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Theme

Investigation of ZnO Thin Films Prepared by Spray Pyrolysis for UV Photodetector Applications

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General introduction

In recent years, ultraviolet (UV) photodetectors have garnered significant attention due to their diverse applications in areas such as environmental monitoring, biomedical devices, and optical communication. Zinc oxide (ZnO) emerges as a promising material for UV photodetection owing to its wide bandgap, high electron mobility, and excellent optical properties. This thesis explores the fabrication and characterization of ZnO-based UV photodetectors, focusing on optimizing device performance through innovative deposition techniques and high detection response,.and low fabrication cost

uv photodetectors based on zinc oxide (ZnO) have emerged as promising candidates for uv 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 uv absorption characteristics. By leveraging the interaction between ZnO and light, these sensors can provide rapid, sensitive, and selective detection of various volatile compounds.

The development of a ZnO-based uv photodetector 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, wide band gap , 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 uv photodetector 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 spectrum of light, measuring the resulting electrical response, and analyzing the data to establish calibration curves and detection limits.

The successful implementation of a ZnO-based uv photodetector 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 uv 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 photodetectors, especially uv photodetector. 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.

Abstract:

Ultraviolet (UV) radiation poses significant health risks and environmental concerns, necessitating advanced detection methods. This study explores the fabrication of zinc oxide (ZnO) thin films on silicon and glass substrates using the spray pyrolysis technique, optimized through careful control of deposition parameters including spray nozzle-substrate distance, deposition temperature, and solution concentration. The deposited ZnO films were utilized to develop UV photodetectors.

Spray pyrolysis, known for its simplicity and cost-effectiveness, enabled the uniform deposition of ZnO films. Optical and structural properties were characterized using UV-Visible spectrophotometry and X-ray diffraction (XRD), respectively. The study specifically investigated the UV detection properties of the ZnO films.

Results demonstrate that the ZnO-based photodetectors exhibited high sensitivity and response to UV light. Electrical conductivity measurements further validated the films' suitability for UV photodetection applications. This research highlights the efficacy of spray pyrolysis in producing ZnO thin films with tailored properties for UV photodetection, suggesting their potential in areas such as environmental monitoring and UV-related health assessments.

Keywords: Thin film, ZnO, X-ray diffraction (XRD), Electrical conductivity, Spray pyrolysis, UV photodetector.

Résumé :

Le rayonnement ultraviolet (UV) pose des risques importants pour la santé et des préoccupations environnementales, nécessitant des méthodes de détection avancées. Cette étude explore la fabrication de couches minces d'oxyde de zinc (ZnO) sur des substrats de silicium et de verre en utilisant la technique de pyrolyse par pulvérisation, optimisée grâce à un contrôle minutieux des paramètres de dépôt, y compris la distance buse-substrat de pulvérisation, la température de dépôt, et concentration en solution. Les films de ZnO déposés ont été utilisés pour développer des photodétecteurs UV.

La pyrolyse par pulvérisation, connue pour sa simplicité et sa rentabilité, a permis le dépôt uniforme de films ZnO. Les propriétés optiques et structurelles ont été caractérisées par spectrophotométrie UV-Visible et diffraction des rayons X (XRD), respectivement. L'étude a spécifiquement étudié les propriétés de détection UV des films ZnO.

Les résultats démontrent que les photodétecteurs à base de ZnO présentaient une sensibilité et une réponse élevées à la lumière UV. Les mesures de conductivité électrique ont confirmé l'aptitude des films pour les applications de photodétection UV. Cette recherche met en évidence l'efficacité de la pyrolyse par pulvérisation dans la production de couches minces de ZnO avec des propriétés adaptées pour la photodétection UV, suggérant leur potentiel dans des domaines tels que la surveillance environnementale et les évaluations de santé liées aux UV.

Mots-clés : Film mince, ZnO, diffraction des rayons X (XRD), conductivité électrique, pyrolyse par pulvérisation, photodétecteur UV.

ملخص:

تشكل الأشعة فوق البنفسجية مخاطر صحية كبيرة وشواغل بيئية، تتطلب أساليب كشف متقدمة. تستكشف هذه الدراسة تصنيع أغشية أكسيد الزنك الرقيقة (ZnO) على ركائز السيليكون والزجاج باستخدام تقنية الانحلال الحراري للرذاذ، والتي تم تحسينها من خلال التحكم الدقيق في معلمات الترسيب، بما في ذلك ركيزة المعالج البعيد من الفوهة إلى الزجاج ودرجة حرارة الترسيب والتركيز في المحلول. تم استخدام أفلام ZnOالمودعة لتطوير أجهزة الكشف عن الأشعة فوق البنفسجية.

سمح الانحلال الحراري بالرش، المعروف ببساطته وفعاليته من حيث التكلفة، بالترسيب الموحد لأفلام .ZnO تميزت الخصائص البصرية والإنشائية بقياس الطيف المرئي بالأشعة فوق البنفسجية وحيود الأشعة السينية (XRD) على التوالي. بحثت الدراسة على وجه التحديد في خصائص اكتشاف الأشعة فوق البنفسجية لأفلام.ZnO

تظهر النتائج أن أجهزة الكشف الضوئي القائمة على ZnO أظهرت حساسية عالية واستجابة للضوء فوق البنفسجي. أكدت قياسات التوصيل الكهربائي ملاءمة الأفلام لتطبيقات الكشف الضوئي بالأشعة فوق البنفسجية. يسلط هذا البحث الضوء على فعالية الانحلال الحراري بالرش في إنتاج أغشية رقيقة ZnO بخصائص مناسبة للكشف الضوئي للأشعة فوق البنفسجية، مما يشير إلى إمكاناتها في مجالات مثل المراقبة البيئية والتقييمات الصحية المتعلقة بالأشعة فوق البنفسجية.

الكلمات الرئيسية: فيلم رقيق، ZnO، حيود الأشعة السينية(XRD) ، التوصيل الكهربائي، التحلل الحراري بالرش، كاشف ضوئي للأشعة فوق البنفسجية..

ABBREVIATIONS :

MOS : metal oxides semiconductors

UV : ultraviolet

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 theconduction 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

I CHAPTER ONE I: Bibliographic Study on metal oxides

I.1 Metal oxide Semiconductor (MOS) :

Semiconductor metal oxide (MOS) materials are promising candidates for various electronic devices. They have attracted considerable attention due to their superior electrical performance, high transparency, excellent stability and uniformity [1]. In this chapter, we introduce mainly some basic ideas of MOS.

I.2 Definition of MOS:

The oxide contains at least one oxygen and another element, existing in the solid, liquid and gaseous phase. A very common example of liquid oxides at room temperature is hydrogen oxide (H_2O) which we call water, used as a universal solvent and necessary for life on our planet. Carbon dioxide (CO_2) is one of the most important gases on the planet, because plants absorb it and use it as an ingredient of photosynthesis, it is considered one of the products of breathing. Besides water and gas oxides, solid (metal) oxides also play an important role in our daily life.

For example, silicon oxide (SiO_2), also called silica, has many applications in everyday needs, architectures and technologies [2]. Semiconductor metal oxides represent a unique class of materials due to their electronic load carrying properties compared to conventional covalent semiconductors such as silicon (Si). Semiconductor metal oxides are valence compounds with a high degree of ionic bonding. Their conduction band minimum and valence band maximum consist mainly of the metal orbital (M) ns and oxygen (O) 2p, respectively. The interaction between metallic and oxides orbitals leads to a significant disparity in the transport of load carriers. In general, the orbitals (M) ns are very dispersive while that of (O) 2p is localized, resulting in a smaller effective mass for the electrons compared to the holes. Typical semiconductor metal oxides, such as ZnO, SnO_2 and TiO_2 as well as their solid solutions, mainly have a conductivity of type n [3]. MOS has a very large group of materials, they differ from each other in their crystal structure, inherent defects, energy band level and other physicochemical aspects [2]. For example, in terms of crystalline structure, ZnO could exist in hexagonal wurtzite or cubic zincblende. However, under ambient conditions, hexagonal wurtzite is more stable and common [4]. The network constants of ZnO in wurtzite form are a = 3.250 Å and c = 5.207 Å, where the c/a ratio is 1.633, close to the ideal value [5]. TiO_2, on the other hand, can have three different crystalline forms: anatase (a = 3.785 Å, c = 9.513 Å), rutile (a = 4.593 Å, c = 2.959 Å) and brookite (a = 5.455 Å, b = 9.181 Å, c = 5.142 Å) [6] while SnO2 belongs to the tetragonal rutile and the network constants are a = 4.738 Å, c = 3.187 Å [7]. These various crystal structures lead to different unique properties of MOS.

I.3 Properties of MOS

The properties of semiconductor metal oxides are also strongly related to processing methods and preparation and deposition conditions. The mastery of these techniques and conditions makes it possible to obtain a semiconductor metal oxide with well-defined physicochemical properties.

I.4 Different types of MOS

Semiconductor metal oxides (MOS) can be divided into two main families. The first family presents an n-type behavior as an example (ZnO, SnO_2, TiO_2, WO_3, Ta_2O_5 and Nb_2O_5) or the load carriers are free electrons. The n-type OMSs fill the majority of photodetector-type applications because they are more stable and have more favorable properties for chemsorption. The second family is characterized by p-type behavior as an example (CuO, NiO, Cr_2O_3, Mn_3O_4 and Co_3O_4) or load carriers are free holes. Therefore, when two semiconductor metal oxides are combined to form a heterojunction, three types of heterojunctions are obtained: p-n junction, n-n junction and p-p junction [1].

Among these metal oxides, zinc oxide (ZnO) may have different and interesting morphologies such as nanowires [8], nanotiges [9], nanoflowers [10], nanobelts [11], nanorings [12] and nanotubes [13]. etc., which make them useful for manufacturing nanodevices for optoelectronic and detection applications.

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

Table 1 Different types of metal oxide

I.5 Application of nanostructured MOS

MOS are widely used in many areas of technology, its applications directly related to their properties, including nanotechnology, microelectronics, photovoltaics, photocatalysis, lithium rechargeable battery (Supercapacitor), electrodes and gas detection. In the latter, the MOS represent a sector of activity in constant evolution. They have been extensively researched and developed as important devices for detecting gas leaks and are also found in various technological fields, including air quality, combustion, industrial processing, the food industry and medical diagnosis through expired air analysis [14].

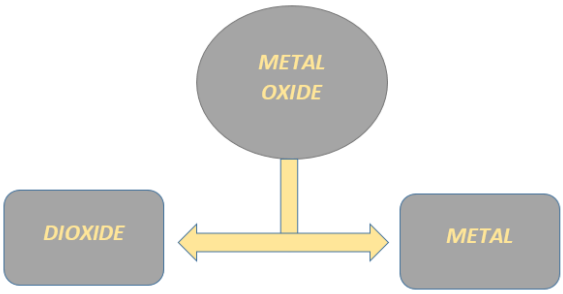

Figure 1 Metal oxides Semiconductor diagram

I.6 THE ZNO CHOICE:

.Zinc oxide has emerged as the most promising material. This is due to its optical and electrical properties, its very high thermal and chemical stability, its non-toxicity and its abundance in nature that have made it a material at a reduced price (unlike, for example, ITO). In addition, it has a gap of 3.3eV and an excitation state with a binding energy of 60meV which allows a sufficient emission of UV [15] and stands for the special qualities needed to create the perfect uv photodetector.

I.7 ZnO Properties

I.7.1. Structure of Zinc Oxide (ZnO)

The most stable thermodynamic form, the wurtzite hexagonal structure [16], is how zinc oxide crystallizes at room temperature and pressure. The zinc atoms in this structure occupy half of the tetrahedral interstitial locations, while the oxygen atoms occupy the tops of a tetrahedron. Zinc oxide's crystalline growth axis is c (002) Figure 2.

Under certain growth conditions, ZnO can also display additional structural forms, such as the blende and rock salt formations. Since the zinc and oxygen atoms only occupy 40% of the crystal's volume, the wurtzite structure of ZnO is known as lacunary [17], leaving vacant spaces with a radius of 0.95Å. This structure permits the introduction of additional zinc atoms or contaminants into these voids in precise interstitial regions when certain conditions are met. This may change a few of the material's characteristics. When mechanical stress is applied, the spatial dispersion of the barycentres of positive Zn2+ and negative O2- charges results in the formation of a piezoelectric polarization field in addition to a spontaneous polar field along the c-axis.

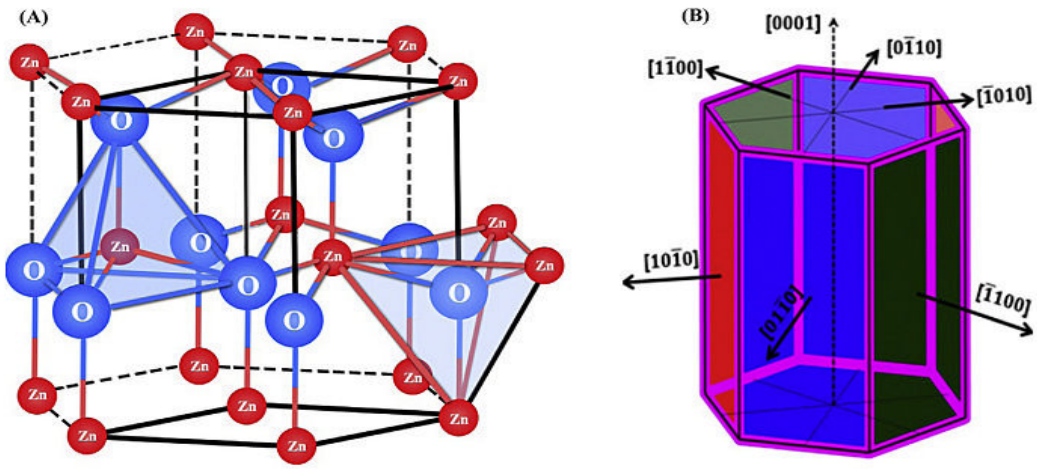

Figure 2 : Structure hexagonale de ZnO [9].

I.7.2. Electrical and electronic properties of Zinc Oxide (ZnO)

ZnO is a type n semiconductor having an excitonic bonding energy of 60 meV and a direct gap of 3.37 eV at room temperature [18]. It is intrinsic, which means that an electron can go from the valence band to the conduction band with just enough thermal energy.

The band structures of the electronic oxygen and zinc are:

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

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

The ZnO semiconductor's valence band is made up of the oxygen 2p states, whereas the conduction zone is made up of the zinc 4s states. ZnO's electrical resistivity can be changed by either forming oxygen gaps that serve as electron donors or by shifting away from the stoichiometric structure by adding extra zinc atoms to the interstitial locations. The latter is likewise dependent on production temperature, doping, deposition process parameters, annealing, etc. [19].

I.7.3. Optical properties of Zinc Oxide (ZnO)

When zinc oxide is in its massive state, its refractive index equals 2.0. The refractive index and absorption coefficient of thin layers change depending on the manufacturing conditions. The author states that the refractive index has a value that ranges from 1.7 to 2.2. The energy of the forbidden band rises and the absorption coefficient falls as a result of the improved ZnO stoichiometry [20].

I.7.4. MECHANICAL PROPERTIES:

ZnO is a relatively soft material with a hardness of about 4.5 on the Mohs scale. Its elastic constants are smaller than those of relevant III-V semiconductors, such as GaN . The high thermal capacity and thermal conductivity, low thermal expansion and high melting temperature of ZnO are beneficial for ceramics. The most stable ZnO phase is wurtzite, ZnO has a very long optical life. Among glued tetrahedral semiconductors, ZnO has the largest piezo tensor, or at least one comparable to GaN and AlN, this property actually makes it a technologically important material for many piezoelectric applications, which require a large electromechanical coupling [21].

I.7.5. APPLICATIONS OF ZnO:

Among the multiple applications of this material in optoelectronic devices [15]:

• Solar cells (transparent electrodes).

• Acousto-optical media.

• Gas detectors (conductive gas sensors).

• Optical waveguide.

• Pression protector.

• Ultrasonic oscillators and piezoelectric transducers.

• Detectors in the (UV) laser and detector photos.

• Transparent and anti-reflective layers.

• Photo electrochemical cells.

I.8 CONCLUSION:

This chapter explores the promising potential of metal oxide semiconductors (MOS) in various technological applications due to their unique properties, including exceptional electrical performance, high transparency, stability, and uniformity. It discusses the definition and types of MOS, highlighting the differences between n-type and p-type oxides and their respective applications.

Zinc oxide (ZnO) is emphasized as a standout material due to its favorable optical and electrical properties, high stability, non-toxicity, and abundance. ZnO's ability to form various nanostructures expands its use in nanodevices for optoelectronics and sensing. Its electrical, optical, and mechanical properties make it suitable for diverse applications such as solar cells, gas detectors, optical waveguides, and photodetectors.

II CHAPTER Two II :(UV) photodetection

II.1 introduction

In recent years, the number of ZnO Nano devices has been developed successfully such as transistors, sensors, solar cells and photodetectors]. UV detector is one of the eye catching devices due to its wide applications in the field of flame sensing, missile plume detection, space-to-space communication, astronomy and biological research [22]. Various wide band gap semiconductors such as GaN, AlGaN, diamond, SiC [23], III–V compounds [24] and II–V compounds [25] have been used to fabricate UV photodetectors. Among them ZnO based UV detector have attracted considerable attention recently because of its properties like wide band gap (3.34 eV), high exciton binding energy (60 meV), non-toxicity, high radiation hardness and higher transparency in the visible region. It has been well known that the conductivity of ZnO can be dramatically increased under UV illumination and fact has been used in UV sensor applications.

II.2 Background of UV photodetectors

UV detection technology has a long history, dating back to the early twentieth century when researchers first investigated the properties and effects of ultraviolet radiation. In the 1920s, Robert W. Wood pioneered the use of UV photography, leading to advances in understanding UV's interactions with diverse materials. By the mid-twentieth century, as semiconductor technology advanced, researchers began employing materials such as silicon carbide (SiC) and gallium nitride (GaN) for UV sensing, boosting sensitivity and stability. Zinc oxide (ZnO)'s potential as a UV detector material was investigated in the 1990s due to its wide band gap and high exciton binding energy, which provided improved performance under difficult conditions. This decade saw substantial developments in UV detector applications, ranging from military to environmental monitoring.establishing the technology's crucial role in modern science and industry.

Ultraviolet (UV) radiation is an important component of solar radiation .which has a significant impact on the development and survival of mankind. Extreme UV radiation can cause various diseases, including cataracts and skin cancer, Photodetectors are one of the popular types of technology used in ultraviolet radiation research. They are widely used in the industrial area (flame detectors, fire alarm systems, extreme UV lithography), national security (missile defense, military recognition, explosives detection, forensic analysis, secure communications), in fields

such as medicine (UV imaging, protein analysis, and DNA sequencing) or biology (biological agent detection), and when dealing with environmental issues (ozone detection, air pollution determination, disinfection, and decontamination).[26]

II.3 Definition of a Photodetector

A photodetector is an optoelectronic device that captures electromagnetic radiation, absorbs it, and converts it into thermal, mechanical, or, in most cases, electrical energy [27]. This device exemplifies the direct phenomenon of light-matter interaction. Here, we focus on devices that generate an electrical signal following optical excitation. There are different types of photodetectors [28]:

- Passive photodetectors: No external power source is required, such as solar cells.
- Active photodetectors: An external power source is required.

II.4 Structure of a Photodetector

In its basic structure, photodetectors are composed of a homogeneous semiconductor material, called photosensitive, which is connected to an electrical circuit using two ohmic contacts (two electrodes). These contacts allow a voltage to be applied across the material, resulting in a current I. The typical bias circuit of a photodetector is shown in Figure 3. Under the effect of an optical beam, the photodetector generates electron-hole pairs that modify the conductivity of the absorbing layer and, consequently, the conductance of the semiconductor. This results in an increase in current I in the circuit due to the generation of photocurrent I_{ph_o}.

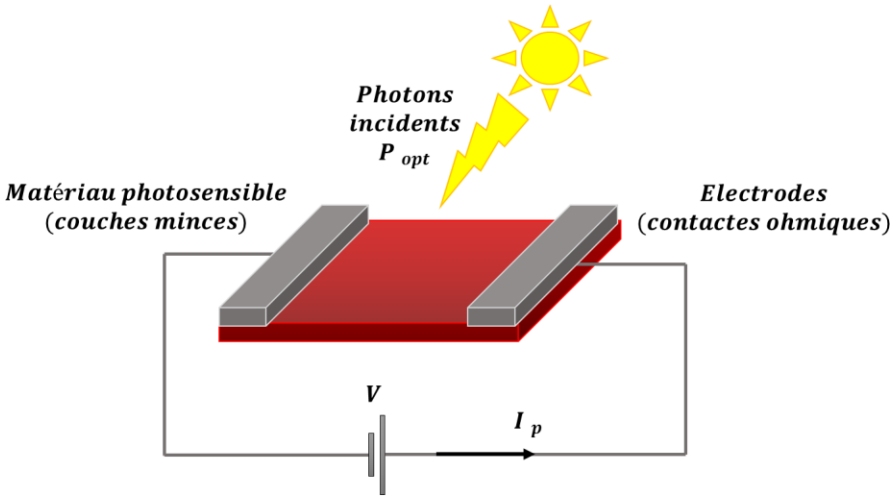

Figure 3 Schematic representation of a photodetector.

II.5 Operating Principle of a Photodetector

The photodetector operates according to the general principle illustrated in Figure 4. Each incident photon transfers its energy $\hbar\, v$ to an electron in the active material, as long as its energy is greater than or equal to the bandgap width E_g of the semiconductor [29].

When a photon with sufficient energy propagates towards an electron in the valence band, the electron absorbs it and moves to the conduction band, producing an electron-hole pair and resulting in photocurrent I_{ph} . In a photodetector, these pairs are separated by the external electric field $\vec{E}_{ext}$, as illustrated in Figure 4; electrons and holes move to respective electrodes. The mechanisms involved depend on the photodetector's structure. This leads to a current of charges in the external circuit, restoring the electrical neutrality of the material [30].

The process of generating photocurrent I_{ph} in a photodetector consists of four distinct steps [31]:

- ✓ Absorption of incident photons
- ✓ Generation of excitons (electron-hole pairs) in the material
- ✓ Separation of charge carriers
- ✓ Collection of charge carriers by the electrodes

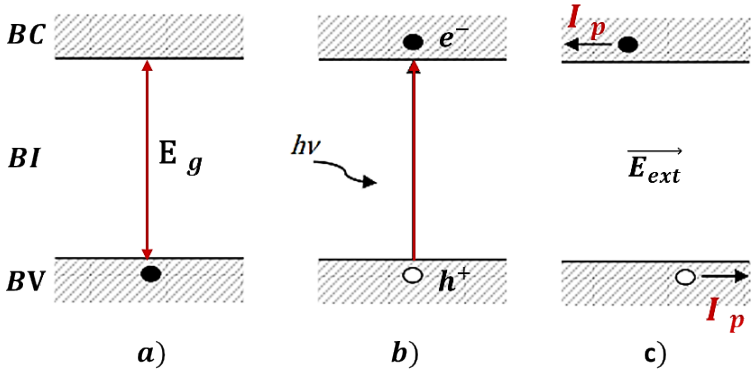

Figure 4 Transition of charges between energy bands: (a) Stable state (absence of incident photon). (b) Creation of electron-hole pairs by photon absorption (photo-excitation) and (c) Creation of displacement current under the action of an external electric fie

II.5.1. Characteristics of a Photodetector

To meet a targeted application, it is important to understand the electrical behavior of a photodetector in response to incident optical radiation. Below are the various characteristics that best describe a photodetector's performance.

II.5.2. The Sensitivity (S) and ON/OFF Current Ratio I_{ON}/I_{OFF}

The ratio between the current measured under illumination I_{ph} and the current measured in the dark I_{obs}, I_{obs} is also a characteristic that evaluates a photodetector's performance. It indicates the quality of the photodetector's response to incident light. The higher this value, the more charge carriers the detector will have generated by absorbing photons [32].

$$s = \frac{I_{ph} - I_{abs}}{I_{abs}} [\%] \qquad (1)$$

II.5.3. Spectral Response (λ)

Responsivity or spectral response R(λ). is a means to quantify a photodetector's sensitivity. This characteristic results from quantum efficiency and directly relates the photocurrent generated by the photodetector to the optical power of the incident light [64]. The responsivity value is given by:

$$R(\lambda) = \frac{I_{ph}}{P_{\text{opt}}}[A/W] \qquad (2)$$

Where:

- ✓ I_{ph} is the photocurrent generated by the photodetector following optical excitation;
- ✓ P_{opt} is the optical power of the incident light.

II.5.4. External Quantum Efficiency (EQE)

To evaluate a photodetector's efficiency, we introduce the term external quantum efficiency (EQE). The external quantum efficiency or quantum yield provides information on the number of electron-hole pairs generated per incident photon. It indicates the ability to convert energy from photons into electrical energy. The quantum yield η of a photodetector is always less than 1 ($0 \leq \eta \leq 1$).

It is expressed as follows [33]:

$$\eta(\lambda) = \frac{I_{ph}hc}{qP_{opt}\lambda}[\%] \qquad (3)$$

Where:

$\hbar$ is Planck's constant, $\hbar = 6{,}582\ 118\ 99 \times 10^{-16}\ eV.s$;

q is the elementary charge of an electron, $q = 1{,}6 \times 10^{-19}\ C$

c is the speed of light in a vacuum, $c = 3 \times 10^{8}\ m.s^{-1}$

λ is the photon's wavelength.

II.5.5. Active area.

A photodetector's active area is typically the physical region that turns incoming optical light into an electric output signal. For detectors with a circular surface, the diameter is often provided,

whereas detectors with a rectangular or square surface are provided with their length and width.

II.5.6. Optical Area

The perceived active area of an optically immersed detector may differ from its physical active area due to optical concentrators. The optical detector area can be considerably magnified in detectors equipped with optical concentrators, also known as immersion lenses (Fig. 5).

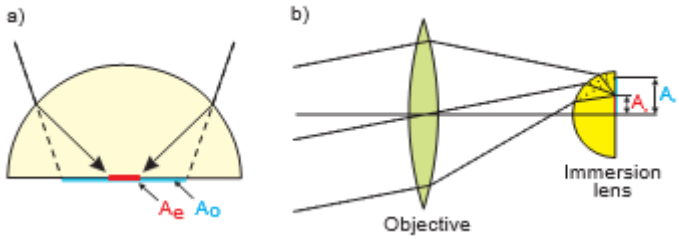

Figure 5 Rays propagation in optical immersion (a), and beam tracing for an optical system with a combination of an objective lens and an immersion lens (b) [11].

II.6 Different Types of Photodetectors

There are different structures of photodetectors, including:

- ✓ Photoconductors
- ✓ p-n junction photodetectors
- ✓ p-i-n photodiodes
- ✓ Schottky photodiodes
- ✓ Phototransistors
- ✓ Heterojunction photodetectors

Photodetector	Advantages	Disadvantages
Photoconductor	Simple design, easy process control, high gain	Large dark current, slow time response
Schottky UV detector	Low dark current, quick time response, high sensitivity, and quantum efficiency	Higher absorption losses, shallow-semiconductor contact
p-n and p-i-n detectors	Fast time response, high impedance, low dark current, low bias operation, high-frequency operation, easier fabrication	The response is dependent on the dopant used which impairs the spectral response
Metal-semiconductor-metal (MSM)	Fast time response, minimally affected by bias, simple fabrication process, low cost, easy integration	Lower gain and spectral response

Figure 6 Classification and advantages and disadvantages of UV detectors

II.7 UV photodetector

Ultraviolet (UV) radiation covers a wide spectral range from the visible limit (400 nm ↔ 3.1 eV) to the boundary of low-energy X-rays (10 nm ↔ 124 eV). It is arbitrarily divided into four regions:

- UV (A), for wavelengths between 400 and 320 nm (from 3.1 eV to 3.87 eV);
- UV (B), for wavelengths between 320 and 280 nm (from 3.87 eV to 4.43 eV);
- UV (C), for wavelengths between 280 and 200 nm (from 4.43 eV to 6.20 eV);
- Far Ultraviolet, for wavelengths between 200 and 10 nm (from 6.2 eV to 124 eV).

II.8 Zinc Oxide for a MSM UV Photodetector

Zinc oxide (ZnO) has a large direct bandgap of about 3.34 eV which corresponds to absorptions in the UVA range.[35] It also has an exciting binding energy of 60 meV which is relatively large, and these qualities in part make ZnO a very suitable candidate for UV photo detection devices. ZnO is even more promising due to its high thermal and mechanical stability, high sensitivity, and ease of which a multitude of morphologies can be made at the nanoscale. A device that is responsive and resistant to high temperature electronic degradation is possible with this metal oxide. This, along with its cheapness, abundance, and non-toxicity make it rival other promising high performance wide bandgap semiconductors such as gallium nitride (GaN).[35]

II.9 Conclusion

UV photodetectors have undergone significant evolution since their inception, beginning with Robert W. Wood's pioneering work in UV photography in the early twentieth century. Advancements in semiconductor technology, notably with materials such as silicon carbide (SiC), gallium nitride (GaN), and zinc oxide (ZnO), have propelled the field forward, enhancing sensitivity and stability. These photodetectors play a crucial role across diverse applications including environmental monitoring, medical diagnostics, and national security. Functioning as optoelectronic devices, they convert incident UV radiation into electrical signals by generating electron-hole pairs within the semiconductor material. Key performance metrics such as

sensitivity, spectral response, and external quantum efficiency characterize their effectiveness. ZnO, with its wide bandgap, high exciton binding energy, thermal stability, and ease of nanostructuring, stands out as a promising material for UV photodetection, rivaling other semiconductors in performance and cost-effectiveness. Ongoing research aims to further improve response times, integration capabilities, and resilience to extreme conditions, ensuring UV photodetectors continue to advance scientific, industrial, and societal applications in the future

III CHAPTE THREE III: Development and Characterization of thin films

CHAPTE THREE III: Development and Characterization of thin films

III.1 Introduction

Thin film deposition technology involves applying an extremely thin film of material to the surface of a substrate, which can range in thickness from a few nanometers to 100 micrometers, or only a few atoms. It can also be used to construct layers on top of previously applied coatings. Thin film deposition techniques and production procedures have been critical to the creation of modern electronics such as semiconductors, optical devices, solar panels, disk drives, CDs, and so on1. The tiny layers are deposited in diverse ways. It refers to the breadth of the domain in which we apply these layers. Scientifically, these methods are classified into two types: physical and chemical, such as spray pyrolysis, which is the focus of our research in this work.

III.2 Thin Film

Thin film technology is at the heart of remarkable advances in solid-state devices. The usefulness of metal films' optical features, as well as scientific curiosity about the behavior of two-dimensional solids, have fueled widespread interest in thin film research and technology. Thin film studies have directly or indirectly expanded numerous new fields of research in solid-state physics and chemistry, based on phenomena that are unique to the film's thickness, geometry, and structure [36,37]. Thin films are ideal for applications in microelectronics and integrated optics. However, the physical properties of the films, such as electrical resistivity, are not significantly different from those of the bulk material. A thin film is a low-dimensional substance formed by condensing individual atomic/molecular/ionic species of matter. A thin film's thickness is considered between tenths of a nanometer and several micrometers [37,38,39]. Some of the factors, such as conditions preparation, which determines the physical, electrical, optical, and other properties of a film rate of deposition, substrate temperature, environmental conditions, residual 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 larger areas, etc.

III.2.1. Thin Film Deposition Definition and application

Thin films nature can be insulating (SiO_2, SiN_4, SiC,), metallic (Al, Cr, Au, Ag...) and semi-conductor (Si, GaAs, CdTe, ZnO...), While its structure can be amorphous, nanocrystalline, microcrystalline or monocrystalline

Thin film deposition is the process of creating thin film coatings and depositing them onto a substrate. These coatings can be made from a variety of materials, including metals, oxides, and compounds. Furthermore, thin film coatings have a number of properties that can be employed to modify or improve a specific component of the substrate's performance. For example, some are translucent, others are strong and scratch-resistant, while yet others change the conductivity of electricity or signal transfer.

Thin Film Deposition is broadly divided into Chemical Deposition and Physical Vapor Deposition Coating Systems [40].

The thin film deposition methods are summarized in (**Figure 7**).

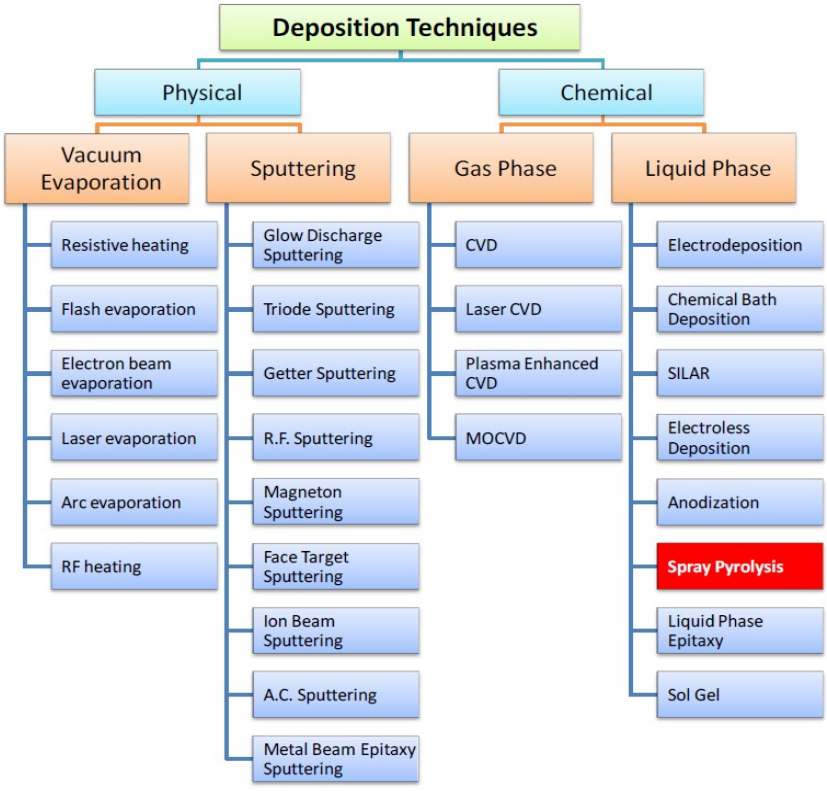

Figure 7Classification of Thin Film Deposition Techniques

III.2.2. Classification of thin films deposition techniques

Thin films deposition techniques divide into two groups, depending on the nature of the deposition process. Physical methods include physical vapor deposition (PVD), laser ablation, molecular beam epitaxy and sputtering. Chemical methods comprise of gas phase and solutiondeposition. The gas phase techniques include chemical vapor deposition (CVD) and atomic layer epitaxy (ALE). The solution deposition techniques include spray-pyrolysis deposition, sol-gel, spin-coating and dip-coating (Figure 7) [41]. Research on optimization of thin filmsmaking techniques lead to the development of new technologies [41].

III.2.3. THE CHOICE OF A THIN FILM DEPOSITION TECHNIQUE:

The realization of ZnO thin films requires the masteries and control of their elaboration. The choice of a deposit method involves several criteria [42]:

- The nature of the material to be deposited.
- Desired deposition rate and layer thickness.
- The constraints imposed by the substrate (vacuum degassing, maximum temperature, etc.).
- The desired stoichiometry.
- Crystalline quality and layer density.
- Adhesion of the deposit to the substrate.
- Finally, reproducibility and cost of implementation.

III.2.4. APPLICATIONS OF THIN FILMS:

In the course of the 20th century, more specific applications have diversified into the following fields [43, 44]:

• Microelectronics: it has developed since the 1960s thanks to the implementation of increasingly thin conductive or insulating layers, and

find them under types of passive layers (electronic contact), PN junction, transistor diode, piezoelectric, laser, LED lamps, superconductors, etc...

• Optical: while maintaining aesthetic applications, the optical applications of the layers have made it possible to develop more efficient radiation sensors, such as anti-reflective layers in solar cells, anti-reflective treatment of camera lenses, photodetection, display of flat screens, optical guides (architectural energy controls, vehicles, energy conversion, etc.).

• Mechanics: tribological coatings (dry lubrication, wear resistance, erosion, abrasion, diffusion barriers) microsystems…

• Chemistry: The main applications of surface coatings are oriented towards better corrosion resistance through the creation of a waterproof film (corrosion resistance), gas sensor, catalytic coatings, protective layers.

• Thermal: For example, the use of a thermal barrier layer (TBC) reduces the surface temperature of the metal of the reactor fins, thus improving reactor performance (increase in internal temperature).

• Biology: biological micro sensors, bio-chips, biocompatible materials…

• Micro and nanotechnology: mechanical and chemical sensors, actuators, detectors, adaptive optics, nano photonics…

• Magnetic: information storage (computer memory), security devices, sensors…

• Decoration: watches, glasses, jewelry, home equipment…

III.3 Spray pyrolysis

The chemical spraying technique known as «SPRAY», was first proposed by Chamberlin and Skarman in 1963 and used for the deposition of CdS films [28]. It has been adapted for the production of several materials such as (Cd, Zn) Sn, $CuInS_2$, FeS_2 [29], as well as for the production of thin films of transparent and conductive oxides (SnO_2, ZnO, etc.) [45].

«Spray pyrolysis» is the most common name given to this technique. It consists of spray and pyrolysis.

Spray: is the English word that indicates the jet of a liquid in fine droplets, launched by a sprayer.

Pyrolysis: comes from pyrolytic and indicates the heating of the substrate.

The definition of pyrolysis (pyrolytic) is identical to the thermal decomposition of a source to release a metal or compound [46, 47]. The temperature of the substrate provides the necessary energy, called activation energy, to trigger the reaction. A solution containing the different components of the compound is sprayed mechanically on substrates that are arranged on a substrate holder heated to a temperature between 200 °C and 450 °C. Because of the temperature, the (volatile) elements of the solution will be immediately eliminated, the compound to be formed remains (zinc oxide) [48].

The choice of this technique was motivated by numerous advantages [48]:

- Possibility to deposit a wide choice of materials.
- Simple method of adding the precursor by means of a spray.
- Easily controllable reaction environment under neutral gas or air at atmospheric pressure.
- Ease of implementation of reactors of this type.
- The speed and simplicity of its implementation.
- It allows you to control the chemical composition of the material you want to obtain.
- The thin films prepared by this technique are of good quality.

- It is a very inexpensive and economical technique. It is industrializable.
- This method can be used to deposit onto large surfaces for solar cells or flat screens.

On the other hand, the major problems of this technique is the control of the evaporation of the spray generated. In fact, too fast or too slow evaporation leads to an unwanted precursor reaction affecting the properties of the deposit. In other words, if the drops reach the hot substrate before complete evaporation, a pyrolysis spray reaction takes the place of the CVD Spray mechanism [49]. Since the spray device is not placed in an isolated enclosure, various impurities may enter the solution or settle on the surface of the substrate, which will change the measurements of the sample properties afterwards [50]

III.3.2. Ultrasonic Pyrolysis Spray (USP) Technique:

In the case of an ultrasonic spray, a thin layer of liquid formed on a high-frequency vibrating surface breaks into a fine, uniform spray. Ultrasonic vibration induces surface waves in the liquid layer. When frequency is adjusted very regular square cells can be observed on the free surface just before reaching the resonance frequency.

When resonance is reached, the amplitude increases until droplet rupture Configuration of standing surface waves during ultrasonic atomization (water,f=50kHz), Mechanism of rupture of droplets during atomization by ultrasonic frequencies.). Very regular square cells generate droplets of uniform size [51].

III.3.3. Precursor Decomposition:

Several processes occur simultaneously when a droplet reaches the surface of the substrate such as evaporation of the residual solvent, spreading of the droplet and solvent decomposition. Several models exist for the decomposition of a precursor.

Viguie and Spitz [8] proposed processes that occur when the substrate temperature increases.

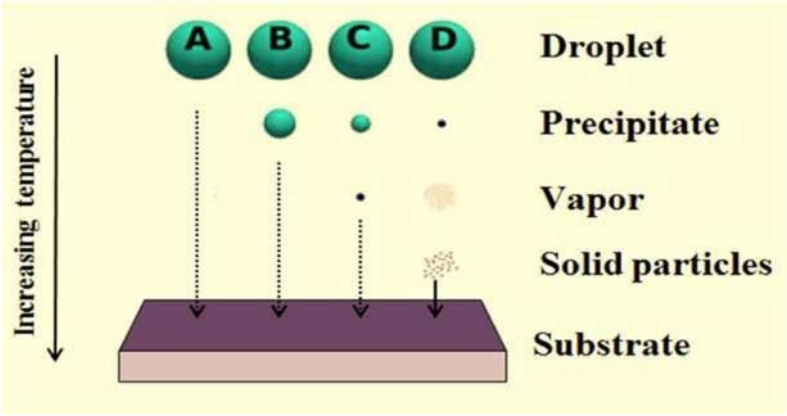

Figure 8 Description of deposition processes that occur as the substrate temperature rises.

Process A: the drop of solution projects directly onto the hot substrate. The solvent evaporates and the precursor breaks down to form a layer of product. For thick films, this process requires continuous deposition to obtain dense films (<1 µm).

Process B: The solvent evaporates before reaching the hot surface of the substrate. The precursor reacts to the surface and breaks down or reacts chemically to form the desired

material layer. It does not pass through the gas phase.

Process C: The solvent also evaporates as it approaches the surface of the substrate. The precursor enters the gas phase near the hot surface. The vapor of the precursor adsorbs to the surface, diffuses, then forms products by further decomposition and/or chemical reactions.

Process D: If the deposition temperature is very high, the decomposition and/ or chemical reactions take place in the vapor phase, giving rise to a homogeneous nucleation (similar to a homogeneous CVD reaction). The formation of fine particles of products takes place in the gas phase. They are then deposited on the substrate. The film thus formed has a porous character and a very low adhesion to the substrate. The powder can be directly collected in the gas phase for the production of ultrafine particles[52]

III.3.4. Pyrolysis spray nebulization technique (NPS)

Spray pyrolysis technique is widely adopted because of its cost effectiveness and applicability to large areas. The critical and efficient operation of the pyrolysis spray technique depends on the preparation of fine droplets of uniform size, followed by the controlled thermal decomposition of these droplets in terms of environment, location and time. In general,

, the spray guns of the marketed spray devices are used for spray and these atomizers are not sufficient to generate droplets smaller than the micron or nanometer in a reproducible way or to control their size distribution. Therefore, some techniques modified atomization have been developed and used effectively for the preparation of thin films[53].

To achieve uniform deposition, the spray nozzle was modified. Raj et al. [54] used a rotating atomizer with a pendulum movement, which allows homogeneous films to be formed with reproducible properties. Gottlieb et al. [55] modified the spray technique to grow films of uniform thickness over a large area (10 cm2 10 cm2) by arranging to move the nozzle in x- y directions above the substrate. Moreover, Sethupathi et al. have designed a spray generator using a jet nebulizer. In another study, Peaker et al. [56] used a method that preheated the spray mist separately from the substrate heating, This resulted in a relatively low temperature drop at the substrate surface compared to other pyrolytic processes. Jet nebulization pyrolysis (JNS) is a method that allows large-scale deposition of high-quality films in a single heating step and at low cost. In addition, this technique has a great advantage, which lies in the fact

that the material can be deposited at a relatively low temperature and with various nanostructures. This is a low-cost, vacuum-free technique for applications on large surfaces, which allows the production of high-quality film with a low precursor volume. The operation of the NSP method is based on the Bernoulli principle. That is, when a flow of pressurized air is directed through a narrowed orifice, the velocity of the air flow increases to create a jet. The impact of a gas jet with a liquid produces aerosol particles (particle size<5 µm). The fog shape of the solution allows to improve the quality of the film and to obtain a uniform growth thanks to a progressive nucleation with a minimum of losses.

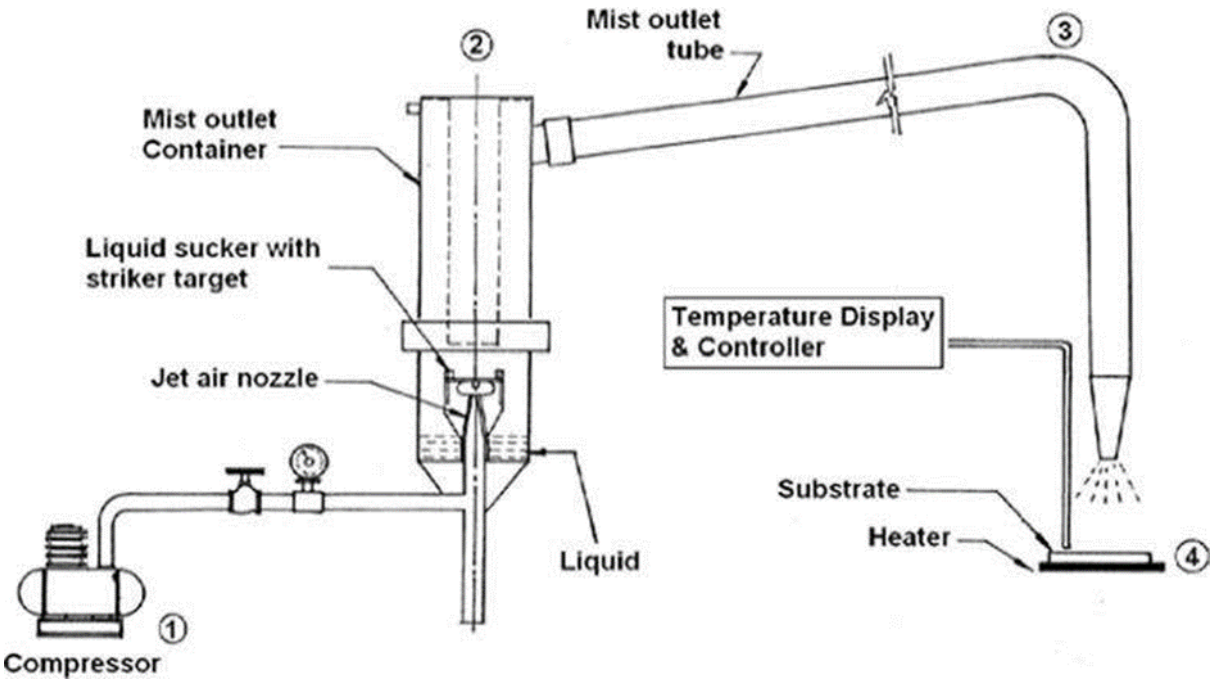

Figure 9 Diagram of the pyrolysis plant of the Jet Nebulizer spray (JNS): (1) air compressor, (2) jet assembly Nebulizer, (3) fog outlet tube and (4) heating with temperature regulator. [48]

which includes an air compressor with a control valve, The main unit of the jet nebulizer assembly consists of a fog carrier tube with a conical spray nozzle and an electric heater connected to a temperature controller. The Jet Nebulizer is a small atomization machine, which acquires the ability to convert the precursor solution into very small droplets by a double collision process, when powered by an air compressor. In the nebulization unit, compressed air is released by the 3 mm diameter Jet nozzle and produces droplets smaller than micron size and an aerosol mist formed and delivered by the nozzle of the carrier tube. When the aerosol mist touches the heated substrate, solvent evaporation takes place, followed

by a heterogeneous reaction, which leads to the formation of a thin layer of metal oxide on the substrate.

The substrate's temperature, topography, and chemical makeup, as well as the chemical makeup and concentration of the spray solution and any additives, all affect how quickly the sprayed films grow. The spray parameters, such as the spray head's scanning speed, distance from the substrate, angle of incidence of the droplet on the substrate, etc., also have an impact on the growth rate. With respect to the volume of solution sprayed, or spraying duration, the film's thickness grows roughly linearly. The substrate surface is impacted by the spray pyrolysis process in general. Neutral substrates, such glass/quartz and ceramics, are used when the substrate shouldn't participate in the pyrolytic reactions. This method is less expensive than other film-making techniques and offers a straightforward experimental setup, mostly because of its basic equipment.

does not need premium substrates and reagents to be used. The chemicals utilized in the precursor solution make it simple to adjust the films' composition. Spray pyrolysis is a process that has been utilized for decades in a variety of industries, including the manufacturing of glass, solar cells, and electrical conductive electrodes [60]. This approach has allowed for the deposition of several types of films.

III.3.5. Characterization techniques

ZnO, SnO_2, and their binary and ternary combinations are materials that are extremely sensitive to preparation conditions, just like all thin coatings. Thus, in order to determine the ideal preparation circumstances, optimization work is required, which calls for a methodical (statistical) examination of the optical and electrical characteristics of the material that is generated.

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.

UV-visible spectroscopy for transmittance measurement in the wavelength range [200-800]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.

III.4 X-ray diffraction

III.4.1. Introduction

Wilhelm Conrad Roentgen's discovery of X-rays in 1895 paved the way for significant advancements across all scientific fields and the creation of new medical and technological uses [61]. Specifically, new avenues for the study of crystalline materials were made possible by Laue, Friedrich, and Knipping's 1912 research on X-ray diffraction (XRD) by crystals [62]. These techniques have since undergone additional development to become extremely potent instruments in the domains of materials science and engineering. Since the initial X-ray studies using crystals and the discovery of X-rays, XRD techniques have developed into highly effective state-of-the-art procedures for advanced material characterisation. The foundation of XRD techniques is a crystal's unique capacity to diffract X-rays, which enables an accurate analysis of the crystalline phases' structures. A sample's micro- and macrostructural characteristics have cumulative contributions in recorded diffraction patterns. Lattice parameters, space group, chemical composition, macrostresses, or qualitative phase analysis can all be studied with the help of the peak position. Considering the highest intensity, It is possible to acquire details on texture and quantitative phase analyses, as well as crystal structure (atomic positions, temperature factor, or occupancy). Lastly, sample broadening contributions (microstrains and crystallite size) are shown by the peak shape[63].

III.4.2. XRD measurements :

To ascertain the phase composition and crystallographic characteristics of thin films, XRD measurements are carried out. The classical electromagnetic theory, which describes how an electron oscillates at the same frequency as the field in an alternating electromagnetic field, is based on XRD observations. The atom's electrons will oscillate in the beam's frequency when it is struck by an X-ray. Electromagnetic radiation is released from an accelerating charge. The radiation that is released most of the time interferes destructively, Nonetheless, the radiation that is released corresponds with and exits the crystal at the appropriate angle of radiation. Bragg's equation (4) describes how X-rays diffraction occurs.

$n\lambda=2d\cdot\sin\theta$ (4)

Where :

λ is the X-ray wavelength

θ is the angle of incidence with the lattice plane

n is an integer.

d is the interplanar distance

X-rays with constant wavelength are radiated towards crystal lattice, radiation reflects from lattice atoms illustrated in Figure 10 which is captured by a detector [64, 65].

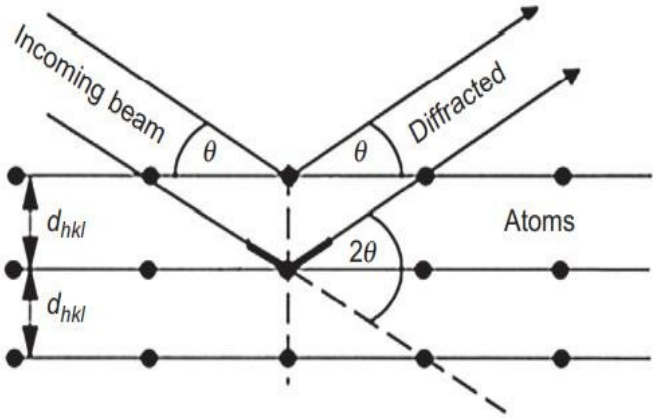

Figure 11 Bragg's geometry of X-ray reflection 66].

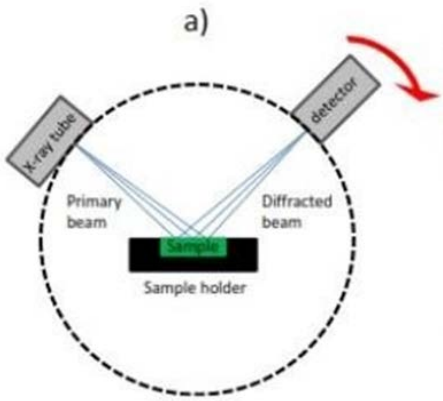

Figure 10 Scheme of XRD measurement

Plotting the observed radiation intensity versus 2θ is done. The radiation angle is changed to determine the angles at which Bragg's equation (4) is satisfied, as shown in Figure 11. When we compare these diffraction peaks with past experimental data, we may determine phase composition, lattice parameters, and crystallite orientation [66]. These angles will produce diffraction peaks in the XRD pattern.

III.4.3. The average crystallite size

(D, in nm) was estimated using Scherrer's equation (5) [67].

$D = 0.9\lambda/\beta \cos\theta$ (5)

where,

λ is the X-ray wavelength for CuKα (0.154056 nm).

β is the full width in radians at the FWHM of the diffraction line

θ is the diffraction angle.

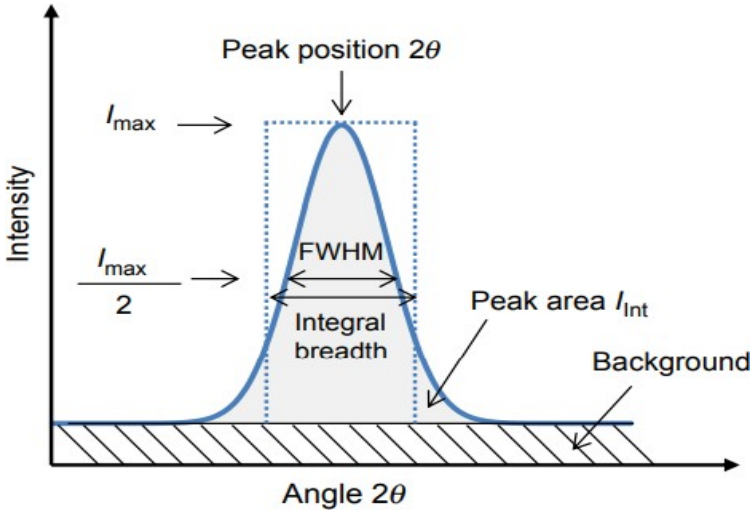

Figure 12 Diffraction peak and information content that can be extracted

III.5 UV-VIS spectroscopy

III.5.1. Introduction

Ultraviolet and visible spectrometers have been in general use for the last 35 years and over this period have become the most important analytical instrument in the modern day laboratory. In many applications other techniques could be employed but none rival UV-Visible spectrometry for its simplicity, versatility, speed, accuracy and cost-effectiveness [68].

The different components of light are characterized by a specific wavelength. The sum of all components i.e. of all wavelengths is called a spectrum. More specifically, a spectrum represents a distribution of radiant energy. For instance, the electromagnetic spectrum of visible light ranges from approximately 390 nm up to approximately 780 nm [69].

III.5.2. Measurement principle

A UV/VIS spectrophotometer measures the intensity of light passing through a sample solution in a cuvette, and compares it to the intensity of the light before it passes through the sample. The main components of a UV/Vis spectrophotometer are a light source, a sample holder, a dispersive device to separate the different wavelengths of the light (e.g. amonochromator), and a suitable detector (figure 13) [70].

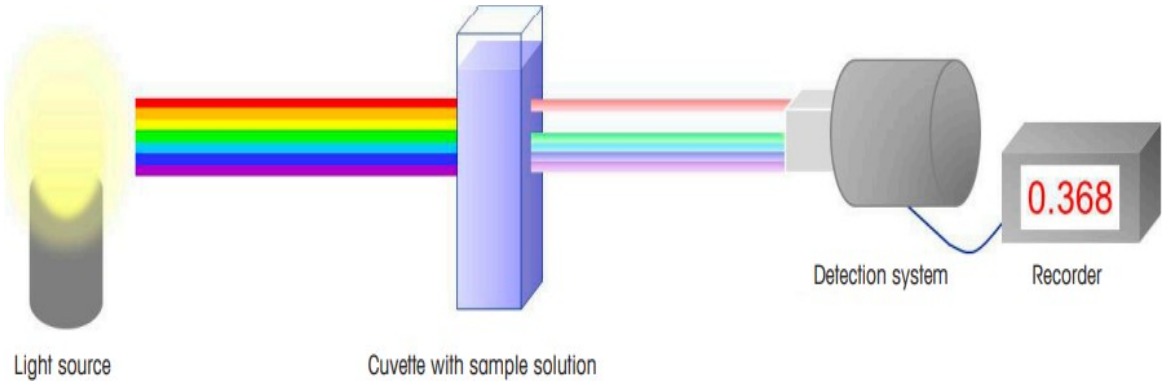

Figure 13 Measurement principle in UV/Vis spectroscopy [70]

III.5.3. Electrical characterization

- **Two-point technique**

In the most basic scenario, two metallic coplanar electrodes are needed for the electrical characterisation of the intrinsic layer. An external electric field between the electrodes guides the carriers in a predetermined

direction. A conduction current that changes depending on the bias voltage supplied between the electrodes is the end result. We sprayed two gold metal electrodes separated by a 2 mm interelectrode distance on samples that had been placed on glass substrates in order to measure the samples. There is a fluctuating voltage applied between the two locations.

- **Technique of the four points**

Four finite-radius tungsten metal tips arranged equally apart make up the 4-point probe arrangement shown in Figure 14. To reduce sample damage during probing, springs are attached to the end of each tip for support. During measurements, an auto-mechanical stage that moves up and down is comprised of the four metal tips. The outer two probes are powered by a high-impedance current source, and the voltage between the inner two probes is measured with a voltmeter to ascertain the resistivity of the sample. Probe spacing is typically about 1 mm [71].

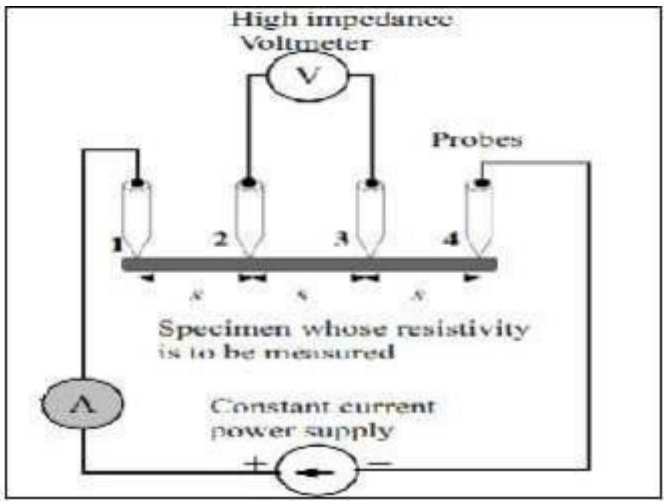

Figure 14 Four probe method of measuring resistivity of a specimen [71].

In figure (14) 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 [72] **:**

$$\rho = \frac{\pi}{\ln 2} \cdot \frac{V}{I} \cdot d \qquad (6)$$

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:

III.6 Experimental part

Development Procedures of ZnO Thin Layer Preparation of spray solution

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

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

.2 Methanol (CH_3OH); Other names (Carbinol, Columbian spirits, Hydroxy methane,MeOH, Methyl alcohol, Methyl hydroxide, Methylic alcohol)

Zinc oxide (ZnO) is a white solid with a molar mass of 81.406 g/mol. It has a density of 5.606 g/cm³. Zinc oxide melts at a temperature of 1,974°C (3,585°F) or 2,247 K and boils at a temperature of 2,360°C (4,280°F) or 2,630 K. The material has a band gap of 3.3 eV, which is an important property for its applications in electronics and optoelectronics.

Methanol, with the chemical formula $CH_3 OH$ or $CH_4 O$, is a colorless liquid that has a molar mass of 32.04 g/mol. It has a density of 0.792 g/cm³. The melting point of methanol is -97.6°C (-143.7°F or 175.6 K), while its boiling point is 64.7°C (148.5°F or 337.8 K). Additionally, at 20°C, the vapor pressure of methanol is 13.02 kPa.

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 15

The Zinc oxide (ZnO) has been dissolved in a mixture of doubly distilled water and methanol. methanol solution (99.995%) of absolute purity is pr

ovided from Sigma Aldrich; a Few drops of Hydrochloric acid (HCl) were added to the solution. The mixed solution was stirred by amagnetic stirrer as in Figure 16

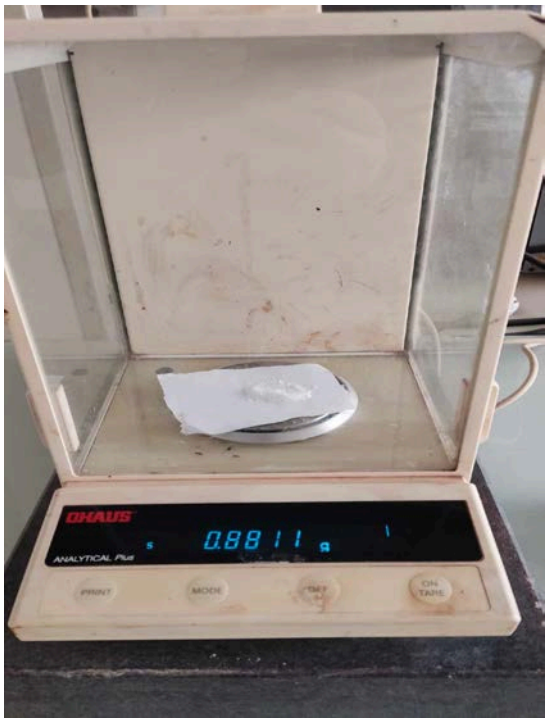

Figure 15 Scale used to weigh materials

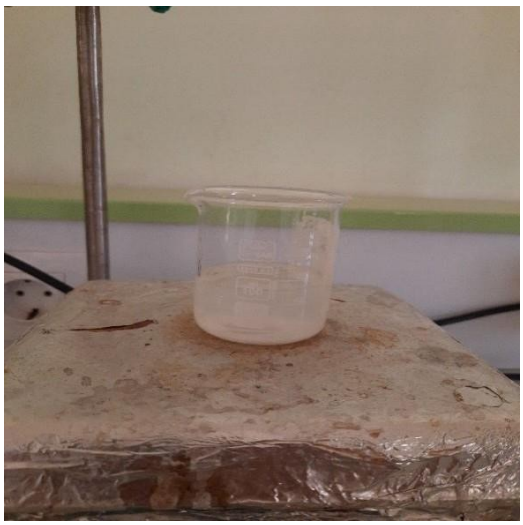

Figure 16 The magnetic mixer

The mixing process relies on the placement of a magnetic component coated with a non-reactive substance. This component is submerged in the solution within a glass bowl, which is then positioned on a magnetic mixer. When an electric current is applied, the magnetic stirrer rotates, mixing the solution at 50°C for 30 minutes until it becomes clear and transparent. The spray solution contains 0.1 M zinc oxide dissolved in methanol

III.6.1. Preparation of doped zinc oxides solutions

For depositing of Al doped zinc oxide, we used with amounts calculated so as to obtain Al concentrations of 5%

And 3% was added to water, in the same conditions used previously.

For depositing of mg doped zinc oxide, we used with amounts calculated so as to obtain mg concentrations of 5%

And 3% was added to water, in the same conditions used previously

III.6.2. Choice of substrate

Thin film requires a substrate to support itself. The substrate is very important for the growth of thin films in terms of the lattice and thermal mismatching between it and the film The physical properties of a thin layer differ depending on whether it is deposited on an amorphous insulating substrate (with a disordered atomic structure, such as glass) or a monocrystalline substrate (with an ordered atomic structure, such as a silicon monocrystal).

In this work, our thin films were deposited in a microscopy slide glass substrates and a silicon substrates

III.6.3. Monocrystalline silicon substrates

Monocrystalline silicon substrates, specifically Si (100), are ideal for optical characterization in the infrared range. They require high resistivity and relatively substantial thickness to prevent absorption from free carriers and interference effects. These commercially available substrates have excellent surface quality.

III.6.4. Glass substrates

The choice of glass as substrate was due to economic reasons, to perform a good optical characterization of our films, and it is adopted because the good thermal expansion that it presents with ZnO, which is minimize the constraints between film interfaceand substrate .

III.6.5. Substrate cleaning

Substrate cleaning in thin film technology is an important step prior to deposition [1]. It is necessary to remove the contaminants that would otherwise affect the properties of the film.

Cleaning involves the removal of contaminants without damage the substrate. While cleaning, the bond between the substrates is broken and contaminants are set free from the substrates. The properties that can be affected by the presence of contaminants includemorphology, nucleation electronic properties and the substrate film interface.

The cleaning is done in an ultrasonic bath (figure 3.1) according to the following steps:

- Rinse the substrates in distilled water for 5 min,
- Cleaning in ethanol for 5min,
- Rinse in distilled water for 5 min,
- Cleaning in acetone for 5min,
- Rinse in distilled water for 5 min,
- Substrate drying using Joseph paper.
- Substrates should not be touched with hands after this treatment to avoid contamination.

III.6.6. Choice of deposition temperature

The spray pyrolysis technique is among the chemical methods that require high temperatures for the realization of the decomposition of the solutions used arriving on heated substrates and converted into oxides [3].

In order to preserve thin films characteristics, we have chosen a temperature set at 350°C.

III.7 Experimental editing

The schematic diagram of the spray paralysis technique is shown in Figure 9 at the laboratory (LPCM) of Ammar Telidji University, Laghouat, the latter is built from simple devicesto which we have made some modifications to achieve the relatively homogeneous layers, chosen materials such as ZnO, it consists of spray nozzle, hot plate, substrate, Spraying device, A compressor, thermocouple:

Figure 17 Pyrolysis spray system

III.7.1. The device comprises:

(a) Spraying Device

This device features three holes:

- The first hole at the top connects to a thin tube that leads to a tank holding about 30 ml of the solution to be sprayed.
- The second hole, positioned horizontally, connects to a tube through which compressed air from an air compressor passes, allowing both the solution and compressed air to be drawn from the bottom of the spraying device.

(b) Spray Nozzle

Made of glass, the spray nozzle consists of:

- An inner tube for the solution, surrounded by a gas tube through which the carrier gas flows.
- When pressure is applied to the carrier gas, a vacuum forms at the nozzle tip, causing the solution to be automatically drawn in and sprayed.

(c) Substrate

Glass and silicon substrates were utilized.

(d) Hot Plate

- An iron disc measuring 18x18 cm is mounted on an electric heater.
- This setup can reach temperatures up to 500°C.
- A Chromel-Alumel thermocouple, fixed at the center of the iron disc, measures the substrate temperature.
- A temperature controller monitors the hot plate's temperature.

(e) Compressor

The compressor decompresses the carrier gas (air in this case) under controllable pressure, ensuring the solution is pushed toward the nozzle.

(f) Supports

Supports are used to stabilize and hold the components in place.

(g) Digital Thermocouple

- This thermocouple consists of a weld of two wires.
- Its tip is placed at the center of the heating plate.
- It provides a direct temperature reading via a digital display.

III.7.2. Spray pyrolysis system set-up

Following the preparation of substrates and solutions, the synthesis process begins. A silicon substrate (2 cm) is placed on a heating plate (sample holder) and slowly heated from ambient temperature to the chosen synthesis temperature (350°C or 400°C). During heating, the solution flow rate is controlled using syringe mode. Fine droplets are sprayed onto the heated substrate, initiating a pyrolysis process that triggers a chemical reaction between the compounds. The solvent evaporates due to the endothermic reaction, forming a thin layer. The samples are then collected.

III.7.3. Experimental Parameters

It is important to note that several experimental parameters can influence the physical and chemical properties of the synthesized thin layer. The pyrolysis spray technique depends on various parameters, such as:

- Properties of the precursor
- Solution concentration
- Distance between the nozzle and the substrate
- Synthesis time
- Substrate temperature

However, the substrate temperature and deposition time are the primary factors affecting layer quality. This study focuses on the following parameters:

- Substrate temperature
- Solution concentration
- Distance between the nozzle and the substrate

III.7.4. Repository Parameters

The study involves varied parameters to analyze different conditions. The solution molarities used are 0.1 mol/l and 0.2 mol/l. Deposition temperatures are set at 350°C and 400°C. Additionally, the nozzle-substrate distance is maintained at 5 cm.

III.8 Conclusion

In this chapter, we have briefly discussed the cognition of thin films . 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.

IV CHAPTE FOUR IV: Results and Discussion

IV.1 Results and Discussion

IV.1.1. X-ray diffraction studies

This X-ray diffraction study aims to determine the structure of crystal growth, layer trends, measurement of network parameters and crystal size. It should also be allowed to examine the situation of warehouse restrictions.

XRD patterns of the film ZnO deposited on silicon (figure 18) and glass (figure 19). All peaks were found in the samples to be consistent with the multi-crystal hexagonal structure of Wurtzite ZnO (COD ID N 9004181). For the silicon-deposited film ZnO we have five main diffraction peaks (100), (002), (101), (102) and (110) corresponding to the stage of the Zincite plane phase. From the first three peaks, we found that the third peak (101) is the preferred peak.

For the ZnO film deposited on the glass, we have seven main diffraction peaks (100), (002), (101), (102), (110), (103) and (200) corresponding to the stage of the Zincite aircraft. From the first three peaks, we found that the first peak (100) is the preferred peak.

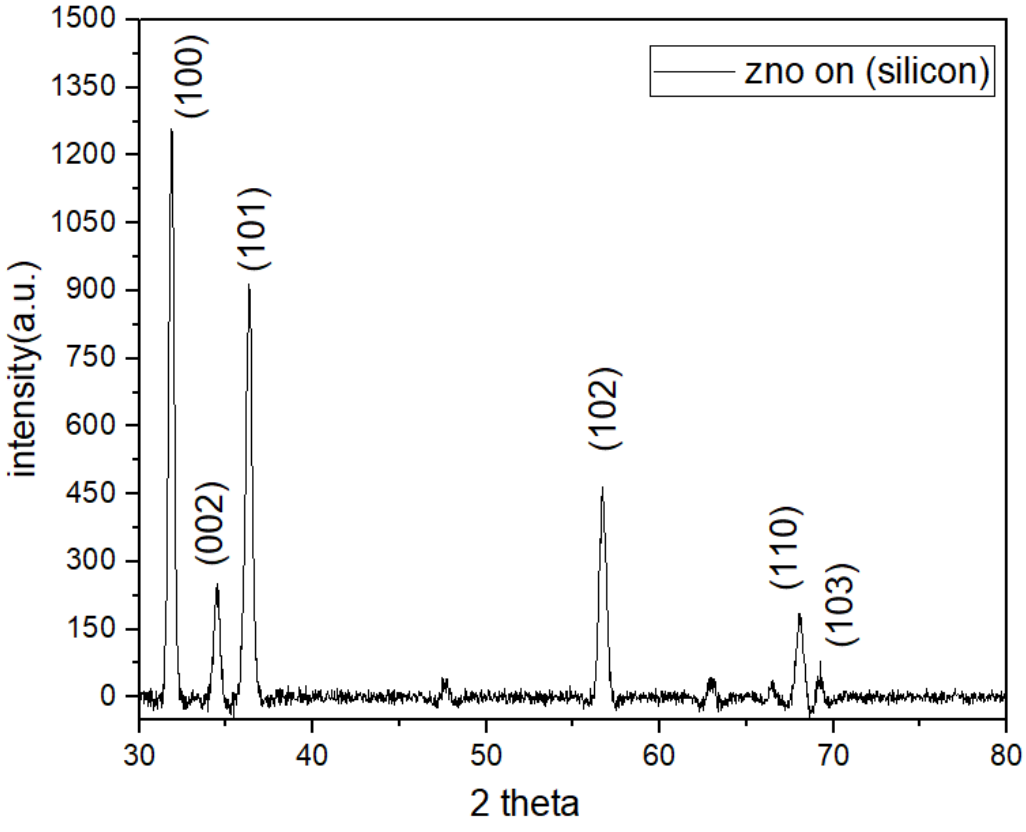

Figure 18 X-ray Diffraction pattern of ZnO thin film deposited on silicon

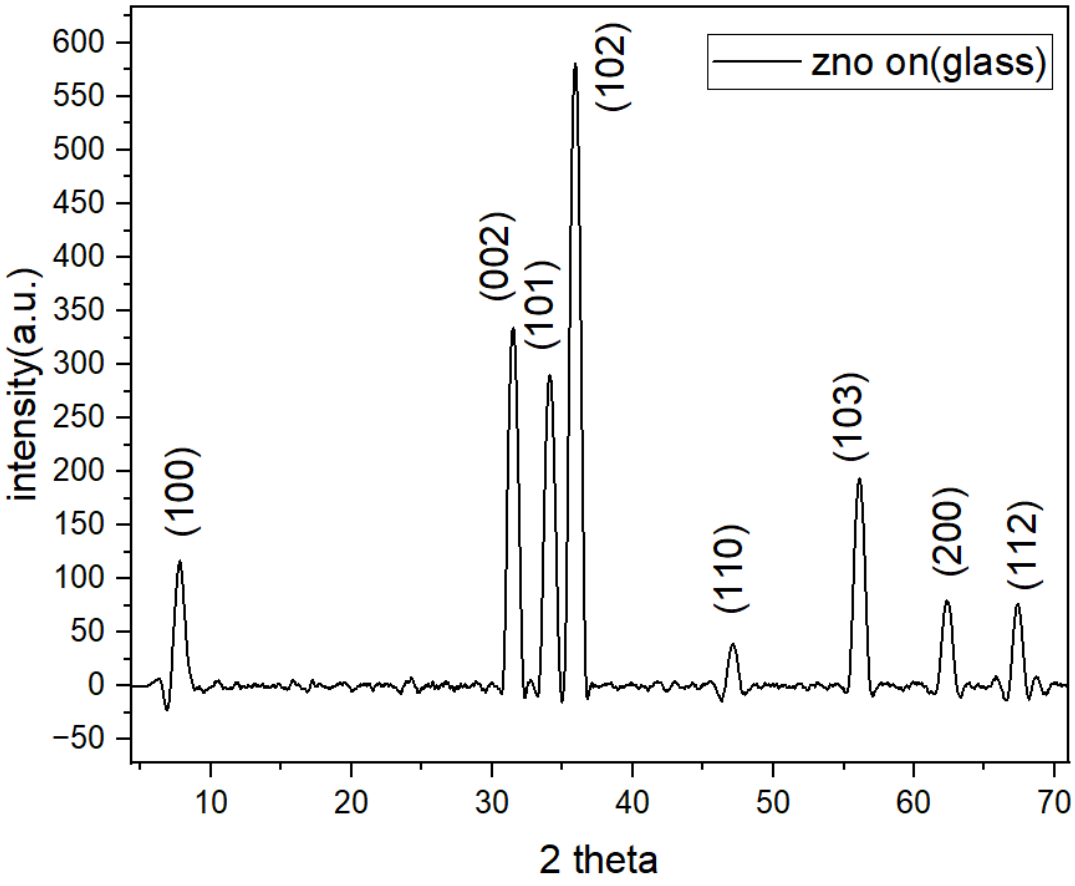

Figure 19 X-ray Diffraction pattern of ZnO thin film deposited on glass

IV.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:

$$\frac{1}{d_{hkl}^2} = \frac{4}{3a^2} \times (h^2 + hk + k^2) + \frac{l^2}{c^2} \quad (7)$$

And

$$d_{hk1} = \frac{\lambda}{2\sin\theta} = \frac{0.15406nm}{2\sin\theta}$$

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

N°	2 Theta(°)	(hkl)	Inte ns(a.u.)	FWHM(°)	d(hkl)
1	31,85975	(100).	476,7368	0,36799	0,028066
2	34,47898	(002).	96,24843	0,38537	0,025991
3	36,3198	(101).	415,7028	0,45141	0,024715

Table 2 ZnO thin film structural parameters

IV.2 crystallite size(D)

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

$$D = \frac{K\lambda}{\beta \cos\theta_{\beta}} \quad (8)$$

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):

$$\delta = \frac{1}{D^2} \quad (9)$$

The value of strain (ε):

$$\varepsilon = \frac{\beta \cos\theta}{4} \quad (10)$$

The results are shown in the following table:

N°	D(nm)	δ (nm-2)	ε
1	22,45046	1,984035	5,625576
2	21,5844	2,146447	5,418805
3	18,52137	2,915101	6,004879

Table 3 ZnO thin films crystallite size, dislocation density and value of strain

IV.3 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 20 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].**

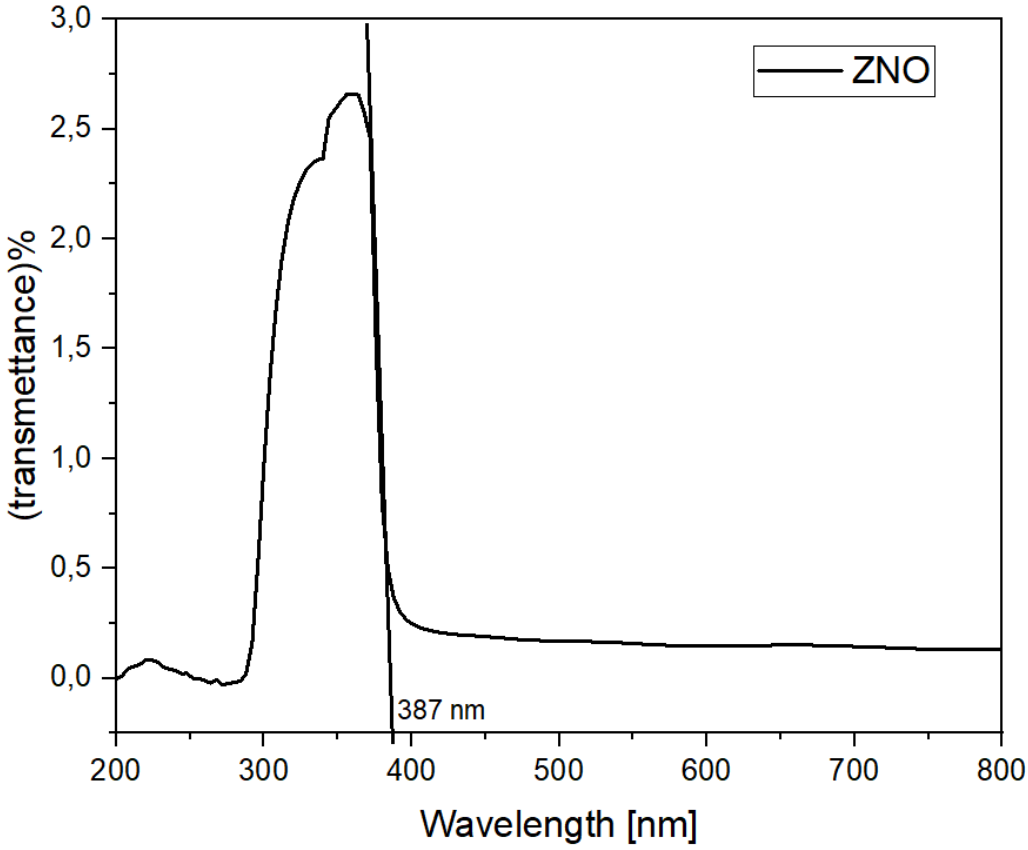

Figure 20 Optical transmittance spectra of ZnO nanofibers

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 21. To cut the power axis at the point (hu = En) we find that the power gap value is equal to 3.24eV.

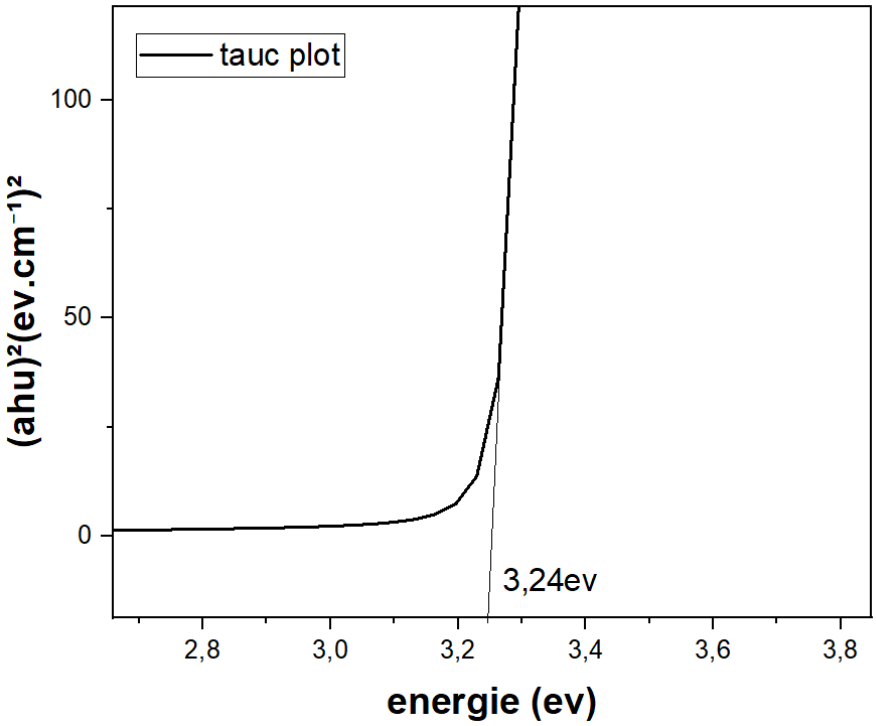

Figure 21 energy gap plot

IV.4 Ultraviolet Sensor System

Form 22 (ultraviolet sensing system) is used to examine the sensor performance of thin membranes. Ultraviolet sensor system consists of light insulating plastic cubic test chamber. A set of UV lamps was installed on the test chamber cover to expose the test sample to UV light. Connected to the feeder to control the operation of the lamps. A digital multimedia scale is used to record the change in sensor resistance over time when exposure to radiation. Resistance changes were observed during the operation and discontinuation of the lamps over a certain time. Where the resistance was constant before the lamps were turned on and on, we observed a marked and rapid change for time. We repeated this process several times in a certain period of time, as this change was recorded and drawn in a curve through a multimedia device. sensitivity, response time and recovery time are calculated based on these measurements.

Figure 22 Experimental setup

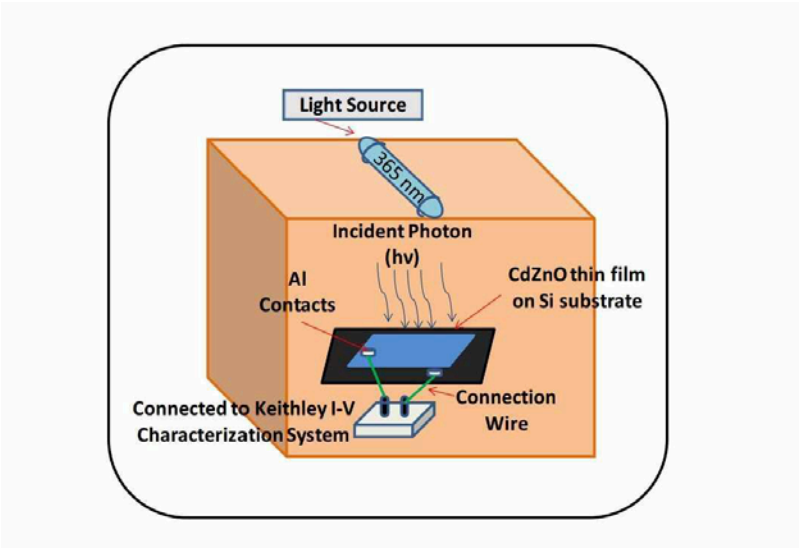

Figure 23 The experimental set up for the i-v measurements in dark and uv light (365nm)

IV.4.1. Sensor detection :

In order to prove the performance of the sensor, we prepared a light-insulated inspection case with UV lamps and we placed the sample inside and showed it to UV light and dark in order to measure the effectiveness of the sensor. These changes were observed at the multi-sized device level in order to study the change in resistance as shown in the figure 24

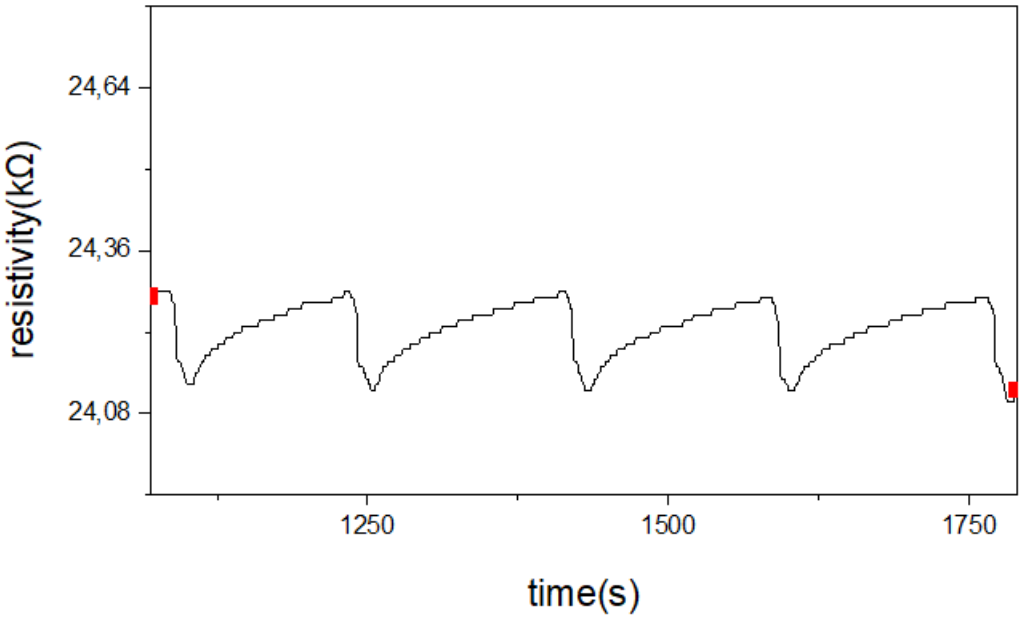

Figure 24 plot of change in resistivity of uv photodetection

IV.5 Characteristics of uv photodetector a sensor

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

$$S = \frac{|\Delta R|}{R_o} \times 100\% = \frac{R_{uv} - R_{dark}}{R_{dark}} \times 100\% \quad (11)$$

Where:

S: Sensitivity.

(R_{uv}) : Electrical resistance.

(R_{dark}): Resistance in dark.

(R_o) : Resistance turning on the uv light

2. Selectivity: selectivity can be defined as the sensor's ability to determine the specific wavelength of UV light within bundles of light; Therefore, ongoing studies to increase the selectivity of oxide semiconductor sensors

3. Response Time and Recovery Time: means the time a sensor takes to respond if UV lamps run from zero to a specified value and reaches a fixed value of about 90% of the final value. It is also defined as the time of recovery. It's time for the sensor signal to return to its initial value after turning off the lamps and reaching 10% [9].

4. Stability: Is the ability of the sensor to stabilize for a specific time while maintaining the selectivity, sensitivity, response time, and recovery time [10].

5. Detection limit :It is the minimum concentration of analysis that can be detected by the sensor.

Dynamic range:It is the range of concentration of examines between the maximum limit and the detection limit.

Resolution:It is the lowest focus that the sensor can detect.

Linearity:Is the relative deviation of the experimental graph on the ideal straight line in the ideal parameters.

Hysteresis:It is the large difference in the value of the output when the value converges with the decrease and increase in the degree of focus [11].

S: Sensitivity :

After taking the values from the data and calculating them, we found

$$S = \frac{|\Delta R|}{R_o} \times 100\% = \frac{24.12 - 24.29}{24.29} \times 100\%$$

$$S = 70\%$$

Response Time :

When dropping the tries and calculating the response time according to the law we found

$$\frac{1428 - 1414}{60} = 0.23s$$

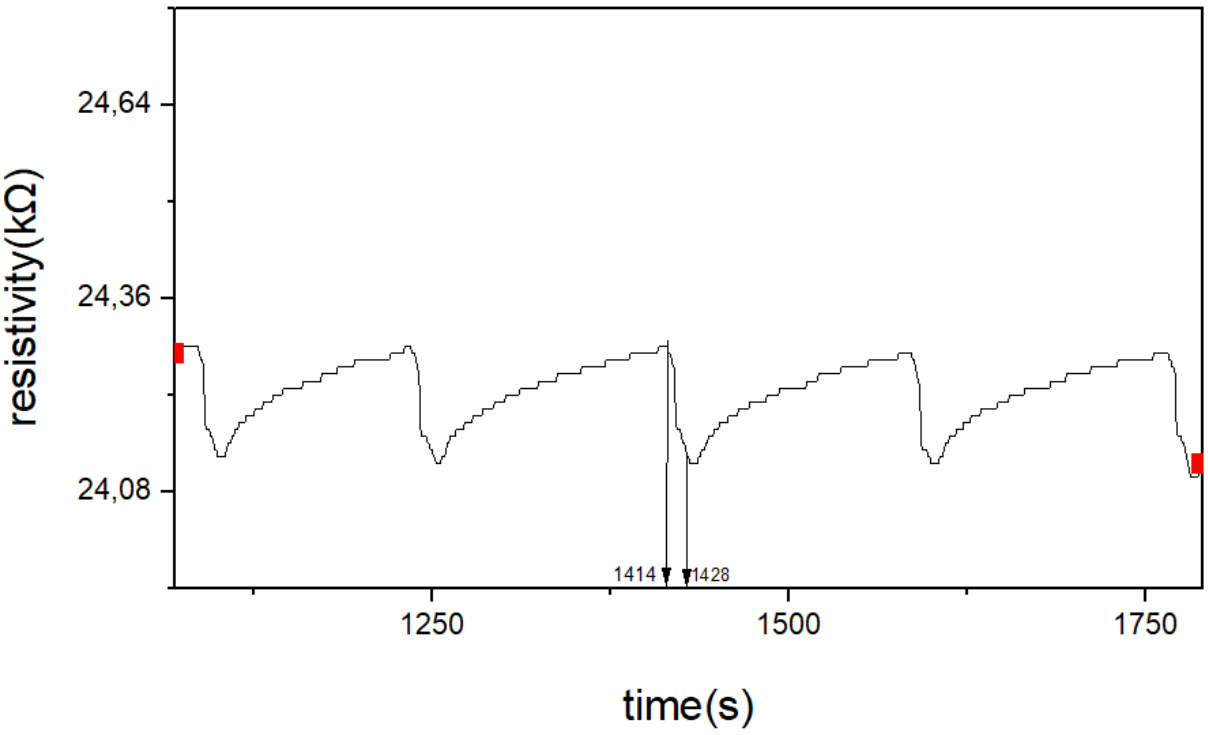

Figure 25 time response calculating

IV.6 CONCLUSION:

In the last chapter we started with the results of ZnO thin layer characterization 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 ZnO transmission results on silicon in the field of UV-VIS. The optical gap is equal to 3.24 electron volts.

The remainder of this chapter is devoted to studying and discussing the results of the sample's UV sensing by recording the change in resistivity when stimulated as well as calculating sensitivity and response time

GENERAL CONCLUSION :

The development of a zinc oxide (ZnO) photodetectors to detect uv represents a significant advance in photodetection 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 photodetector to detect uv . We were able to deposit the thin layer of ZnO by a very simple method called pyrolysis spray. We used silicon and glass substrates,

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 .

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 3.24 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. . 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 photodetectors for detection of uv. The results clearly show that the ZnO-based sensors were too responsive and sensitive

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 optical area, and to Improve sensors manufactured so they can operate

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

LIST OF FIGURES:

LIST OF TABLES :

LIST OF EQUATIONS:

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