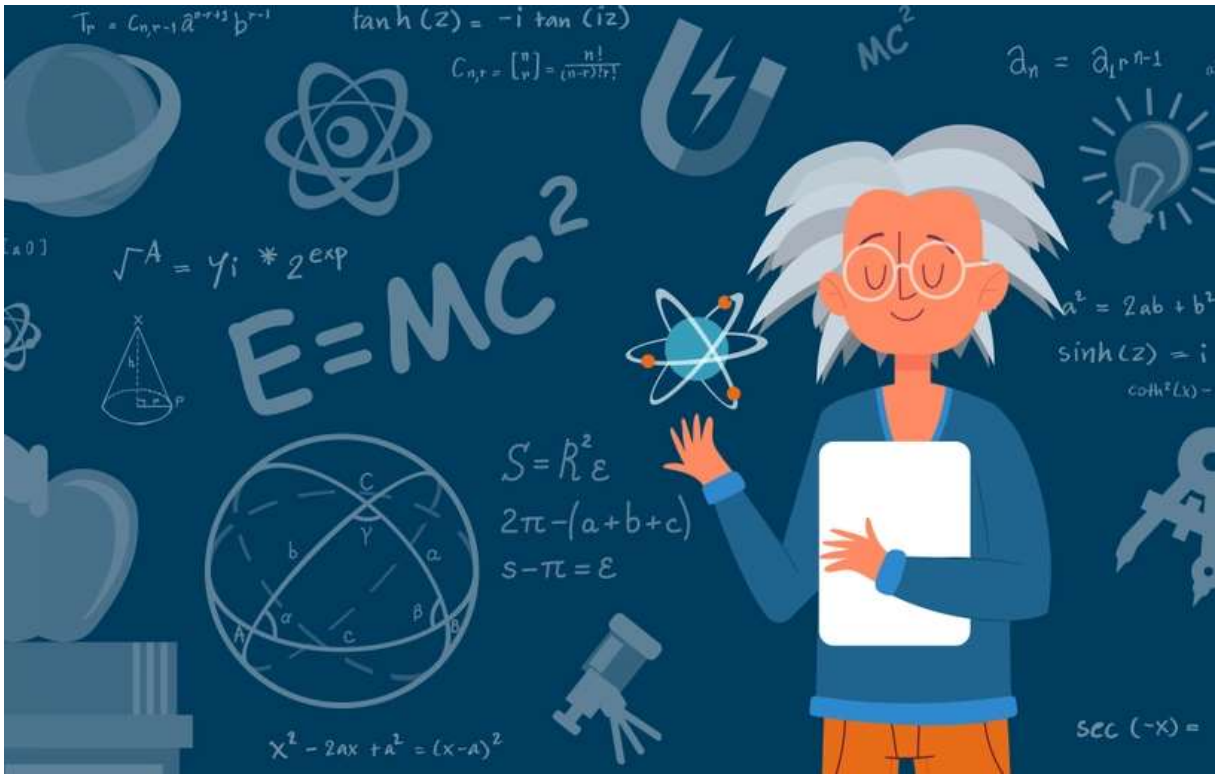
Symbol	Signification	Unit
M	Mass molar	g/mol
C	Solution concentration	mol/l
m	Mass	g
V	Volume	l
Ø	Diameter	m
T	Temperature	^{o}C
α	Absorption coefficient	cm^{-1}
n	Refractiveindex	
k	Extinction coefficient	
E_g	Energy of optical band gap	eV
T	Optical transmittance	%
I	Intensity of light	
t	Film thickness	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

List of abbreviations

SnO_2	Tin dioxide
PLD	Pulsed-laser deposition
MBE	Molecular Beame Eitaxy
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
SnCl2·2H2O	Tin (II) chloride dihydrate
SnCl4·5H2O	Tin tetrachloride pentahydrate
TCD	Tin (II) chloride dihydrate
V_{TCD}	Volume of tin (II) chloride dihydrate
$UV-Vis-NIR$	Ultraviolet-visible-near infrared
(v/v) methanol	Methanol volumetric concentration of an aqueous solution

General introduction



General introduction

In recent years, significant efforts have been made in the field of the development of thin films of transparent conductive oxides (TCOs) [1]. They are remarkable materials in many fields. The existence of their dual property, electrical conductivity and optical transparency [2]. TCOs films like SnO_2, ZnO and In_2O_3 have attracted the attention of many research workers due to their wide range of applications, such as solar cells and flat panel displays [3].

Tin dioxide (SnO_2) is one of the most widely used transparent conductive oxides (TCOs) in technology. In fact, over the last few decades it has experienced growing scientific and industrial interest in the form of thin layers due to its remarkable physical properties , tin dioxide is an n-type semiconductor and it has a wide band gap with high transparency and electrical conductivity [4], the films are chemically inert, mechanically hard, and can resist high temperature. It mainly occurs in the mineral cassiterite, and crystallizes with a tetragonal structure [3].

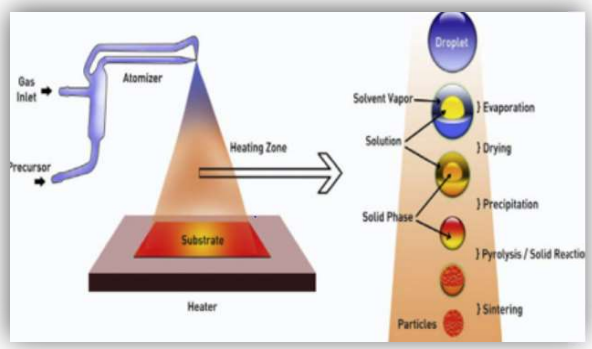
SnO_2 films can be prepared by different techniques, these techniques can be divided into two groups according to the nature of the sedimentation process. Physical methods include physical vapor deposition vacuum thermal evaporation technique, laser beam evaporation, Molecular Beam Epitaxy, and Electron beam evaporation [5]. Chemical methods include chemical vapor deposition, Sol-gel process, chemical bath deposition method, electrodeposition, and spray pyrolysis technique [6].

Spray pyrolysis is a processing technique to prepare dense and porous oxide films, ceramic coatings, and powders [7]. Unlike many other deposition techniques, spray pyrolysis represents a very simple and relatively cost-effective method that it does not require high quality substrates or chemicals [8].

The purpose of this work is the elaboration of thin films onto glass substrates heated at 350°C, by ultrasonic spray pyrolysis technique, from precursor in alcoholic solution of tin chloride (II) dihydrate ($SnCl_2{\cdot}2H_2O$), and the study of the effect of the solution concentration and solvent concentration 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

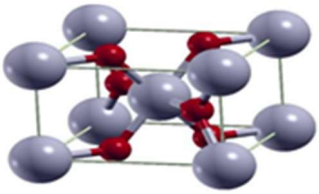
(LMSSEF) of Larbi Ben M'Hidi University in Om El Bouaghi. These films are characterized by UV-Visible-NIR double beam spectrophotometer and four-point probe technique to determine their optical and electrical properties, respectively. Our work is organized into three chapters as follows:

- The first chapter was devoted to the notions of thin films, the techniques of their elaboration, transparent conductive oxides, the essential properties of tin dioxide and the field of its applications.
- The second chapter is devoted to how to prepare thin films by adding to the various experimental techniques to distinguish our coating layers.
- The third chapter is devoted to discussing the experimental results obtained from the study of thin films.

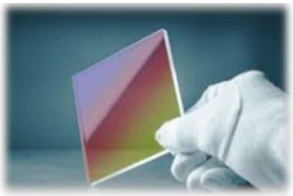


Chapter I

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

Thin film technology is the basic of astounding development in solid state electronics [3], they are material layers with thicknesses ranging from one atomic layer up to several micrometers. They are ubiquitous in the modern world and can be found in such diverse applications as mirrors, cutting tools eyeglasses, microelectronics, window glass, and solar cells [9].

I.1.2. Classification of thin films deposition techniques

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. The vast varieties of thin film materials use in their deposition processing and fabrication techniques methods which are possible [3].

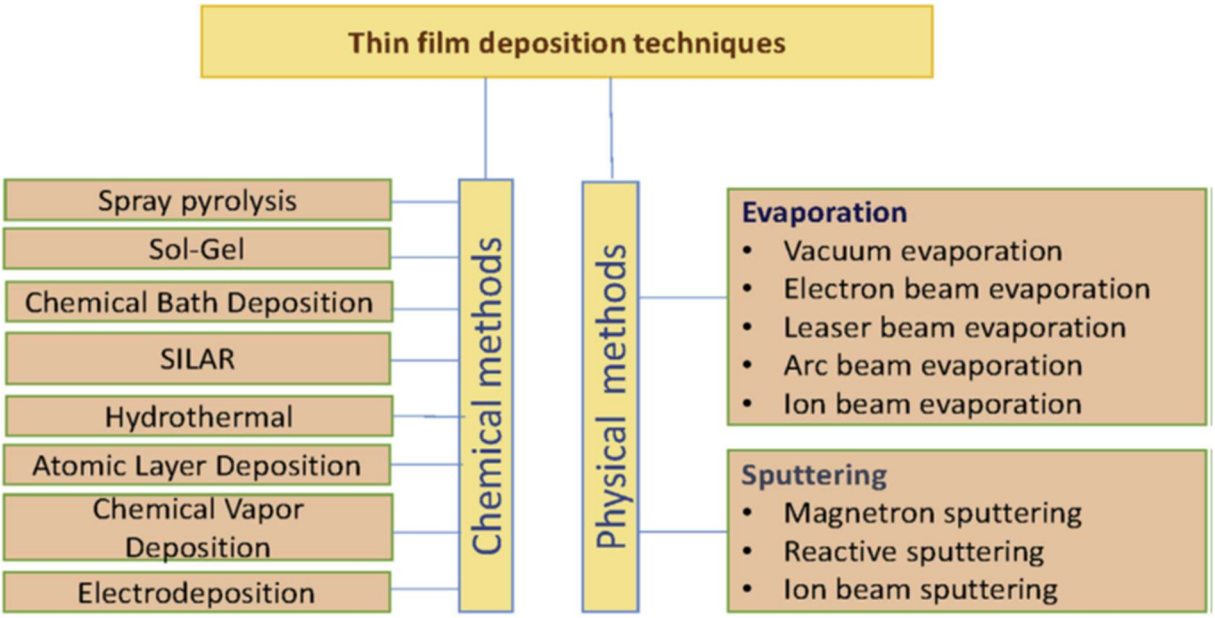


Figure I.1. Classification of thin film deposition technique [10].

The thin film materials are obtained by different ways of deposition[3], deposition methods are roughly divided in two categories, chemical vapor deposition (CVD) and physical vapor

deposition (PVD), although hybrid processes are not unheard of. PVD and CVD processes are differentiated by how material transport and film deposition is facilitate [9]. Figure I.1 shows the schematic of classification of thin film deposition technique.

I.1.2.1. Physical deposition techniques

PVD technology simply consists of evaporation or sublimation of the material to be deposited. The crucible of the latter is heated in a vacuum crucible at high temperature [2].

I.1.2.1.1. Evaporation techniques

In this method, the interconversion between the solid and vapor phase takes place in a vacuum environment. There are several evaporation methods available for thin-film deposition [10].

A. Vacuum thermal evaporation technique

Vacuum evaporation technique is one of the oldest and extensively used method for semiconducting thin film deposition at industrial scale. It is a simplest technique for synthesis of amorphous film especially chalcogenide films such as CdSSe, MnS, Ge-Te-Ga, and used to protect textiles from metal nanoparticles deposition [10, 11]. The vacuum helps to settle vapors of coating particles on the substrate where it convert back into the solid phase. The evaporation is carried out by electron beam heating or electrical heating.

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} to 10^{-9} mbar [12]. Figure I.2. Shows the schematic diagram of vacuum thermal evaporation technique.

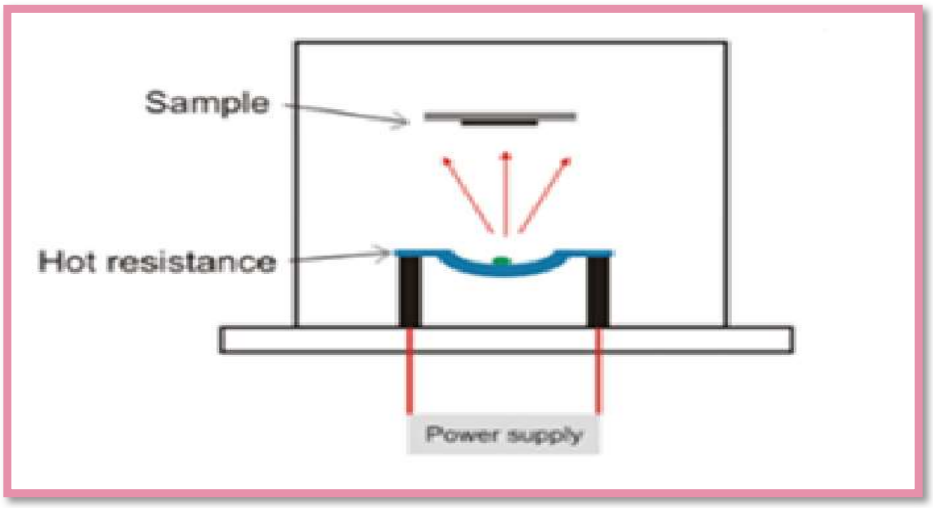


Figure I.2. Schematic of vacuum thermal evaporation technique.

B. Laser beam evaporation (Pulsed laser deposition)

For physical depositions, PLD requires lenses to focus the laser beam, in order to focus large energy density to ablate the target source and the vaporized materials eventually sublimate on the substrates. PLD is a clean and simple method to obtain a wide range of structures, compositions, and properties [13].

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.3 [12]. 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. 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) [14].

In the case of metal oxide thin films, oxygen is used to deposit the oxides metals. The coating of thin films through PLD follows three modes: Frank–van der Merwe, Volmer–Weber, and Stranski– Krastanov. PLD has some advantages over other physical deposition. Among them is the availability of less space for the board and the availability of software design [15].

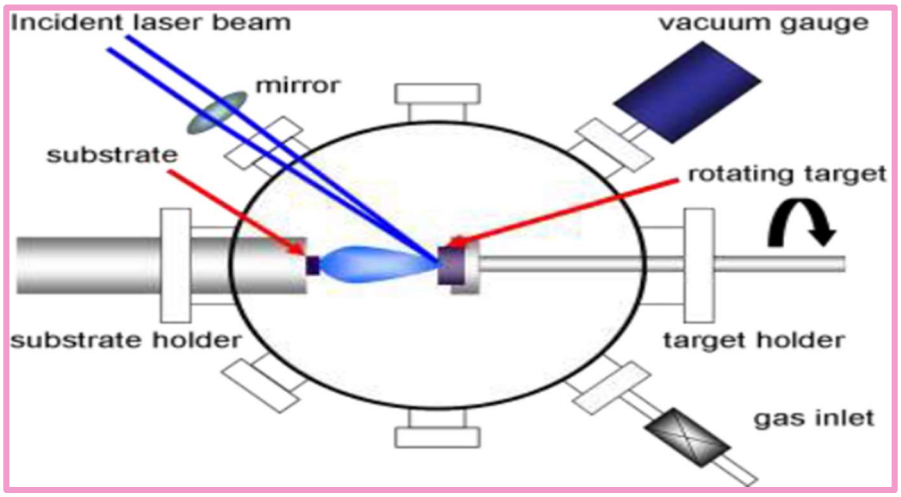


Figure I.3. Schematic of pulsed-laser deposition [9].

C. Molecular Beam Epitaxy

Molecular Beam Epitaxy (MBE) is an epitaxial process by which growth of materials takes place under ultra-high vacuum (UHV) conditions on a heated crystalline substrate by the interaction of adsorbed species supplied by atomic or molecular beams. The layers or deposits

have: (1) the same crystalline structure of the substrate or a structure with a similar symmetry and (2) a lattice parameter differing from that of the substrate by no more than ~10%. The beams generally have thermal energy and are produced by evaporation or sublimation of suitable materials contained in ultra-pure crucibles [16].

MBE have been considered the sophisticated technique in obtaining high-purity films because of its complexity in the process and expensive equipment is needed to achieve the purpose [17].

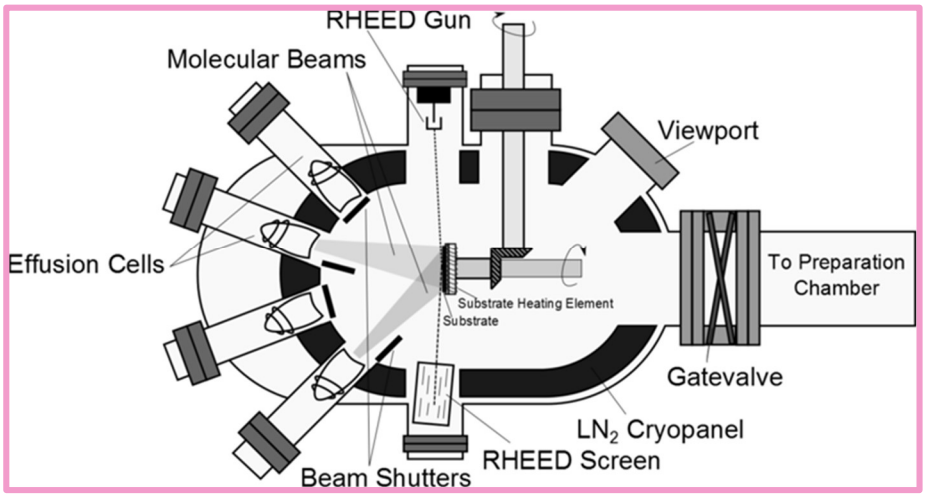


Figure I.4. Schematic of a typical system for molecular beam epitaxy (MBE).

E. Electron beam evaporation

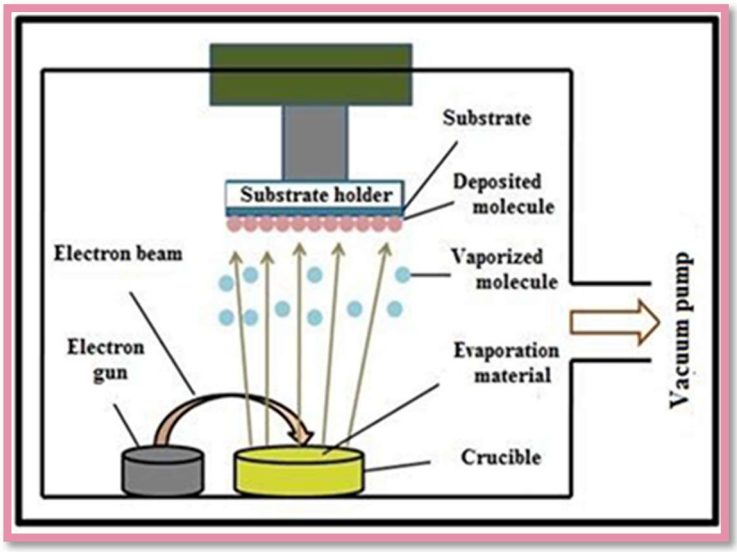


Figure I.5. Schematic diagram of electron beam evaporation [18].

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.5. Thin films prepared by electron beam evaporation are good quality and purity [18].

I.1.2.1.2. Sputtering

Sputtering is another physical vapor deposition process occurs in a vacuum chamber. A large piece of the material to deposited, known as a target, is bombarded with high energy argon ions from a glow discharge. When the argon ions strike the target, they knock off target atoms and molecules, which are then conveyed through the vacuum to the substrate, where they condense and form a thin film. Sputtering is most commonly used for depositing metal films, but, like evaporation, can also deposit insulating films with some slight process and equipment variations [9]. There are many other types of sputtering are: Magnetron Sputtering, Reactive Sputtering, and Ion Beam Sputtering [10].

It has several advantages, high-melting point materials can be easily formed by sputtering. The deposited films have composition similar to the composition of the starting materials [15]. The general sputtering method can be used to prepare a variety of materials such as metals, semiconductors, insulators, etc., and has the advantages of simple equipment, easy control, large coating area, and strong adhesion [19]. The diagram of the sputtering system is shown in Figure I.6.

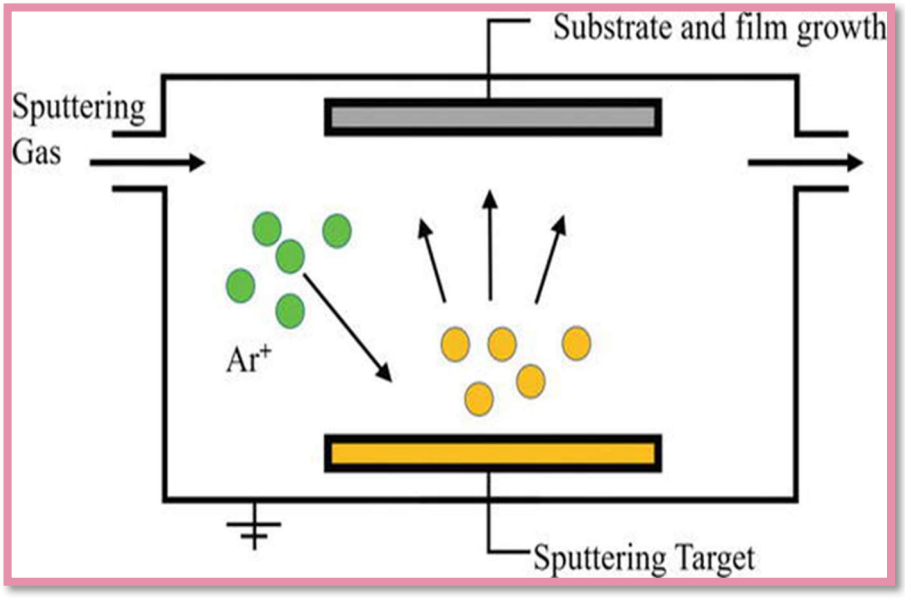


Figure I.6. Sputtering system diagram.

I.1.2.2. Chemical deposition methods

Chemical deposition involves a reaction wherein the product self-assembles and coats the substrate. It can be further divided into chemical vapor deposition, and chemical solution deposition [20].

I.1.2.2.1. Chemical Vapor Deposition (CVD)

Chemical Vapor Deposition (CVD) is a process in which the substrate is exposed to one or more volatile precursors, which react and/or decompose on the substrate surface to produce the desired thin film deposit [21]. CVD has been used historically for the fabrication of thin films composed of inorganic materials [22]. It includes many methods, the most important of which is:

A. Plasma Enhanced Chemical Vapor Deposition (PECVD)

PECVD is a plasma-enhanced CVD process where deposition is achieved by introducing reactant gases between a grounded electrode. The capacitive coupling between the electrodes excites the reactant gases into plasma, which induces a chemical reaction and results in the reaction product being, deposited on the substrate. The gear, which is placed on the grounded electrode, is typically heated to 300°C.

PECVD is used to deposit thin films of various materials on substrates at lower temperature than that of standard CVD technique [23]. The Figure I.7 below shows the method.

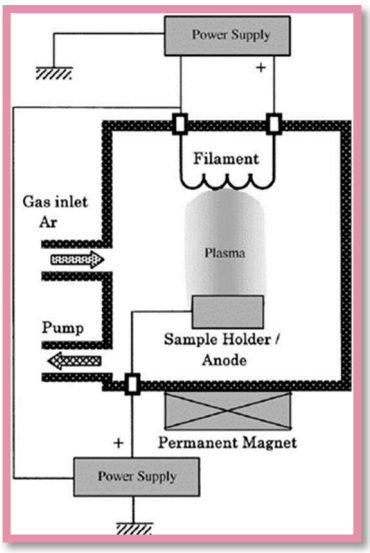


Figure I.7. PECVD system diagram.

There is a method that based on low pressure (LPCVD: Low Pressure Chemical Vapor Deposition) which ranges from 0.1 to 10 torr. Reactor configurations that have been used for LPCVD thin film processes include resistance heated tubular hot-wall reactors, vertical flow batch reactors and single-wafer reactors [24]. The figure I.8 shows the schematic of PECVD.

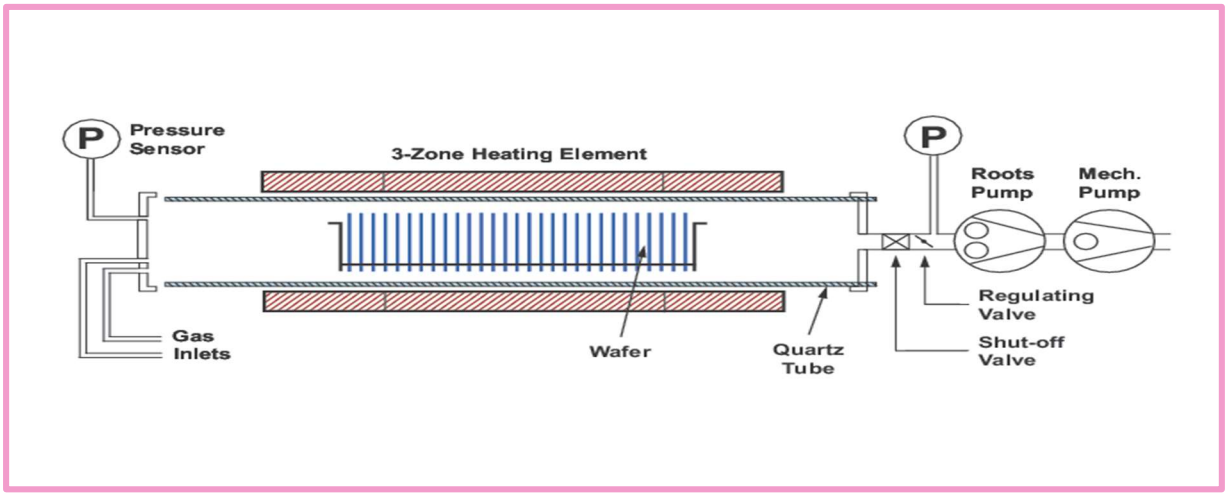


Figure I.8. Schematic description of LPCVD system.

I.1.2.2.2 Chemical solution deposition (CSD)

Chemical solution deposition (CSD) is an overarching term used to describe any technique whereby a chemical precursor solution is used to create a film [25]. The CSD is a very versatile method as it provides excellent stoichiometry control and coverage of large surface areas. The application procedures used for CSD are quite similar to what is used in the semiconductor industry for application of photoresist, which is a proven high throughput process [26].

It contains many methods, including the following:

A. Sol–Gel process

Sol-gel process is used for production of solid materials from small molecules. Oxides of silicon and titanium are the most popular materials for this process. The process involves conversion of monomers into a colloidal solution (sol) that acts as the precursor for an integrated network (or gel) of either discrete particles or network polymers [27]. There are two processes for the production of the films:

A.1. Dip coating

In this method (Figure I.9.a), the substrate is normally withdrawn vertically from a desired coating solution, which causes a complex process involving gravitational draining with

concurrent drying and continued condensation reactions. Environmental conditions (temperature, humidity, airflow) are very important parameters as much as pH of the solution, substrate surface, and withdrawn speed. They all affect film parameters the resulting [28].

A.2. Spin Coating

Spin coating process consists of putting the drops of liquid precursor on the surface of a spinning substrate (Figure I.9.b). The film formed on the substrate results from two balancing forces:

The centrifugal force (due to spinning) which drives the viscous sol radially outwards and viscous force (due to friction) which acts radially inwards. Spin coating is the cheapest film production method in silicon technology. However, thinner films (<100 nm) are hard to make and can waste 98% of the process materials [29].

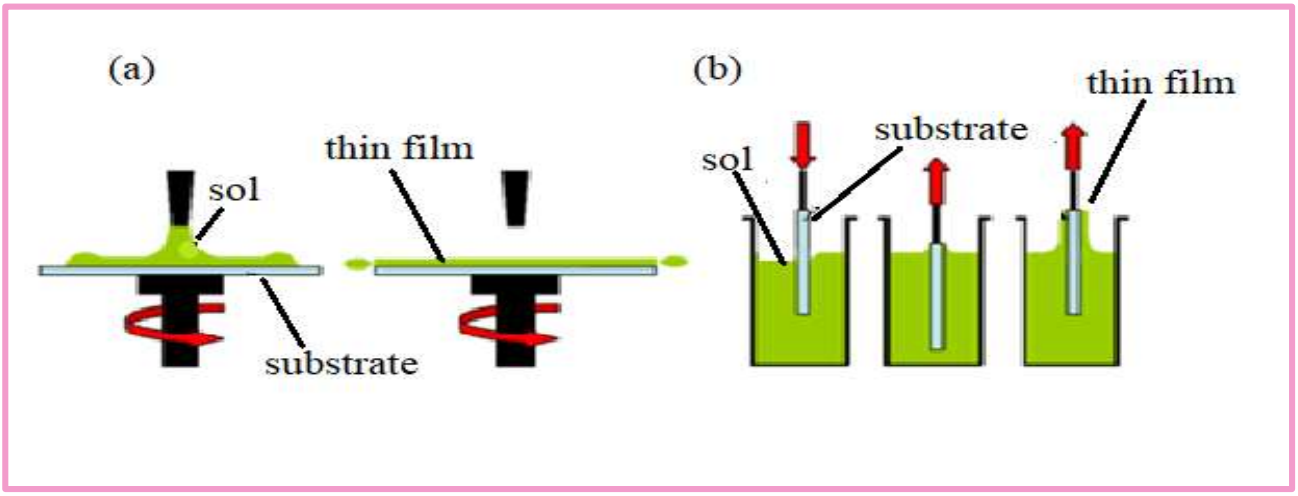


Figure I.9. Sol-gel process diagram **(a): Spin-coating, (b): Dip-coating.**

B. Chemical bath deposition process

The chemical bath deposition (CBD) method uses a controlled chemical reaction to deposit a thin film. In the typical experimental approach, the substrates are immersed in solution containing the chalcogenide source, metal ion, and complexing agent [30].

The preparation and characterization of thin films by chemical bath deposition have been reporting by many researchers [30]. The FigureI.9 shows the CBD method.

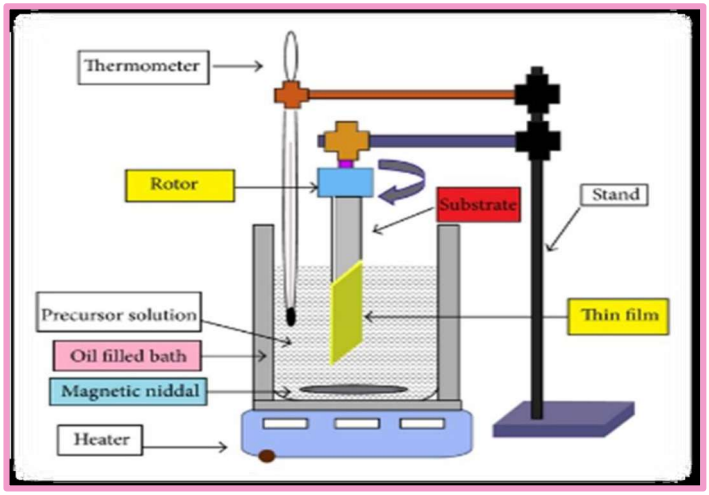


Figure I.10. Chemical bath deposition technique.

C. Electrodeposition

Electrodeposition is a non-vacuum electrochemical technique preferable for thin film deposition owing to its ability to deposit multicomponent alloys at low temperature. In this method deposition of thin metallic films is done onto the substrate by the reduction of cations without any unwanted reactions [31]. The FigureI.9 shows the thin films electrodeposition process.

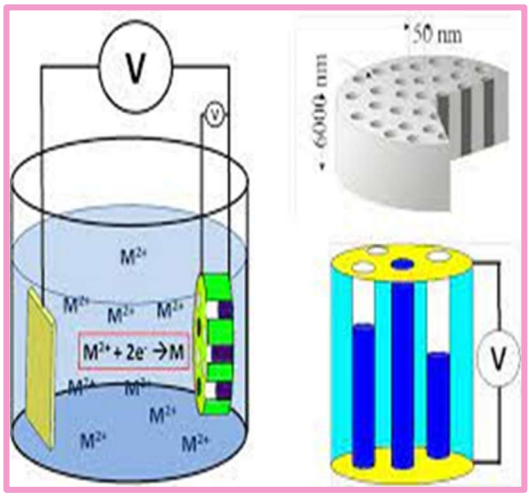


Figure I.11. Electrodeposition process to deposit thin films.

D. Spray pyrolysis technique

The thin films will be produced in this study by this technique. Due to its advantages, ease of use, and the advantages of the obtained thin films.

Spray pyrolysis is a technique that requires a precursor solution, a heated substrate, and atomizer. In this process, the solution is atomized into small drops and transferred to the heated substrate due to gas that generates thin films. The atomic cloud aerosol generates larger droplets due to the ultrasonic spraying method that determines the smaller droplets. That influences the surface morphology of the material. Spray pyrolysis is very efficient, cost effective, and utilizes simple equipment. The thin films produced have large surface area of substrate coverage and potential and homogeneity of mass synthesis [32]. The Figure I.12 shows the spray pyrolysis technique.

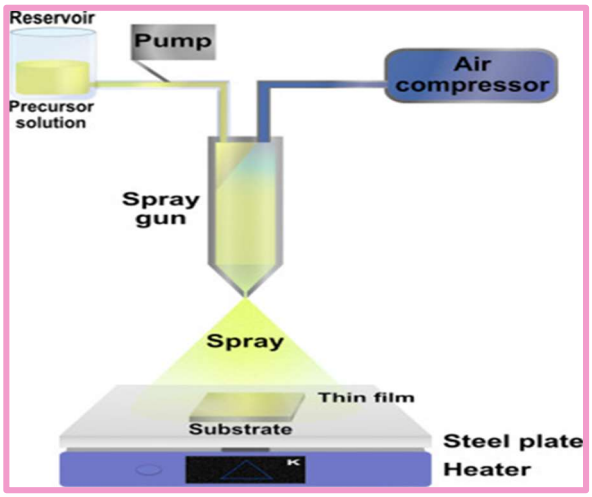


Figure I.12. Principle of spray process [33].

I.2. Transparent Conductive Oxides

Based on Electromagnetic Theory (Maxwell's equations), which could not permit a material to be both electrically conducting and optically transparent simultaneously. Optically transparent materials tend to be electrical insulators by virtue of their large band gaps. However, Transparent Conductive Oxides (TCOs) is a group of materials with unique optoelectrical properties [3].

TCOs are interesting materials for several applications, such as photovoltaic cells, optoelectronics, and catalytic applications. SnO_2 as TCO is available materiel and easy to deposit as thin films using several techniques such as sol-gel and pulsed laser deposition [34].

The TCO semiconductors suitable for transparent electrodes should have a band gap energy approximately above 3.1 eV (i.e., degenerate n-type or p-type semiconductors) [35, 36]. TCO are materials that exhibit a low electrical resistivity of the order of 10^{-4} (Ω.cm), and high carrier

concentration in the range (0.1-1.0)x10^{21} cm^{-3} while being transparent in the visible part of the electromagnetic spectrum, typically having an average visible transmittance of 80% [3].

I.2.1.Applications of TCOs materials

For their luminescence properties introduction TCO films have been widely used as a transparent conducting thin film materials for application in various fields such as solar cells, flat panel displays, smart windows, touch screens, optoelectronic devices, heat mirrors, liquid crystal displays (LCDs), organic light emitting diodes (OLEDs) and gas sensors[12].

Figure I.13. Some applications of TCOs [9].

I.2.2. Metal Oxides

Metal oxides are one of the most important where they widely characterized solid catalysts. Metal oxides are considered as heterogeneous catalysts and are applied for acid–base and redox reactions. Certain groups of metals, particularly transition metals, have attracted much attention because of their outer electron configuration [37]. They are chemical compounds formed into 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 [38].

They are applied widely in various reactions, which include oxidation, dehydration, dehydrogenation, and isomerization. The oxides of transition metals such as Nb_2O_5, WO_3, and TiO_2 are widely used as heterogeneous acid nanocatalysts. The mesopores of these transition metal -oxides allow the substrate inside the metal pores for the catalysed reaction [39].

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. The second family includes n-types (electron conduction). They fill the majority of gas sensor applications, as they are more stable [12].

I.3. Properties and applications of tin dioxide

I.3.1. Properties of tin dioxide

Is an inorganic compound with the chemical formula SnO_2. It mainly occurs in the mineral cassiterite and crystallizes with a tetragonal structure. It is a colorless, amphoteric and diamagnetic solid [38]. That is usually thought of, as an oxygen deficient n-type semiconductor. It is insoluble in water, but dissolves in alkalis and acids [9].

I.3.1.1. Structural properties of tin dioxide

SnO_2 has the tetragonal structure it (a = b = 4.738 Å and c = 3.186 Å) [9], it is a n-type semiconductor with wide energy band gap (3.7 eV). Its unit cell contains two tin and four oxygen atoms as is shown in Figure I.14 the tin atom is at the center of six oxygen atoms placed at the corners of a regular octahedron. Every oxygen atom is surrounded by three tin atoms at the corners of an equilateral triangle. If tin dioxide was completely stoichiometric, it would be an insulator [39].

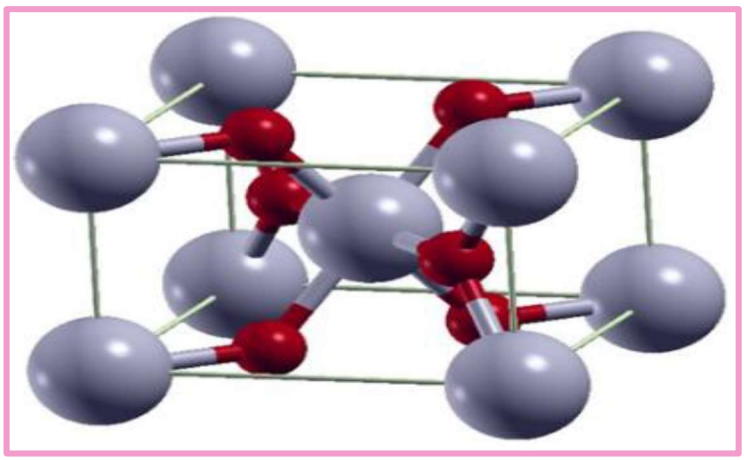


Figure I.14. Unit cell of SnO_2 in the rutile structure [41].

I.3.1.2. Optical properties of tin dioxide

The optical properties of a semiconductor are associated with the intrinsic and extrinsic effects. Intrinsic optical transitions take place between electrons in the conduction band and the holes in the valence band, including the effects of excitants due to the coulomb interaction. Extrinsic properties are related to dopants or defects which usually create discrete electronic states in the band gap, and influence absorption and emission processes [1].Due to its large gap energy, SnO_2 has optical transparency in the visible range and the near infrared which sometimes exceeds the 85% threshold [42]. Tin dioxide (SnO_2) is a semiconductor n-type with wide energy band gap (Eg= 3.6-4.2 eV) .The optical properties of SnO_2 depend on the electromagnetic wave interaction with the semiconductor electrons. And a direct band gap [43].

I.3.1.3. Electrical properties of tin dioxide

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 [3].

Table I.1. The optical and electrical properties of a tin dioxide film [44, 45].

Optical properties of SnO_2			**Electrical properties of SnO_2**		
Transmission in the visible range	**Refractive index**	**Optical band gap**	**Optical band gap nature**	**Conductivity type**	**Free carrier concentration (cm^{-3})**
85%	**1.8-2**	**3.6–4.2 eV**	**Direct**	**n**	**10^{18}-10^{20}**

1.3.2. Applications of tin dioxide

Some of the applications of tin dioxide are given below [46]:

- Magnetic properties of tin dioxide nanoparticles are used in magnetic data storage and magnetic resonance imaging.
- As catalysts, energy-saving coatings and anti-static coatings.
- As electrodes and anti-reflection coatings in solar cells.

- In the making of gas sensors, optoelectronic devices and resistors.
- Making of liquid crystal displays.

Very thin (100 nm), transparent films of tin dioxide are deposited on glass containers in order to increase their mechanical surface resistance. Thicker tin dioxide films (1 μm) provide electrically conductive layers, after appropriate doping with antimony or fluorine, which can be used as electrodes, light-emitting devices (for low-intensity light panels or display panels), fluorescent lamps, antistatic double glazing, heated windshields (mainly for aircraft), etc. Another property of these thick films is their ability to reflect a large proportion of IR radiation, while remaining transparent to visible radiation (use in double glazing for thermal insulation of windows) [12, 38].

Chapter II

Elaboration of tin dioxide thin films

Chapter II: Elaboration of tin oxide thin films

This chapter is divided into two parts, the first part will study the method of ultrasonic spray pyrolysis with the steps of preparing tin oxide thin films. While the methods of optical and electrical characterization of our films will be studied in the second part.

Part one: Ultrasonic spray pyrolysis technique

II.1. Choice of ultrasonic spray pyrolysis technique

The ultrasonic spray pyrolysis method is a cost-effective and adaptable technique based on an aerosol process for synthesizing nanoparticles and depositing thin films [43]. The spray pyrolysis technique has several advantages and the most important is:

- Ultrasonic spraying and atomization allow for full process control resulting in homogeneous high-quality output. Ultrasonic spray pyrolysis excels conventional techniques, e.g. CVD by its homogeneous distribution and its cost-efficiency.
- Due to its easy feasibility, flexibility, and cost-efficiency.
- Ultrasonic spray pyrolysis gives you full control over the most important process parameters such as: ultrasonic amplitude, precursor solution, precursor composition, viscosity, flow rate, deposition temperature, and substrate temperature.

II.2. Thermal effects of the substrate on droplets

Droplets impact on the substrate surface, spread into a ball-shaped structure, and undergo thermal decomposition. The shape and size of the ball depends on the momentum and volume of the droplet, as well as the substrate temperature (Figure II.1). Consequently, the film is usually composed of overlapping disks of metal salt being converted into oxides on the heated substrate [47].

In process A: In the lowest temperature regime, the droplet splashes onto the substrate and decomposes.

In process B: At medium temperature regime, the solvent evaporates completely during the flight of the droplet and dry precipitate hits the substrate, where decomposition occurs.

In process C: At high temperature regime, the solvent also evaporates before the droplet reaches the substrate. Then the solid precipitate melts and evaporates without decomposition and the vapor diffuses to the substrate to undergo the CVD process.

In process D: At very high temperature regime, the precursor evaporates before it reaches the substrate, thus solid particles are formed after the chemical reaction in the vapor phase.

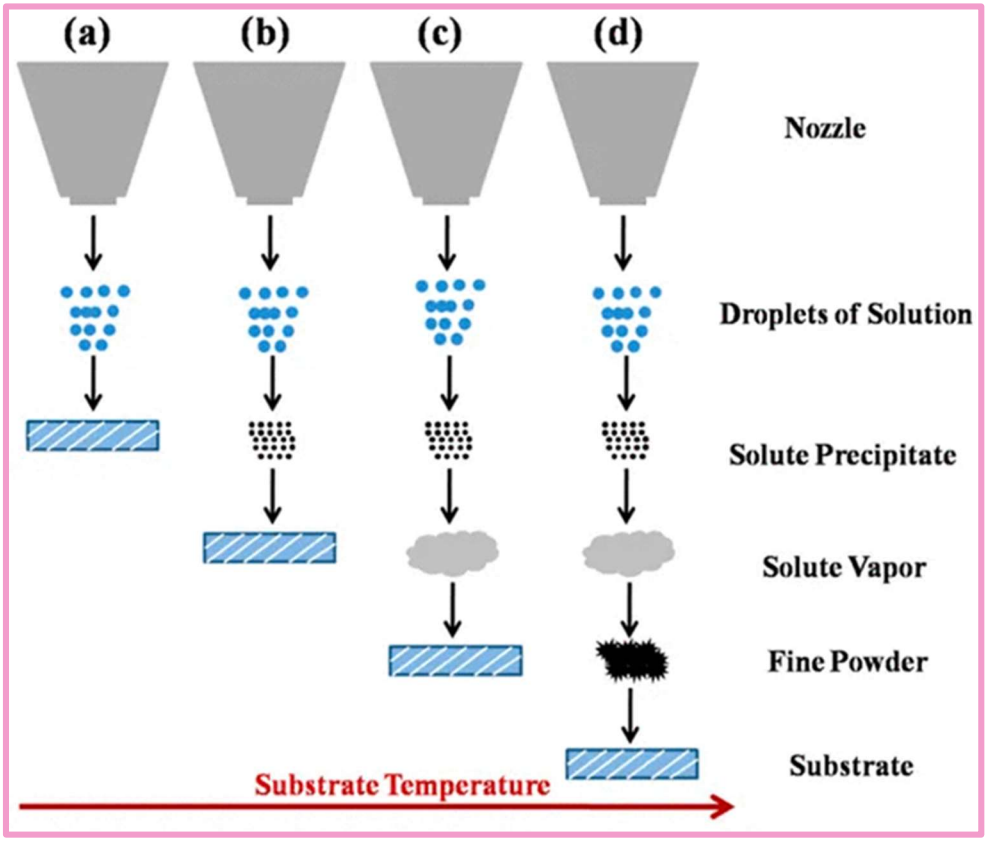


Figure II.1. Thermal effects of the substrate on droplets.

As the droplets move through the ambient, they experience physical and chemical changes depicted in FigureII.1. As the droplet traverses the ambient, there are four forces simultaneously acting on it, describing its path [44]. Those forces are gravitational, electrical, thermophoretic, and the Stokes force.

II.3. Elaboration of tin oxide films

On a glass substrate, we deposit thin films form aqueous solution alcohol containing tin chloride dihydrate ($SnCl_2 \cdot 2H_2O$) (99.8 %, Aldrich) was dissolved in a wide variety of precursor solution; solvent A (methanol: water; 25:75; v/v) and solvent B (methanol: water; 75:25; v/v) at different molarities (0.02M, 0.04M, 0.06M ,0.08M, and 0.10M).

II.3.1. Choice and preparation of substrate

In our work, the glass substrates used are equidistant (Figure II.2) that are sterilized by solvent solutions (distilled water, acetone, and ethanol) and dried with Joseph paper in the following steps:

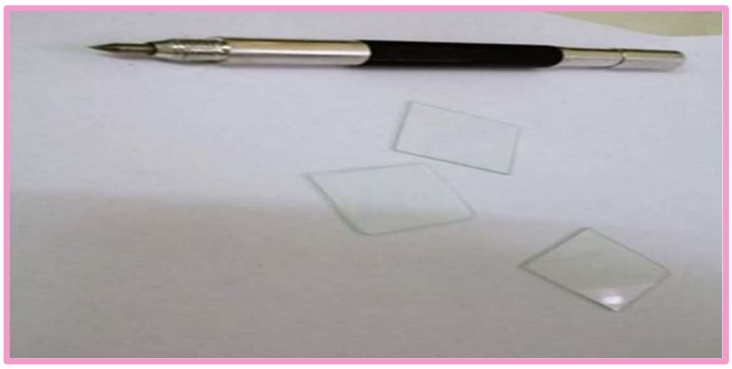


Figure II.2. Isometric glass substrates and diamond pen.

- The glass substrates have cut into equal dimensional substrates by pen of diamond point (Figure II.2 and Figure II.3.a),
- Soak the substrates in acetone to remove grease and fats,
- The substrates are immersed in distilled water to remove traces of acetone,
- Soak the substrates in ethanol to remove the organic matter. The substrates are again immersed in distilled water to remove traces ethanol (Figure II.3.b),

- The glass slides ultrasonically cleaned in each for about 5 min (Figures II.3.c and d), Drying the substrates using Joseph paper, so as not to leave any traces or impurities.

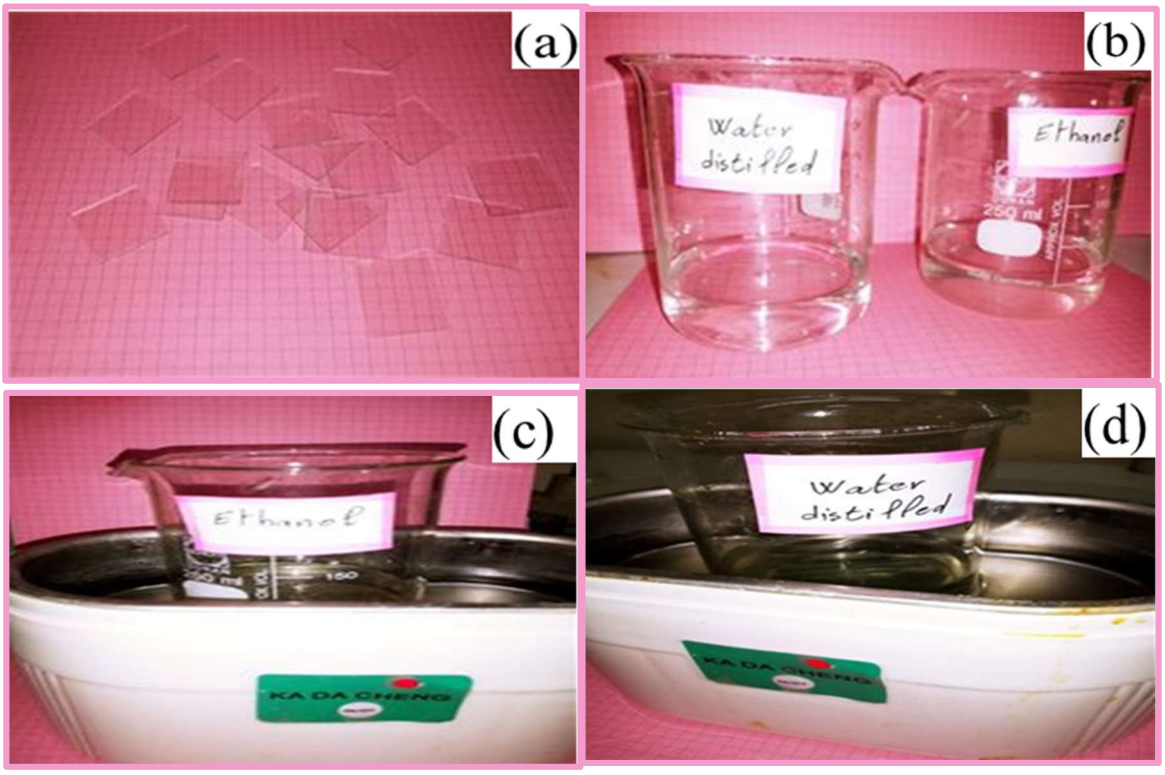


Figure II.3. Substrate preparation and cleaning process.

II.3.2. Preparation of precursor solutions

There are several precursors to obtain thin films of tin oxide such as tin tetrachloride pentahydrate ($SnCl_4 \cdot 5H_2O$) and tin dichloride dihydrate ($SnCl_2 \cdot 2H_2O$) [48].

In our work, we chose tin dichloride dihydrate (Figure II.4.a) dissolved in two different aqueous alcohol solutions; 25% (v/v) Methanol and 75% (v/v) Methanol. To obtain solution (V_{TCD}) of ($SnCl_2$ $2H_2O$) with molar mass (M = 225.63 g/mol), and molarity (C_1 = 0.1 mol/l).

By following these steps:

- Measure a mass of tin dichloride dihydrate **m**=C_1.M.V_{TCD} = (0.90±0.02)g, (Figure II.4.b) using a balance (**KERN442-432N)**.
- The previous mass was dissolved in an aqueous alcohol solution by volume V_{TCD}=40ml (Figures II.4.c and d).
- The solution was stirred with ultrasonic bath cleaners for about five minutes.
- From the main solution (C_1=0.1mol/l) for the both solvents, we prepare solutions with different molarities (C_2=0.08 mol/l, C_3=0.06mol/l, C_4=0.04mol/l, and C_5=0.02mol/l), the following relationships:

$$C_{n1}V_{n1}=C_{n2}V_n \qquad \text{(II.1)}$$

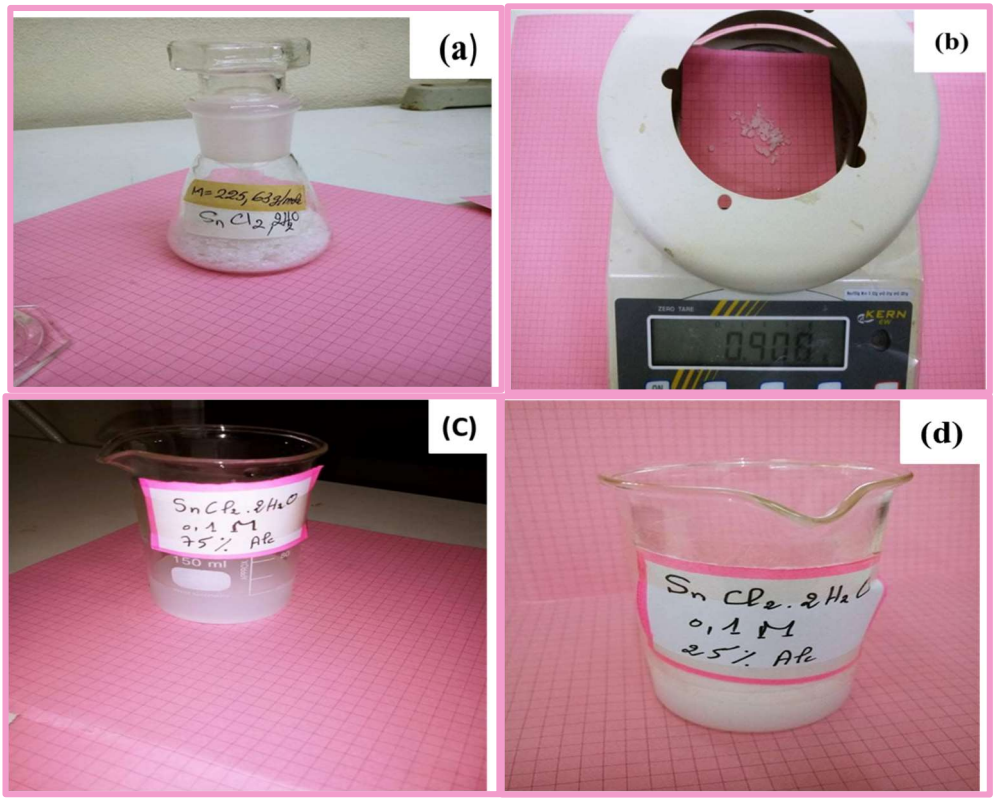


Figure II.4. Preparation of spraying solutions; **(a):** TCD, **(b)**: mass TCD, **(c):** TCD dissolved in methanol 75 % (v/v), **(d):** TCD dissolved in methanol 25 % (v/v).

II.3.3. Ultrasonic spray pyrolysis's equipment

We have developed tin oxide thin films using ultrasonic spray pyrolysis technique (FigureII.5) , at laboratory of material and structure of electromechanically systems and their reliability (LMSSE: *Laboratoire des Matériaux et Structure des Systèmes électromecaniques et leur Fiabilité*) of the University of Larbi Ben M'Hidi in Om El Bouaghi.

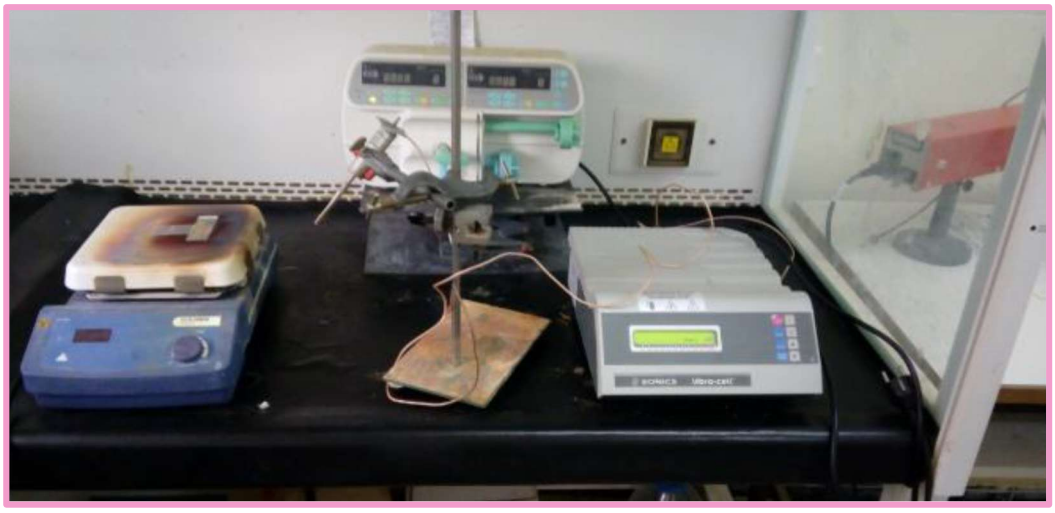


Figure II.5. Complete experimental devices of the ultrasonic spray pyrolysis technique.

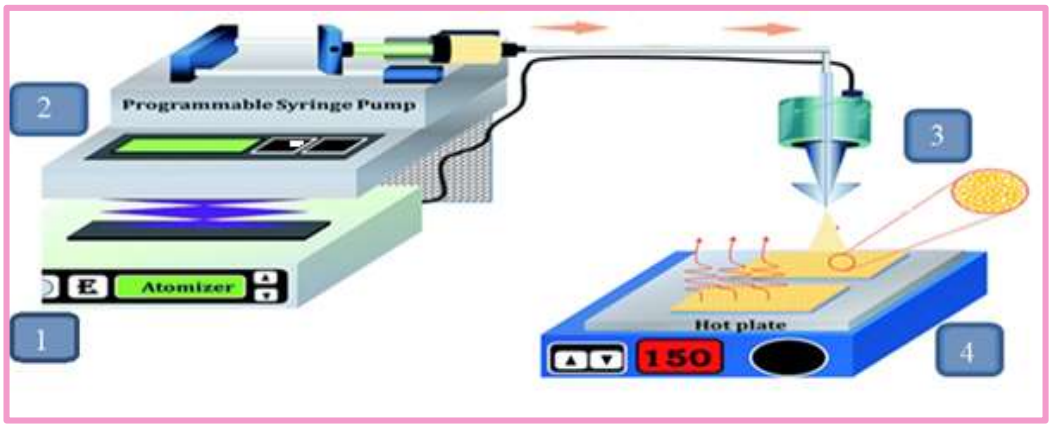


Figure II.6. The schematic experimental set up of the spray pyrolysis system [45].

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

1. **Ultrasonic generator (40 KHz)**: allows decomposing the solution at the atomizer to very fine droplets (Ø ~40 µm).

2. **Syringe pump with Syringe contains the solution:** Model PHOENIX D-CP (GF-FOURES) to control the precursor solution flow rate.
3. **Atomizer:** the atomizer is placed on a support height adjustable to control the nozzle spray distance.
4. **Substrate heater:** it is substrate holder (Ø =25 cm) heated by joule effect. The used temperature in our experiment is 350 C.

II.3.4. Preparation of thin films

After preparing the substrates and solutions, all samples are preparation through the following steps:

1. The prepared precursor solution of tin (II) chloride dihydrate ($SnCl_2 \cdot 2H_2O$) with different molarities (0.02M, 0.04M, 0.06M, 0.08M, and 0.01M) by using two different solvents (75 % Vol. mathanol+25 % Vol. distilled water) and (25 % Vol. methanol +75 % Vol. distilled water) is placed in the syringe to be sprayed in the form of very thin drops, using both ultrasonic generator and syringe pump, that precipitate over the glass substrate. Before deposition, the substrates (0.12 x 2.54 x 2.54) cm^3 were kept at ambient temperature to avoid thermal shock.
2. The substrates were heated to (350 °C) temperature for film.
3. The nozzle was kept at a distance of 5 cm from the substrate during deposition.
4. The spray rate was maintained at 60 ml/h using an ultrasonic generator (40 kHz).
5. The spraying time (5 min) was maintained each time. When aerosol droplets came close to the substrates, the compounds reacted to become a new chemical compound. SnO_2 formulation can be represented as[46]:

$$SnCl_2 + 2H_2O \rightarrow SnO_2 + Cl_2\uparrow + 2H_2\uparrow \qquad \text{(II.2)}$$

Table II.1. Process parameters for the spray deposition of SnO2 thin films.

Solvent	Aqueous alcohol solutions
(SnO_2 $2H_2O$) solution concentration	0.1M, 0.08M, 0.06M, 0.04M, 0.02M
Substrate temperature (°C)	350±10
Nozzle-substrate distance (cm)	5±0.5
Spray rate (ml/h)	60
Deposition time (min)	5

Part two: Characterization techniques of thin films

II.1. Optical characterization and measurement

Characterizations methods of transparent conductive oxides thin films are different, there are a lot of structural, electrical and optical methods which specialize the thin films and help to obtain characteristics (band gap, absorption coefficient, grain size, thickness, film types) of the deposited thin films [3]. Which is obtained by studying the transmission spectrum (optical transmittance curve as a function of wavelength) data given by UV-Vis Spectrophotometer.

II.1.1. Ultraviolet-visible spectroscopy

Ultraviolet-visible spectrophotometry is based on the interaction between electromagnetic radiation and matter in spectral fields. This method is considered non-destructive and depends on the transition from the ground state to the excited state of the electron [2].

Ultraviolet-visible spectroscopy or ultraviolet-visible spectrophotometry (UV-Vis or UV/Vis) 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 reference I_0. The ratio I/I_0 is called the transmittance and it is usually expressed as a percentage (T %). The absorbance, A is based on the transmittance [9].

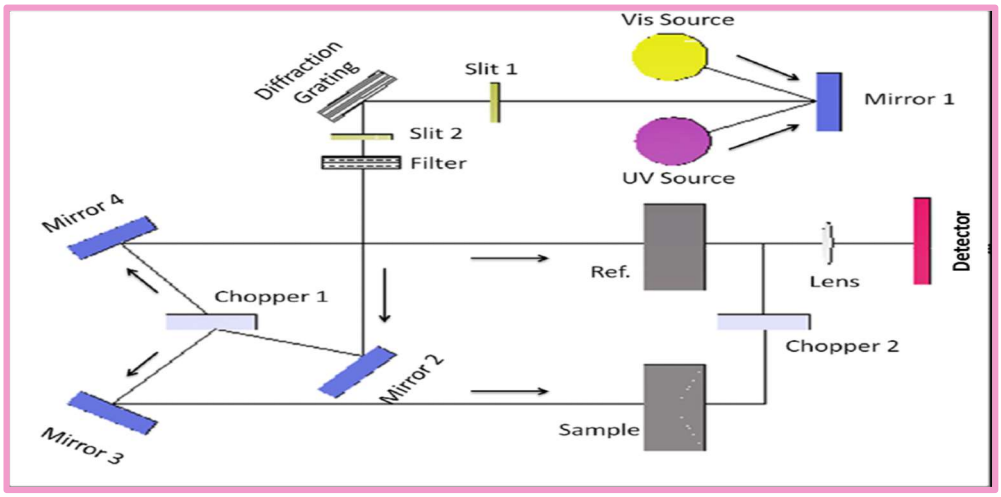


Figure II.7. Schematic spectrometer of UV-Vis [49].

Source consisting of two lamps which provide a continuum of emission over the entire UV-Visible wavelength range. A monochromator, by moving, makes it possible to select

wavelengths and therefore to scan the spectral range. The beam of photons of selected wavelength crosses a mirror which synchronizes the movement of the monochromator then the beam crosses the sample (glass+layer) and the reference (glass) [1].

The transmission curves of the thin layers studied are obtained using a UV-Vis type (V-630), the operating principle of which is represented by the diagram in Figure II.7. Computer-controlled, it can perform spectral scanning between (190 nm- 1100 nm). Spectra are processed using UVPC software. Then, we manage to record curves representing the variation of the transmittance as a function of the wavelength in the Ultra-Violet and Visible range. The exploitation of these curves makes it possible to determine optical characteristics such as the optical absorption threshold, the absorption coefficient. Figure II.8**.** Experimental device for UV-Vis-NIR spectroscopy.

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

II.1.1.1. Determination of film thickness and refractive index

The Method of Least Squares is a procedure to determine the best fit line to data; the proof uses simple calculus and linear algebra. The basic problem is to find graph y=f(x) given that, for $n \in \{1,\ldots.N\}$, the pairs (x_n, y_n) are observed [50]. Least squares regression is used to predict the behavior of dependent variables. We determine the thickness and refractive index of tin oxide thin films from the spectrum of transmittance, using Fit software that allows to vary a number of parameters. We use the least squares method to adjust a simulated transmittance curve to that measured (Figure I.9) [51].

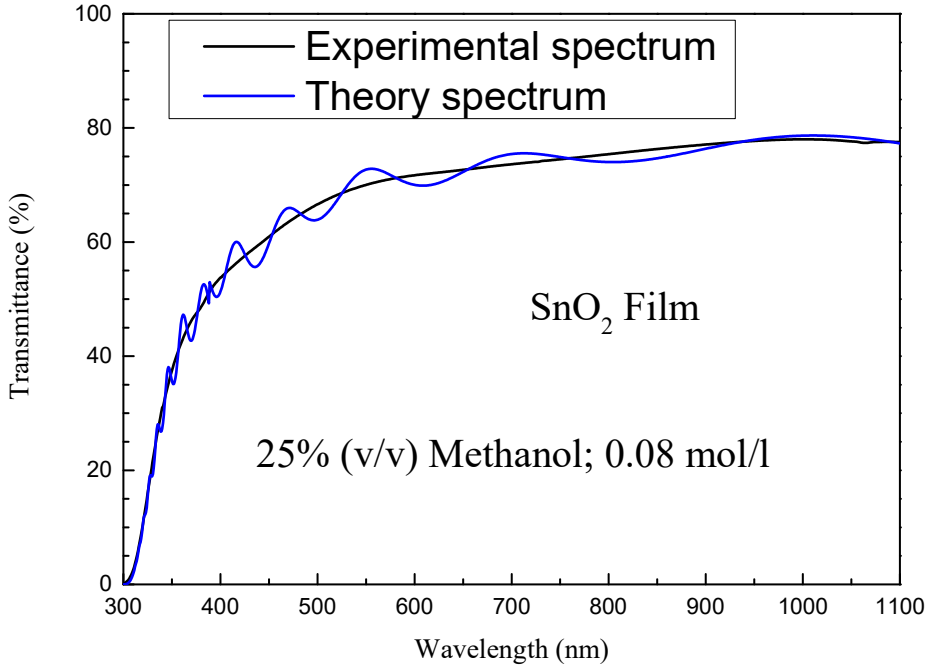


Figure II.9. Fitting the measured transmittance spectra to Swanepoel's method.

II.1.1.2. Determination of absorption coefficient and optical band gap

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, the band gap energy. A diagram illustrating the band gap is shown in FigureII.10 [9].

In order to find the band gap *(E_g)* values of films, initially the absorption coefficient *(α)* should be identified by the relation [52]:

$$\alpha = \frac{1}{d} ln \left(\frac{1}{T}\right) \qquad \text{(II.6)}$$

In the spectrum domain where light is absorbed and knowing the film thickness *(d),* the film absorption coefficient *α (λ)* is deduced from *T (λ)* through the Beer–Lambert law [2]:

$$T = e^{-\alpha d} \qquad \text{(II.7)}$$

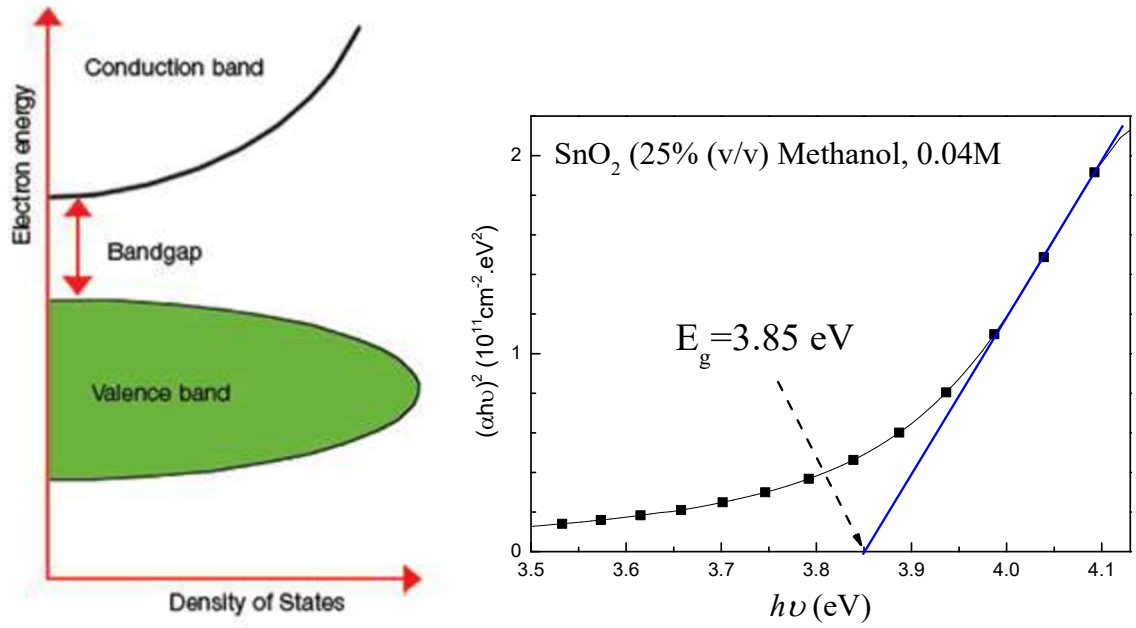


Figure II.10. Explanation of band gap [9].

where:

T is the transmittance and d is the film thickness. The optical band gap of SnO_2 thin film is obtained from the Tauc formula [52]:

$$(\alpha h\nu)^n = A(h\nu - E_g) \qquad \text{(II.8)}$$

where:

h ν: Energy of incident photon (eV).

A: Constant dependent on electron-hole mobility.

E_g: Energy of the optical gap (eV).

The Eg value is determined for direct transition (n=2) by plotting $(\alpha h\nu)^2$ versus $(h\nu)$ and extrapolating the linear region of the plot to zero absorption ($(\alpha h\nu)^2 = 0$).

II.1.1.3. Determination of Urbach Energy

Another important parameter that characterizes the disorder of the material is the energy of the Urbach tail. According to Urbach's law, the expression of the absorption coefficient is according to the equation II.9 [2].

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

where:

α_0: Constant.

E_{Urb}: Energy of Urbach.

By plotting lnα as a function of hυ (Figure II.11), we can access the value of E_{Urb}

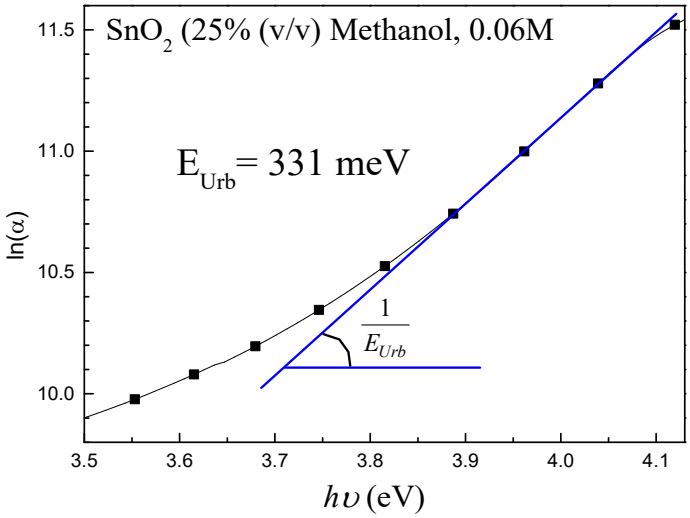


Figure II.11. Determination of Urbach energy

II.2. Electrical properties

Besides the basic optical properties, the electronic properties are of particular interest in thin films. Especially the conductivity/resistivity is of interest for electrical applications. To reliably determine the resistance of the manufactured layers, a four-terminal sensing method was applied [53].

This method is employed when the sample is in the form of a thin wafer, such as a thin semiconductor material deposited on a substrate. The sample is millimeter in size and having a thickness *(d)*. It consists of four probesarranged linearly in a straight line at equal distance (S) from each other. A constant current *(I)* is passed through the two external probes and the potentialdrop of voltage *(V)* across the middle two probes is measured (Figure I.11) [2].

Since each pair of the four pins was equidistant during the measurement, and the thickness of the layer is much smaller than its lateral dimension as well as the distance between the pins, the sheet resistance (ρ_s) can be calculated as follows [54].

$$\rho_s = \beta\left(\frac{V}{I}\right) \qquad \text{(II.10)}$$

β It is a geometric factor and in the case of semi-infinite thin films it is equal to $\frac{\pi}{ln2}$.

Since the film thickness *(d)* is known from the optical transmittance measurements, the material electrical conductivity (σ) can be calculated:

$$\sigma = \frac{1}{\rho_s d} \qquad \text{(II.11)}$$

In order to know the electrical surface resistivity (ρ_s) and electrical conductivity (σ) of tin oxide thin films, we used jandel four-point probe device where the LMSSEF laboratory of Larbi ben M 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.12).

Figure II.12.Four-point probe + keitheley 2400 Source Meter.

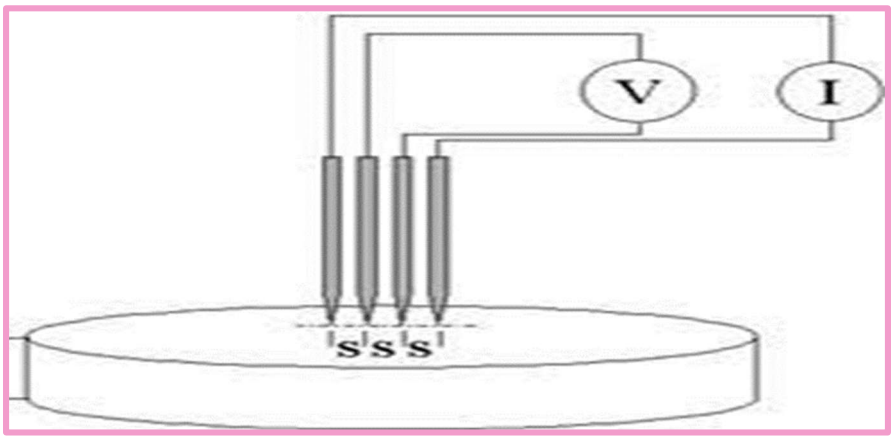


Figure II.11.Diagram representing the principle of the four-point method.

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 0.10 mol/l) using two different solvent concentrations with constant deposition conditions.

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

III.1. Effect of solvent concentration and solution concentration on color of our samples

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 0.10 mol/l) using two different solvent concentrations (75 % Vol. methanol+25 % Vol. distilled water) and (25 % Vol. methanol+75 % Vol. distilled water).

A gradation in color from light to dark yellow was observed for samples deposited with different solution concentrations from 0.02 to 0.10 mol/l using an aqueous alcohol solution. This may be due to the increase in the thickness of the samples due to the increase in the amount of material deposited with increasing molarity [55].

It was also noticed that the color of samples prepared with 25% (v/v) methanol is dark yellow compared to samples prepared with 75% (v/v) methanol. Through observation, it can be said that the latter has high transparency compared to the other.

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

	Bare substrate	**C_1=0.10M**	**C_2=0.08M**	**C_3=0.06M**	**C_4=0.04M**	**C_5=0.02M**
25% (v/v) methanol						
75% (v/v) methanol						

III.2. Effect of solvent concentration and solution concentration on the optical transmittance of tin oxide

The transmittance spectra obtained by UV-visible spectroscopy as function of wavelength over spectral range 300-1100 nm are showing.

Figure III.1 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 ultrasonic spray pyrolysis technique, with different solution concentrations of tin (II) chloride dihydrate using 25% (v/v) methanol (Figure III.1.a), and 75% (v/v) methanol (Figure III.1.b) as a solvent with the precise experimental conditions (T_S=350°C and t_D=5 min).

The change of curves is convergent and can be divided into two fields:

- In the field [300-450 nm], we observe a low optical transmittance followed by a strong energy absorption, and a large energy. Which corresponds to the basic absorption ($\lambda <$ 450 nm). This absorption is due to the band-to-band electronic transition (from the valence band to the conduction band). This region is exploited for the determination the energy of the optical gap (Eg), the Urbach parameter (E_{Urb}), and the type of transition (direct or indirect) according to the method detailed in chapter II [2, 51].

- A region of strong transparency is located between 450 and 1100 nm. The value of the transmission is about 50-70 % for 25% (v/v) methanol and about 70-85% for 75% (v/v) methanol. In this wavelength range which corresponds to the visible and near-infrared region. This region is exploited for the determination of the layer thickness [2, 56]. Where the following was observed.

✓ Interference fringes are not observed in the of the solvent concentration "25 % (v/v) methanol and 75 % (v/v) methanol". This can be explained by preparation conditions, oxygen deficiency in the material, surface roughness of the thin films, and also the change of our samples color [57, 55].

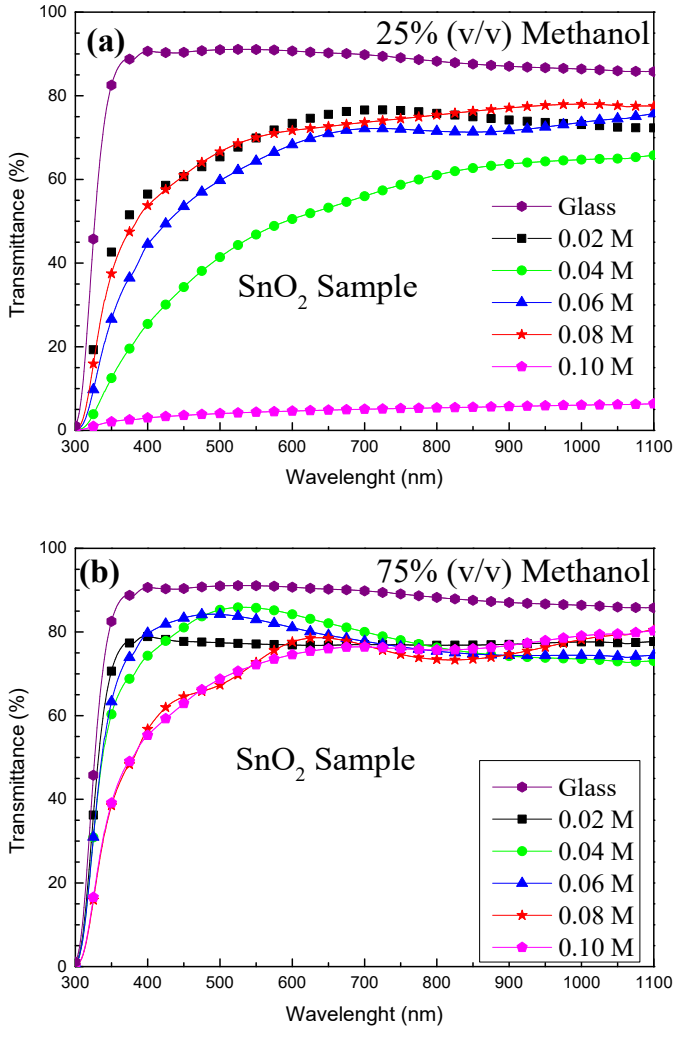


Figure III.1. Optical transmittance spectra of SnO_2 samples at different solution concentrations using two different solvent concentrations **(a):** 25% (v/v) methanol **(b):** 75% (v/v) methanol.

Figure III.2 incident photon in the UV-Vis-NIR range, recorded in the range from 300 to 1100 nm obtained of tin oxide thin films prepared by ultrasonic spray pyrolysis technique represents typical spectra of the variation in optical transmittance as a function of the wavelength of the incident photon in the UV-Vis-NIR domain.

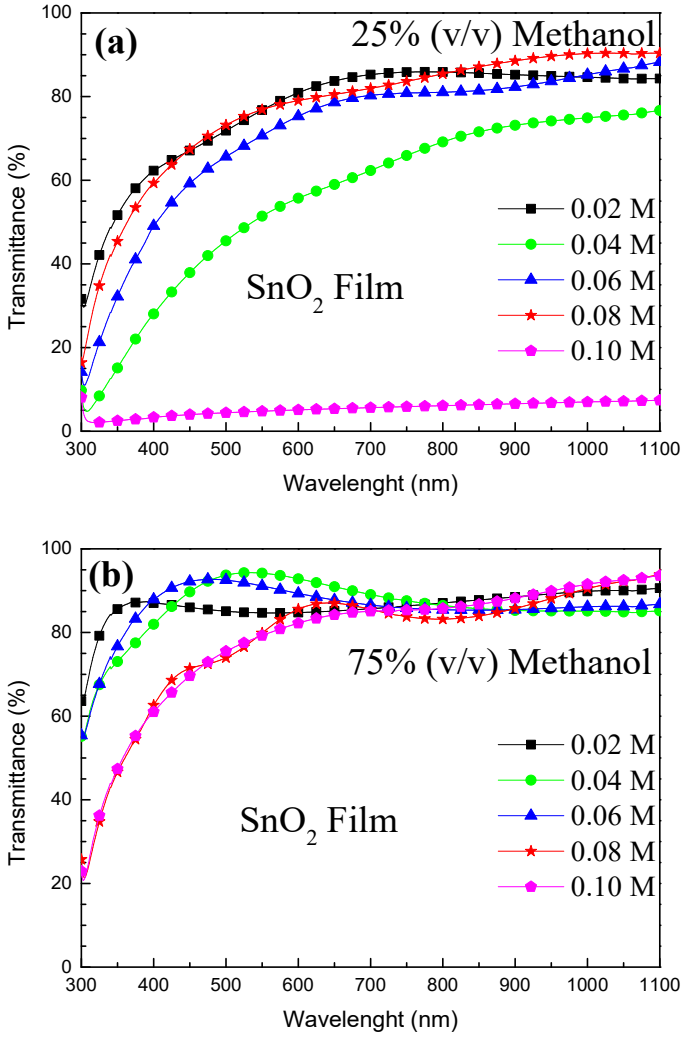


Figure III.2. Optical transmittance spectra of SnO_2 thin films at different solution concentrations using two different solvent concentrations; **(a):** 25% (v/v) methanol, **(b):** 75% (v/v) methanol.

Where the following has been noted:

- The decrease in the percentage of transparency with an increase in molarity, this is due to the increase the tin atoms (Amount of material), which is the reason for the change in color from lighter to darker, which is followed by an increase in the thickness of the sample.

- The transparency in the case of 25% (v/v) methanol is less than the transparency in the case of 75% (v/v) methanol. We can explain this that the solubility of ($SnCl_2.2H_2O$) in 75% (v/v) methanol is better than 25% (v/v) methanol, since in a 75% (v/v) methanol solution the drop will take time for enough. Therefore, the SnO_2 precipitates well compared to a solution of 25% (v/v) methanol and also the Cl evaporates during preparation the film, and1 the membranes are rich in oxygen, unlike a solution of 25% (v/v) methanol.

- The variation of transparency of all samples prepared with 25% (v/v) methanol decreases with the decrease in the wavelength of the incident photon and this indicates oxygen significant poverty compared to samples prepared with 75% (v/v) methanol that there are diffractions in the visible region [57], as shown in the figure III.3, which represents the change in the transparency ratio in terms of the wavelength of the tin oxide films in both cases 25% (v/v) and 75% (v/v) methanol at a concentration of 0.08M.

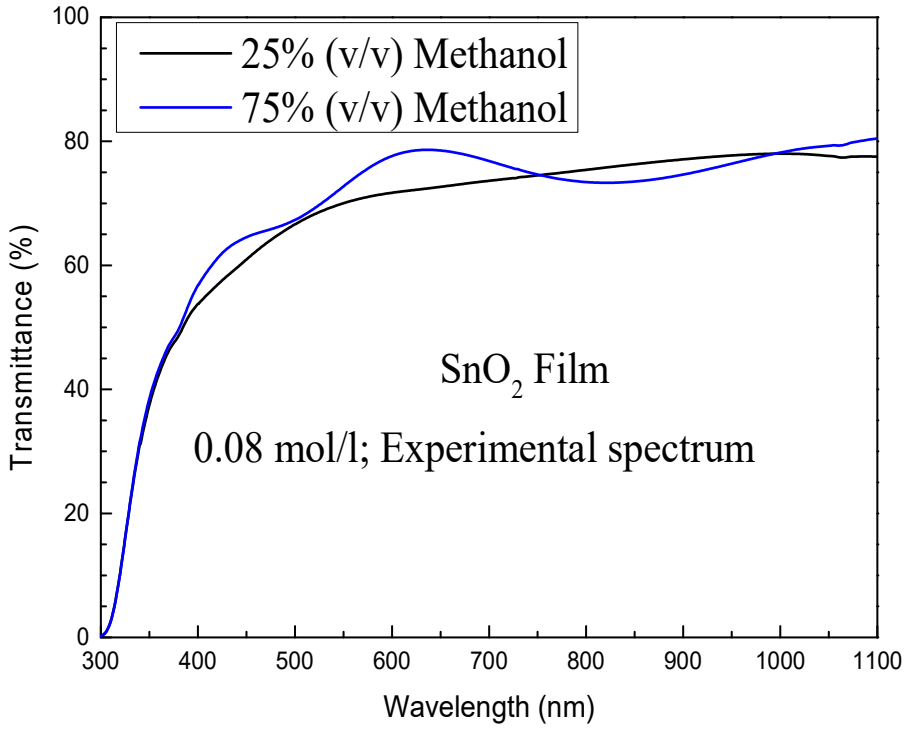


Figure III.3. The change in the transparency ratio in terms of the wavelength of the tin oxide films deposited at 0.08 M with different solvent concentrations.

III.3. Effect of solvent concentration 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 least squares methods which was explained than in chapter II.

Figure III.4 shows the variation of thickness of tin oxide thin films deposited by ultrasonic spray pyrolysis as a function of the solution concentration of the solution using two alcoholic solutions.

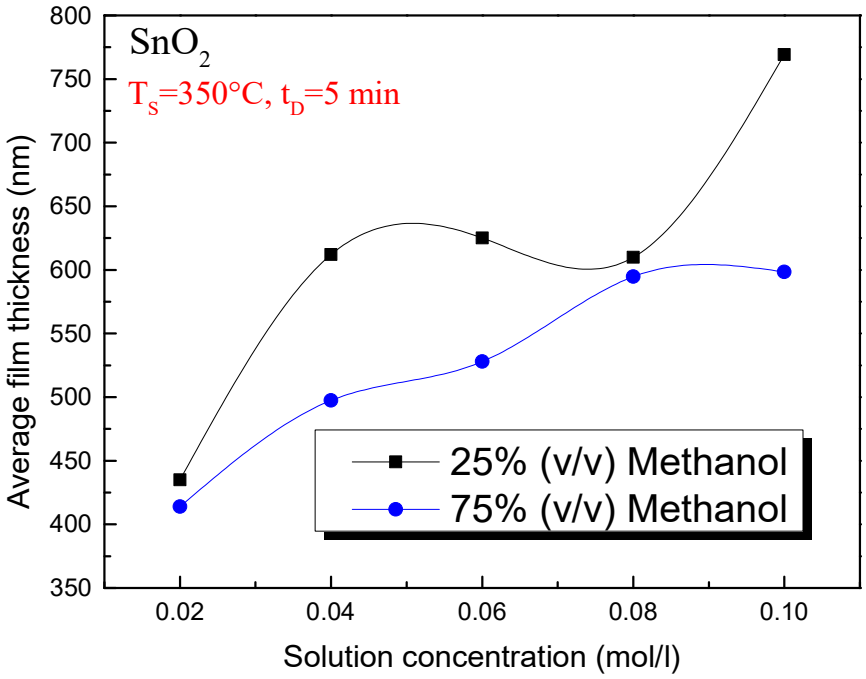


Figure III.4. Variation of average thickness of SnO_2 film with solution concentration.

The proportionality between increasing the thickness and increasing the concentration of the solution was observed, and it was noted that the thickness values ranged between 425 and 775 nm at 25% (v/v) methanol and between 150 and 250 nm at 75% (v/v) methanol.

The increase in thickness can be explained by an increase in the amount of material deposited (that is, there are more materials that contribute to the formation of membranes) [12].

It was also observed that the thickness of the films obtained with 25% (v/v) methanol is greater than the thickness of the films obtained with 75% (v/v) methanol. This may be due to:

The reaction rate of a 75% (v/v) methanol solution is greater than the reaction rate of a 25% (v/v) methanol solution with heat, since the increase in the reaction corresponds to a decrease in the volume of solute (granules), which means that the precipitated particles of smaller size give a smaller thickness and a denser substance, unlike 25 % (v/v) methanol, whose molecules are larger, resulting in an unorganized crystal structure and the presence of porosity in the film.

III.4. Effect of solvent concentration and solution concentration on the optical band gap of tin oxide

By using the optical process (Chapter II), the optical bandgap energy values E_g for tin oxide were determined.

As a reminder, we know that the band gap is an energy field in which electrons are not present. It represents the energy difference between the highest valence band and the lowest conduction band [56].

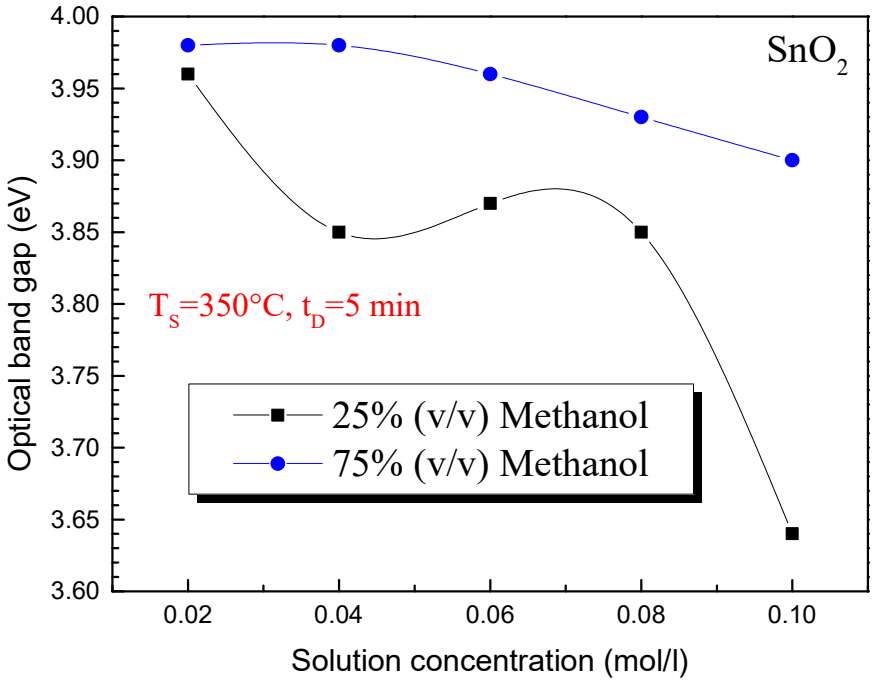


Figure III.5. Variation of optical band gap of SnO_2 with solution concentration using different solvent concentrations.

Figure III.5 represents the change of the optical bandgap as a function of solution concentration. From the previous information, we know that the optical bandgap of tin oxide

varies between 3.6 and 4.2 eV [57], which corresponds to the optical bandgap values of the prepared tin oxide films, which range from 3.63 to 3.98 eV.

Where it was observed that the optical bandgap decreases with increasing solution concentration in both cases of solvent concentration (75% (v/v) methanol and 25% (v/v) methanol).

This decrease may be due to the increases of number of molecules that therefore there is not enough time to set them in the right place, which leads to: creates crystal defects [9], the enhancement in photon scattering, create lattice strain, and the decreases of the grain size [12,15,9].

As these defects are more in the materials prepared using the solvent 25% (v/v) methanol compared to the other solvent (75% (v/v) methanol), which led to a decrease in the band gap value.

There is also be seen an obvious difference in the drop of optical bandgap that according to the solvent concentration used, as observed in the case of 25% (v/v) methanol, decreasing with higher values compared to 75% (v/v) methanol. This may be due to the difference in oxygen poverty. That is, the amount of tin deposited in 25% methanol is much greater than that in 75% (v/v) methanol. This results in an increase in charge carriers, which in turn can be observed at the 0.10 M point at 25% (v/v) methanol. The value of the gap is that films are almost lost at this point. A semiconductor becomes a conductor.

III.5. Effect of solvent concentration and solution concentration on the Urbach energy of tin oxide

In the process of deposition by ultrasonic spray pyrolysis the growth of the film takes place by thermal decomposition of a precipitate at the level of the substrate resulting from the vaporization of the droplets of the aerosol. In this situation, the material that forms contains different types of defects leading to disorder in the structure [2].

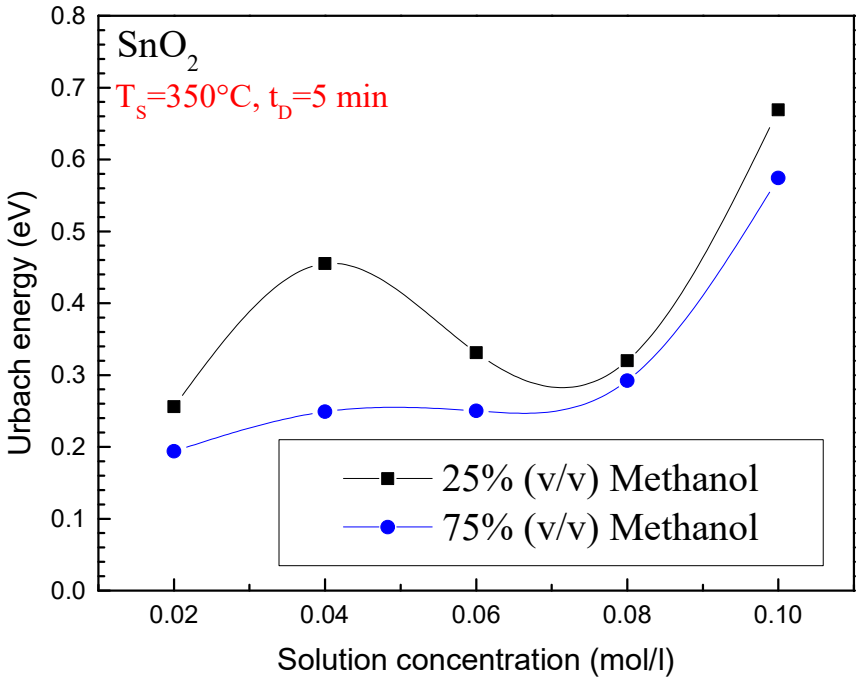


Figure III.6. Variation of Urbach energy of SnO_2 thin films with solution concentration.

In Figure III.6, we reported the variation of Urbach energy of SnO_2 films as a function of solution concentration using two different solvent types (25% (v/v) methanol and 75% (v/v) methanol).

By the increase in solution concentration from 0.02 mol/l to 0.10 mol/l by using both precursors, the Urbach energy is increase from 0.20 eV to 0.56 eV and from 0.24 eV to 0.66 eV for using 75% (v/v) methanol and 25% (v/v) 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 [58].

The increase in Urbach energy can also be explained by the decrease in the optical bandgap [56]. Figure 7.III. (a and b) showed the inverse relationship between the optical bandgap and the Urbach energy as a function of concentration using two different solvent concentrations.

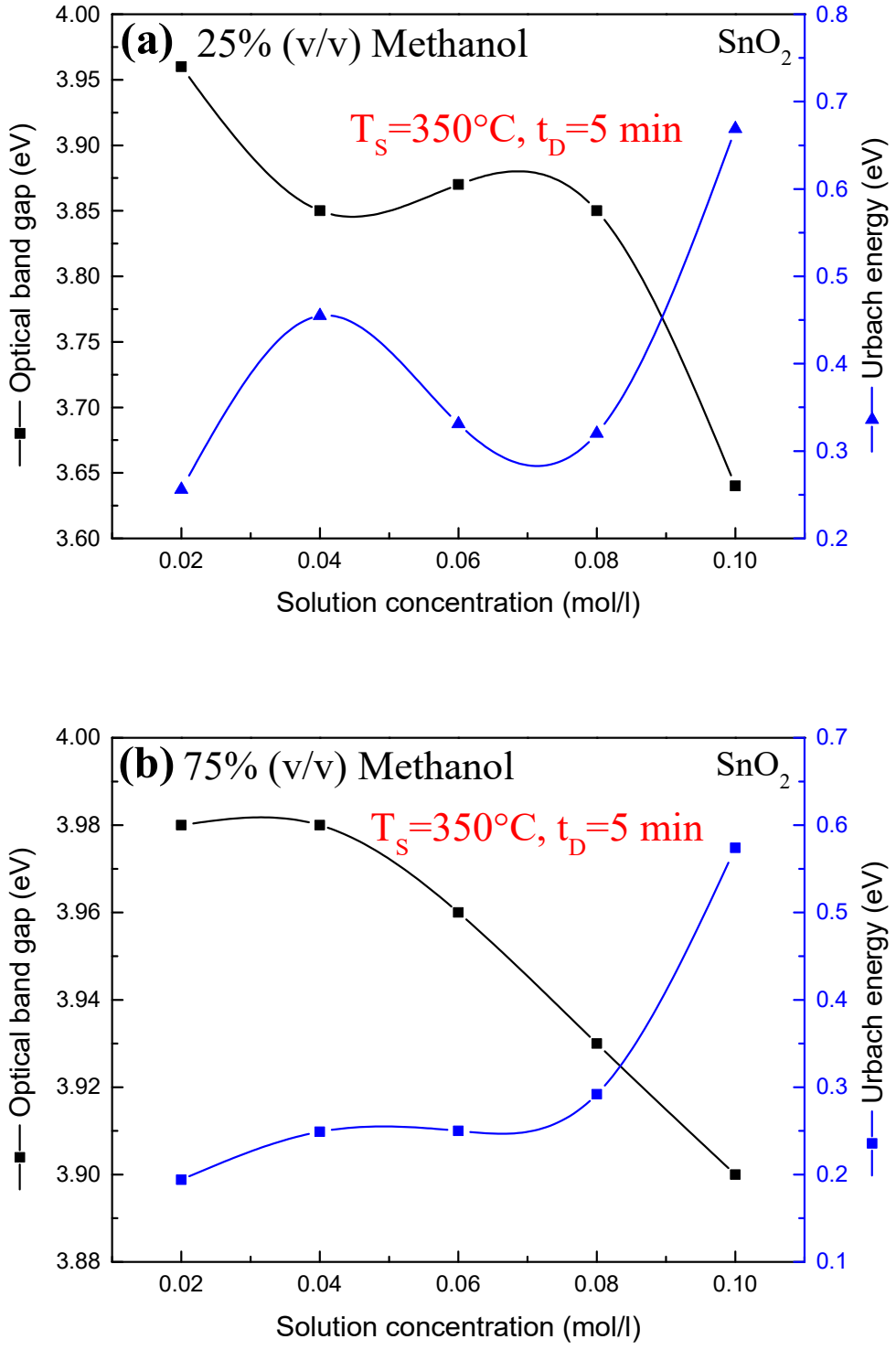


Figure III.7. Variation of E_g and E_{Urb} of SnO_2 thin films versus solution concentration using: **(a):** 25% (v/v) methanol, **(b):** 75% (v/v) methanol.

The Urbach energy value for thin films prepared with 25% (v/v) methanol is greater than 75% (v/v) methanol that is show as less structured, more random, and more impurities compared to 75% (v/v) methanol (Figure III.6).

III.6. Effect of solvent concentration and solution concentration on the refractive index of tin oxide

Figure III.8 represents the changes of the refractive index of tin oxide thin films in terms of the concentration of the solution in the two cases (25% (v/v) methanol and 75% (v/v) methanol).

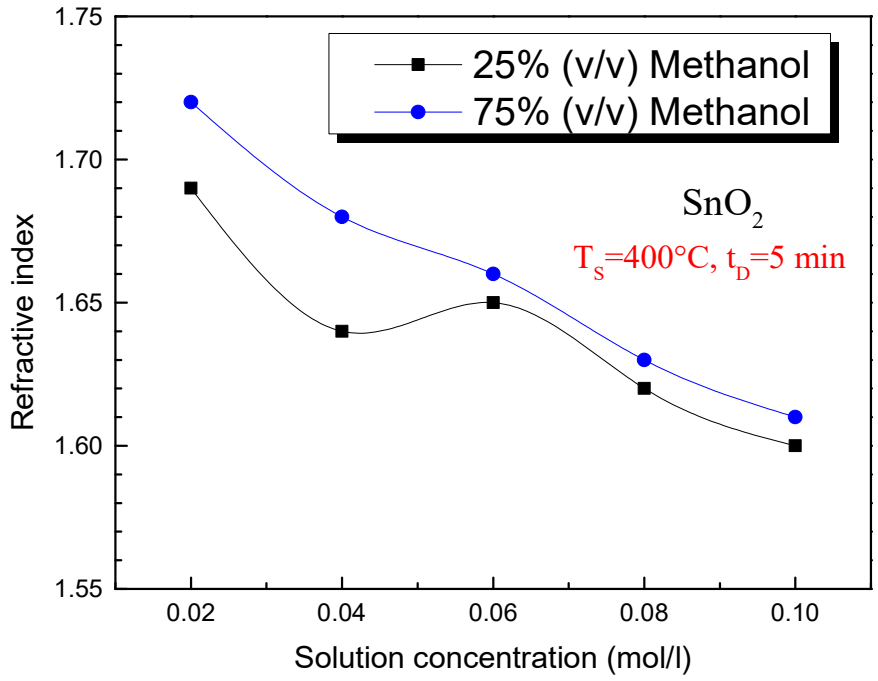


Figure III.8. Variation of refractive index of SnO_2 thin films with solution concentration.

We know that the refractive index depends on the scattering of photons in the material [59]. Where observed:

The value of the refractive index decreases with the increase in the concentration of both solutions, as the curve of 75% (v/v) methanol decreases from 1.72 to 1.62 and in 25% (v/v), it decreases from 1.69 to 1.61. The photon is scattered well [60].

- Refractive index values by using the solvent of 25% (v/v) methanol of the less compared to 75% (v/v) methanol, and this is because the 25% (v/v) methanol sample is less dense, where the size of the precipitated particle is bigger and therefore more porous, and from it good scattering of the incident photon [61].

Figure III.9 shows the inverse relationship between the refractive index and film thickness. This may be due to the presence of porosity in the films with decreasing of refractive index that it the increases of film thickness [61].

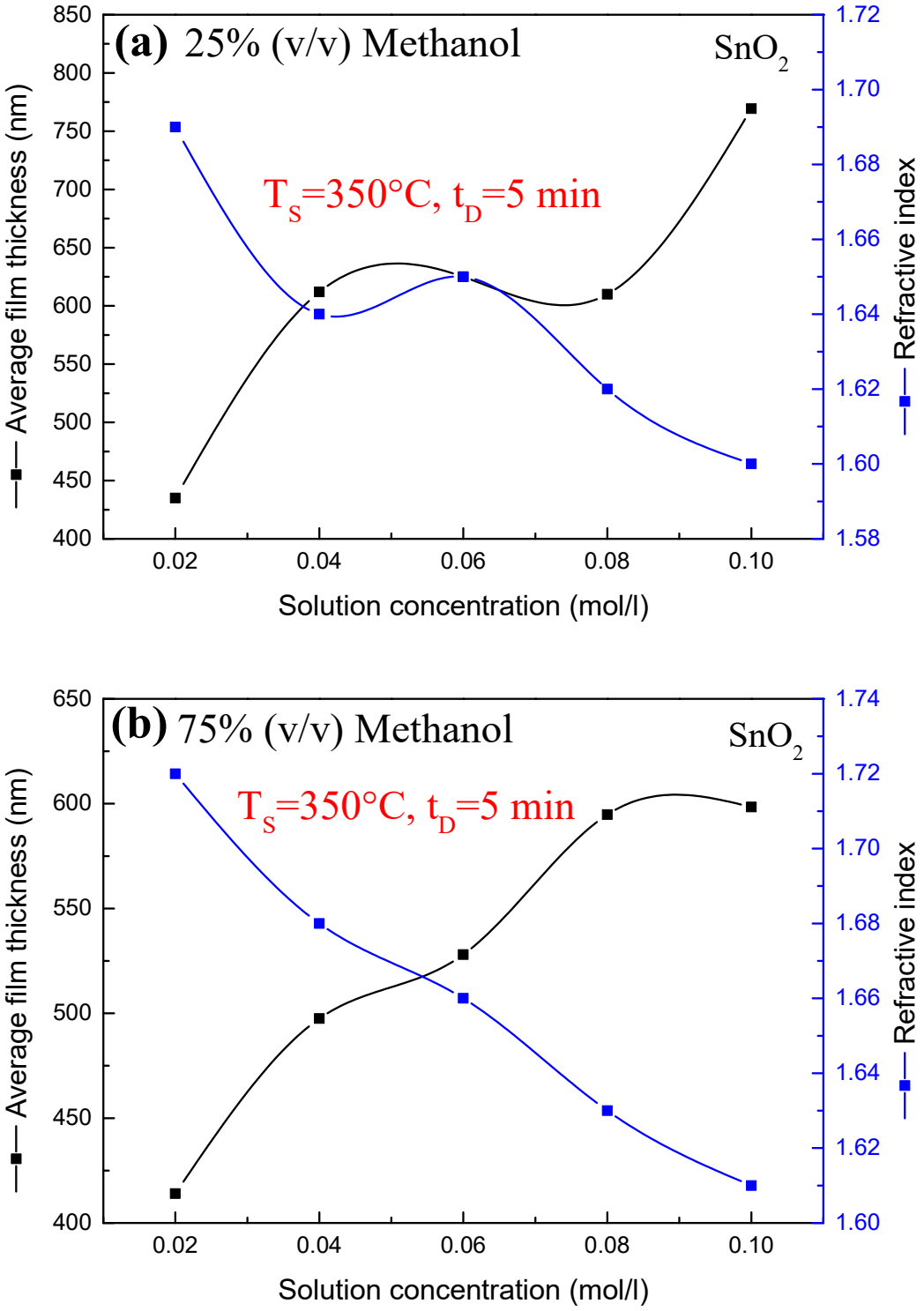


Figure III.9. Variation of and n of d SnO_2 thin films versus solution concentration using: **(a):**25% (v/v) methanol and **(b):** 75% (v/v) methanol.

III.7. Effect of solvent concentration and solution concentration on the electrical conductivity of tin oxide

The results were obtained by examining our samples with a four-point probe device.

Figure III.10 represents the electrical conductivity values of SnO_2 films in terms of concentration in both 25 % (v/v) methanol and 75% (v/v) methanol.

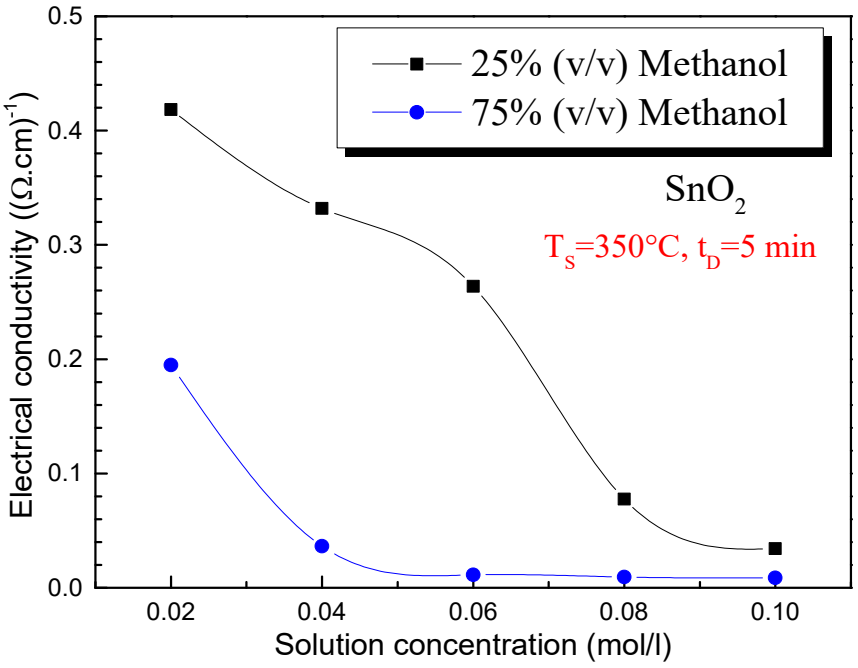


Figure III.10. Variation of electrical conductivity of SnO_2 thin films with solution concentration.

A decrease in the electrical conductivity is observed in terms of concentration in both cases, we explain this by the decrease in the grain size, that is, the increase in the granular boundary which impedes the movement of charge carriers [62]. Also, As can be seen the drop of electrical conductivity of SnO_2 prepared with 75 is a few compared to 25, which is due to the decrease rate in the grain size due to the solubility of solution which is related to the solvent concentration.

General conclusion

General conclusion

In this work, tin oxide thin films are deposited by ultrasonic spray pyrolysis it is an easy and low-cost chemical technique. We get good quality films.

On glass substrates tin (II) chloride dihydrate dissolved in two different alcohol concentrations (25% (v/v) methanol and 75% (v/v)) methanol at different molarities (0.02, 0.04, 0.06, 0.08, 0.10 mol/l) were deposited. Substrate temperature (350°C), nozzle substrate distance (5cm), flow rate (60ml/h), and spray time (5min) were kept constant throughout the sedimentation process. The effect of solvent concentration and solution concentration on the optical and electrical properties of samples deposited are studied which have good adhesion to substrate.

To characterize these samples, UV-Vis spectroscopy for optical characterization and the four-point method for electrical characterization were used. The characterization of the films led us to the following:

Increase in molarity leads to an increase in the change of our samples color (from lighter to darker), film thickness, crystal defects with decreasing optical transmittance, refractive index, optical band gap, and electrical conductivity, due to increase amount of material, an increase in the gaps in the material which leads to increase in disorder of films structure the decrease in the grain size, the increase in the granular boundary which leads to increased crystal defects, decreased mobility of charge carriers and increased scattering of photons.

The increase in the concentration of methanol as a solvent leads to an increase in: transmittance, refractive index, and optical band gap, with decreasing opacity, thickness, crystal defects, and electrical conductivity due to an increase in solubility and an increase in chemical reaction, which led to a decrease in the poverty of oxygen atoms in the material. Surface roughness, the gaps in the material decrease to become more dense.

We conclude that when the proportion of methanol in water is predominant, it has a good solubility compared to with a lower percentage in water, so a solvent containing 75% (v/v) methanol is better than 25% (v/v) methanol and gives films with good optical and electrical properties.

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Abstract

Elaboration of tin dioxide thin films by spray pyrolysis using different concentrations of solution and solvent

Abstract

In this work, tin dioxide thin films (SnO_2) were prepared onto glass substrates, using ultrasonic spray pyrolysis technique.

These films are prepared from tin (II) chloride dihydrate dissolved in two solutions of different volume concentrations of methanol (25% and 75%) with different molarities (0.02, 0.04, 0.06, 0.08, and 0.10 mol/l) under constant conditions of preparation. These films are characterized by UV-Visible-NIR spectrophotometer and four-point probe technique to study the effect of precursor concentration and solvent concentration 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.

It is observed that the optical and electrical properties are influenced by the variation of solution concentration and solvent concentration. All the samples obtained are n-type semiconductor and have high optical absorption in the ultraviolet domains. With the increase of solution concentration or the reducing

the volumetric ratio of methanol as a solvent (from 75% to 25%); the optical transmittance, refractive index optical band gap and decrease with increasing the Urbach energy and increasing molarity or volume ratio of methanol in solution. It was found that the films prepared with a higher concentration of methanol had better optical and electrical properties than those prepared with a small proportion of methanol.

Key word: *Thin films, Tin oxide, Spray pyrolysis, Optical gap, solvent concentration, Electrical conductivity.*

Résumé

Élaboration de couches minces de dioxyde d'étain par spray pyrolyse en utilisant différentes concentrations de solution et de solvant

Résumé

Dans ce travail, des couches minces de dioxyde d'étain (SnO_2) ont été préparées sur des substrats en verre, en utilisant la technique de pulvérisation pyrolyse ultrasonique.

Ces films sont préparés à partir de chlorure du d'étain (II) dihydraté dissous dans deux solutions de différentes concentrations volumiques de méthanol (25 % et 75 %) avec des molarités différentes (0.02, 0.04, 0.06, 0.08 et 0.10 mol/l) dans des conditions de préparation constantes. Ces films sont caractérisés par un spectrophotomètre UV-Visible-NIR et une technique de quatre points pour étudier effet de la concentration de précurseur et de la concentration de solvant sur les propriétés optiques et électriques des films préparés, afin d'obtenir une bonne propriété photoélectrique, ce qui en fait un candidat important dans de nombreuses applications technologiques.

On observe que les propriétés optiques et électriques sont influencées par la variation de la concentration de la solution et de la concentration du solvant. Tous les échantillons obtenus semi-conducteur de type n et ont une absorption optique élevée dans les domaines ultraviolets. Avec l'augmentation de la concentration de la solution ou réduire le pourcentage volumétrique du méthanol en tant que solvant (de 75 % à 25 %); la transmittance optique, l'indice de réfraction et l'énergie de gap optique diminuent avec l'augmentation de l'énergie d'Urbach et de l'épaisseur du film. D'autre part, la conductivité électrique diminue avec l'augmentation de la molarité ou pourcentage volumique du méthanol en solution. Il a été constaté que les films préparés avec une concentration plus élevée de méthanol avaient de meilleures propriétés optiques et électriques que ceux préparés avec une faible proportion de méthanol.

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

ملخص

تحضير أغشية رقيقة من ثاني أكسيد القصدير بواسطة الرش بالانحلال الحراري باستعمال تركيزات مختلفة من المحلول والمذيب

ملخص

في هذا العمل، قمنا بإعداد أغشية رقيقة من ثاني أكسيد القصدير SnO_2 على ركائز زجاجية، باستخدام تقنية الرش الأمواج فوق الصوتية. لقد قمنا بدراسة تأثير كل من المولارية وتركيز المذيب على الخواص الضوئية والكهربائية للأغشية المحضرة، من أجل الحصول على خاصية كهروضوئية جيدة، مما يجعل هذه الأفلام مرشحًا مهمًا في العديد من التطبيقات التكنولوجية.

قمنا بإعداد هذه الأفلام على ركائز زجاجية انطلاقا من محلول كحولي لكلوريد القصدير ثنائي الهيدرات تمت إذابته في محلولين بتركيزات مختلفة (25٪ (حجم / حجم) ميثانول و75٪ (حجم / حجم) ميثانول) مع موليات مختلفة (0.02، 0.04، 0.06، 0.08 و0.10 مول / لتر) في ظل ظروف تحضير ثابتة. شخصت هذه العينات باستعمال مطيافية الأشعة الفوق بنفسجية-المرئية-تحت الحمراء القريبة وطريقة المسابير الأربعة لدراسة تأثير كل من المولارية وتركيز المذيب على الخواص الضوئية والكهربائية للأغشية المحضرة، من أجل الحصول على خاصية كهروضوئية جيدة، مما يجعل هذه الأفلام مرشحًا مهمًا في العديد من التطبيقات التكنولوجية.

لوحظ أن الخصائص الضوئية الكهربائية للأفلام تتأثر بتغير المولارية وتركيز المذيب. جميع العينات التي تم الحصول عليها هي أشباه موصلات من نوع n ولهم امتصاص عالي للأمواج الفوق بنفسجية. بزيادة تركيز المحلول أو التقليل من النسبة الحجمية للميثانول كمذيب (من 75 إلى 25 بالمئة)؛ تنخفض كل من الشفافية الضوئية، معامل الانكسار وعرض العصابة الممنوعة بتزايد طاقة اورباخ (اللاتنظيم) وسمك العينات. من ناحية أخرى تتناقص الناقلية الكهربائية بزيادة المولارية وزيادة النسبة الحجمية للميثانول في المحلول. كما وجد أن الأفلام المحضرة بتركيز أعلى من الميثانول لها خصائص بصرية وكهربائية أفضل من تلك المحضرة بنسبة صغيرة من الميثانول.

الكلمات المفتاحية *الأفلام الرقيقة، أكسيد القصدير، الرش بالانحلال الحراري، تركيز المذيب، عرض عصابة الطاقة، الناقلية الكهربائية.*