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MASTER THESIS

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Theme

ZnO thin films deposition for the manufacture of (VOCs) gas sensor

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Our parent for their support

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Finally, we want to say that we are really proud of ourselves for the hard work we've put in over the past months as well as all of our patience and passion

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ملخص

تعتبر المركبات العضوية المتطايرة المصادر الرئيسية للملوثات في البيئة الداخلية وتعتبر ضارة جدًا بجسم الإنسان. لذلك، هناك حاجة إلى مزيد من العمل فيما يتعلق باكتشاف الأبخرة وتطورها، وقد طورنا في هذا العمل طبقات رقيقة من أكسيد الزنك (ZnO) من خلال تقنية الانحلال الحراري بالرش على ركيزة السيليكون، مع ظروف الترسب (المسافة الركيزة، درجة حرارة الترسب، مولية المحلول). تم بناء مستشعر غاز بترسبZnO ، يستخدم للكشف عن المركبات العضوية المتطايرة الغازية. تقنية الانحلال الحراري للرذاذ هي تقنية بسيطة سهلة التنفيذ واقتصادية. لقد درسنا الخصائص البصرية لهذه الطبقات بواسطة قياس الطيف المرئي فوق البنفسجي، وخصائصها الهيكلية بواسطة .DRX يعتبر أكسيد الزنك (ZnO) ذا أهمية كبيرة لأنه مادة ثنائية ذات خصائص بصرية إلكترونية جيدة حيث أنه شفاف وناقل. تمت دراسة خصائص الكشف عن المركبات العضوية المتطايرة، وأظهرت النتائج أن المستشعرات القائمة على ZnO كانت أكثر حساسية لبخار الأسيتون (VOC) من المركبات العضوية المتطايرة الأخرى (الإيثانول والميثانول)

الكلمات المفتاحية: غشاء رقيق، XRD،ZnO , التوصيل الكهربائي، رذاذ الانحلال الحراري، مستشعر الغاز.

Abstract

Volatile organic compound (VOCs) are the main sources of pollutants in the indoor environment and are considered to be very harmful to the human body. Therefore, more work is needed regarding the detection and development of vapor detection methods. In this study, we have developed thin layers of zinc oxide (ZnO) on a silicon substrate using the spray pyrolysis technique. The deposition conditions such as the distance between the spray nozzle and the substrate, deposition temperature, and molarity of the solution were carefully controlled. The ZnO deposit was used to build a gas sensor capable of detecting vapors of volatile organic compounds. The spray pyrolysis technique is a simple and cost-effective method that is easy to implement. The optical and structural properties were investigated using UV-Visible spectrophotometry and X-ray diffraction (DRX). We specifically investigated the detection properties of the ZnO film for different VOCs type. The results indicated that the ZnO-based sensors exhibited higher sensitivity towards acetone vapor (VOC) compared to the other two tested VOCs, namely ethanol and methanol.

Keywords: Thin film, ZnO, DRX, Electrical conductivity, Pyrolysis spray, Gas sensor.

Résume

Les composés organiques volatils (COV) sont les principales sources des polluants dans l'environnement intérieur et sont considérées comme très nocives pour le corps humain. Par conséquent, plus de travail est nécessaire concernant la détection des vapeurs et son développement, Dans ce travail, nous avons élaboré des couches minces d'oxyde de zinc (ZnO) par la technique **spray pyrolyse** « pulvérisation pyrolytique » sur un substrat de silicium, avec des conditions de dépôt (distance bec-substrat, température de dépôt, molarité de la solution). Un capteur de gaz a été construit avec ces couches de ZnO et utilisé pour détecter les vapeurs de composés organiques volatils gazeux. La technique spray pyrolyse est une technique simple, facile à mettre en œuvre et économique. Nous avons étudié les propriétés optiques et structurelles de ces couches par spectrophotométrie UV-visible et par DRX. Les propriétés de détection du film ont été étudiées pour les COV, Les résultats ont montré que les capteurs à base de ZnO étaient plus sensibles aux COV d'acétone que les deux autres COVs (éthanol, méthanol).

Mots-clés : Couche mince, ZnO, Si, DRX, Conductivité électrique, Spray pyrolyse, Capteur de gaz.

NOMENCLATURE

ABBREVIATIONS :

MOX : metal oxides

VOCs: volatile organic compounds

TCO : transparent conductive oxide

PVD : physical vapor deposition

CVD : Chemical vapor deposition

DRX: x-ray diffraction

SEM: scanning electron microscopy

UV-VIS: Ultraviolet-visible spectroscopy

SYMBOLS:

FWHM: width at half height [radians]

eV: The electron-volt (eV) is the unit of energy used in particle physics 1eV=1.6 10^{-19} J

Eg: represents the energy to be supplied to the valence band electrons to pass through the conduction band [eV]

D: crystallite size, [nm]

k: Shape constant, 0.9

λ:1.54 Å is the wavelength of CuKα radiation, nm

θ: Bragg's angle in degrees

β: the FWHM in radians

d : the interplanar distance

θ : the angle of incidence with the lattice plane

General Introduction

In recent years, the need for effective and reliable gas sensing technologies has grown significantly, driven by the demand for monitoring and controlling air quality, industrial safety, and environmental preservation. Among the various types of gases, (VOCs) play a crucial role due to their wide presence in numerous industrial processes, indoor environments, and outdoor pollution sources. (VOC) vapors are the primary sources of indoor environmental pollutants and are considered seriously harmful to the human body **[1]**. There are notable correlations between VOC emissions and different kinds of cancers **[2]**. Among the VOC, acetone is widely used in many applications, notably as abiomarker for diabetes since it can be found in the exhaled breath of the diabetes patient.Therefore, more work is needed concerning vapors detection and its development **[2,3]**.

Gas sensors based on zinc oxide (ZnO) have emerged as promising candidates for VOC detection due to their unique properties and compatibility with scalable fabrication techniques. ZnO is a wide-bandgap semiconductor with excellent sensing capabilities attributed to its high surface-to-volume ratio, large specific area, and gas adsorption characteristics. By leveraging the interaction between ZnO and VOCs, these sensors can provide rapid, sensitive, and selective detection of various volatile compounds.

The development of a ZnO-based gas sensor involves several key steps, including material selection, film deposition, sensor fabrication, and characterization. The choice of ZnO as the sensing material stems from its favorable properties, such as high chemical stability, sensitivity to a wide range of gases, and low cost. To obtain a suitable ZnO layer, deposition techniques such as spray pyrolysis, chemical vapor deposition, or physical vapor deposition are commonly employed, with each method offering its own advantages and considerations.

Once the ZnO film is fabricated, it is integrated into a gas sensor device through appropriate electrode patterning and electrical connections. The sensor's performance is then characterized by evaluating its sensitivity, selectivity, response time, and stability under controlled conditions. This characterization process involves exposing the sensor to different concentrations and types of VOCs, measuring the resulting electrical response, and analyzing the data to establish calibration curves and detection limits.

The successful implementation of a ZnO-based gas sensor requires optimization at multiple stages, including material synthesis, film deposition, device design, and data analysis. Furthermore, the development of advanced signal processing techniques, such as machine learning algorithms, can enhance the sensor's accuracy and reliability by enabling real-time monitoring and automated VOC identification.

Our brief is organized into four chapters, which can be listed as follows:

1. In the first chapter, we will present a bibliographical study on the basic concepts of metal oxides and their most important characteristics. Then, we will shed light on Zinc oxide (ZnO) and its different physical properties, as well as its optical and structural properties and applications.

2. In the second chapter, we offer a general study of gas sensors, especially (MOX) gas sensors. We will explore the characteristics of these sensors, the principle of their detection, and the structural characterization techniques associated with them.

3. The third chapter focuses on the methods employed for achieving thin film deposition in an optimal manner. We will particularly emphasize the techniques of spray pyrolysis, which serve as the foundation of our research laboratory. Additionally, we will study various methods used to define the electrical, optical, and structural properties of thin films. This chapter will also encompass the experimental methods employed for the preparation of the ZnO thin films.

4. In the fourth and final chapter, we will explain and analyze the results obtained, finalized by a general conclusion.

CHAPTER ONE: Bibliographic Study on metal oxides

CHAPTER ONE I: Bibliographic Study on metal oxides

1.1 Metal oxides

Metal oxides (MOs) are the most common materials in the Earth's crust and are present in traditional ceramics. MO semiconductors are distinguished by their lack of similarity to conventional inorganic semiconductors like silicon with regard to the concepts of material design, electronic structure, defect states, thin-film processing, and optoelectronic properties. As a result, they have the potential to completely redefine both conventional and entirely new capabilities

1.2 Metal oxides definition

A metal is a simple body, usually endowed with a special metallic luster. It is a good conductor of heat and electricity at ordinary temperatures **[4]**, it is malleable and ductile and has two characteristic chemical properties: oxide formation and basic hydroxides when the metal is at the degree of oxidation +1 or +2 and the formation of simple cations (hydrated) in aqueous solution **[5]**. Most metals react with oxygen. And any metal that reacts in contact with the dioxygen (hot or cold) undergoes oxidation to become a metal oxide.

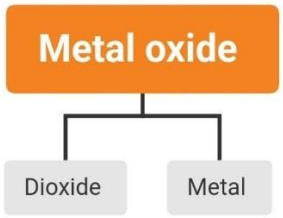


Figure I.1:Metal oxides diagram

A metal oxide, in general, is a body consisting of metallic atoms and oxygen atoms (M1xM2yOz), or M is the chemical symbol of the metal atom in question, O is the symbol of the oxygen atom, “x” and “y” and “z” of the natural integers.

1.3 Types of metal oxide

1.3.1 Metal oxides type n and type p

There are two large families of metal oxides. The first is type P (hole conduction). They are known to be relatively unstable because they tend to exchange oxygen from their network

easily with air. However, P types are used for certain applications such as high-temperature oxygen sensors **[6,7,8]**, The second family groups the N types (electron conduction). They fulfill the majority of gas sensor applications because they are more stable and have more chemical-friendly properties.

Table I.1: List of metal oxides.

Metal oxide type n	Metal oxide type p
TiO_2	La_2O_3
WO_3	PdO
ZnO	NiO
SnO_2	TeO_2
In_2O_3	$BaTiO_3$

1.3.2 Simple and complex metal oxides

Metal oxides are classified into two main categories: simple metal oxides consist of a metal such as SnO_2, TiO_2, SiO_2, etc. and mixed metal oxides consist of two or more metals such as $BaTiO_3$, $CaTiO_3$, Mg_2SiO_4, etc.

1.4 Application of metal oxides

Metal oxides also have applications directly related to their properties. There are many applications in various fields of technology, including microelectronics, photovoltaic industry, gas sensors, anti-corrosion, paints, biotechnology, photocatalysis, and nanotechnology. Metal oxide nanostructures represent a sector of activity in constant evolution. They have been involved in the miniaturization of the systems in which they are integrated, and we will never be able to cite all those systems.

1.5 Zinc oxide (ZnO)

Various oxides have been used in gas sensor applications **[9]**. Among them, zinc oxide has emerged in recent decades as a promising and competing material for tin oxide. Composed of zinc and oxygen atoms, this material has a set of advantages: like interesting electrical and morphological properties, it is infinitely recyclable and not toxic. ZnO is also a chemo-resistive material, its gas detection is mainly controlled by the change of sensor resistance when gas

molecules react on its surface **[10]**. It represents the unique features required for an ideal gas sensor. **[11]**

1.5.1 ZnO Properties

1.5.1.1 Structure of Zinc Oxide (ZnO)

Zinc oxide crystallizes under normal temperature and pressure conditions according to the wurtzite hexagonal structure **[12]**, which is the most stable thermodynamically. In this structure, the oxygen atoms occupy the tops of a tetrahedron and the zinc atoms occupy half of the tetrahedral interstitial positions. The crystalline growth axis of zinc oxide is c (002) **Figure I.1**. ZnO can also exhibit other structural forms under specific growing conditions, such as the blende and rock salt structures. The wurtzite structure of ZnO can be described as lacunary, meaning that the zinc and oxygen atoms only fill 40% of the crystal's volume **[13]**, leaving empty spaces with a radius of 0.95Å. Under certain conditions, this structure allows for the insertion of excess zinc atoms or impurities into these empty spaces, specifically in the interstitial positions. This can alter some properties of the material. The spatial dispersion of the barycentres of positive Zn2+ charges and negative O2- charges creates a spontaneous polar field along the c-axis and also gives rise to a piezoelectric polarization field when mechanical stress is applied to ZnO **[11].**

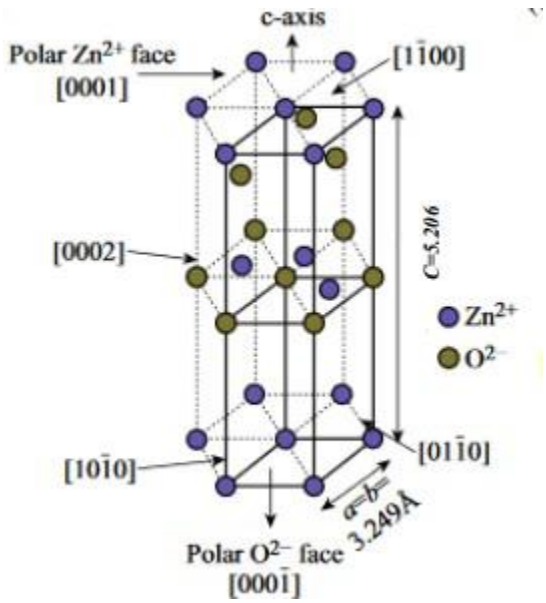


Figure I.2: Structure hexagonale de ZnO [12].

1.5.2 Electrical and electronic properties of Zinc Oxide (ZnO)

ZnO is a type n semiconductor with a direct gap of 3.37 eV at ambient temperature and an excitonic bonding energy of 60 meV **[14]**. It is intrinsic, meaning that its thermal energy is sufficient to pass an electron from the valence band to the conduction band.

The electronic oxygen and zinc band structures are:

O: $1s^2\ 2s^2\ 2p^4$

Zn: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}4s^2$

The 2p states of oxygen form the valence band and the 4s states of zinc form the conduction zone of the ZnO semiconductor. The electrical resistivity of ZnO can be modified by moving away from the stoichiometric structure by introducing excess zinc atoms into the interstitial positions, or by creating oxygen gaps that act as electron donors. The latter also depends on the temperature of production, doping, the parameters of the deposition method, annealing, etc **[12]**.

1.5.3 Optical properties of Zinc Oxide (ZnO)

The refractive index of zinc oxide in the massive form is equal to 2.0. In thin layers, its refractive index and absorption coefficient vary according to the conditions under which the layers are made. The refractive index has a value varying between 1.7 and 2.2 according to the author. The improved ZnO stoichiometry leads to a decrease in the absorption coefficient and an increase in the energy of the forbidden band **[15].**

1.5.4 Applications of ZnO thin films

Zinc oxide (ZnO)-regardless of its use in the research has a wider range of applications, some of which are:

- **Lithium-Ion Batteries (LIBs):** Similar to other batteries, a rechargeable lithium-ion battery is made of one or more power-generating compartments called cells. **[16].**
- **Solar cells:** Tin dioxide coatings are widely used in thin film solar cells prepared from hydrogenated amorphous silicon. This kind of solar cell is composed of a glass plate, coated with a transparent conducting oxide for example tin dioxide. **[17].**
- **Low-Emissivity coatings:** Low-Emissivity glass (low-E glass) is employed to reflect the heat transmitted by infrared radiation with a long wavelength, generally about 10μm. **[18].**
- **Gas Sensors**

1.5.4.1 Gas Sensors

The activity of an electrical semiconducting gas sensor depends on the variation in electrical conductivity that semiconductor materials face while exposed to a gaseous atmosphere of different components. Thus, an electrical circuit assesses this response and the producing change in resistance is employed as the output signal for the instrument. The sensor comprises an oxide semiconductor film on an insulating substrate with two linked metal electrodes. Zinc oxide is one of the most employed oxides for this application. A model of a ZnO gas sensor is displayed in Fig **I.2** to detect carbon monoxide CO. The reaction of CO with surface-adsorbed oxygen ions leads to the formation of CO2 and free electrons which augment the electrical conductivity to fulfill the aim of CO detection **[18].**

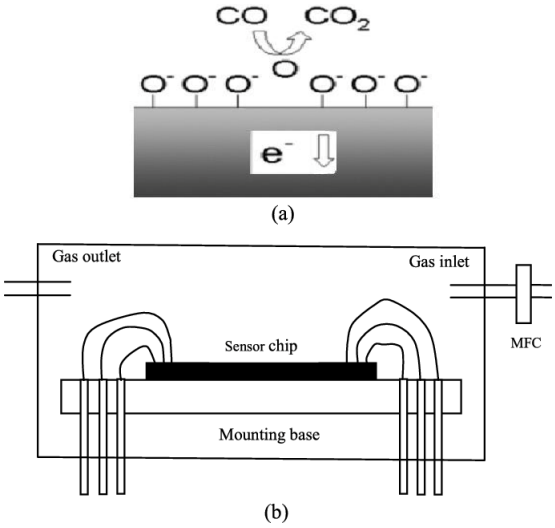


Figure I.3: Example of CO detector based in ZnO thin film

2. Volatile organic compounds

(VOCs) encompass a heterogeneous group of organic chemicals characterized by their propensity for high vapor pressure at ambient temperature. This attribute facilitates their rapid evaporation into the atmosphere. VOC emissions originate from a wide array of sources, including combustion of fuels, solvents employed in paints, varnishes, and cleaning agents, building materials, consumer products, and tobacco smoke. VOCs engender notable health effects, ranging from mild irritations of the ocular, nasal, and pharyngeal mucosae to more severe manifestations such as headaches, dizziness, nausea, fatigue, respiratory disorders, and potential carcinogenicity.

Intriguingly, indoor environments often harbor higher VOC concentrations compared to outdoor settings, owing to the pervasive use of VOC-laden products within residential and commercial premises. Consequently, proactive measures to mitigate excessive exposure are imperative. To curtail risks associated with VOCs, regulatory bodies, exemplified by the US Environmental Protection Agency (EPA), have promulgated stringent standards governing VOC emissions across diverse sources. These regulatory frameworks, designed to safeguard public health, endeavor to minimize human exposure to VOCs. It is worth noting that VOCs bear environmental implications as well. They constitute key contributors to the formation of atmospheric smog and engage in intricate chemical reactions with other air pollutants, culminating in the formation of deleterious compounds that detrimentally impact ecosystems and air quality **[19]**.

Conclusion

In this chapter, we have summarized the fundamental properties of Metal oxides (MOs) and their applications. Then, the identification of zinc oxide (ZnO) in terms of their properties and wide applications.

CHAPTER TWO: gas sensor

CHAPTER TWO II: GAS SENSOR

1 Sensor definition

Sensors are an essential part of the detection chain in a functional system. These are the first elements encountered in the measurement chain and they gather information about the behavior of the operating part exploited by the controlling part, that is, they transform the quantity we want to measure, called the measured quantity. This measurement can be a physical (light, pressure, heat, etc.) or chemical (gas, liquid, acid, etc.) electrical signal from a process or device.

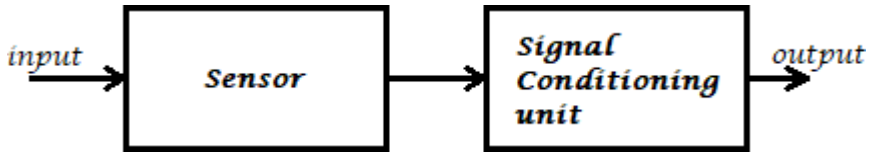


Figure II.1: Transducer blocks diagram showing the sensing and transduction elements

The sensor measuring chain gives us a relation between these two quantities which is characterized by the following concepts:

- ✓ Linearity
- ✓ Bandwidth, response time
- ✓ Aging
- ✓ Sensitivity to measured quantity
- ✓ Influence of disturbances
- ✓ Calibration **[20].**

2 Types of sensors

The sensors can be defined according to the measured quantity (measured), we distinguish the sensors of position, temperature, speed, force, pressure, gas, etc. They can also be defined based on the character of the information.

We can distinguish two types of sensors: sensors in direct contact with the size we want to capture and proximity sensors that do not require direct contact with the size but it is enough to approach it to obtain the information, each of these two types are divided into three categories: mechanical, electrical and pneumatic sensors.

3 Structure and operation of a sensor

The sensor is defined as a component that converts the measurement into a signal that can be exploited. The block diagram of the sensor structure is shown in figure **(II.2) [21].**

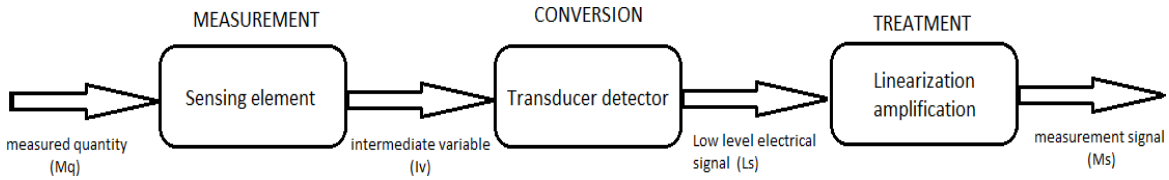


Figure II.2: Schematic diagram of the structure of a sensor

3.1 Sensing element

In principle, the quantity to be measured is not convertible directly into an electrical signal, but rather it is the sensitive element called a measuring element which converts the quantity to be measured (Mq) into an intermediate quantity (Iv) which is easy to convert into an electrical signal; the law that links the intermediate (Iv) to the measured (Mq) must be perfectly known. The intermediate magnitude is often a deformation or a force.

This sensitive element characterizes the sensor. The design of the sensors is based on the principles which make it possible to obtain a quantity which can be exploited from the quantity to be measured.

3.2 Transducer detector

We are in the conversion part with main element the transducer. It converts the intermediate size into an electrical size, usually a voltage or frequency. The transducer also called primary sensor behaves in principle like a generator, it is an active sensor or as impedance, we speak in this case of passive sensor. It is then combined with an electrical circuit designed to measure this impedance.

3.3 Linearization amplification

Since the signal from the transducer to the treatment part is of low power, it is difficult to transfer it as it is. If we know the transfer function linking the transducer signal to the quantity to be measured, it is rarely linear (the signal emitted by the sensor must vary linearly with the quantity to be measured), it is sensitive to disturbing quantities called influence quantities such as the temperature of the sensitive-transducer element.

To cope with such problems, electronic circuits are designed to amplify, linearize and correct the transducer signal.

With specially designed microprocessors and microcontrollers, we can envisage any treatment necessary to obtain the performance of the sensor we want to manufacture. The signal emitted is usually an analog current or voltage signal. The electrical energy supply of the sensor is made by the communication line, that is to say that each element receives from the other electrical signals of different sizes which are in reality only information on the measured **[21].**

4 Chemical sensors

The chemical sensor is an analyzer that responds to a particular analyte in a selective and reversible way and transforms input chemical quantity, ranging from the concentration of a specific sample component to a total composition analysis, into an analytically electrical signal.

The chemical information may originate from a chemical reaction by a biomaterial, chemical compound, or a combination of both attached onto the surface of a physical transducer toward the analyte. The chemical sensor subject is an emerging discipline formed by the multidisciplinary study among chemistry, biology, electricity, optics, mechanics, acoustics, thermology, semiconductor technology, microelectronics technology, and membrane technology **[22].**

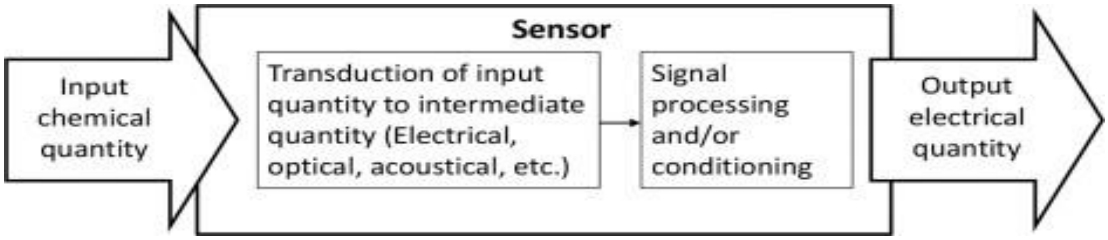


Figure II.3: Sensor principle. Schematic diagram of a sensor that produces an electrical output in response to the presence of an input quantity**. [22]**

4.1 Characteristics of chemical a sensor

The main characteristics that make it possible to evaluate the performance of a gas sensor are:

4.1.1 Sensibility

is the variation of the measured signal (output signal) in relation to the variation of the target gas concentration. It is defined by the following relationship:

$$Si = \frac{\Delta X}{\Delta Ci} \quad (1)$$

with:

Si: gas sensitivity i,

X: the measured quantity; in the case of MOX sensors, it is the electrical resistance.

Ci: the gas concentration i.

Since in general the sensitivity is not constant (linearity problem), we therefore use the relative response extracted from the differential and relative calculation. This depends on the nature of the gas to be detected.

-**Oxidizing gas:** Differential and relative response**:** $\frac{R_{gas}-R_{air}}{R_{gas}}$ (2)

or Relative Response: $\frac{R_{gas}}{R_{air}}$ (3)

-Reducing gas: Differential and relative response: $\frac{R_{air}-R_{gas}}{R_{air}}$ (4)

or Relative Response: $\frac{R_{air}}{R_{gas}}$ (5)

4.1.2 Reproducibility

This parameter is probably the most important for both physical and chemical sensors. It is the ability of a sensor to give, under defined conditions, very similar responses when repeatedly applying the same input signal. **[23]**

4.1.3 Response time and recovery time

This is the time required for the sensor to react to an initial change in concentration at a certain concentration value. Recovery time is defined as the time required for the sensor signal to return to its original value after a change in concentration from a certain value to zero. In most cases, these two parameters are calculated from 90% of the response variation **[24].**

4.1.4 Selectivity

The selectivity of a sensor is also a decisive parameter. This selectivity will allow to discriminate a target gas within a gas mixture. It is defined as the ratio of sensitivities (or relative responses) between two gases for

the same gas concentration:

$$\text{selectivity}_{\text{gas1 / gas2}} = \frac{response_{relative(gas\ 1)}}{response_{relative(gas\ 2)}} \quad (6)$$

In contrast to sensitivity, the selectivity of sensors designed with metal oxides appears as their weak point. In fact, they appear to be not very selective with regard to a particular gas unless they use doping treatments of the semiconductor **[25].**

4.1.5 Reversibility

Refers to the ability of the sensor to return to its original state when the gas concentration returns to normal **[26].**

4.1.6 Detection limit

This is the lowest concentration variation that can be detected by the sensor under given conditions. For MOX sensors, this detection limit is in the order of ppm (part per million) or ppb (part per billion) **[27].**

The performance of the gas sensors depends on the properties of the material used but also on the method of preparation of the material used and the measuring environment.

4.2 Classification of chemical sensor

According to the working principle, the chemical sensor can be classified into many types such as optical, electrochemical, mass, magnetic, and thermal. The optical chemical sensor is based on the changes in optical phenomena analysis arising from the interaction between the analyte and the receiver. The electrochemical sensor utilizes electrochemical effect among the analytes and featured electrodes. The working principle of the mass sensor depends on the quality change induced by the mass loading from the adsorption toward the analyte by the special modification of sensor surface. The magnetic device is based on the magnetic properties in analyte adsorption, whereas the thermal sensor utilizes the thermal effect generated by the specific chemical reaction or adsorption process.

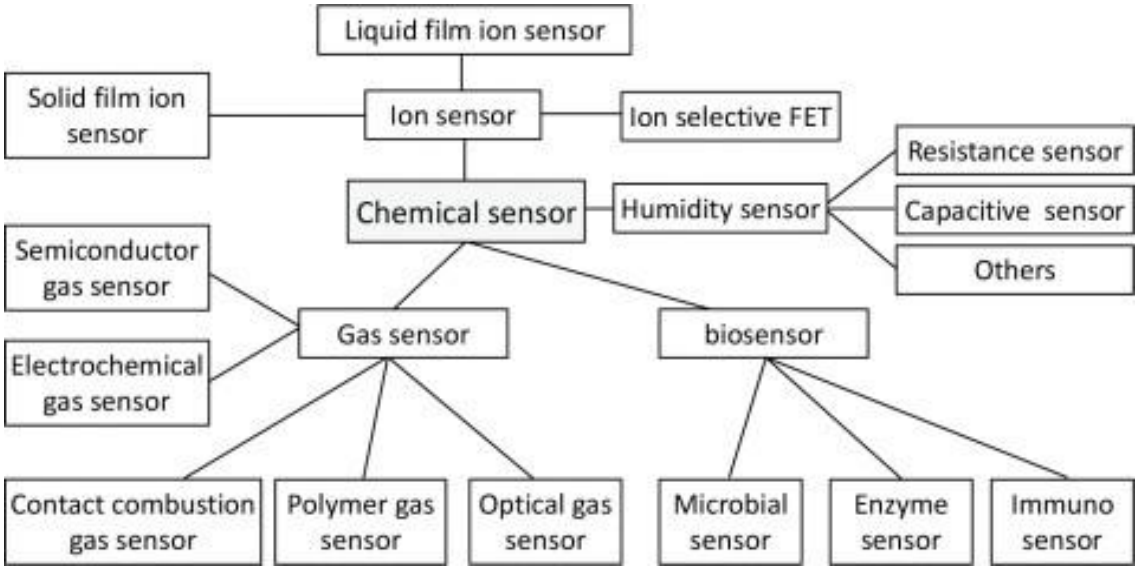


Figure II.4: Classification of chemical sensors based on sensing objects **[22]**

5 Gas sensor

Gas sensors are chemical sensors that are of paramount importance. A chemical sensor comprises of a transducer and an active layer for converting the chemical information into

another form of electronic signal like frequency change, current change or voltage change. As the air surrounding us contains different amount of gases which could be hazardous to human health, atmospheric pollutants or of significance to an industrial or medical process, It becomes therefore very imperative to detect the presence of these gases since the environment we dwell in consists of humans, plants and animals as its main inhabitants, so the safety of their lives is of topmost priority. Basically, traditional detection methods which produce systems that sounds an audio alarm to notify people when there is a gas leakage that is harmful or poisonous is not very reliable because it is required to obtain accurate real-time measurements of the concentration of a target gas. However, for many centuries, different gas sensor technologies have been used for different gases detection including semiconductor gas sensors, catalytic gas sensors, electrochemical gas sensors, optical gas sensors and acoustic gas sensors. The performance characteristic of every sensor is based on some properties including sensitivity, selectivity, detection limit, response time and recovery time.

5.1 Semiconductor gas sensor

Semiconductor gas sensor is a sensitive element made by metal oxides or metal semiconductor oxide materials **[28].** As regards the electrical conductivity sensors, the resistance of their active sensing layer changes due to contact with the gas to be detected. Since the first semiconductor metal-oxide-ceramic gas sensor was reported in 1962, the semiconductor gas sensors have become the most comprehensive and widely used gas sensors **[22].**

5.2 Electrochemical gas sensor

The electrochemical gas sensor can be categorized into galvanic cell type, controlled potential electrolysis type, coulometric type, and ion-selective electrode type. The galvanic cell gas sensor evaluates the target gas composition by measuring the shift in current. The controlled potential electrolysis gas sensor senses the target gas by measuring the electrolytic current and is different from the galvanic cell sensor, and a specific voltage should be imposed externally. Furthermore, the oxygen in blood can also be detected in addition to CO, NO, NO_2, and SO_2. The coulometric gas sensor detects the target species by measuring the current generated by the interaction between the gas and the electrolyte.

The ion-selective electrode gas sensor has appeared earlier, and it detects the gas by measuring the ion current with high sensitivity and excellent selectivity **[22].**

5.3 Sensors based on metal oxides

Metal oxide sensors use semiconductor materials that exhibit variations in electrical resistance depending on the gaseous atmosphere in which they are placed. These gas sensors have a wide range of gas detection capabilities that covers market demands for detecting oxygen, flammable gases and toxic gases... But they suffer from low sensitivity when operating at room temperature and a lack of selectivity. However, these types of sensors have many advantages such as: low cost, production flexibility, ease of use, easy integration into portable systems. The many potentialities of oxide materials offer increasing research and development axes for gas sensors in order to improve them, and significant advantages compared to other types of sensors which are constrained by certain limits such as the complexity of operation and a high price.

Increasing development for gas sensors in order to improve them, and significant advantages compared to other types of sensors that are constrained by certain limits such as operational complexity and high price **[23].**

5.3.1 Metal oxide gas sensors

5.3.1.1 Presentation

In very general terms, a MOX gas sensor consists of a sensitive layer deposited on a substrate on which are deposited contact electrodes:

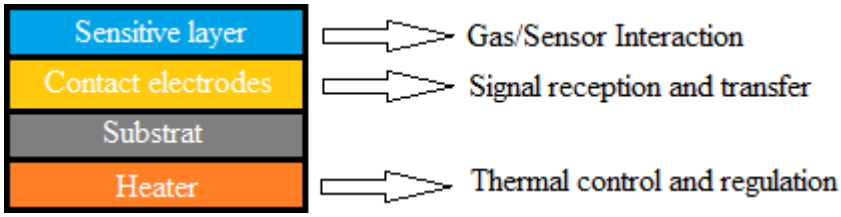


Figure II.5: Different components of a gas sensor

Sensitive layer: It is based on metal oxide such as ZnO, SnO_2, etc.

Substrate: There are several substrates for depositing gas-sensitive metal oxides, such as Al_2O_3, Si, MgO, ZrO, sapphire, quartz, glass, or other ceramics.

Contact electrodes: The electrodes will make it possible to establish electrical contact with the sensitive layer in order to measure its response to the gas by conducting the loads of the host

material to the external measuring circuit. They are often gold or platinum, but can be found in tungsten, silver, or aluminum.

Heater: the heating system will control and regulate the temperature of the sensitive layer **[25].**

5.3.1.2 Gas/sensor interaction principle:

This part deals essentially with the elementary mechanisms of surface physics, relative to the operation of a gas sensor.

• **Adsorption:** part of the gaseous phase attaches to the surface of the solid. There are two types of absorptions: Physical absorption (physisorption) and Chemical absorption (chemisorption)

• **Reaction:** Gas adsorption in the solid creates a reaction that creates a new material.

• **Desorption:** Adsorption of gaseous molecules creates another gaseous species.

In a semiconductor imagined infinite, its volume presents energetic states that allow to determine its type of conduction. These energy states are formed, after the creation of structural defects resulting from stoichiometry deviations or impurities introduced by doping.

In a real case, when you cut an infinite semiconductor to create a new surface, bonds between atoms on the surface are broken and topology defects (gaps, steps, etc.) appear. These surfaces are called clean surfaces and must be distinguished from the actual surfaces on which atoms from the surrounding gas phase are adsorbed. In the forbidden band they then appear additional energy states or surface states which are classified into two categories.

- the intrinsic states due to the abrupt discontinuity of the crystalline network,

- Extrinsic states due to the presence of alien species on the surface of the semiconductor.

Absorption is a surface phenomenon by which molecules of gas called absorbate attach to a solid surface of ZnO called absorbent. The reverse phenomenon of desorption is activated by a growth in the temperature gradient or by a decrease in pressure **[20].**

5.3.1.3 Detection principle

When a MOX gas sensor is placed in a gaseous environment, an adsorption phenomenon of the gas molecules occurs on the surface of the metal layer. This adsorption leads to interactions

between the gas and the sensitive layer which results in electron exchanges and subsequently causes changes in the resistance of the layer. These mechanisms of surface physics will then be described in detail to better understand the operation of a gas sensor.

Depending on the energy involved during the interaction between the gas and the sensitive layer, two types of adsorptions can be found:

- Physisorption or physical adsorption: during this process, weak Van der Waals and electrostatic interactions occur between the surface of the sensitive layer and the gaseous molecules with adsorption heats of 1 to 20 kJ/mol. But there is no exchange of electrons. Physical adsorption is reversible and is favored by a decrease in temperature.
- Chemisorption or chemical adsorption: requires the formation of high-energy interactions (covalent, ionic or metallic bonds) with significant adsorption heats of the order of 40 to 200 kJ/ mol. During chemisorption, an exchange of electrons occurs between the surface of the layer and the gaseous molecules which subsequently modify the electronic properties (electrical resistance). Chemisorption may or may not be irreversible.

The metallic oxides used in gas detection show variations in electrical properties after the chemisorption of gaseous molecules. These variations depend on the type of gas to be detected but also on the type of the semiconductor layer.

- **In type n semiconductors**

  Oxidizing gases (electron acceptors), (Figure 4): oxidizing gases such as NO_2 **[29]**, NO **[30]**, O_3 **[31]** and O_2 **[32]** interact with the surface of the sensitive layer. The oxygen atom O of these gases removes electrons from the layer instead of releasing them. This subsequently produces the increase in resistance. The depletion zone becomes thicker due to the decrease in carrier concentration which leads to increased resistance

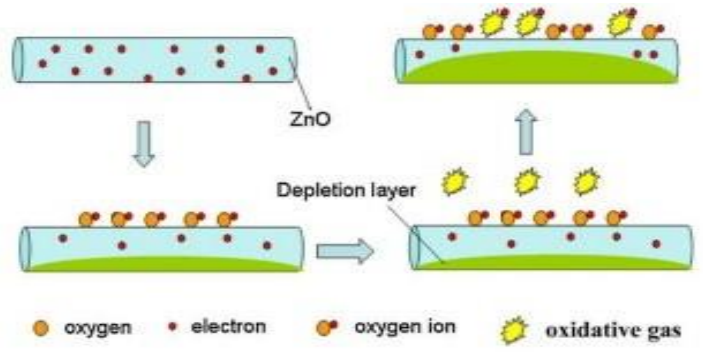


Figure II.6: Oxidizing gas reaction with a Type n (ZnO) semiconductor **[33]**

Reducing gases (electron donors) (cf. **Figure II.7**): the reaction of reducing gases such as H_2 **[34]**, CO **[35]**, CO2 **[36]**, H_2S **[37]**, NH_3 **[38]** and CH_4 **[39]** with a sensitive layer of a semi-layer conductor type n, will lead to an increase in conductivity by the release of electrons in the depletion zone that comes from interaction with oxygen molecules previously absorbed at the surface. The surface conductivity of the material varies with the amount of gas adsorbed.

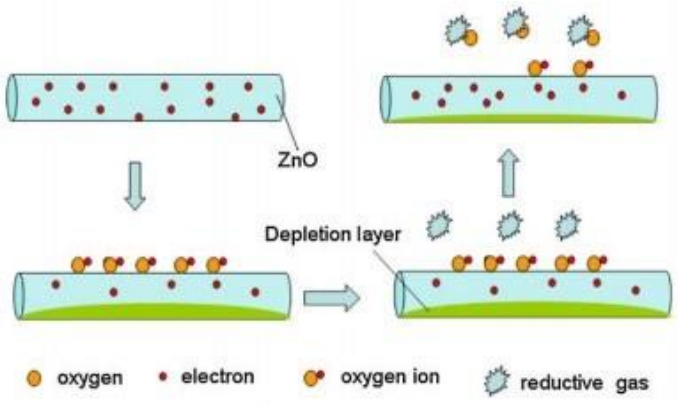


Figure II.7: Reaction of a reducing gas with a type n semiconductor (ZnO) **[33]**

- **In type p semiconductors**

The reaction mechanism in the p-type semiconductors is opposite to that of the n-type semiconductors, since the conduction is deficient, that is, the oxidizing gases increase the conductivity while the reducing gases reduce it.

5.3.1.4 Oxygen adsorption

The operating principle of semiconductor oxide-based sensors is based on the variation of conductivity due to doping by the adsorption of gas on the surface of the host material. The reaction

mechanism between the sensor and the target gas (or air) is based on the interaction between the target gas and the oxygen species adsorbed to the surface of the host material **[40- 41].** Because metal oxides are oxygen gaps, their concentration depends on the method of production, they will naturally react with the dioxygen present in the environment. Oxygen is therefore the precursor of the detection reaction. Adsorbed to the surface, it can exist in several forms depending on temperature **[42,43]**, each form having its own reactivity. At room temperature, oxygen is present on the surface in a physiosorbed form $O_{2,phys}$, but it does not participate in the detection mechanism. For higher temperatures (from T = 160°C), oxygen willbe chemically is orbed as $O_{2}^{-}{}_{ads}$ At higher temperatures (T > 300°C), the chimisorption will take the dissociative form O^{-}_{ads} and O^{2-}_{ads}(unstable form). If, however, the temperature has become too high (T > 600 C°), the network's oxygens will then migrate to the surface and desorb (**Figure II. 8**); The corresponding balances are **[44, 45, 46]**.

Physisorption of oxygen $$O_{2,gas} \rightarrow O_{2,phys} \rightarrow O_{2,ads} \quad (7)$$

Oxygen chemisorption $$O_{2,ads} + e^{-}_{ZnO} \rightarrow O^{-}_{2,ads} \quad (8)$$

$$O^{-}_{2,ads} + e^{-}_{ZnO} \rightarrow 2\,O^{-}_{ads} \quad (9)$$

$$O^{-}_{ads} + e^{-}_{ZnO} \rightarrow O^{2-}_{ads} \quad (10)$$

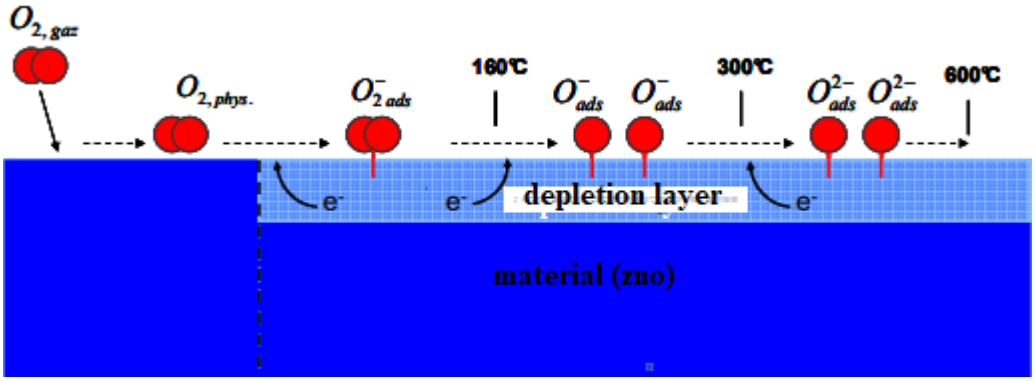


Figure II.8: Principle of oxygen adsorption on the sensor surface **[46]**.

Oxygen adsorbed on the surface of the sensitive layer, due to its oxidizing properties, will capture electrons from the conduction band of the host material (ZnO), leaving an electron-depleted area on the surface of the sensitive layer, the depletion zone. This electronic depletion will immediately decrease the conductivity (or increase the resistivity) on the surface. The reverse effect can be observed in sensors using p-type semiconductors as host material.

The oxygen present in the gas phase is at all times in equilibrium with the oxygen adsorbed on the surface of the host material. As a result, any phenomenon that causes a variation in the amount of oxygen (gas phase or adsorbed) results in a variation in resistance.

Conclusion

This chapter explains the general concepts of gas detection. We will present the different types of sensors under study, with particular attention to metal oxide-based sensors. We will see the essential characteristics of a sensor and the fundamental mechanisms of gas detection.

CHAPTER THREE: Development and Characterization of thin films

1 Introduction

Thin film deposition technology involves coating the surface of a substrate with a very thin film of material that ranges in thickness from a few nanometers to 100 micrometers, or just a few atoms. It can also be used to build up layers on top of already-deposited coatings. Thin film deposition technology or manufacturing processes have become integral to the development of modern electronics such as semiconductors, optical devices, solar panels, disk drives, CDs, etc**[47].** The deposition ways of the thin layers are different from one another. It refers to the diversity of the domain where we use these layers. Scientifically, these ways are divided into two parts: physical and chemical such as Spray pyrolysis which is the spot of our study in this work.

2 Thin Film

Thin film technology is the basis of astounding development in solid-state electronics. The usefulness of the optical properties of metal films, and scientific curiosity about the behavior of two-dimensional solids have been responsible for the great interest in the study of science and technology of thin films. Thin film studies have directly or indirectly advanced many new areas of research in solid-state physics and chemistry which are based on phenomena uniquely characteristic of the thickness, geometry, and structure of the film **[48,49].** Thin films are especially appropriate for applications in microelectronics and integrated optics. However, the physical properties of the films like electrical resistivity do not substantially differ from the properties of the bulk material. A thin film is defined as a low–dimensional material created by condensing, one–by–one, atomic/molecular/ionic species of matter. For a thin film, the limit of thickness is considered between tenths of a nanometer and several micrometers **[49,50,51].** Some of the factors, such as conditions preparation, which determines the physical, electrical, optical, and otherproperties of a film rate of deposition, substrate temperature, environmental conditions, theresidual gas pressure in the system, purity of the material to be deposited, inhomogeneity of the film, structural and compositional variations of the film in localized or wider areas, etc **[52,53].**

3 Thin Film Deposition: Definition and Importance

Thin film deposition is a process in which thin film coatings are produced and deposited onto a substrate. Many different materials can be used to create these coatings, including metals, oxides, and compounds. Additionally, thin film coatings have a variety of traits that can be used to change or enhance a particular aspect of the performance of the substrate. For instance, some are transparent, others are powerful and scratch-resistant, and still, others alter the conductivity of electricity or signal transfer.

Thin films are typically used to improve the surface properties of solids or bulk materials. These properties include but are not limited to transmission, reflection, absorption, hardness, abrasion resistance, corrosion, permeation, and electrical behavior. Hence, it is an important manufacturing step in the production of many solid-state, optoelectronic, and medical devices and products, including consumer electronics, precision optics, compound semiconductors, semiconductor lasers, fiber lasers, microscopy & microanalysis sample slides, LED displays, optical filters, medical implants, and even nanotechnology.

Thin Film Deposition is broadly divided into Chemical Deposition and Physical Vapor Deposition Coating Systems **[47]**.

The thin film deposition methods are summarized in (**Figure III.1**).

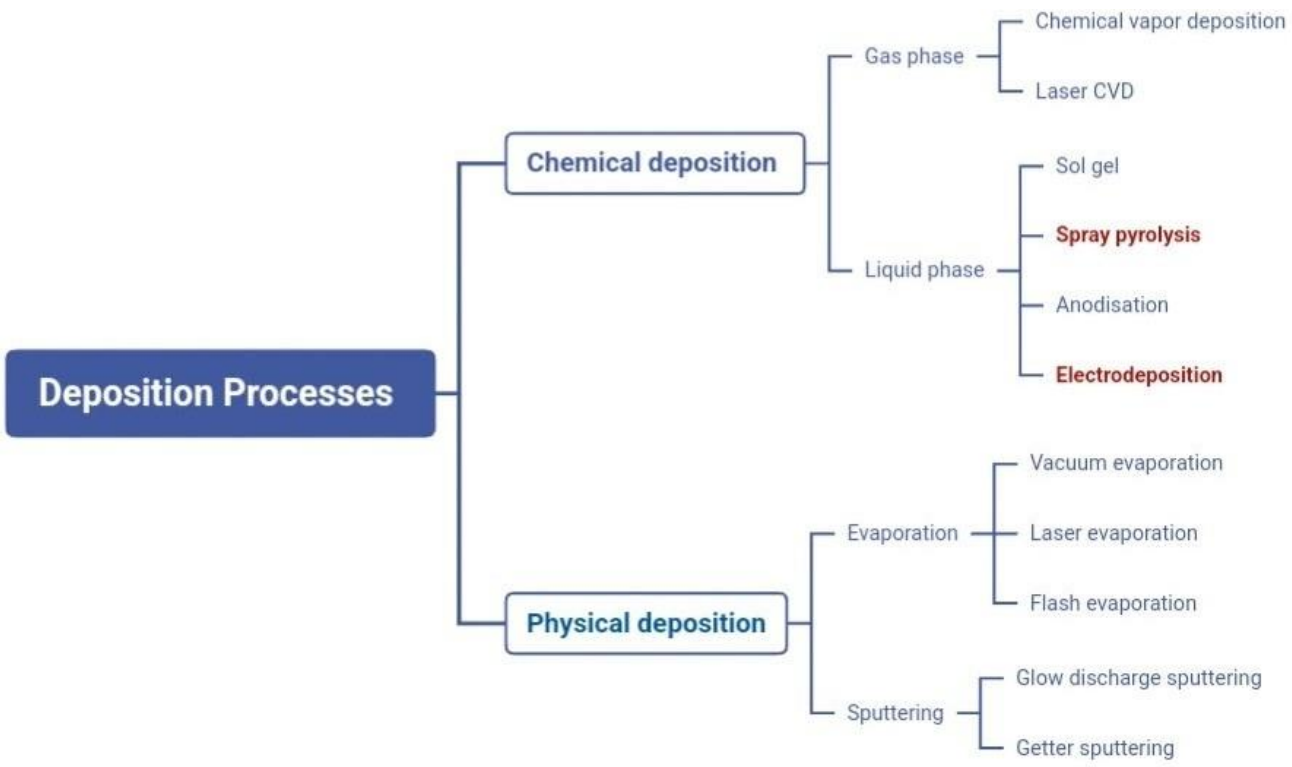


Figure III.1: Classification of Thin Film Deposition Techniques

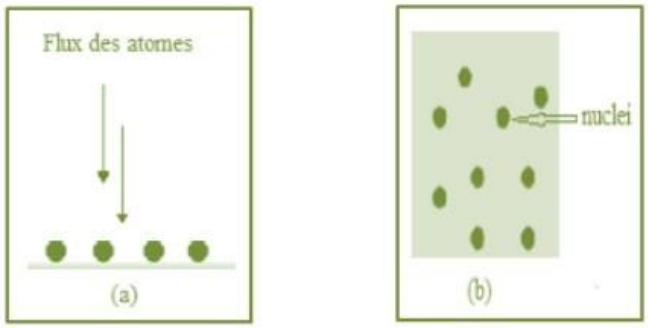
3.1 Thin layer growth mechanisms

To obtain fine-quality thin films for device applications and for a better understanding of their properties, the concepts regarding the nature of the films should be understood. The ideal condition of the film formation involves the deposition of the material atom by atom (or molecule by molecule) and layer by layer with proper time intervals between the two successive depositions so that, they can occupy the minimum potential energy configuration concerning the substrate and subsequently on the previously deposited layers **[54].** For more understanding of thin films, the following properties illustrate various mechanisms occurring at different stages of film growth. There are several stages in the growth process, from the initial nucleation of the deposits to the final continuous three-dimensional film formation states

3.1.1 Nucleation

This is the phenomenon that accompanies changes in the state of matter and consists in the appearance, within a given medium, of points of transformation from which a new physical or

chemical structure develops. Sprayed species arriving on the substrate lose their normal components to the substrate of their speed and are physically adsorbed by the surface of the substrate. These species are not thermodynamically in equilibrium with the substrate and move over the entire surface of it. In this state, they interact with each other and form what are called "clusters". These "clusters" also called nuclei, are unstable and tend to desorb. Under certain depositional conditions, they collide with other adsorbed species and begin to grow. After reaching a critical size, these clusters become thermodynamically stable and the nucleation barrier is breached. The nucleation step is shown in **Figure III.2 [55].**



(a):the arrival of atoms on a substrate. (b): substrate morphology

Figure III.2: Thin-layer nucleation scheme

3.1.2 Coalescence

Nuclei's grow in size and number until they reach a maximum nucleation density. This and the average size of these nuclei's also called islets depend on a number of parameters such as the energy of the sprayed species, the rate of spraying, the energy of activation, adsorption, desorption, thermal diffusion, the temperature of the substrate, the topography and the chemical nature of the substrates. A nucleus can grow simultaneously parallel to the substrate by a phenomenon of surface diffusion of the sprayed species. It can also grow perpendicular to the substrate by spraying species. In general, lateral growth in this stage is much more important than perpendicular growth **Figure III.3** shows the coalescence phase.

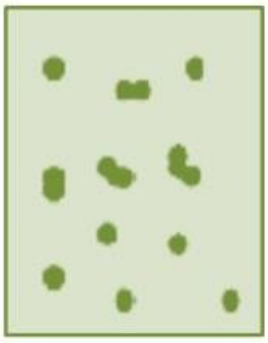


Figure III.3: Diagram representing coalescence.

3.1.3 Growth

The final step in the film manufacturing process is the coalescence step in which the islands begin to regroup. This tendency to form larger islands is enhanced by the growth in surface mobility of adsorbed species. This improvement is achieved by increasing the temperature of the substrate. These larger islets still grow, leaving channels and holes on the substrate.

The structure of the film in this step changes from a type of discontinuous island to a type of porous network. A continuous film is formed by filling the channels and holes **[56].**

(a):Stage after coalescence. (b): growth

Figure III.4: Thin Layer Growth

4 Thin Layer Development Methods

4.1 Physical Processes

The physical method covers the deposition techniques which depend on the evaporation or ejection of the material from a source.

4.1.1 Evaporation

Evaporation is a physical vapor deposition (PVD) process in which the wafer (substrate) is placed in a chamber and subjected to very low pressures as the chamber is removed using a vacuum pump. Once the chamber is free of residual gases, the material to be deposited is subjected to a temperature sufficient to cause it to evaporate. The evaporated molecules are dispersed throughout the chamber, landing on the wafer (and the chamber walls) and condensing, coating the wafer uniformly. Evaporation or sublimation techniques are widely used for the preparation of thin layers. A very large number of materials can be evaporated and, if the evaporation is undertaken in a vacuum system, the evaporation temperature will be very considerably reduced, the number of impurities in the growing layer will be minimized **[57]**.

4.1.2 Sputtering

Sputtering is another physical vapor deposition process that occurs in a vacuum chamber. A large piece of the material to be 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 wafer (i.e. 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 **[58].**

4.2 Chemical Process

Chemical methods depend on physical properties. Structure-property relationships are the key features of such devices and the basis of thin-film technologies. Underlying the performance and economics of thin film components are the manufacturing techniques for a specific chemical reaction **[59].**

4.2.1 Chemical Vapor Deposition

Chemical vapor deposition can be defined as a material synthesis method in which the constituents of the vapor phase react together to form a solid film at the surface. The chemical reaction is an essential characteristic of this method; therefore, besides the control of the usual deposition process variables, the reactions of the reactants must be well understood. Various types of chemical reactions are used in CVD for the formation of solids are pyrolysis, reduction, oxidation, hydrolysis, synthetic chemical transport reaction, etc, several forms of CVD are in wide use and are frequently referenced in the literature **[60].**

- ✓ Metal-organic CVD (MOCVD), CVD processes based on metal-organic precursors;
- ✓ Photo-Enhanced Chemical Vapor Deposition (PECVD)
- ✓ Laser-Induced Chemical Vapor Deposition (LCVD);
- ✓ Low-pressure CVD (LPCVD), CVD processes at sub-atmospheric pressures. Reduced pressures tend to reduce unwanted gas phase reactions and improve film uniformity across the wafer;
- ✓ Plasma-enhanced CVD (PECVD), CVD processes that used plasma to enhance chemical reaction rates of the precursors. PECVD processing allows deposition at lower temperatures, which is often critical in the manufacture of semiconductors.

4.2.2 Sol-gel

Sol-Gel is a chemical method used for the preparation of metal oxide-type materials such as ceramics and glasses. Initially, it consists of a stable suspension (Sol) of chemical precursors in solution. This "Sol" was transformed into a "Gel" during the gelling step result of chemical interactions between species in suspension and solvent, to give an expanded three-dimensional solid lattice through the liquid medium. The obtained gel is "wet" subsequently it was transformed into dry amorphous material by removal of solvents (to obtain an air-gel) or by evaporation under atmospheric pressure (to obtain xerogel) **[61].**

4.2.3 Electrodeposition method

- **Definition:** Electroplating is an electrochemical method of film formation, both metallic and oxide **[60].** This is a process widely used in the industry for many types of applications **[61].**

- **Principle of electrodeposition:** The purpose of electroplating is to apply a surface layer to a metal to confer on this surface the desired properties: aesthetic, magnetic and/or electrical. The principle of electrodeposition is very simple: it is an electrolysis. These are redox reactions (oxydo-reduction), which are triggered by a current source.

$$M^{n+} + ne \rightleftharpoons M \quad \textbf{[62]}$$

This electrochemical method is often operated from traditional electroplating baths. The electrolysis bath is most of the time the critical element of the cell.

It contains the appropriate metal salt (sulphates, chlorides or other salts). The substrate (working electrode) on which the deposit is to be made constitutes the cathode of an electrolytic assembly, the electrolyte in which it is bathed containing metallic ions M^{n+} of positive charge. Polarization of the electrodes will cause these ions to migrate to the cathode, the substrate. The metal ion is neutralized by the electrons supplied by the cathode and deposited on it as metal M following the reaction **[63].**

5 Spray pyrolysis

Chemical spray pyrolysis is a processing technique being considered in research to prepare thin and thick films, ceramic coatings, and powders. Unlike many other film deposition techniques, spray pyrolysis represents a very simple and relatively cost-effective processing method (especially equipment costs). It provides an extremely easy technique for preparing films of any composition. Spray pyrolysis does not require high-quality substrates or chemicals **[64].**

Chemical spray pyrolysis is a process in which a thin film is deposited by pulverization of a precursor solution in the form of micron dimension droplets onto a preheated substrate where the precursor salts undergo pyrolysis to form a desired chemical compound as an adherent film from the more thermally stable compound and volatile by-products evaporate. This process is especially useful for the thin film deposition of metal oxides **[65]**. In the CSP method, thin films are synthesized by nebulizing fine droplets of precursor solutions containing metal salts and different additives (acids, complexing agents, etc.) onto preheated substrates. The schematic diagram of the spray pyrolysis system is presented in **Figure III.5**. The typical CSP system is composed of an atomizer, which helps to produce aerosols, a solution vessel, a heater, and a

temperature controller **[66].** Depending on the atomizer type used, the CSP method can be categorized into three modes: pneumatic, ultrasonic, and electrostatic **[65, 67, 68, 69].** Different parameters such as the deposition temperature, carrier gas, solution spray rate, concentration of starting chemicals in a solution, the distance between a spray nozzle and substrates, nature of the substrates and solvents have been reported to influence the film properties **[70]**.

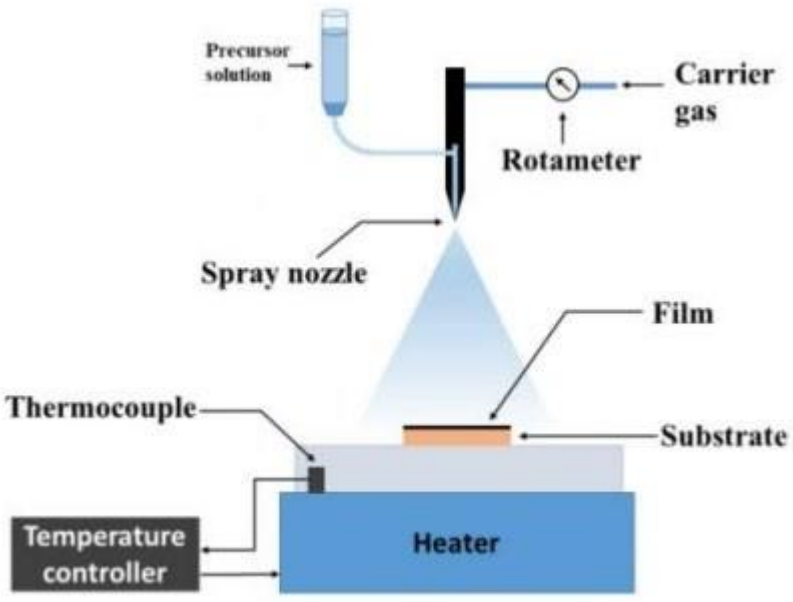


Figure III.5: Scheme of the chemical spray pyrolysis system **[66]**.

5.1 Characteristic features of the spray pyrolysis process

The growth rate of the sprayed films depends upon the chemical and topographical nature and temperature of the substrate, the chemical nature and concentration of the spray solution, and its additives. Another factor that affects the growth rate is the spray parameters like the scanning speed of the spray head, the distance of the spray head from the substrate, the angle of incidence of the droplet on the substrate, etc. The thickness of the film increases almost linearly with spraying time, i.e. with the amount of sprayed solution. In general, the spray pyrolysis process affects the substrate surface. When the substrate shouldn't take part in the pyrolytic reactions, neutral substrates such as glass/quartz, and ceramics are employed. Compared with other techniques for obtaining films, this technique presents a simple experimental arrangement and is a cost-effective method, mainly due to its simple equipment. It

does not require the use of high-quality reagents and substrates. The composition of the films can be easily controlled with the reagents used in the precursor solution. Several types of films have been deposited by spray pyrolysis, and this technique has been used for decades in various industries, such as in the production of glass, solar cells, and electrical conductive electrodes **[71].**

5.2 Advantages and Disadvantages of Spray Pyrolysis

Advantages

- ✓ Low cost (inexpensive apparatus, does require high-quality targets or vacuum);
- ✓ Easy control of composition and microstructure (facile way to dope material by merely adding the doping element to the spray solution;
- ✓ Deposition at moderate temperatures of 100-500°C;
- ✓ Technological ability for mass production.

Disadvantages

- ✓ Possible oxidation of sulfides when processed in air atmosphere;
- ✓ Difficulties with growth temperature determination;
- ✓ After a long processing time spray nozzle may become cluttered;
- ✓ Films quality may depend on the droplet size and spray nozzle **[72].**

6 Characterization techniques

Like all thin coats; ZnO, SnO_2 and their binary and ternary mixtures are materials very sensitive to the conditions of preparation. Therefore, optimization work is necessary to define the best conditions for preparation, which requires a systematic (statistical) analysis of the optical and electrical properties of the material produced.

It is for this purpose that the samples have been analyzed by various material characterizations. To do this we used the following techniques:

- ✓ X-ray diffraction (DRX) for structural study and evaluation of grain size and stresses.
- ✓ Scanning electron microscopy (SEM) for microstructural layer studies.

- ✓ UV-visible spectroscopy for transmittance measurement in the wavelength range [00-00] nm and deduce the value of the optical gap and the disorder in the film network.
- ✓ Electrical measurements using the technique of two spikes.

We present, in detail, these different characterization techniques.

6.1 X-ray diffraction

XRD measurements are conducted to determine the phase composition and crystallographic properties of thin films. On the basis of XRD measurements lays the classical electromagnetic theory when an electron is oscillating in an alternating electromagnetic field with the same frequency as the field. When an X-ray beam hits the atom, electrons of that atom will oscillate in the frequency of the beam. An accelerated charge emits electromagnetic radiation. In most cases the emitted radiation interferes destructively, however, at the right angle of radiation, the emitted radiation coincides and leaves the crystal. The diffraction of X-rays is described by Bragg's equation (11).

$$n\lambda = 2d \cdot \sin\theta \qquad (11)$$

Where :

λ is the X-ray wavelength

d is the interplanar distance

θ is the angle of incidence with the lattice plane

n is an integer.

X-rays with constant wavelength are radiated towards crystal lattice, radiation reflects from lattice atoms illustrated in **Figure III.6**which is captured by a detector **[73, 74].**

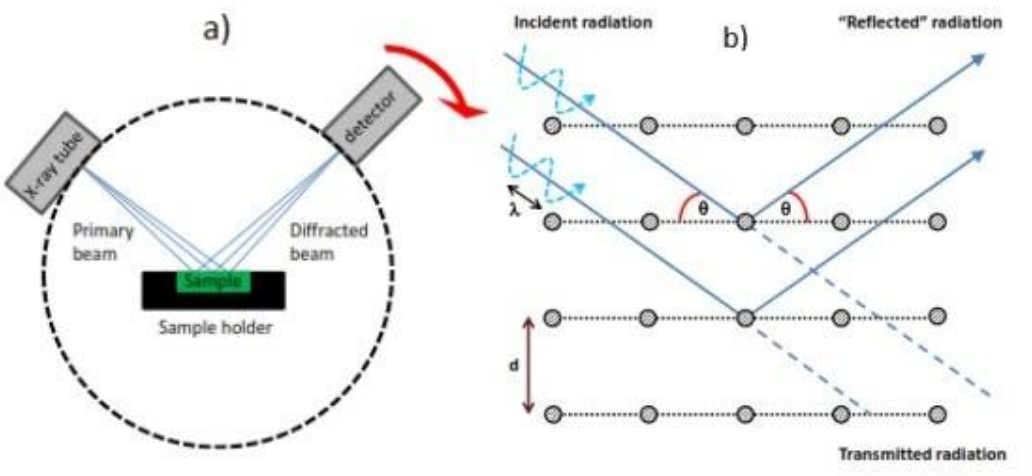


Figure III.6: Scheme of XRD measurement and b) Bragg's geometry of X-ray reflection **[75].**

The intensity of detected radiation is plotted against 2θ. As it is seen in **Figure III.6**, the angle of radiation is varied to find angles where Bragg's equation (11) is satisfied. These angles will generate diffraction peaks in the XRD pattern and these peaks can be compared with previous experimental data giving us information of phase composition, lattice parameters and crystallites orientation **[75].**

6.2 UV-VIS SPECTROSCOPY

Spectroscopy: Spectroscopy is the measurement and interpretation of radiation electromagnetic [EMR] absorbed and emitted when molecules, atoms, or ions in a sample change from one energy state to another.

UV-VIS Spectroscopy: Ultraviolet (UV) spectroscopy is a physical optical spectroscopy technique that uses light in the visible, ultraviolet, and near-infrared domains. It is based on the law of Beer-Lambert, according to which the absorbance of a solution is directly proportional to the concentration of the absorbing species in the solution and the length of the path. For example, for a path length, it can be used to determine the concentration of the absorber in a solution. It is necessary to know how quickly absorbance changes with concentration. UV-VIS spectroscopy has been in use for 37 years and has become the most important analytical instrument in the modern laboratory. In many applications, other techniques can be used, but

none compete with UV-VIS spectroscopy for simplicity, versatility, precision, speed, and cost-effectiveness **[76].**

6.2.1 Principle of UV-VIS spectroscopy

A molecule or ion has an absorption in the visible or ultraviolet region when the radiation causes an electronic transition within its structure. Thus, the absorption of light by a sample in the ultraviolet or visible region is accompanied by a change in the electronic state of the molecules in the sample. The energy provided by the light will move the electrons from their fundamental orbital state to an excited state orbital or a higher energy anti-bond orbital. Potentially, three types of fundamental-state orbitals may be involved.

1. σ (bond) molecular

2. molecular orbital π (binding)

3. Atomic orbit n (not binding) **[76].**

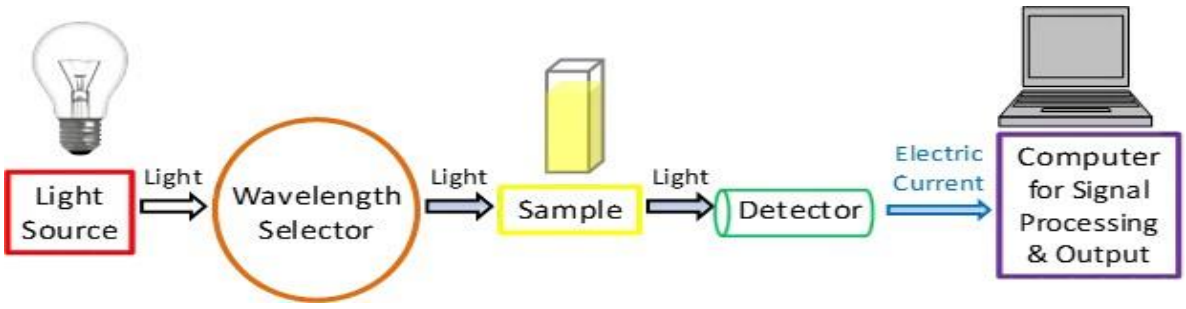


Figure III.7: A simplified schematic of the main components in a UV-Vis spectrophotometer **[77]**.

6.3 Electrical characterization

6.3.1 Two-point technique

The electrical characterization of the intrinsic layer, requires in the simplest case, two metallic coplanar electrodes between which an external electric field directs the carriers towards a well-determined direction. The result is a conduction current that varies with the bias voltage applied between the electrodes. The measurements were made on samples deposited on glass substrates; we sprayed two gold metal electrodes separated by an interelectrode distance of 2mm. A variable voltage is applied between the two points.

6.3.2 Technique of the four points

The 4-point probe setup **Figure III.8** consists of four equally spaced tungsten metal tips with finite radius. Each tip is supported by springs on the end to minimize sample damage during probing. The four metal tips are part of an auto-mechanical stage that travels up and down during measurements. A high-impedance current source is used to supply current through the outer two probes; a voltmeter measures the voltage across the inner two probes, to determine the sample resistivity. Typical probe spacing is ~ 1mm **[78].**

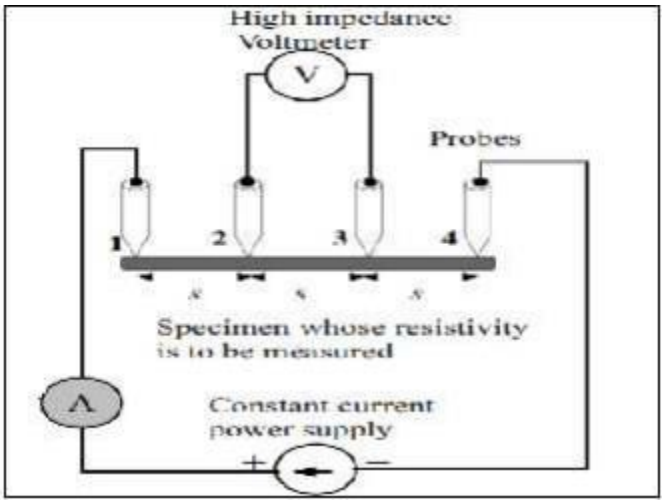


Figure III.8 : Four probe method of measuring resistivity of a specimen **[78].**

In figure (6) for the Four probe method, s is spacing between point probes, unit by meter (m). The two outer probes are used for sourcing current and the two inner probes are used for measuring the resulting voltage drop across the surface of the sample. The volume resistivity is calculated as follows **[79]:**

$$\rho = \frac{\pi}{ln2} \cdot \frac{V}{I} \cdot d \qquad (12)$$

where:

ρ the volume resistivity (Ω.cm);

V: the measured voltage (volts);

I: the source current (amperes);

d: the sample thickness (cm);

Based on a formula (13), we deduce the following:

$$Rs = \frac{\pi}{ln2} \cdot \frac{V}{I} = 4.53 \cdot \frac{V}{I} \quad (13)$$

Experimental part

7 Development Procedures of ZnO Thin Layer

7.1 Preparation of spray solution

The solution used was prepared in distilled water with the following chemicals products:

- ✓ Zinc oxide (ZnO); Other names (Zinc white, calamine, philosopher's wool, Chinese white, flowers of zinc)

Chemical formula	ZnO
Molar mass	81.406 g/mol
Appearance	White solid
Density	5.606 g/cm^3
Melting point	1.974°C (3.585°F ; 2.247K)
Boiling point	2.360°C (4.280°F ; 2.630K)
Band gap	3.3 eV

- ✓ Methanol (CH3OH); Other names (Carbinol, Columbian spirits, Hydroxy methane, MeOH, Methyl alcohol, Methyl hydroxide, Methylic alcohol)

Chemical formula	CH_3OH or CH_4O
Molar mass	32.04 g/mol
Appearance	Colourless liquid
Density	0.792 g/cm^3
Melting point	-97.6°C (-143.7°F ; 175.6K)
Boiling point	64.7°C (148.5°F ; 337.8K)
Vapor pressure	13.02KPa (at 20°C)

To prepare the solution we weighed a certain amount of Zinc oxide (ZnO) by a sensitive electronic scale of the type (OHAUS) with high sensitivity with an accuracy of 10^{-4} grams illustrated in **Figure III.9**

Figure III.9: Scale used to weigh materials

The Zinc oxide (ZnO) has been dissolved in a mixture of doubly distilled water and methanol. methanol solution (99.995%) of absolute purity is provided from Sigma Aldrich; a Few

drops of Hydrochloric acid (HCl) were added to the solution. The mixed solution was stirred by a magnetic stirrer as in **Figure III.10**

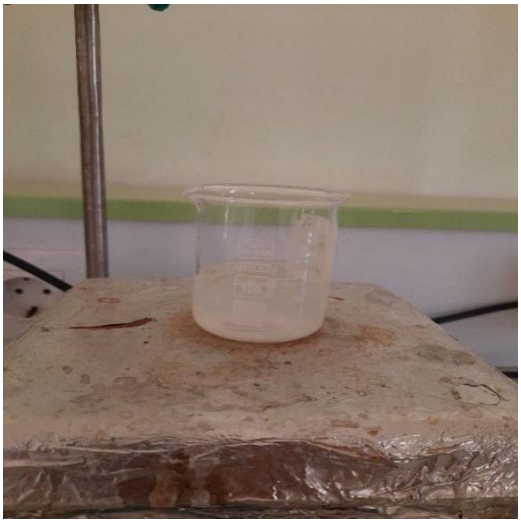


Figure III.10: The magnetic mixer

The mixing process depends on the location of a magnetic part covered by a substance that does not interact with chemical compounds. So that this part is placed in the solution in a glass bowl and the bowl is placed on a magnetic mixer and an electric current is passed, the magnetic stirrer rotates in the solution and mixes the solution at 50°C for 30 min to yield a clear and transparent solution. The spray solution consists of a concentration of 0.1 M of zinc oxide dissolved in methanol.

7.2 Choice of substrate

The type of substrate significantly affects the physical properties of the deposited thin layer compared to those of the same solid material. The physical properties of a thin layer vary depending on whether it is deposited on an amorphous insulating substrate (disordered atomic structure, such as glass) or a monocrystalline substrate (ordered atomic structure, such as a silicon monocrystal)

7.2.1 Monocrystalline silicon substrates

These monocrystalline substrates Si (100) are well suited for optical characterization in the infrared domain, where high resistivity and relatively high thickness are essential to avoid absorption due to free carriers and interference effects.

They have marketed platelets that have excellent surface condition. In our study, we chose these substrates for the determination of the refractive index by spectroscopic ellipsometry

7.3 Substrate cleaning

The choice and preparation of substrates are essential to allow the development of thin layers of good quality. Cleaning them is therefore a very important step to avoid contamination of the surface and the detachment of the deposited layers. Proper cleaning removes grease and dust. Also, the surface condition of the substrate must be free from scratches and flatness.

The process of cleaning the substrate surface is as follows:

- Rinse with distilled water,
- Ultrasonic washing at room temperature in an acetone bath for 15 minutes and then in a methanol bath for 15 minutes to remove traces of grease and impurities glued to the surface of the substrate, then cleaning in an ultrasonic distilled water bath.

Air-reactive substrates, in the case of silicon, are chemically stripped in a dilute hydrofluoric acid bath to remove the native oxide layer.

This is done just before depositing to avoid the formation of oxide during substrate storage.

7.4 Experimental editing

The schematic diagram of the spray paralysis technique is shown in **Figure III.11** at the laboratory (LPCM) of Ammar Telidji University, Laghouat, the latter is built from simple devices to which we have made some modifications to achieve thi relatively homogeneous layers, chosen materials such as ZnO, it consists of spray nozzle, hot plate, substrate, Spraying device, A compressor, thermocouple:

Figure III.11: Pyrolysis spray system

The device comprises:

(a) Spraying device: This is a three-hole device attached from the first hole from above with a thin tube at the end of a tank that contains about 30 ml in which the solutions to be sprayed are placed. It is fixed from the second hole in a horizontal plane with a tube through which

the compressed air from the air compressor passes to extract both the solution and the compressed air from the bottom of the spraying device

(b) Spray Nozzle: It is made up of glass and consists of the inner solution tube surrounded by the gas tube through which carrier gas flows. With the application of pressure to the carrier gas, a vacuum is created at the tip of the nozzle and the solution is automatically sucked and the spray starts.

(c) Substrate: we used glass and silicon substrates

(d) Hot Plate: The iron disc, with a diameter of 18x18 cm, was supported on the electric heater. Maximum temperature up to 500°C can be obtained with this arrangement. Chromel-alumni thermo-couple was used to measure the temperature of the substrates and is fixed at the center of the iron disc. The temperature of the hot plate was monitored with a temperature controller.

(e) A compressor: that decompresses the carrier gas (in our case it is the air) under a controllable pressure. This guarantees that the solution is pushed toward the spout.

(f) Supports.

(g) A digital thermocouple: This thermocouple consists of a weld of two wires. Its tip is placed in the center of the heating plate, it allows to read the temperature to give the direct reading of the temperature using a digital display.

7.5 Spray pyrolysis system set-up

The synthesis procedure comes immediately after the preparation of substrates and solutions; The silicon substrate (2 cm) is placed on top of a heating plate (sample holder) resistor, the sample holder is slowly heated from ambient temperature to the temperature chosen for the thin film syntheses (350, 400°C). When heating is carried out, the flow rate of the solution is fixed, the syringe mode is used. Very fine droplets are sprayed on the heated substrate, which, by pyrolysis, activates the chemical reaction between the compounds. the solvent evaporates due to the endothermic reaction of the two compounds forming the thin layer, finally, we collect our samples.

It is important to note that several experimental parameters are scalable and can influence physical and chemical properties.

As mentioned earlier the technique used pyrolysis spray is a method of synthesis that depends on several parameters such as the properties of the precursor, the concentration of the

solution, the distance between the beak and the substrate, the synthesis time, and the temperature of the substrate, however, the temperature and the deposition time remain the main parameters influencing the quality of the layer.

Therefore, in this work, we limit ourselves only to the parameters which are the temperature of the substrate and the concentration of the solution and the distance between the beak and the substrate.

The repository parameters are varied

• Solution molarities: 0.1mol/l, 0.2mol/l.

• Deposition temperatures: 350°C, 400°C.

• Spout-substrate distances: 5cm.

Conclusion

In this chapter, we have briefly discussed the cognition of thin films for TCOs and the various stages of their growth. Additionally, we have provided an overview of the methods used to deposit these films, along with their respective benefits and drawbacks. Our primary focus has been on the chemical process, specifically the technique of Spray Pyrolysis, which serves as the foundation for our experimental study.

CHAPTER FOUR: Results and Discussion

1. Results and Discussion

1.1 X-ray diffraction studies

This X-ray diffraction study aims to specify crystal growth structure and layer directions and measure mesh parameters and crystal size. It must also allow the state of constraints in the repositories to be examined.

XRD patterns of ZnO film deposited upon silicon (**Figure IV 1**). All peaks in the samples were found to be consistent with the polycrystalline hexagonal structure of Wurtzite ZnO (COD id N 9004181). we have eight major diffraction peaks (100), (002), (101), (102), (110), (103), (202), and (104) corresponding to the Zincite plane phase. from the first three peaks, we found that the third peak (101) is the preferred one.

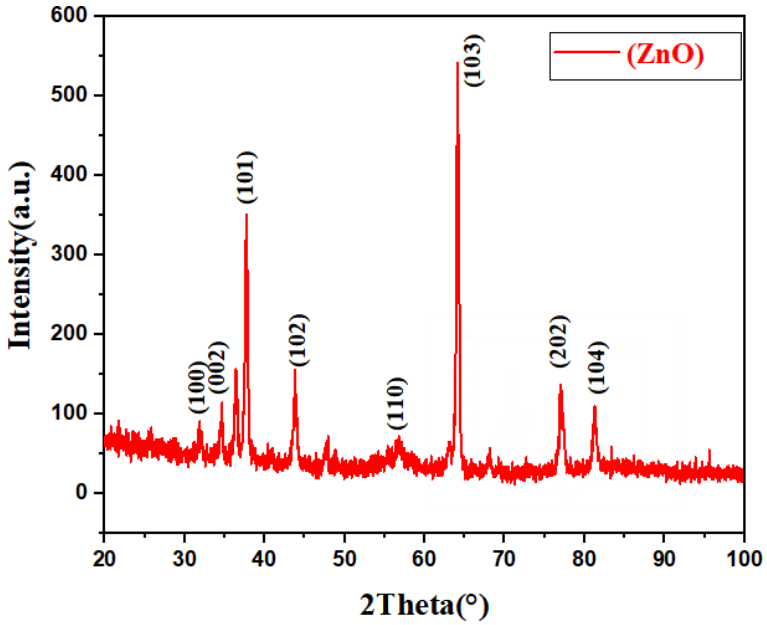


Figure IV 1: X-ray Diffraction pattern of ZnO thin film

1.2 Lattice parameters (a and c)

ZnO has a hexagonal unit cell with two lattice parameters a and c (a = 3.249 Å and c = 5.206 Å in JCPDS No. 5-664). Lattice parameters a and c represent the edge length of the basal plane hexagon and the axial height of the unit cell perpendicular to the basal plane respectively.

According to the following equations:

$$\frac{1}{d_{hkl}^2} = \frac{4}{3a^2} \times (h^2 + hk + k^2) + \frac{l^2}{c^2} \qquad (14)$$

And

$$d_{hkl} = \frac{\lambda}{2\sin\theta} = \frac{0.15406\,nm}{2\sin\theta} \qquad (15)$$

We have found that the calculated lattice parameters a and c show a slight increase in comparison to the standard lattice parameters of ZnO

Table IV.1: ZnO thin film structural parameters

N°	2 Theta(°)	(hkl)	Intens(a.u.)	FWHM(°)	d(hkl)
1	21.65485	(100).	4690.22843	19.41866	0.41005801
2	22.88315	(002).	-2941.16671	14.90905	0.38831752
3	37.69059	(101).	117.59516	0.40174	0.23847266
4	43.78633	(102).	54.71648	0.53159	0.20658282
5	64.12626	(110).	6718.61141	110.60993	0.14510599
6	64.12626	(103).	196.89775	0.39637	0.14510599
7	77.07501	(202).	55.88104	0.57016	0.12363834
8	81.26436	(104).	38.32528	0.58668	0.11828921

1.3 crystallite size(D)

The crystallite size of the ZnO thin films was calculated by applying Scherrer's formula. The equation is below [1-2]:

$$D = \frac{K\lambda}{\beta \cos\theta_{\beta}} \qquad (16)$$

Where:

D: crystallite size, nm

k: Shape constant, 0.9,

λ=1.54 Å is the wavelength of CuKα radiation, nm,

θ: Bragg's angle in degrees,

β: the FWHM in radians.

And

The dislocation density (δ):

$$\delta = \frac{1}{D^2} \qquad (17)$$

The value of strain (ε):

$$\varepsilon = \frac{\beta \cos\theta}{4} \qquad (18)$$

The results are shown in the following table:

Table IV.2: ZnO thin films crystallite size, dislocation density and value of strain

N°	D(nm)	δ (nm-2)	ε
1	0.41652107	5.94715704	4.76823957
2	0.54365388	6.63171771	3.65319245
3	20.8947842	17.5842076	0.0950511
4	16.1059398	23.4321219	0.12331303
5	0.08475002	47.4929689	23.4344752
6	23.6501093	47.4929689	0.0839773
7	17.8131285	65.4174549	0.11149486
8	17.8429208	71.4676877	0.1113087

1.4 Optical study

The optical properties of thin films and bulk materials are extremely important in the optoelectronics applications. The optical characterization of deposited films gives information about the deposited thin films like refractive index, disturbance intensity (energy Urbach), and energy bandgap. optical properties of the sprayed ZnO thin films were investigated via UV-Visible spectroscopy using the transmittance mode at room temperature as a function of the wavelength. Figure 2 shows the transmittance of the ZnO nanofibers deposited on glass and measured at (0.2 Mol) in the range of 320–1100 nm. The transmittance for the sample is effectively increasing rapidly as the wavelength increases in the range of 370–390 nm and then increases slowly at higher wavelengths. The transmittance in the visible region is about 75% **[3].**

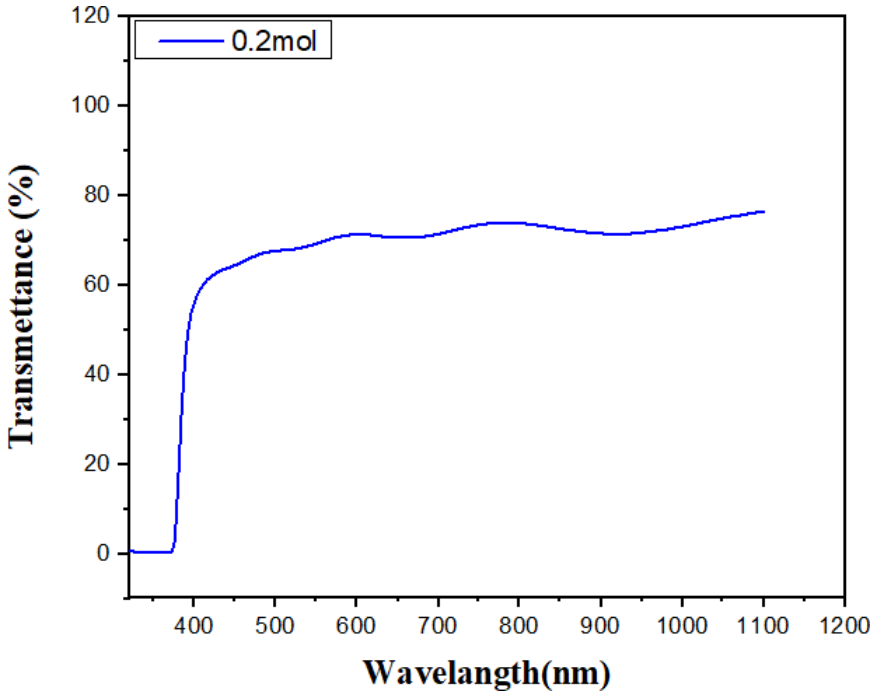


Figure IV 2: Optical transmittance spectra of ZnO nanofibers

Gap energy is one of the distinctive factors in semiconductors. Gap energy, is defined as the energy needed to transport electrons from the top of the equivalence range to the bottom of the conduction range. To determine this energy in the prepared thin layers, we track the curve between $(ahu)^2$ and the photon power (hu) and extend the line (tangent) to the curve **Figure IV.3**. To cut the power axis at the point (hu = En) we find that the power gap value is equal to 3.282eV.

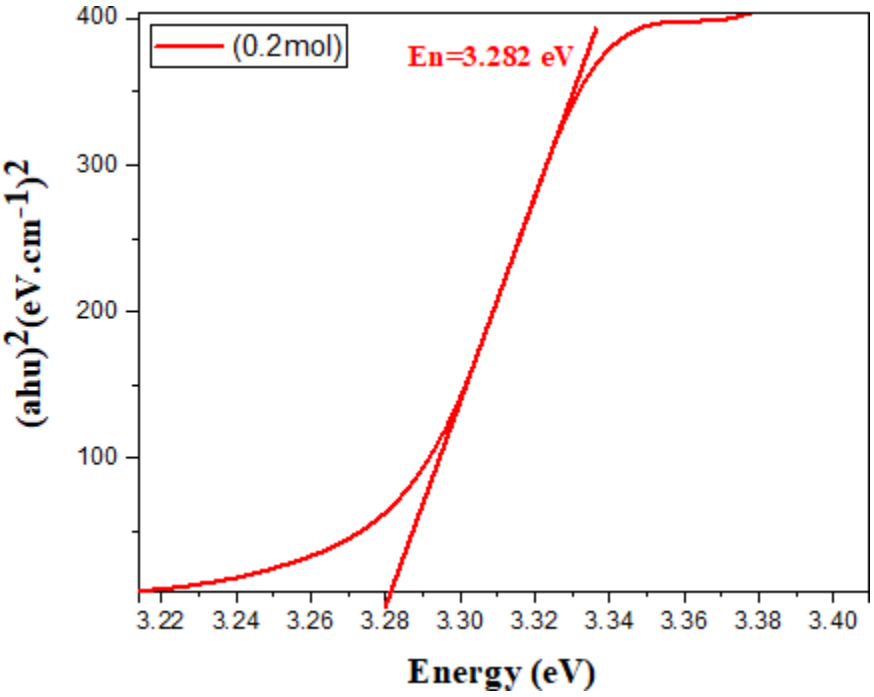


Figure IV.3: The plots of (ahu) ^{2} versus hu of ZnO film

8 The Gas Sensing System

Figure IV.4 represents (a gas sensing system) to examine the sensing performance of thin films. The gas sensor system consists of a movable glass cylindrical test chamber. The heater was fixed on the base plate to heat the sample under test up to the required operating temperatures. Connected to a thermocouple to control the operating temperature. A digital multimeter is used to record the change in resistance of the sensor over time when exposed to the gas. The required gas concentration inside the system was achieved by injecting a known volume of (ethanol, methanol, and acetone) using an injecting syringe to allow it to flow and evaporate on the heater by evaporating to produce VOCs inside the test chamber. Air was allowed to pass into the glass dome. The resistance of the airflow bias is recorded using a multimeter. Subsequently, the VOC gas is introduced, and the resulting change in resistance is measured. Following this, the VOCs are released, and the resistance undergoes further changes. Finally, the sensitivity value, response time, and recovery time are computed based on these measurements.

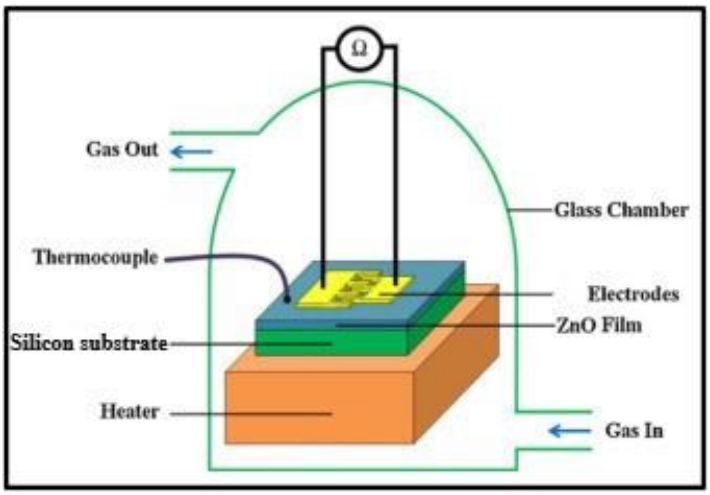


Figure IV.4: experimental setup schematic **[4].**

Figure IV.5: experimental setup **[5].**

In order to examine the influence of gas concentration on our sensor, we studied the detection properties of different concentrations of VOCs (0.1ml,0.2ml,0.4ml) at a constant temperature of 200°C.

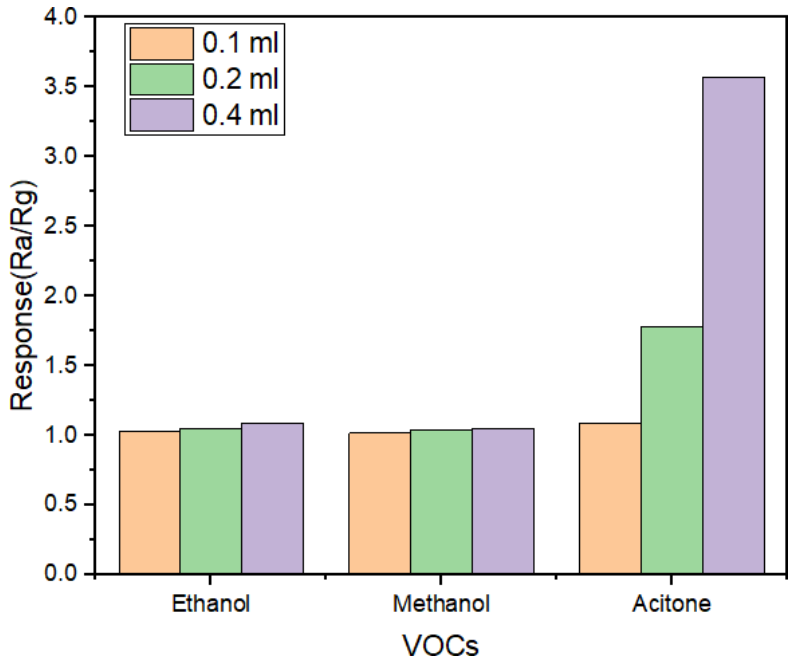
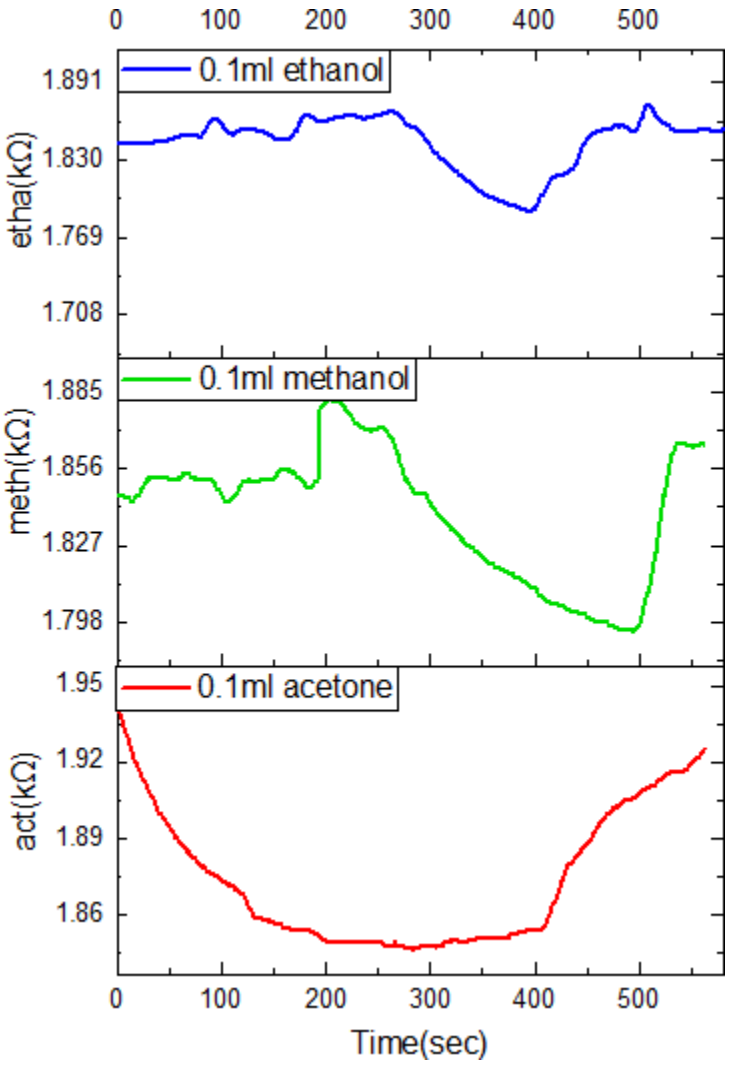


Figure IV.6: the response (Ra/Rg) of the three analytic vapors at different concentrations

Figure IV.6 represents a graphic column showing the response (Ra/Rg) of the three analytic vapors at different concentrations at constant temperature. The highest sensor response has been demonstrated for acetone vapor. From the figure it is clear that the prepared ZnO gas sensor is highly sensitive to acetone; however, at the same temperature the sensitivity of both ethanol and methanol is still high, which makes it difficult to distinguish between them in real-life measurements, where both acetone and ethanol have the same chemical behavior



FigureIV.7: resistance changes of VOCs by time of constant concentration (0.1ml)

Figure IV.7 represents three curves of three different VOCs (acetone, methanol, and ethanol) representing resistance changes by time of constant concentration (0.1ml) and constant temperature. Through the results obtained, we observe a decrease in resistance when exposed to the gas.

These results are interpreted as follows:

As a typical n-type semiconductor. When ZnO thin films are exposed to the air, oxygen molecules will be adsorbed on the surface, capturing free electrons from the conduction band to form negative oxygen species, such as O^{2-}, O, and O^{2-} , resulting in an electron depletion layer (LD) and higher resistance. As reductive gases such as acetone, methanol, and ethanol vapors get

to the sensor, they will react with the oxygen species on the ZnO surface, the trapped electrons can be released to the conduction band, leading to a resistance decrease.

The response time, τ_{res}, is defined as the time taken by the resistor ranging from Ra to [Ra - 90% (Ra - Rg)] when the sensor is exposed to the target gas. And the recovery time, τ_{rec} is defined as the time taken by the resistor changing from Rg to [Rg + 90% (Ra - Rg)] when the sensor is retrieved from the target gas. For acetone, the response time was the best (τ_{res}=126 sec) in comparison to ethanol (τ_{res}=130 sec) and methanol (τ_{res}=239.24 sec)

CONCLUSION

In last chapter we started with the results of the characterization of the ZnO thin layer where the results of structural X-ray diffraction confirmed the formation of ZnO with a hexagonal structure and The gap energy is calculated by the Taucplot method using the results of the ZnO transmittance on silicon in the UV-VIS domain. The optical gap is equal to 3.758 eV

The rest of this chapter is devoted to the detection of VOCs (aceton, ethanol and methanol).The results clearly show that the ZnO-based sensors were more responsive to aceton vapor (VOCs) than the other two VOCs (ethanol, methanol).

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GENERAL CONCLUSION

The development of a zinc oxide (ZnO) gas sensor to detect volatile organic compounds represents a significant advance in gas sensing technology. Through this project, we explored ZnO's potential as a sensor material and its compatibility with manufacturing techniques, its unique properties including a surface-to-volume ratio, large specific area, and gas adsorption properties, the main goal of this work was to create a gas sensor to detect volatile organic compounds. We were able to deposit the thin layer of ZnO by a very simple method called pyrolysis spray. We used silicon substrate, zinc molar oxide solution (0.2 mol/l).

Many technologies have been used to characterize ZnO layers. Structural characterization was performed by X-ray diffraction (DRX). optical transmission was obtained by UV spectrometry, and was used to determine optical gap energy and Auerbach's parameter.

Structural X-ray diffraction analyses confirmed the formation of ZnO with a hexagonal structure. It was also used to assess the different sizes of crystal crystals that make up our thin layers. The peaks are consistent with ZnO peaks according to map (JCPDS) No. 0.06-0395.

The gap energy is calculated by the Taucplot method using the results of the ZnO transmittance on silicon in the UV-VIS domain. The optical gap is equal to 3.282 eV.

Images of prepared samples show that there are no overlapping colors in the layers deposited on silicon confirming the suction of deposition of the ZnO thin layers and that these layers are homogeneous. The transparency of the deposited layers on glass confirms that the deposited layers belong to the TCO family. Changing the color of the layer deposited on the glass in the same conditions confirms the type of effect of the substrate in the form of the ZnO layers.

ZnO thin layers deposited on silicon were used to manufacture gas sensors for detection of (VOCs). The results clearly show that the ZnO-based sensors were more responsive to acetone vapor (VOCs) than the other two VOCs (ethanol, methanol)

As with any research project, there are limitations and areas for future exploration. For instance, further investigation can be conducted to optimize the sensor's response time, stability, and selectivity towards specific VOCs, and to Improve sensors manufactured so they can operate

at room temperature, The use of other metal oxide layers deposits (ZnO@Al , ZnO@Co,etc.) to compare the sensors made Additionally, the integration of multiple sensing materials or functionalization techniques could enhance the sensor's performance and broaden its detection capabilities.

Overall, the gas sensor based on ZnO presented in this project provides a solid foundation for continued research and development in the field of gas sensing. By further refining the fabrication processes, exploring new materials, and incorporating advanced data analysis techniques, we can unlock even greater potential in VOC detection and contribute to a safer and healthier environment for all.