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The effect of pH on the Synthesis of MgO-ZnO Alloys

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Abstract

In this work, MgO-ZnO thin films were deposited on galas substrate (450°C) by pneumatic technique. The effects of PH solution in the range of ((2.6; 5.0; 7.0 and 7.9 of Ph) were successfully investigated. MgO-ZnO thin films were observed in high crystallinity with a hexagonal wurtzite structure with a strong preferential, the maximum value of crystallite size 42.12 nm is attained of deposit MgO-ZnO thin film at 450 °C with 5 of PH. The optical transmission spectra showed all the sprayed MgO-ZnO thin films are transparency within the visible wavelength region. The band gap of MgO-ZnO thin films increases from 2.53 to 3.18 eV as the PH increases, The Urbach energy values decreased as the PH increased from 820 to 305 meV.

Key words: MgO-ZnO; Thin films; PH solution; spray technique.

ملخص

في هذا العمل ، تم ترسيب الأغشية الرقيقة من MgO-ZnO على ركيزة الزجاج درجة حرارتها 450 درجة مئوية وهذا بتقنية الهواء المضغوط. تمت دراسة تأثير محلول PH في المجال (2.6 ؛ 5.0 ؛ 7.0 و 7.9 درجة الحموضة) بنجاح. لوحظت الأغشية الرقيقة MgO-ZnO في درجة تبلور عالية مع بنية wurtzite سداسية مع تفضيلية قوية، وأعلى قيمة من البلورات تم الحصول عليها هي 42.12 نانومتر من غشاء رقيق MgO-ZnO المترسب عند 450 درجة مئوية مع 5 درجة حموضة. أظهرت أطياف الإرسال البصري أن جميع الأغشية الرقيقة MgO-ZnO التي تم رشها شفافة داخل منطقة الطول الموجي المرئي لحظنا زيادة في فجوة النطاق من 2.53 إلى 3.18 إلكترون فولت مع زيادة PH ، وانخفضت قيم طاقة Urbach مع زيادة PH من 820 إلى 305 ميلي إلكترون فولت.

الكلمات الأساسية: MgO-ZnO ، الأغشية الرقيقة، محلول PH ، تقنية الرش.

تشكرات

بادئ ذي بدء نود أن نشكر الله عز وجل و نحمده حمدا كثيرة الذي منحنا القوة والصبر لإنجاز هذا العمل المتواضع. نود أن نشكر بحرارة كبيرة مشرفنا البروفيسور الدكتور سعيد بن رماش على نصائحه الثمينة ومساعدته طوال فترة العمل بأكملها. كما نتوجه بالشكر إلى أعضاء لجنة التحكيم على رأسها الدكتورة بودور بريزة والدكتور فريد لطرش على قبول عملنا وإثرائه بمقترحاتهم. كما نشكر أيضا أستاذتنا الكريمة شاوش نجاة التي لم تبخل علينا طوال عملنا هذا بنصائحها القيمة وندعو الله أن يوفقها في مشوارها العلمي و العملي. كما نود أن نشكر جميع الأشخاص الذين شاركوا بشكل مباشر أو غير مباشر في تحقيق هذا العمل. كما أود أن أشكر جميع أفراد عائلتي على تشجيعهم. أخيراً ، أشكر جميع أصدقائي.

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General Introduction

General Introduction

In the field of semiconductors, doping is the action of adding impurities in small quantities to a pure substance in order to modify its conductivity properties. The properties of semiconductors are largely governed by the quantity of carriers of charge they contain.[1] .

The properties of semiconductors are largely governed by the amount of charge carriers they contain. These carriers are the electrons or the holes. The doping of a material consists in introducing, into its matrix, atoms of another material. These atoms will replace certain initial atoms and thus introduce more electrons or holes .[2].

Doping is carried out by introducing impurities into the crystal of a semiconductor in order to increase the number of free carriers. This insertion is carried out by diffusion or by transmutation.

The doping of ZnO by the element Mg to obtain the ternary alloy Zn-MgO. This new material which has a wider forbidden band than ZnO has received much attention due to its potential applications in ultraviolet optoelectronic devices. These new thin films $Zn_{1-x}Mg_xO$ has emerged as one of the important compounds in semiconductors in due to the high binding energy. $Zn_{1-x}Mg_xO$ thin films of various compositions were deposited on glass substrates using the pyrolysis spray technique.[3] .

This manuscript is organized as follows:

- The first chapter presents, first of all, some definitions of the layers thin, deposition techniques which to date make it possible to obtain layers of transparent conductive oxides, a definition of TCO then a review on the essential properties of the oxide used (MgO). Finally, we present some data on the potential applications of oxides conductive transparencies.
- The second chapter describes the different experimental steps followed to the elaboration of MgO thin films. First, we describe the conditions and technique used for the deposition of MgO layers. In a second part we quote the different techniques used for the characterization of our layers.
- In the third chapter, we expose and discuss, in detail, the results of all our films. From this study, the result is a summary which highlighting the figure of merit of all samples.
- Finally, we end this manuscript with a general conclusion in which we highlight all the significant results we have obtained during this work journey.

General Introduction

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Chapter I: MgO Thin Films

Chapter I MgO Thin Films

I.1 Introduction

Several studies has been reported on the processing of magnesia thin films over the past few decades [1,2,3], as many fruitful advances in thin film deposition technique have occurred. The formation of thin films depends on many parameters including deposition technique due to their structure and properties [4, 5]. Among the factors which determine the physical, electrical, optical and other properties of a film we cite for example rate of deposition, environmental conditions, substrate temperature, presence of foreign matter in the deposit or its purity and inhomogeneity of the film. Various deposition methods have been used to understand the influence of these parameters on the formation of MgO thin films [4, 6].

In this chapter we report the definition of the thin layer, MgO thin films and its main alloys as well as some elaboration methods and finishing with some applications in different fields.

I.2 Definition of thin layer

A thin layer of a given material is an element of this material which its thickness has been greatly reduced to the Angstrom Å scale and this small distance between the two limits (almost two dimensional), in general, causes instability and degradation over time [7]

The essential difference between the material in the bulk state and the thin layer state is related to the fact that in the massive state we usually neglect, with reason, the roles of the boundaries in the properties, whereas in a thin layer these are at contrary the effects related to the surface that are preponderant. It's pretty obvious that the lower the thickness, the more this bidimensionality effect will be important. Conversely, when the thickness of a thin layer exceeds a certain threshold, the thickness effect will become minimal and the material will regain the well-known properties [8].

The second essential characteristic of thin layer is that, whatever the procedure used for its fabrication, a thin layer is always built on a support (although sometimes it is separated of the support). Consequently it will be imperative to take into account this major fact in the design, namely that the support has a very strong influence on the structural properties of the

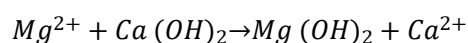
Chapter I MgO Thin Films

deposited layer. So a thin layer of a same material and same thickness may have significant difference depending on whether it will be deposited on an amorphous insulating substrate such as glass or a monocrystalline silicon substrate for example. Consequently to these characteristics, thin layer is anisotropic by construction.

In practice we can distinguish two main families of methods, those that use a carrier gas to move the deposited material from a container to the substrate and which are similar to the diffusion techniques used in manufacturing active compounds, and those that involve a very low pressure environment and in which the material to be deposited will be conveyed by means of an initial pulse of thermal or mechanical nature [9].

I.3 MgO thin films

Magnesium oxide is produced by the calcination of magnesium carbonate or magnesium hydroxide. The latter is obtained by the treatment of magnesium chloride solutions, typically seawater, with lime[10].



Calcining at different temperatures produces magnesium oxide of different reactivity. High temperatures 1500 – 2000 °C diminish the available surface area and produces dead-burned (often called dead burnt) magnesia, an unreactive form used as a refractory. Calcining temperatures 1000 – 1500 °C produce hard-burned magnesia, which has limited reactivity and calcining at lower temperature, (700–1000 °C) produces light-burned magnesia, a reactive form, also known as caustic calcined magnesia. Although some decomposition of the carbonate to oxide occurs at temperatures below 700 °C, the resulting materials appear to reabsorb carbon dioxide from the air [11].

The use of MgO, With a low dielectric loss, shows a wide application in semiconductor systems. In addition, due to its low refractive index ($n = 1.7$), MgO is especially suitable as a buffer for epitaxial optical waveguide films [12]. Moreover, textured MgO thin films could provide a possible template for epitaxial growth of textured perovskite oxides. However, in spite of its growing relevance in science and technology, the understanding and control of the growth process of MgO thin films are limited so far, especially the strain relaxation process. Strain relaxation in MgO thin films plays a pronounced role in influencing the crystal quality and subsequent performance in devices.

Chapter I MgO Thin Films

The structure assigned to MgO can be regarded as a cubic close packing of O^- ion and all the octahedral sites are filled with Mg^+ ions (**Fig. I.1**). Each O^- ion is surrounded by six Mg^+ ions and each Mg^+ ions is surrounded by six O^- ions to produce 1:1 co-ordination. The radius ratio falls within the range of 0.41–0.73 \AA , which is the radius ratio of stable octahedral coordination. Existing high bond strength in ionic crystal is due to the strong electrostatic forces between ions and hence MgO an ionic crystal, exhibits hardness and high melting point and low electrical conductivity. Its structural, physical, optical and electronic properties are listed in **Table I.1**.

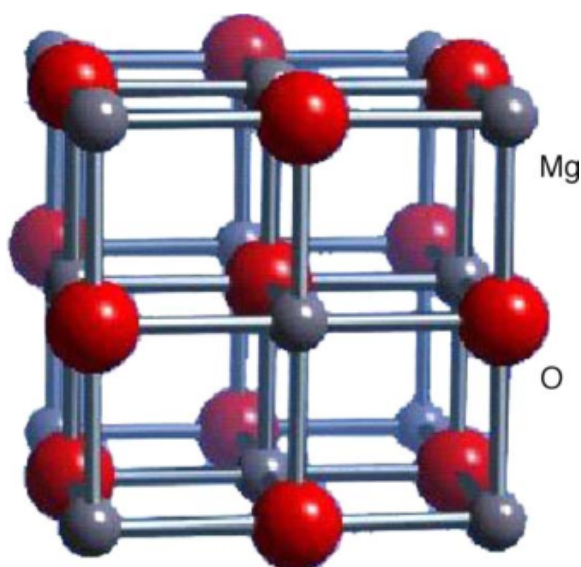


Fig I.1: MgO crystal structure.

Table I.1: Summary of Material properties of MgO[13]

Property	Parameters	values
Physical	Crystal type	Cubic
	Density	3.85 g/cm ³
	Melting Point	2800 °C
	Boiling point	3600°C
Chemical	Color	White
	Chemical formula	MgO
	Molecular weight	40.304 g/mol
	Number of atoms /cm ²	2×10 ²³
Optical	Optical band gap eV	7.2
	Absorption coefficient/cm (2μm)	0.05
Dielectric	Dielectric constant	9.8
	Refractive index	1.739

I.4 The thin films alloys

I.4.1 MgO-ZnO alloys

ZnO is a large gap semiconductor, it is transparent in the visible and in the near infrared. It has a set of properties which allow its use in a certain number of applications such as for example a chemical sensor in thin layers [14].

To enhance the efficiency, the electronic structure, ZnO can be alloyed with MgO to form a ternary $Mg_xZn_{1-x}O$ compound, thus, enabling bandgap engineering and luminescence in the UV regime [15] Often, the combination of these group-II oxides in alloys leads to crystal structure mismatch: undoped ZnO prefers the hexagonal wurtzite (B4) structure or the fourfold coordinated zinc-blende structure (B3), while MgO favors the cubic rock salt (B1) structure at ambient conditions.[16, 17] Experiments have shown that $Mg_xZn_{1-x}O$ exhibits the (B4) structure for high ZnO concentration,[18] while preferring the B1 structure at high MgO concentration.[19] At intermediate concentrations, it exhibits phase separation [20] due to its compositional gradient, which often leads to a thermodynamically unstable crystal structure. In general, the isovalent and isostructural II–VI alloys are thermodynamically unstable because the mixing enthalpy in either the B1, B3, or B4 structure is always positive.[20,21] The difficulty in synthesizing stable phases of MgO–ZnO alloys has hindered the adequate exploitation of their promising properties for technological applications. This prompted earlier calculations on the stability of the $Mg_xZn_{1-x}O$ alloy system.[20,22]

I.4.2 MgO-SnO₂

Tin dioxide (SnO₂) has very remarkable electrical properties linked to surface adsorption; it is an n-type semiconductor with a large band gap (between 3.5 and 4.1 eV, [23-24]). Like the majority of semiconductor oxides, the crystal of SnO₂ presents breaks in the periodicity of the network: the oxygen vacancies have been designated as being the predominant intrinsic defects in SnO₂ [23, 25, 26], making it sub stoichiometric in oxygen. These particular properties have long attracted the attention of scientists who have tried to improve electrical performance by different methods (microstructural stabilization, doping ...)

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I.5 Elaboration methods of MgO thin film

Thin films are generally used to enhance the surface properties of solids. Transmission, reflection, absorption, etc. permeation and electrical behaviour are only some of properties that can be improved by using a thin film. Thin film technologies are divided into PVD (Physical Vapour deposition) and CVD (Chemical Vapour deposition) processes (Table I.2).

Thin film of all materials created by any deposition technique exhibits different features such as:

- the beginning of a random nucleation process follows by nucleation and growth stages. These stages are dependent on deposition conditions.
- The nucleation stage can be modified significantly by external agencies, such as electron or ion bombardment.
- Film microstructure, associated defect structure, and film stress depend on the deposition conditions at the nucleation stage.
- The crystal phase and the orientation of the films are governed by the deposition conditions.

The basic properties of, such as film composition, crystal phase and orientation, film thickness, and microstructure, are controlled by the deposition conditions and methods.

The MgO films have been deposited by various methods including molecular beam epitaxy [27], sol-gel process [28-31], successive ionic layer adsorption and reaction (SILAR) [32], ultrasonic spray pyrolysis (USP) [33,34], and ion beam assisted deposition [35].

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Table I.2:Thin Film Deposition Techniques [36]

Thin Film Deposition techniques		
Physical Vapour Deposition (PVD)		Chemical Vapour Deposition (CVD)
Thermal Process	Athermal Process	
1)Thermal deposition	1) Direct current Diode sputtering	1) Thermally activated CVD
2)Electron Beam Deposition	2) Radio Frequency sputtering	2) Plasma Enhaanced CVD
3)Molecular Beam Epitaxy deposition	3) Magnetron sputtering	3)Photo-assisted CVD
4)Pulses Laser Deposition	4) Unbalanced Magnetron Sputtering	4) Metal organic CVD

I.5.1 Physical vapour Deposition (PVD)

Physical vapour Deposition technique is the transfer of atoms and molucules from a source to a substrate by a process that relies on physical methods to produce the vapour species. Physical vapour deposition is carried out in high vacuum to avoid contamination of the film by ambient atmosphere [37].

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I.5.1.1 Molecular Beam Epitaxy (MBE):

This process is based on the deposition of thermal beam of atoms or molecules on the clean surface of a single-crystalline substrate held at high temperature under ultra-high vacuum conditions to form an epitaxial film [38]. **Figure I.2** shows a typical MBE system. MBE is a sophisticated and finely controlled method for growing single-crystal epitaxial films in high vacuum. Limitations of MBE are the expensive equipment and its complex operation [39].

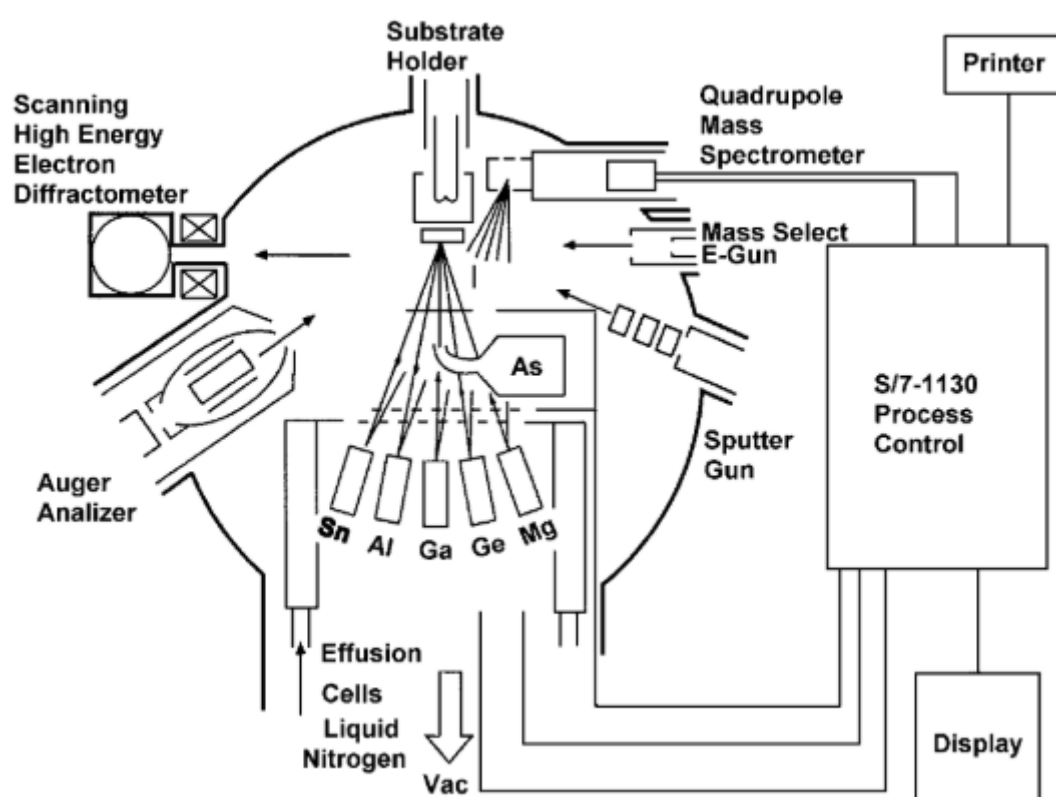


Fig I.2 : Molecule Bean Epitaxy (MBE) system.[38]

I.5.2 Chemical Vapour Deposition (CVD)

The process by which the non-volatile products of a gas phase reaction are allowed to deposit onto a substrate is known as chemical vapour deposition [39]. The main feature of CVD is its versatility for synthesizing both simple and complex compounds with relative ease. Fundamental principles of CVD encompass an interdisciplinary range of gas-phase reaction

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chemistry, thermodynamics, kinetics, transport mechanisms, film growth phenomena and reactor engineering [40]. The advantages of CVD include high deposition rate, low price and flexibility in composition control. However, due to high deposition temperature, CVD is not suitable for substrates which are thermally unstable at high temperatures [41]

I.6 Applications

The modification of the surface of a substrate permit to couple its properties and the properties of the surface material (deposited). The modification of the surface of a substrate gives it one or more additional physicochemical properties (resistance to corrosion, electrical insulation, etc.): the use of a low added value substrate leads to deduct manufacturing costs while having the required physical and chemical surface properties.

The first surface modifications had an aesthetic purpose (painting, gold plating ...) while more technical applications concerned metallurgy [ref].

During the 20th century, more sophisticated applications diversified in the following fields: [ref]

Microelectronics: it was able to develop from the 1960s through the implementation of layers becoming thinner conductive or insulating, and can be found subtypes passivating layer (electronic contact), PN junction, diode, transistor, material piezoelectric, LED lamp, superconductor,

Optic: while retaining the aesthetic applications, the optical applications of the layers were used to develop more effective radiation sensors, such as anti-reflection layers in solar cells, mirror glass, anti-reflection treatment of camera lenses, photo-detection , flat screen displays, ophthalmic applications, optical guide (energy controls - architecture, vehicles, energy conversion, etc.)

Mechanic: tribological coatings (dry lubrication, erosion, abrasion; diffusion barriers...)

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

Thermal: the use of a thermal barrier layer decreases for example the surface temperature of the metal of the fins of the reactors thus making it possible to improve the performances of the reactors (increase in the internal temperature),

Biology: biological micro sensors, biochips, biocompatible materials ...

Micro and nanotechnologies: mechanical and chemical sensors, microfluidics, actuators, detectors, adaptive optics, nano photonics...

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

Decoration: watches, glasses, jewelry, home equipment, etc.

I.7 Conclusion

Magnesium oxide (MgO) seems to have many interesting properties as MgO thin films such as high electrical resistivity, high optical transparency, good chemical resistance, excellent thermal and thermodynamic stabilities, high secondary electron emission stability, low dielectric constant and low refractive index. These unusual properties caused that MgO films have been widely used in a lot of applications.

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Chapter II

Experimental Section

Chapter II Experimental Section

II.1. Introduction

In this study, a new route to produce pure and composite ZnO-MgO thin films has been presented. In the process the pure ZnO thin films were the starting point, ending up with MgO by doping various concentration of Mg with the help of spray pyrolysis technique. The crystal phases in all doping levels have been obtained when the samples annealed at 450 °C. The X-ray diffraction spectra, the scanning electron microscopy micrographs and UV-Vis absorption spectra have been performed to elucidate the composed film structures.

II.2. Elaboration

The principle of the spray pyrolysis method (or spray pyrolysis or also pyrolytic spraying) consists in mechanically spraying a solution of precursors chemicals, containing the different constituents of the compound ZnO (zinc acetate and manganese chloride (MgCl₂) on substrates arranged on a substrate holder heated. After spraying the solution, a chemical reaction occurs on the hot surface (substrate), which provides a thin layer of ZnMgO after evaporation elements of the reaction (volatile elements).

In our work, we have studied the influence of solution pH (Sm, Sm1, Sm2, Sm3 and Sm4) on the structural and optical properties of the layers thin from ZnMGO. The different layers were produced on glass substrates heated to temperature of 450 °C.

II.3. Spray pyrolysis technique (SPT)

Spray pyrolysis is a technique widely used to prepare materials in different forms: thin, thick, dense, porous and even deposits multilayer and ceramic coatings can be prepared using this technique [1]. The principle of this technique is based on the formation of droplets of a solution containing the different constituents of the compound transported by a flow to be deposited on a substrate heated by a heating system to temperatures appropriate (activation of the chemical reaction between compounds). Thus the solvent evaporates and the other elements react to form the final compound (hence the name pyrolysis: "pyro" for heat and "lysis" for decomposition). This experience may be carried out under a normal atmosphere [2].

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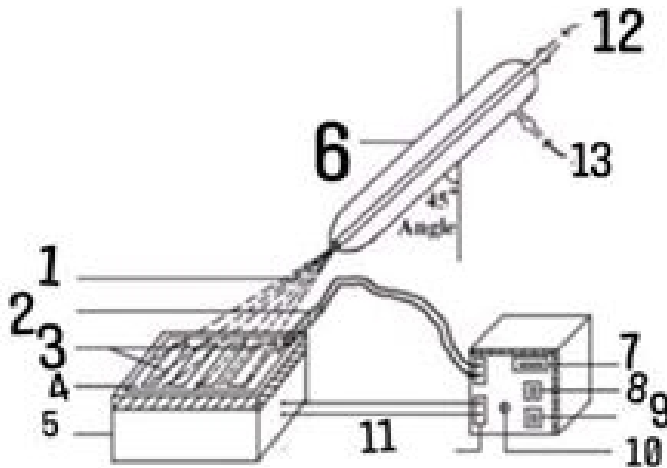


Figure II.1: Experimental diagram of the spray pyrolysis process [3].

- | | | |
|-----------------|----------------------|---------------------|
| 1 – Spray | 7 - Billboard | 13 – Compressed air |
| 2- Thermocouple | 8 - Voltmeter | |
| 3 - Substrats | 9 - Ampermeter | |
| 4 - Low plate | 10 - Reset | |
| 5 - Heater | 11 - Energy supplied | |
| 6 – Aerosol gun | 12 – Solution | |

II.4. The advantages of the spray pyrolysis technique

The droplet size is $5\ \mu\text{m}$; it is $\approx 40\ \mu\text{m}$ in the case of the ultrasonic spray and $30\ \mu\text{m}$ for the sol-gel.

-It allows good control of the chemical composition of the material.

-We can use several products at the same time, in particular for doping [4].

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II.5. Experimental procedure

II.5.1. Preparation of the substrate

The structural properties of the layer to be deposited are strongly linked to the nature of the substrate. Thus a thin layer of the same material, of the same thickness may have significantly different physical properties depending on whether it is deposited on a substrate amorphous insulator such as glass, a monocrystalline silicon substrate for example, or a conductive substrate such as ITO (indium tin oxide) [5].

II.5.1.1. Choice of deposition substrate

The choice of substrates is dictated by:

- ↪ **Adhesion:** The solution should adhere to the substrate.
- ↪ **Physical properties:** the physical properties of the substrates must be in agree with the type of study you want to conduct, for example:
 - ❖ For the study of the optical properties of wave guiding it is imperative to choose a substrate with a refractive index lower than that of the material to be deposited [6].

Some applications require the use of conductive substrates such as ITO while others ask for insulating substrates like glass. In our work, we used glass substrates.

II.5.1.2. Cleaning of substrates

As we have mentioned, these substrates require special preparation in order that they serve as a support for the deposit.

Cleaning the substrates is a very important step which takes place in a place clean, because this step determines the qualities of adhesion and homogeneity of the layers filed.

The substrates must be free from grease, scratches and impurities such as dust. The procedure for cleaning the substrates that we have chosen is the following:

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- Soap cleaning
- Rinsing with distilled water
- Cleaning with methanol
- Finally, drying with an optical paper [7].

II.5.2. Preparation of the solution

In this work we used the following precursors: zinc acetate ($C_4H_6O_4Zn \cdot 2H_2O$), as source material which we dissolved in methanol, we get $[ZnO] = 0,1 \text{ mol/l}$, and we dissolve $MgCl_2$ in water, we obtain $[MgO] = 0,158 \text{ mol/l}$.

We take 70 ml of MgO and 30 ml of ZnO , then stir for 2 hours to obtain a homogeneous solution.

Table II.1: The experimental conditions for the production of $ZnMgO$ thin films.

Precursors	Concentration of solution M	T C°
Zinc acetate ($C_4H_6O_4Zn \cdot 2H_2O$)	0,1	450C°
Magnesium chloride ($MgCl_2$)	0,158	

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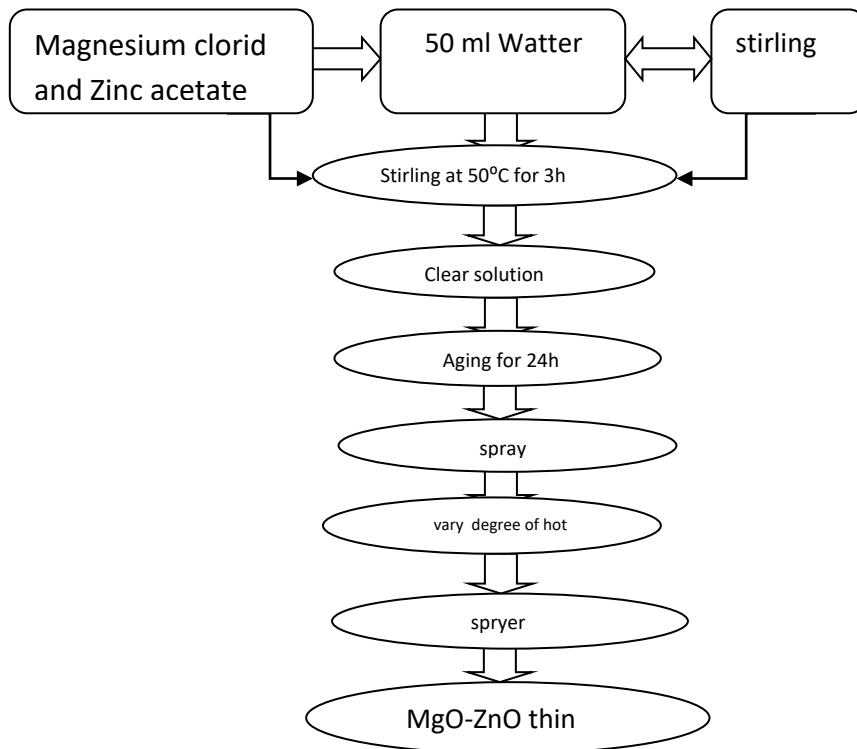


Figure II.2 Flow chart of Spray pyrolysis method for preparation of MgO thin films.

II.5.3. Preparation of the substrate

A) Glass Substrates

During this study, spray pneumatic MgO thin films were deposited on glass substrates (see Figure II.2). Which have a length of 2.5cm and a width of 2.5cm the choice of glass for these reasons:

- The thermal compatibility with MgO (thermal dilation coefficients are $\alpha_{\text{glass}} = 8.5 \times 10^{-6} \text{ K}^{-1}$, to minimize the constraints with the interface film/substrate,
- For their transparency which adapts well for the optical characterization of films in the visible one.
- For economic reasons.

In order to obtain good adherence and uniformity for the films.

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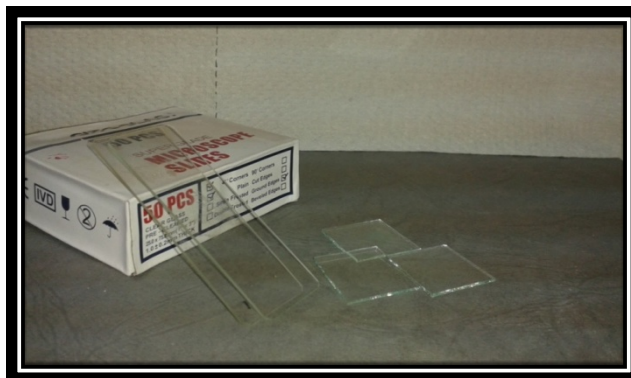


Figure II.3 Glass Substrates

B) Substrate Cleaning Process

The adherence and the quality of the depot repose on purity and the state on substrate thus the cleaning of the substrate is one of the most important steps to remove any contaminated organic compounds, the cleaning of our substrates surfaces is as follows:

- The substrates are cut using a pen with diamond point.
- Washing with soap solution to clean any dusts or attachments.
- Washing with distilled water to remove soap, and then with acetone during 2 min.
- Rinsing with distilled water again.
- Washing with ethanol during 2 min at ambient temperature.
- Cleaning in water distilled bath.

II.6. Thin Film Deposition

The deposition procedure comes immediately after the preparation of the substrates and solutions and is presented in several stages:

The substrates are placed above a substrate holder and to avoid thermal shock from substrates the substrate holder is gradually heated from room temperature gradually up to the temperature chosen for the deposits (450 ° C). Very droplets fines are sprayed onto the heated substrate which causes, by pyrolysis, the activation of the chemical reaction between the

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compounds, the solvent evaporates due to the reaction endothermic of the two compounds forming the thin layer. At the end of the deposit process, we stop heating and allow the substrates to cool above the substrate holder until the ambient temperature, in order to avoid thermal shocks which risk breaking the glasses, and then we collect our samples (Table 2).

Table II.2: Preparation of solutions at different pH

	Solution	pH	T C°
Sm	([MgO] = 0,158 + [ZnO] = 0,1) = 0,258 mol/l	7	450 C°
Sm1	[ZnMgO] + HCl (diluted)	2,6	
Sm2	[ZnMgO] + HCL (diluted)	5	
Sm3	[ZnMgO] + Ethano-amin (diluted)	7,9	
Sm4	[ZnMgO] + Ethano-amin (concentrated)	9,03	

II.6.1. Charaterization of the films

As it is known, that the techniques of characterization of thin films are very numerous, the aim of this work is to study the effect of ph on the synthesis of ZnMgO alligae deposited on glass substrates, by spray pyrolysis. It is for these purposes that these layers were analyzed by different material characterization techniques. The characterization of ZnMgO layers is based on a variety of strong methods:

- X-ray diffraction (XRD), for structural characterization.
- UV-VIS spectrophotometry for optical characterization.

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II.6.2. Structural characterizations

This study made by X-ray diffraction aims to specify the structure and the crystallographic growth directions of the layers, to measure the parameters of mesh size and crystallite size. It should also make it possible to examine the state of the constraints in the depots

II.6.3. Optical characterization

The optical techniques which characterize thin films are numerous such as:

- A) Visible spectroscopy: Is a technique based on the interaction of electromagnetic radiation and matter in the near UV to very near range IR. This technique makes it possible to determine the optical constants of the material studied (the rate transparency, the absorption coefficient, the optical gap and the extinction coefficient) [8].



Fig II.4 : Ultraviolet-visible spectrophotometer [9]

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B) Principle of ultraviolet-visible absorption

Principle of UV-Visible Spectroscopy. The Principle of UV-Visible Spectroscopy is based on the absorption of ultraviolet light or visible light by chemical compounds, which results in the production of distinct spectra. Spectroscopy is based on the interaction between light and matter [10].

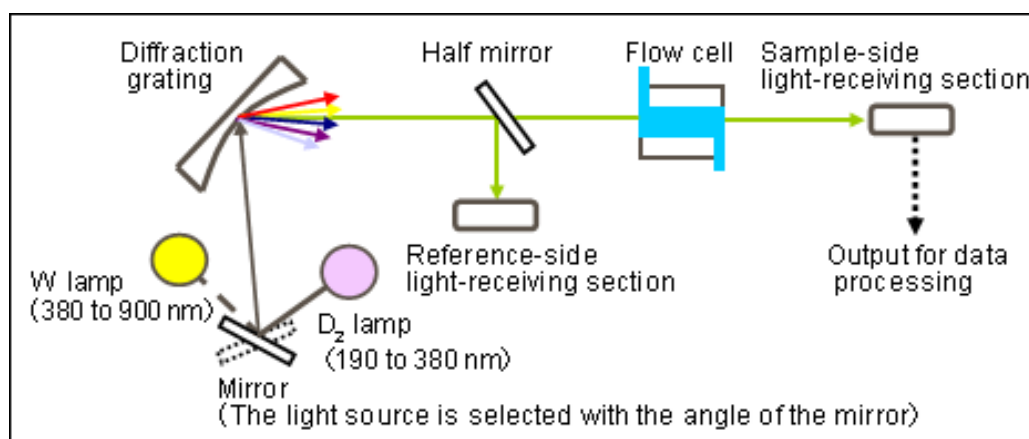


Figure II. 5 : The principle of operation of UV-visible

II.7. Conclusion

In this chapter we have presented the deposition and characterization technique adopted in our study. We recalled the principle of spray deposition and then presented the deposition system that we carried out in the laboratory, after we described the different characterization techniques used to analyze and determine the different optical and electrical properties of the films produced.

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Chapitre III: Results and Discussion

Chapter III Results and Discussion

III.1.Introduction:

Spay pneumatic method has been successfully employed for the deposition of magnesium oxide - zinc Oxide (MgO-ZnO) thin films [1]. The films were deposited with different PH (2.6; 5.0; 7.0 and 7.9 of Ph). The structural and electrical properties of magnesium oxide - zinc Oxide (MgO-ZnO) thin films were studied.

In the present work, we study the molarity effect on structural and electrical properties of MgO-ZnO thin films. The structural, optical and electrical properties of MgO-ZnO thin films were characterized by X-ray diffraction (XRD, Bruker AXS-8D) with $\text{CuK}\alpha$ radiation ($\lambda = 0.1541 \text{ nm}$) in the scanning range was between $2\theta = 10^\circ$ and 90° to find the crystallographic and phase structures. The ultraviolet-visible spectrophotometer (UV, Lambda 35) to find the absorption, band gap and urbach energy.

III.2. Ph effect on structural properties of MgO-ZnO thin films:

The results of X-ray diffraction pattern of deposit MgO-ZnO thin films as a function of Ph are presented in Figure III.1. The observations found that there are four diffraction peaks were observed and highest at $2\theta = 34.1^\circ$, 36.1° , 41.8° and 60.9° corresponding to following plans (002) of ZnO, (101) of ZnO, (200) of MgO and (220) of $\text{Mg}(\text{OH})_2$ respectively [1,2].

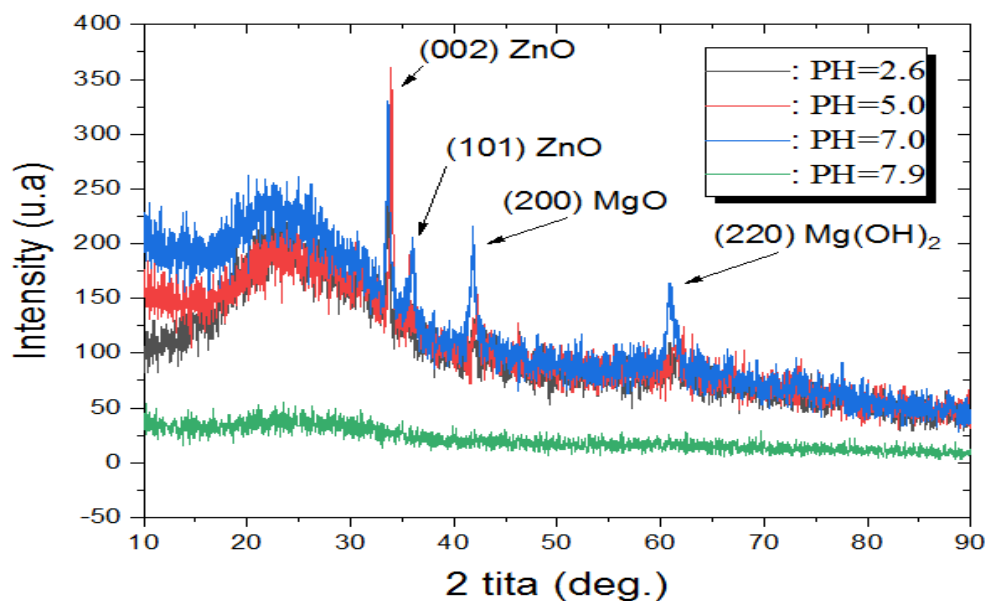


Figure III.1: The XDR of MgO-ZnO thin film deposited with different PH.

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The structure information according to the hexagonal structure as well as the lattice constants can be calculated by the following formula [2]:

$$d_{hkl} = \left(\frac{4}{3} \frac{h^2 + hk + k^2}{a^2} + \frac{l^2}{c^2} \right)^{-\frac{1}{2}} \quad (\text{III.1})$$

where a , c are the lattice parameters, (h, k, l) and d_{hkl} the Miller indices of the planes and the interplanar spacing. These parameters are presented in Table 1. On the other hand the crystallite size of (002) of ZnO plan for MgO-ZnO thin films can be determined by Debye–Scherer formula [3]:

$$G_{(hkl)} = \frac{0.9\lambda}{\beta \cos \theta} \quad (\text{III.2})$$

where $G_{(hkl)}$, λ , β , θ , and are the crystallite size, the X-ray wavelength ($\lambda = 1.5406 \text{ \AA}$), the full width at half-maximum (FWHM), the Bragg angle of (002) of ZnO peak and the average crystallite size, These parameters are presented in Table III.1.

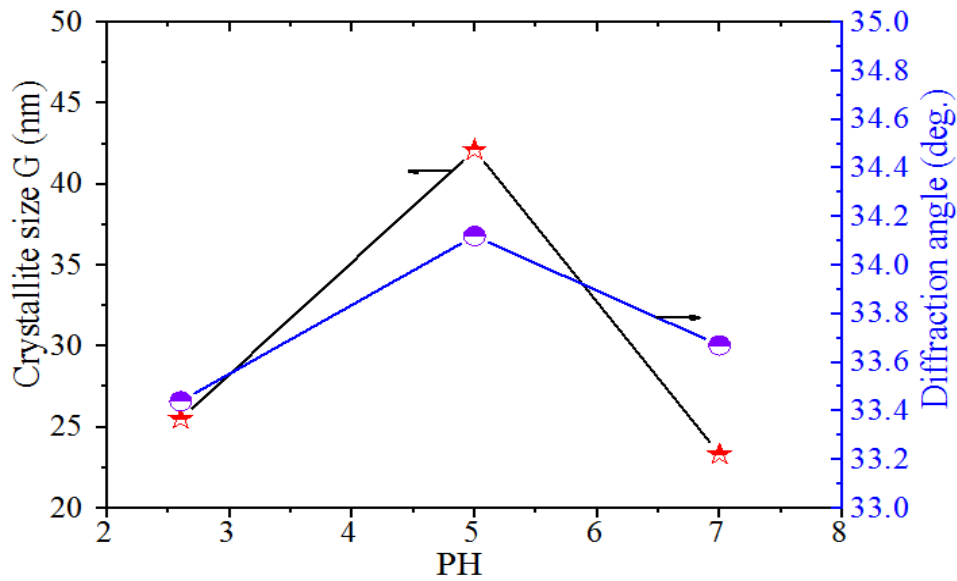


Figure III.2: Variation of crystallite size and diffraction angle of (002) ZnO peak for MgO-ZnO thin film deposited with different PH.

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Table III.1: Variation of the crystallite size and diffraction angle of (002) ZnO peak for MgO-ZnO thin film deposited with different PH.

PH	Crystallite size (nm).	Diffraction angle of (002) ZnO (deg.).
2.6	25.51	33.44
5.0	42.12	34.12
7.0	23.32	33.67
7.9	-	-

III.3. Ph effect on optical properties of MgO-ZnO thin films:

Transmittance (T)

Figure (III.3) shows the relation between transmittance and wavelength in the range of (300- 900 nm) for MgO-ZnO thin films. The transmittance for all thin films increases as the wavelength increases in the range of (300- 400 nm), which it is corresponds the region between the valence band and conduction band. The spectrum shows high transmittance in the visible and infrared regions, and low in the ultraviolet region. The transmittance of MgO-ZnO thin films increased with increasing of Ph from 2.6 to 7.9 in all deposited films. The optical property was affected by the Ph.

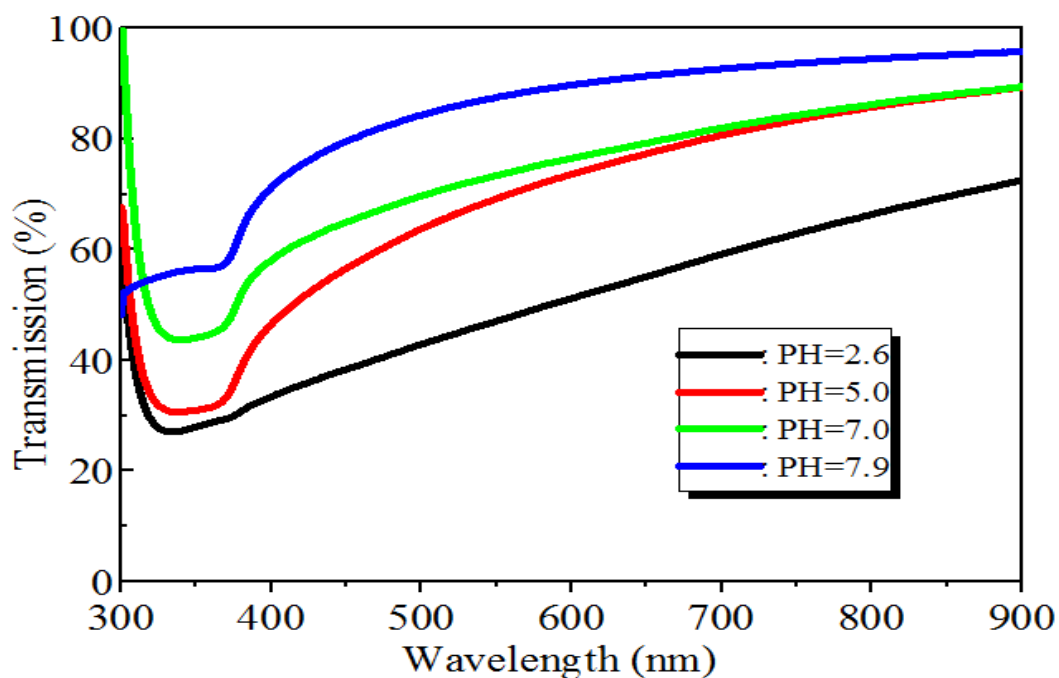


Figure III.3: Variation of transmittance spectra (T) with wavelength (λ) of MgO-ZnO thin film deposited with different PH.

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Absorption

Reflectance R can be obtained from absorption and transmission spectrum in accordance to the law of conservation of energy by the relation [4]:

$$R + T + A = 1 \quad (\text{III.3})$$

where R is the reflectance, T is the transmittance of the films and A is the absorption.

R is related to the refractive index and extinction coefficient of the material as follows [6]:

$$R = \frac{(n - 1)^2 + k_0^2}{(n + 1)^2 + K_0^2} \quad (\text{III.4})$$

where R is the reflectance, n is the Refractive Index, and K_0 is the Extinction Coefficient.

The optical absorption coefficient can be calculated from relation [7]:

$$\alpha = 2.303 * A/t \quad (\text{III.5})$$

where α and t are the absorption coefficient and film thickness. Figure III.4, it have been noticed that all the prepared thin films have a different absorption in visible range of the spectrum, which shows the relation between the absorption (A) with Transmission (T). The high absorption edge value can be find with Ph = 2.6 because the increases in the film thickness.

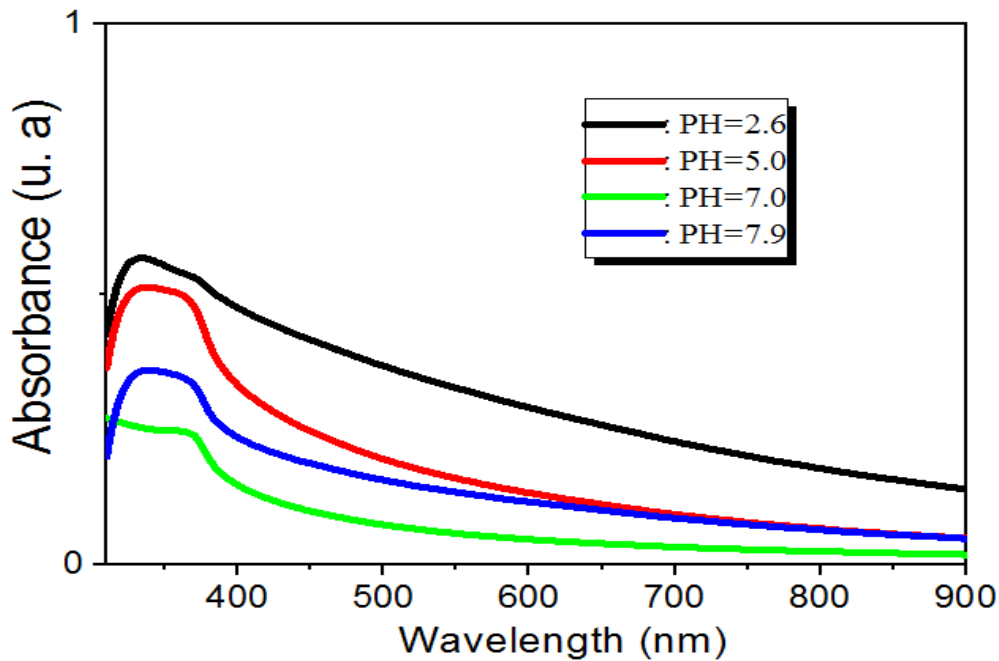


Figure III.4: The relation between absorption and wavelength of deposited MgO-ZnO thin films at various PH.

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The refractive index (n) of the nanostructure thin films was calculated using the following relation [8]:

$$n = \frac{1+R}{1-R} + \sqrt{\left(\frac{4R(\lambda)}{(1-R(\lambda))^2} - k^2\right)} \quad (\text{III.6})$$

Optical Energy gap (E_g):

The optical energy gap (E_g) was derived assuming allowed direct transitions between the edge of the valence and conduction band [9]. For MgO-ZnO thin films, we can calculate using Tauc's equation [10]

$$(\alpha h\nu) = A(h\nu - E_g)^n \quad (\text{III.7})$$

where α is the absorption coefficient, A is a constant, $h\nu$ is the energy of incident photon and n depends on the quantum selection rules for different materials which may be equal to 1/2 for direct and 2 for indirect band gap. In our case, we have used $n=1/2$ because it gives an excellent linear fit curve in the band-edge region [11].

The absorption coefficient (α) has been used to determine the band gap of the evolving MgO-ZnO film by measuring the absorption coefficient as a function of the incident photon energy ($h\nu$). The absorption coefficient may be approximated by [8,11]:

$$\alpha = \frac{1}{t} \ln\left(\frac{1}{T}\right) \quad (\text{III.8})$$

where t represents the film thickness and T the wavelength dependent transmittance.

The graphs of $(\alpha h\nu)^2$ versus $(h\nu)$ plots of MgO-ZnO films fabricated at different molarities are shown in Figure III.5. It can be seen that the extrapolation of linear portion of the graph to the energy axis at $A=0$ [12] in the range between 300–350 nm gives band gap energy E_g is shown in Table III.2.

Urbach energy

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In the addition of we have used the tail width, which can be calculated using the Urbach rule for the absorption coefficient at lower photon energy [13].

$$\alpha(h\nu) = \alpha_0 \exp\left(\frac{h\nu}{E_u}\right) \quad (\text{III.9})$$

where α_0 is the constant and E_u is the Urbach energy, Figure III.6 shows the graph of $\text{Ln}\alpha$ versus $(h\nu)$ plots for which used to deduce the Urbach energy of the MgO thin films, these values are shown in Table III.2.

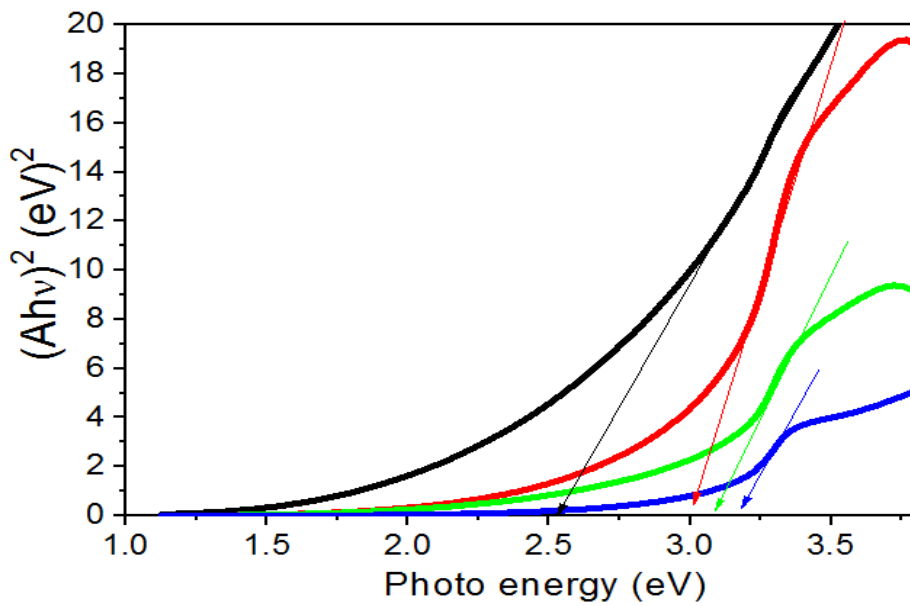


Figure III.5: Plot of $(Ah\nu)^2$ versus $(h\nu)$ of MgO-ZnO thin film for different Ph.

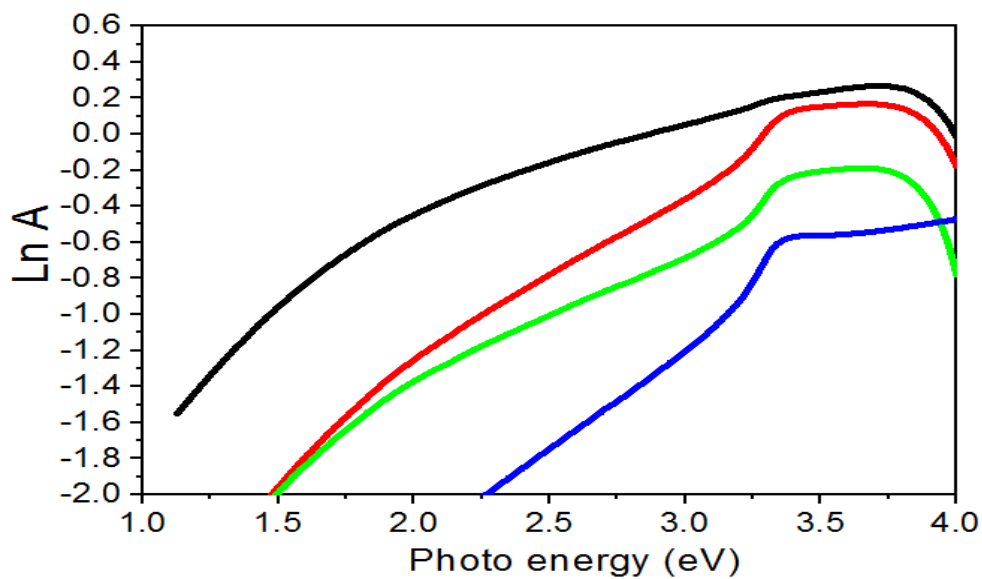


Figure III.6: Plot of $(\text{Ln}A)$ versus $(h\nu)$ of MgO-ZnO thin film for different Ph.

Chapter III Results and Discussion

The Table III.2 below gives as the values of E_g and E_u at different Ph to MgO-ZnO solution. In the other hand, Figure III.7 shows the variation of optical band gap and Urbach energy of MgO-ZnO thin films as a function PH. As can be seen, that the band gap energy E_g and Urbach energy E_u are dependent to the change in PH solution, it is clear that the values of E_g are agreements to E_u variation. However, can be observe that the band gap energy of MgO-ZnO thin films increased slowly with incassating the PH solution, this result can be explained by oxygen vacancy. As mentioned above, As a result, both an increase in the optical gap and a broadening of the Urbach tail occurred.

Table III.2: Variation of the optical band gap energy E_g and the Urbach energy of MgO thin films with different molarities.

PH	Optical gap energy E_g (eV).	Urbach energy E_u (meV).
2.6	2.53	820
5.0	3.02	355
7.0	3.08	340
7.9	3.18	305

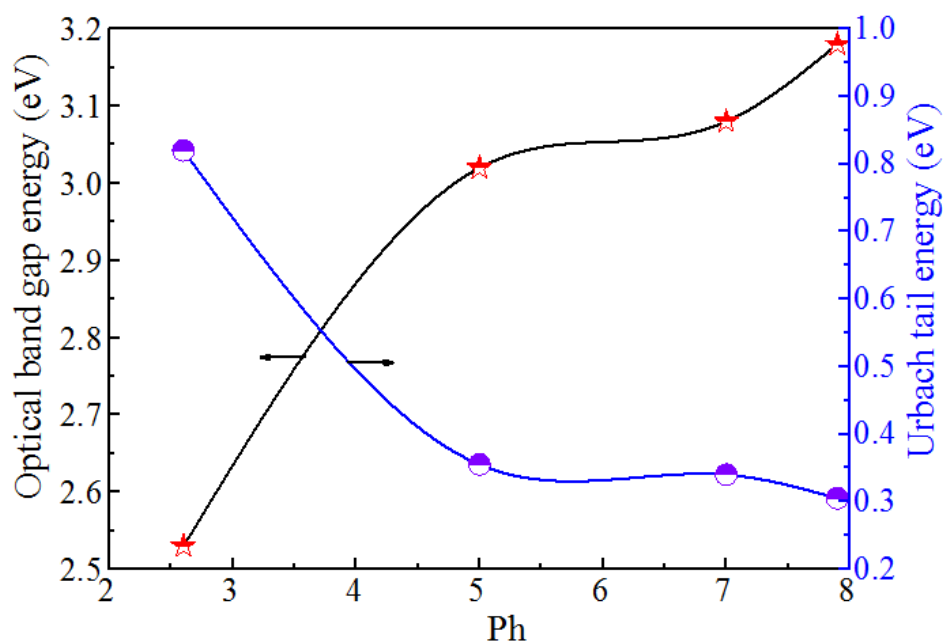


Figure III.7: The variation of optical band gap and Urbache energy of MgO thin films as a function of PH.

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III.4. Conclusion:

In this study MgO-ZnO thin films were deposited on galas substrate by pneumatic technique. The effects of Ph solution (2.6; 5.0; 7.0 and 7.9 of PH) were successfully investigated. MgO-ZnO thin films were observed in high crystallinity with a hexagonal wurtzite structure with a strong preferential, the maximum value of crystallite size 42.12 nm is attained of deposit MgO-ZnO thin film at 450 °C with 5 of PH. The optical transmission spectra showed all the sprayed MgO-ZnO thin films are transparency within the visible wavelength region. The band gap of MgO-ZnO thin films increases from 2.53 to 3.18 eV as the PH increases, The Urbach energy values decreased as the PH increased from 820 to 305 375-519 meV.

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General Conclusion

General Conclusion

The interest in magnesium oxide thin films is fast growing due to their importance in many applications in science and technology. Besides acting as an EC material, it can also be used as a functional layer material for photovoltaic applications. MgO is an insulator with a resistivity of the order of $10^{10} \Omega \cdot \text{cm}$ at room temperature.

In conclusion, highly transparent conductive MgO-ZnO thin films have been deposited on glass substrate by spray pneumatic method. The influence PH solution in the range of ((2.6; 5.0; 7.0 and 7.9 of Ph) on structural and optical properties were investigated.

MgO-ZnO thin films were observed in high crystallinity with a hexagonal wurtzite structure with a strong preferential, the maximum value of crystallite size 42.12 nm is attained of deposit MgO-ZnO thin film at 450 °C with 5 of PH.

The optical transmission spectra showed all the sprayed MgO-ZnO thin films are transparency within the visible wavelength region. The band gap of MgO-ZnO thin films increases from 2.53 to 3.18 eV as the PH increases, The Urbach energy values decreased as the PH increased from 820 to 305 meV.

The best estimated structural and optical characterisation MgO-ZnO thin films are achieved in prepared MgO-ZnO thin films 2.6 and 5 of PH.

General Conclusion

Abstract

In this work, MgO-ZnO thin films were deposited on galas substrate (450°C) by pneumatic technique. The effects of PH solution in the range of ((2.6; 5.0; 7.0 and 7.9 of Ph) were successfully investigated. MgO-ZnO thin films were observed in high crystallinity with a hexagonal wurtzite structure with a strong preferential, the maximum value of crystallite size 42.12 nm is attained of deposit MgO-ZnO thin film at 450 °C with 5 of PH. The optical transmission spectra showed all the sprayed MgO-ZnO thin films are transparency within the visible wavelength region. The band gap of MgO-ZnO thin films increases from 2.53 to 3.18 eV as the PH increases, The Urbach energy values decreased as the PH increased from 820 to 305 meV.

Key words: MgO-ZnO; Thin films; PH solution; spray technique.

ملخص

في هذا العمل ، تم ترسيب الأغشية الرقيقة من MgO-ZnO على ركيزة الزجاج درجة حرارتها 450 درجة مئوية وهذا بتقنية الهواء المضغوط. تمت دراسة تأثير محلول PH في المجال (2.6 ؛ 5.0 ؛ 7.0 و 7.9 درجة الحموضة) بنجاح. لوحظت الأغشية الرقيقة MgO-ZnO في درجة تبلور عالية مع بنية wurtzite سداسية مع تفضيلية قوية، وأعلى قيمة من البلورات تم الحصول عليها هي 42.12 نانومتر من غشاء رقيق MgO-ZnO المترسب عند 450 درجة مئوية مع 5 درجة حموضة. أظهرت أطياف الإرسال البصري أن جميع الأغشية الرقيقة MgO-ZnO التي تم رشها شفافة داخل منطقة الطول الموجي المرئي لحظنا زيادة في فجوة النطاق من 2.53 إلى 3.18 إلكترون فولت مع زيادة PH ، وانخفضت قيم طاقة Urbach مع زيادة PH من 820 إلى 305 ميلي إلكترون فولت.

الكلمات الأساسية: MgO-ZnO ، الأغشية الرقيقة، محلول PH ، تقنية الرش.