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Optical and electrical properties of MgO thin films

Jury :

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General Introduction

General Introduction

Recently, MgO thin films have been gaining interest for their potential advantage as a chemically stable buffer layer for high temperature superconductor and ferroelectric materials applications [1]. MgO is a highly insulating solid with NaCl structure. The lattice constant of MgO is 4.213 Å, which is close to that of several important ferroelectric and superconducting materials. Highly c-axis-oriented PbTiO₃ ferroelectric thin films and good characteristic YBCO thin films have been prepared on MgO single crystal substrates [2–4]. However, for device applications, it is promising to form superconductor and ferroelectric films on Si because the oxide substrates are not only expensive but also incompatible with the current semiconductor technology. Recently, interest in the growth of oxide-based devices on semiconductors has led to the use of oriented MgO films to provide a chemically stable buffer layer between thin films and Si substrate. Especially, epitaxial or oriented MgO films are preferred for such applications, since MgO films can be used as lattice templates for growing oriented overlayers. For example, the high-T_c superconductor YBa₂Cu₃O₇ grows with c-axis orientation when crystallized on 220 oriented MgO films [5] as well as highly textured LiNbO₃, BaTiO₃ and PZT etc. Ferroelectric thin films have been prepared on Si substrates using an intermediate layer of MgO thin film [6–9].

MgO thin films have been prepared by a variety of techniques such as pulsed laser deposition [10], electron beam evaporation [11], metal organic chemical vapor deposition [12], etc. The nebulized spray pyrolysis (NSP) is considered to be a very useful method because of the simplicity of the apparatus and the low price of the raw materials used. The commonly used spray pyrolysis process, which is generated by a piezoelectric transducer, however, has some limitations. The yield of the process is limited by the power and frequency of the ultrasonic generator; therefore, the concentration of the solutions has to be small because the larger concentration of the solutions the greater energy has to be needed to stimulate the process of forming spray. Meanwhile, the piezoelectric transducer would produce heat and therefore, need a cooling system during spray pyrolysis. There have some reports of preparing MgO films by spray pyrolysis by using magnesium acetylacetonate MgC₁₀H₁₄O₄ as the starting material [13]. MgC₁₀H₁₄O₄ is rather expensive and hard to handle.

The present work is divided into three chapters, each addressing a major aspect related to the MgO thin films of the applications and properties, experimental, Results and Discussion.

General Introduction

The first chapter is devoted to a literature study on definitions, applications, some physical properties of MgO thin films. In the second, we have investigated the spray pneumatic method for study the deposition of MgO at different concentrations in same substrate temperature, it has been explained the characterizations techniques. In the end, we have discussed the results, which were investigated the optical and electrical properties of MgO thin films.

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Chapitre I

MgO Thin Films

Chapitre I MgO Thin Films

I.1. Introduction

Number of methods has been reported for deposition of MgO thin films such as vacuum arc deposition [1], magnetron sputtering [2,3], electron beam evaporation [4,5], spray pyrolysis [6] and ion beam assisted deposition [7]. The interesting properties of magnesium oxide thin film has attracted a number of application [1–4,8]. The refractive index of these films is in the range suitable for optical waveguide purpose [8–10]. To the authors knowledge there are no reports on the deposition of MgO thin films by thermal oxidation of vacuum evaporated Mg thin films. Compared to other technique this is a more cost effective method, since oxidation is done in ambient air at relatively low temperature. In this paper, we report the optical properties of thermally oxidized (in air) vacuum evaporated magnesium oxide thin films. Optical transmittance, refractive index, optical band gap, crystal structure and surface morphology have been studied with respect to change in oxidation temperature and duration. A very simple vapour chopping technique [11–14] has been used to modify the properties of the MgO thin film.

Table I.1 Summary of the basic physical and chemical properties of MgO material [wikipedia]

| Property | Value |
|--------------------------------|------------------------|
| Appearance | White powder |
| Molecular mass | 40.3044 g/mol |
| Density (N) (cm ³) | 3.58 g/cm ³ |
| Melting point | 3125 °C |
| Refractive index | 1.736 |
| Band gap energy (Eg) | 7.8 eV |

I.2 Definition of a thin layer

A thin layer of a given material is an element of this material of which one of the dimensions called thickness has been greatly reduced so that it expresses itself in Angstrom Å and that this small distance between the two surfaces limits (almost two-dimensional) causes a disruption of most properties physical [15].

The essential difference between the material in the bulk state and the layer state thin is related to the fact that in the massive state we usually neglect, with reason, the role of the boundaries in the properties, whereas in a thin layer these are at contrary the effects related to

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the surface areas 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 effect thickness will become minimal and the material will regain the well-known properties of solid material [16].

The second essential characteristic of a thin layer is that, whatever the procedure used for its manufacture, a thin layer is always supportive of a support on which it is built (although it sometimes happens that we separate the thin film of said 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 layer deposited therein. So a thin layer of a same material, of the same thickness, may have substantially different depending on whether it will be deposited on an amorphous insulating substrate such as glass, or a monocrystalline silicon substrate for example. It results from these two varieties essential characteristics of a thin layer, the following consequence: a 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 material to be deposited from a container to substrate and which are similar to the diffusion techniques used in manufacturing active components, 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 [17].

I.3 MgO Thin films

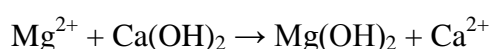
Magnesium oxide (MgO), or magnesia, is a white hygroscopic solid mineral that occurs naturally as periclase and is a source of magnesium (see also oxide). It has an empirical formula of MgO and consists of a lattice of Mg^{2+} ions and O^{2-} ions held together by ionic bonding. Magnesium hydroxide forms in the presence of water ($MgO + H_2O \rightarrow Mg(OH)_2$), but it can be reversed by heating it to separate moisture [18].

Magnesium oxide was historically known as magnesia alba (literally, the white mineral from magnesia – other sources give magnesia alba as $MgCO_3$), to differentiate it from magnesia negra, a black mineral containing what is now known as manganese [19].

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While "magnesium oxide" normally refers to MgO, magnesium peroxide MgO₂ is also known as a compound. According to evolutionary crystal structure prediction [20], MgO₂ is thermodynamically stable at pressures above 116 GPa (gigapascals), and a semiconducting suboxide Mg₃O₂ is thermodynamically stable above 500 GPa. Because of its stability, MgO is used as a model system for investigating vibrational properties of crystals [18-20].

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 [21].



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 appears to reabsorb carbon dioxide from the air [22]

MgO is one of most semi conductors matriel because their opical transparency and high magnetic field. In the latest research was found as a thin film, magnesium oxide (MgO) has been widely studied because it is a unique solid of high ionic character, simple stoichiometry and crystal structure (see Figure I.1), and surface structural defects, but the use of MgO thin films can be enhancement the various applications as a applications in areas such as electronics, adsorption, catalysis, ceramics, petrochemical products, solar cels ,reflecting and antireflecting coatings, detection and remediation of chemical waste and warfare agents, and many other fields [18-22].

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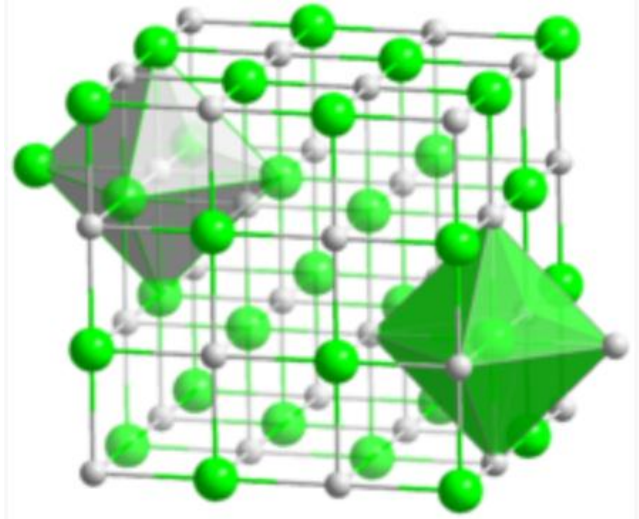


Figure I.1 The structural prosperity of MgO [22]

I.4 Elaborations Methods of MgO thin films

Thin film deposition is the process of adding a thin layer of one material on another. The underlying material on which the layer is added is known as substrate and the layer itself is called thin film. Thin films have become a significant part of microelectronic circuitry because of their small thickness, i.e. a nearly two-dimensional structure, which permits the fabrication of very small devices or microcircuits [23].

Thin film technology is based on three foundations; fabrication, characterization and applications [24]. Thin films are used for electronic components, electronic displays, optical coatings, magnetic data storage, optical data storage, anti-static coating and hard surface coatings, etc. There are dozens of thin film deposition techniques for various applications. Thin film deposition techniques can be conveniently divided into two classes; (1) Physical Vapor Deposition and (2) Chemical Vapor Deposition. However, a considerable number of deposition techniques combine both physical and chemical processes as-well [25].

The common steps to all techniques of film deposition are:

- Generating a supply of atoms or molecules from a source that may be solid, liquid or vapor. This is done by supplying energy to the source by heating, by

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kinetic energy from incident energetic particles or by using chemical reaction to produce volatile species.

- Transport of the constituent atoms or molecules to the substrate. From a technological point of view, this is the crucial part of a deposition, because the manner of transport determines the quality of the film.
- Deposition of atoms or molecules on the substrate. The condition of the substrate surface plays important role in this part of the deposition process. If the substrate surface is contaminated with a fraction of monolayer of impurity atoms, the surface mobility of the arriving atoms may be effected to an extent that the crystal orientation of the film bears little relationship to that of the substrate, and the structure is likely to be polycrystalline. Conversely, if the substrate surface is essentially clean, the arriving atoms are likely to adsorb on sites related to substrate orientation, and the film may be preferentially oriented or even epitaxial.
- Post-deposition treatment. In this part of the process, a prolonged annealing of the film at elevated temperature may yield a film with superior properties as a result of crystal grain growth in the film, stress reduction, the changes in composition produced by diffusion of constituents, etc.
- Process analysis. Modern in-situ analytical techniques are used to monitor the deposition or post-deposition parameters in order to improve quality of the film in term of structure or purity, or both [26].

I.4.1 Physical Vapor Deposition Techniques:

Physical vapor deposition technique is the transfer of atoms and molecules from a source to a substrate by a process that relies on physical methods to produce the vapor species. Physical vapor deposition is carried out in high vacuum to avoid contamination of the film by ambient atmosphere [27]. Some common and well-known physical vapor deposition techniques are:

- **Pulsed Laser Deposition (PLD):**

This technique is based on physical vapor deposition processes arising from the impact of high-power short pulsed laser irradiation of solid targets that leads to the removal of material from the focused zone [28]. PLD is relatively new but very

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efficient technique to deposit epitaxial films. It is a somewhat costly process, but can produce high quality films with high accurate thickness control [24]. However, reproducibility, large area deposition and reduction of particulate emission have yet to be improved [26].

- **Sputtering:**

This technique relies on the removal of atoms from the target by bombarding the target surface with high energetic particles. The target, which is called cathode, is the material to be deposited and substrate is referred to as anode [28]. Sputtering is relatively cost-effective compared with PLD and large area deposition is possible by this process [26].

- **Thermal Evaporation:**

This process comprises evaporating source materials in a vacuum chamber and condensing the evaporated particles on a substrate. Thermal evaporation is conventionally called vacuum deposition. Resistive heating is commonly used in this deposition; therefore this technique cannot be applied to high melting point materials and poor thermal conductors [29].

- **Electron Beam Evaporation:**

This technique is an improvement over thermal evaporation in which a preheated target is bombarded with a highly accelerated beam of electrons in order to vaporize the target. Source electrons as well as secondary electrons trapping and electron beam arcing are the problems associated with this technique [29].

I.4.2 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 [30]. 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 [31].

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- **Chemical Deposition Techniques :**

A deposition technique, in which chemical components react on the surface of the substrate to form a solid film is called chemical deposition technique [30]. In contrast to physical deposition technique, the chemical deposition often utilizes inert gases and may be carried out at atmospheric pressure [31].

Some of the commonly used chemical deposition techniques are:

- **Chemical Vapor 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 vapor deposition [32]. 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 chemistry, thermodynamics, kinetics, transport mechanisms, film growth phenomena and reactor engineering [33]. 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 [34].

- **Spin Coating:**

Spin coating process consists of putting the drops of liquid precursor on the surface of a spinning substrate [35]. The film formed on the substrate results from two balancing forces: the centrifugal force (due to spinning) which drives the viscous sol radially outwards and viscous force (due to friction) which acts radially inwards [39]. Spin coating is the cheapest film production method in silicon technology [36]. However, thinner films (<100 nm) are hard to make and can waste 98% of the process materials [37].

- **Dip Coating:**

Dip coating or immersion coating is a simple old way of thin film deposition by immersing a substrate in the solution of the coating material at a constant speed (preferably judder free). Film thickness is set by the competition among viscous force, capillary (surface tension) force and gravity. Thickness and uniformity can be sensitive

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to flow conditions of the substrate in the liquid bath and gas overhead. The withdraw speed of the substrate, the thicker of the film deposited. Theoretical prediction of process performance is more difficult, and the control of the process more demanding [38].

- **Spray Pyrolysis (SP):**

In this deposition technique, liquid precursors are sprayed by atomization processes and condensed by thermal decomposition on substrates maintained at elevated temperatures. The sprayed micro-droplets reaching the hot substrate surface undergo pyrolytic decomposition and form a single crystallite or a cluster of crystallites of the sprayed materials. Spray pyrolysis was used as early as 1910 to obtain transparent oxide films [39].

I.5 Applications

MgO is prized as a refractory material, i.e. a solid that is physically and chemically stable at high temperatures. It has two useful attributes: high thermal conductivity and low electrical conductivity. "By far the largest consumer of magnesia worldwide is the refractory industry, which consumed about 56 % of the magnesia in the United States in 2004, the remaining 44 % being used in agricultural, chemical, construction, environmental, and other industrial applications." [40] MgO is used as a basic refractory material for crucibles.

It is a principal fireproofing ingredient in construction materials. As a construction material, magnesium oxide wallboards have several attractive characteristics: fire resistance, termite resistance, moisture resistance, mold and mildew resistance, and strength [41]. Besides, MgO films are used in thermal shock transducers for electrical insulation [42] and in AC plasma display panel for protecting layer [43].

Table I.2 Magnesium oxide parameters [4-7]

| | |
|--------------------------------|------------------|
| Dielectric constant (low) | $k' = 9.05$ |
| Optical refractive index (low) | $\Gamma = 1.736$ |
| Lattice constant | ~ 4.213 |

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Medical applications

Magnesium oxide has poor solubility in water and is poorly absorbed from the gut. For this reason, magnesium oxide is relatively ineffective for correcting magnesium deficiency. Magnesium oxide is used for relief of heartburn and dyspepsia, as an antacid, magnesium supplement, and as a short-term laxative. It is also used to improve symptoms of indigestion. Side effects of magnesium oxide may include nausea and cramping.[44] In quantities sufficient to obtain a laxative effect, side effects of long-term use include enteroliths resulting in bowel obstruction.[45]

I.6 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.

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Chapitre II

Experimental Section

Chapitre II Experimental Section

II.1.Introduction

In the present study, we have investigated the variation of experimental details and characterization techniques, which were used in this study. The experimental details can be devised in two sections are related to deposition and characterization of the MgO thin films. The first section describes the sample preparation procedure. However, in the second part, we also describe the various methods adopted for characterizations of MgO thin films.

II.2. Elaboration

The first section we discuss how to use the spray pneumatic process to obtain an MgO thin films and talk about the steps of substrate Cleaning Process (to obtain good adherence and uniformity for the films), and the preparation of spray pneumatic solution for MgO films. In this work, we have studied the effect of concentration pneumatic on optical and electrical properties of MgO thin films.

II.2.1. Spray pneumatic technique (SPT)

The spray pneumatic is a method deposition of thin films in this method we prepared the substrate of thin film to high temperature, this method consists from the oven, air pressure an sprayer of solution, it has pros and cons.

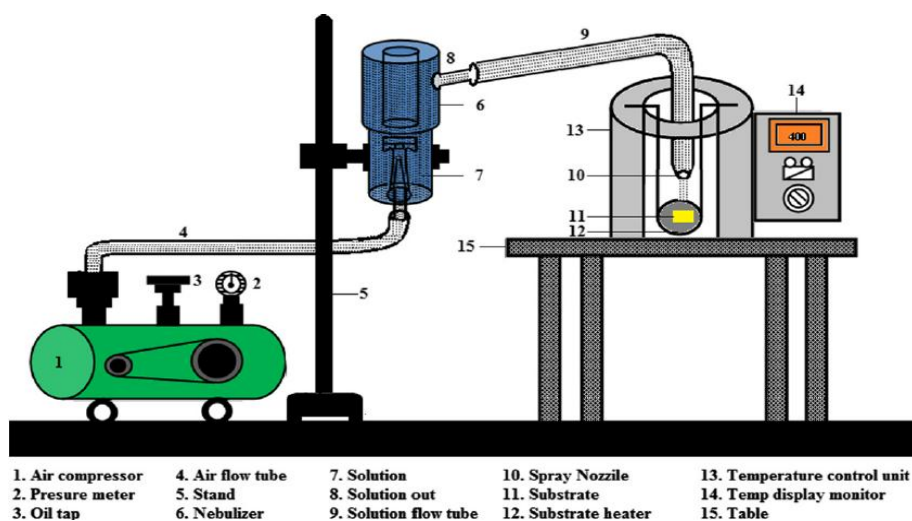


Figure II.1 Spray pneumatic technique

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II.2.2. Advantages of spray pneumatic

This spray pneumatic system has the subsequent advantages: (1) smart size selectivity of the droplets, (2) a suppression of vortices owing to the spray gas within the spraying chamber, and (3) reduced convection flow of the recent gas within the deposition chamber [1].

II.2.3. 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 α 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.



Figure II.2 Glass Substrates

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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.2.4. Preparation of the solution

Magnesium chloride hydrate $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ was used as the starting materials sources a homogeneous and stable solution with many concentration of 0.05 ,0.1 ,0.15 and 0.2 mol/L. MgO coating solutions were prepared by mixing, 0.508,1.016,1.525 and 2.033 g of Magnesium chloride hydrate, which was salved in 50 ml of water distilled and the mixture was stirred by a magnetic stirrer at 50 °C for 3h until obtained a clear, transparent and homogeneous solution. Then allowed to ageing for 24 h, until obtained a clear and homogeneous solution. Then used for the Spray pyrolysis step.



Figure II.3 Magnesium (II) chlorid

Chapitre II Experimental Section

Table (II.1): The physical and chemical properties of Magnesium chloride [2]

| | |
|-------------------|--------------------------------------|
| Chemical name | Magnesium chloride hydrate |
| Molecular formula | MgCl ₂ ·6H ₂ O |
| Molecular weight | 203.31 g/mole |
| Color | Black |
| Density | 2.32 g/cm |
| Melting point | 714 °C |

II.2.5. Depositing of thin films

The MgO thin films were synthesized by the spray pyrolysis process using many solution to study the effect of concentration on MgO thin film, which were deposited at same temperature 350 (see Table II.2).

Table II.2 The experimental conditions of preparation MgO thin films

| S.N | Deposition Alternate (min) | Temperature (°C) | Deposition duration (min) | concentration (ml.l ⁻¹) |
|-----|----------------------------|------------------|---------------------------|-------------------------------------|
| 1 | 1 | 350 | 9 | 0.05 |
| 2 | 1 | 350 | 8 | 0.10 |
| 3 | 1 | 350 | 7 | 0.15 |
| 4 | 1 | 350 | 6 | 0.20 |

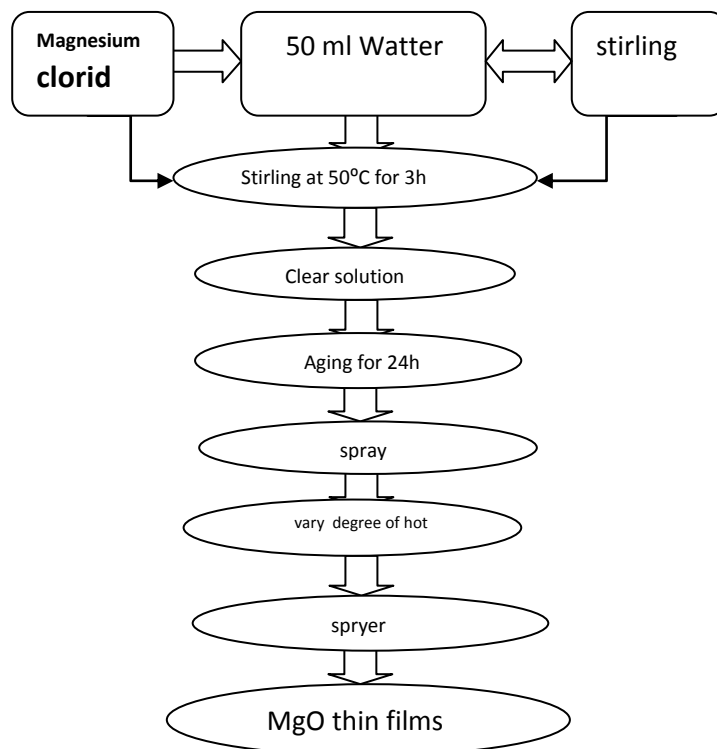


Figure II.4 Flow chart of Spray pyrolysis method for preparation of MgO thin films.

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II.3. Characterization of the films:

The microstructure, electrical and optical properties of Magnesium oxide thin films were evaluated using different characterization techniques such as:

- Ultraviolet visible spectroscopy, for the determination of transmittance and the optical gap and the refraction index of films.
- The electrical characterization was measured the electrical conductivity by the mean of four points.

A brief introduction for each characterization technique will be provided in the following section.

II.3.1. Electrical Conductivity Measurement:

The four-point probe is a very versatile device used widely for the investigation of electrical phenomena. The effect of the contact resistance could be eliminated with the use of such configuration. The most common in-line configuration has been adopted in this work (see figure II-5).

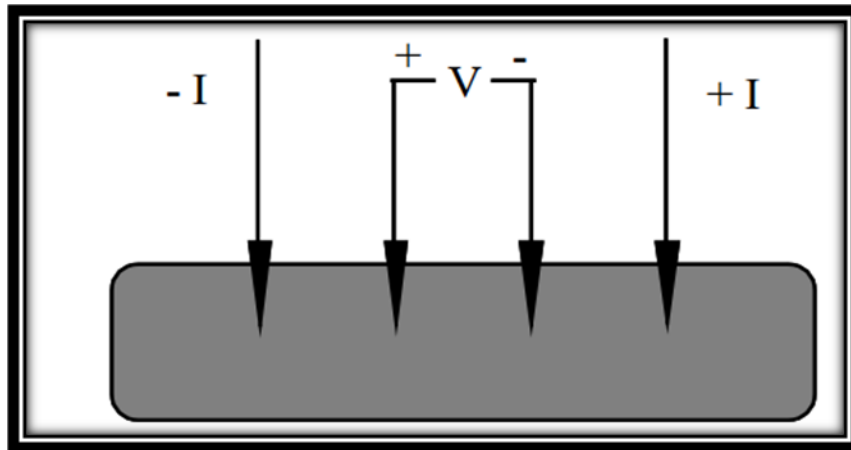


Figure II-5: Schematic of in-line four-point probe configuration

In the measurement, the four metal tips have been attached to the test sample. A high impedance current source of $I = 0.5 \mu\text{A}$ has been used to supply current through the outer two probes; a voltmeter measured the voltage V across the inner two probes. The probe

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spacing was 1 mm. Consequently, the sheet resistance of the film is derived from the formula [3]:

$$R_s = \frac{\pi}{\ln 2} * \frac{V}{I} \quad (\text{II.1})$$

where the factor of $\pi/\ln 2$ is on account of the effect of the current extending. If the film thickness is known, the resistivity is readily obtained from [3]:

$$\rho = R_s * d \quad (\text{II.2})$$

where d is the film thickness. The mean value of three measurements has been taken in order to reduce the measuring error [4].



Figure II. 6 Experimental dispositif.

II.3.2. Optical characterization

A) Ultraviolet–visible spectroscopy

Ultraviolet–visible spectroscopy or ultraviolet-visible spectrophotometry (UV-Vis or UV/Vis): refers to absorption spectroscopy or reflectance spectroscopy in the ultraviolet – visible spectral region. This means it uses light in the visible and adjacent (near-UV and near – infrared [NIR]) ranges. The absorption or reflectance in the visible range directly affects the perceived color of the chemicals involved. In this region of the electromagnetic

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spectrum, molecules undergo electronic transitions. This technique is complementary fluorescence spectroscopy, in that fluorescence deals with transitions from the excited state to the ground state, while absorption measures transitions from the ground state to the excited state.

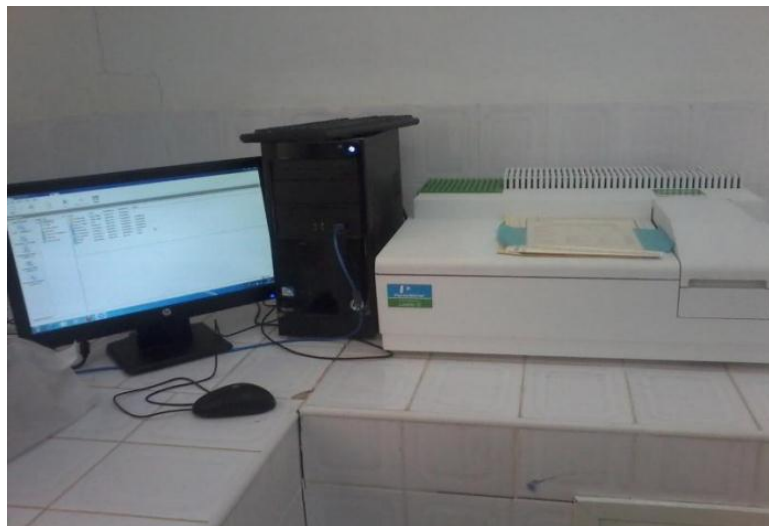


Figure II.7 Ultraviolet-visible spectrophotometer (LAMBDA 25).

B) Principle of ultraviolet-visible absorption

Molecules containing π -electrons or non-bonding electrons (n-electrons) can absorb the energy in the form of ultraviolet or visible light to excite these electrons to higher antibonding molecular orbitals. The more easily excited the electrons (i.e. lower energy gap between the HOMO and the LUMO), the longer the wavelength of light it can absorb [5].

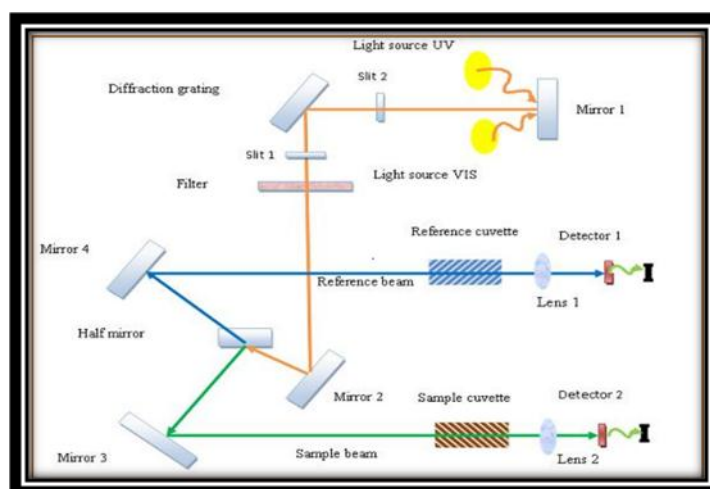


Figure II.8 The principle of operation of UV-visible [6].

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II.4. Conclusion

In this chapter, we have studied the spray polyrisis method for deposition of MgO thin films and also we describe the steps of preparation of MgO solution, which citing the various characterization methods such as: The UV-VIS spectroscopy and electrical characterizations (the four point technique).

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Chapitre III

Results and Discussion

Chapitre III Results and Discussion

III.1.Introduction:

Spay pneumatic method has been successfully employed for the deposition of magnesium oxide (MgO) thin films [1]. The films were doped with different molarities (0.05; 0.10; 0.15 and 0.20 mol.l⁻¹). The optical and electrical properties of magnesium oxide (MgO) thin films were studied.

In the present work, we study the molarity effect on optical and electrical properties of MgO thin films. The optical transmission of the deposited films was measured in the range of 200–1000 nm by using an ultraviolet-visible spectrophotometer (LAMBDA 25) and the resistance R was measured in a coplanar structure obtained with evaporation of four golden stripes on the deposited film surface; the measurements were performed with Keithley Model 2400 Low Voltage Source Meter instrument.

III.2. molarity effect on optical properties of MgO thin films:

Transmittance (T)

Figure (III.1) shows the relation between transmittance and wavelength in the range of (300- 1000 nm) for magnesium Oxide thin films. The transmittance for all thin films increases as the wavelength increases in the range of (300- 400 nm), which corresponds to 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 thin films decreases with increasing of molarities from 0.05 to 0.2M at.% in all deposited films. The effect of concentration molarity on optical property was observed at up to 0.05 or 0.1M.

Absorption

Reflectance R can be obtained from absorption and transmission spectrum in accordance to the law of conservation of energy by the relation [2]:

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

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

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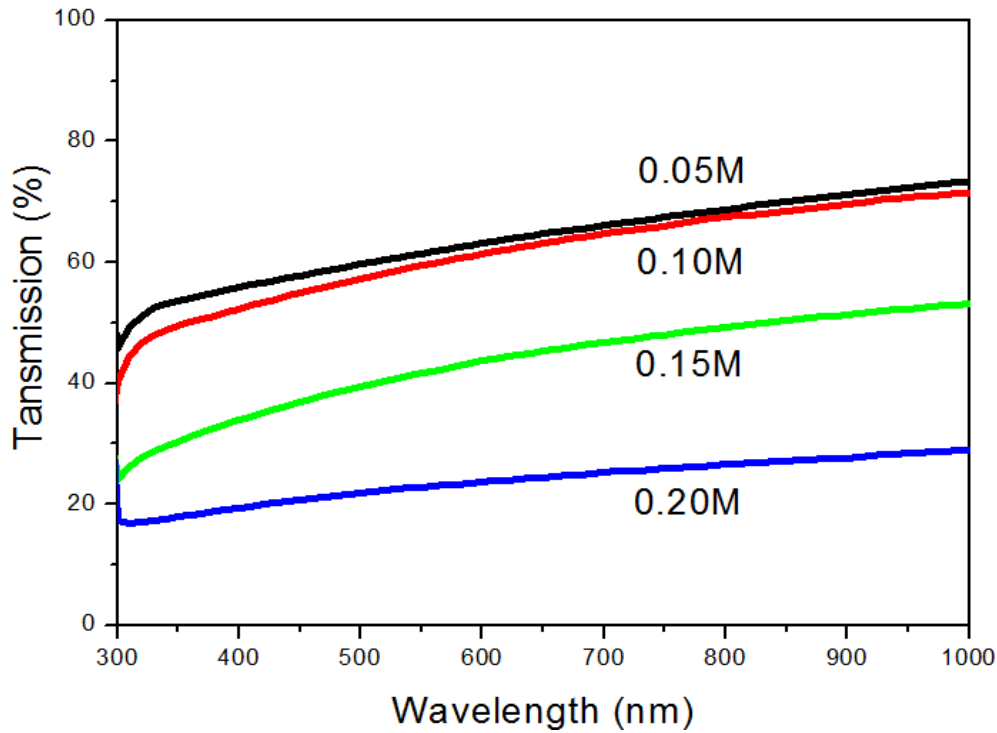


Figure III.1: Variation of transmittance spectra (T) with wavelength (λ) of MgO thin film deposited with different molarities.

R is related to the refractive index and extinction coefficient of the material as follows [3]:

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

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 [4]:

$$\alpha = 2.303 * A/t \quad (\text{III.3})$$

where α and t are the absorption coefficient and film thickness. Figure III.2, 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 0.2M because the increases in the film thickness.

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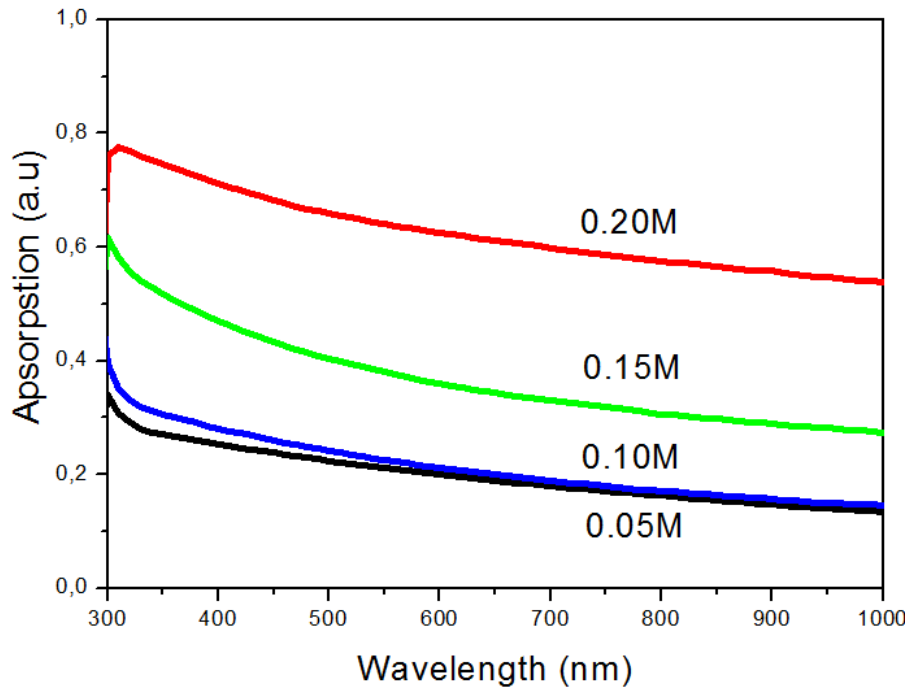


Figure (III.2): The relation between absorption and wavelength of deposited MgO thin films.

The refractive index (n) of the nanostructure thin films was calculated using the following relation [5]:

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

Table III.1 Variation of film transmission of MgO as a function of molarity.

| Molarity (mol.l^{-1}) | 0.05 | 0.1 | 0.15 | 0.2 |
|---|------|-----|------|-----|
| Transmission (%) between 400 and 800 nm | 62 | 59 | 41 | 22 |

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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 [5]. For MgO thin films, we can calculate using Tauc's equation [6]

$$(\alpha h\nu) = A(h\nu - E_g)^n \quad (\text{III.5})$$

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 [7].

The absorption coefficient (α) has been used to determine the band gap of the evolving MgO film by measuring the absorption coefficient as a function of the incident photon energy ($h\nu$). The absorption coefficient may be approximated by [8,9]:

$$\alpha = \frac{1}{t} \ln\left(\frac{1}{T}\right) \quad (\text{III.7})$$

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 films fabricated at different molarities are shown in Figure III.3. It can be seen that the extrapolation of linear portion of the graph to the energy axis at $A=0$ [10] in the range between 300–350 nm gives band gap energy E_g is shown in Table III.2.

Urbach energy

In addition, we have used the tail width, which can be calculated using the Urbach rule for the absorption coefficient at lower photon energy [11].

$$\alpha(h\nu) = \alpha_0 \exp\left(\frac{h\nu}{E_u}\right) \quad (\text{III.6})$$

where α_0 is the constant and E_u is the Urbach energy, Figure III.4 shows the graph of $\ln\alpha$ 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.

Chapitre III Results and Discussion

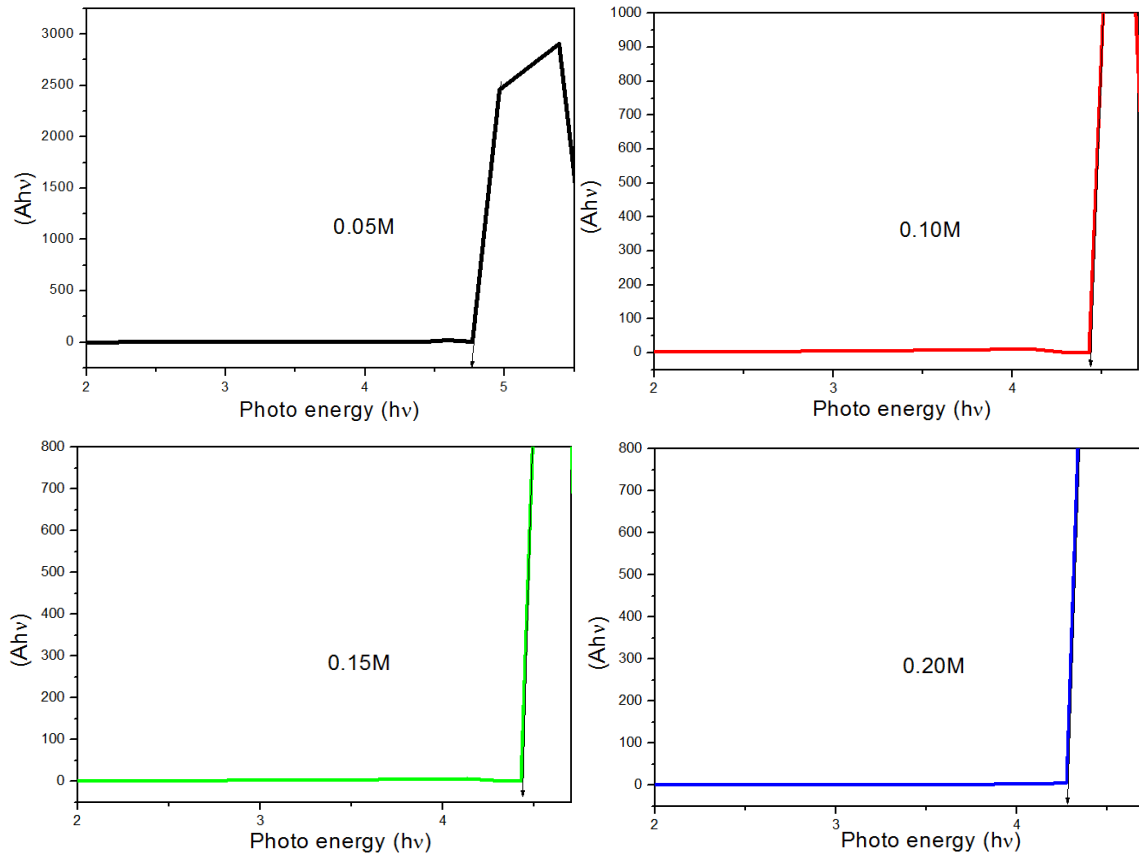


Figure III.3: Plot of $(ah\nu)^2$ versus $(h\nu)$ of MgO thin film for different molarities.

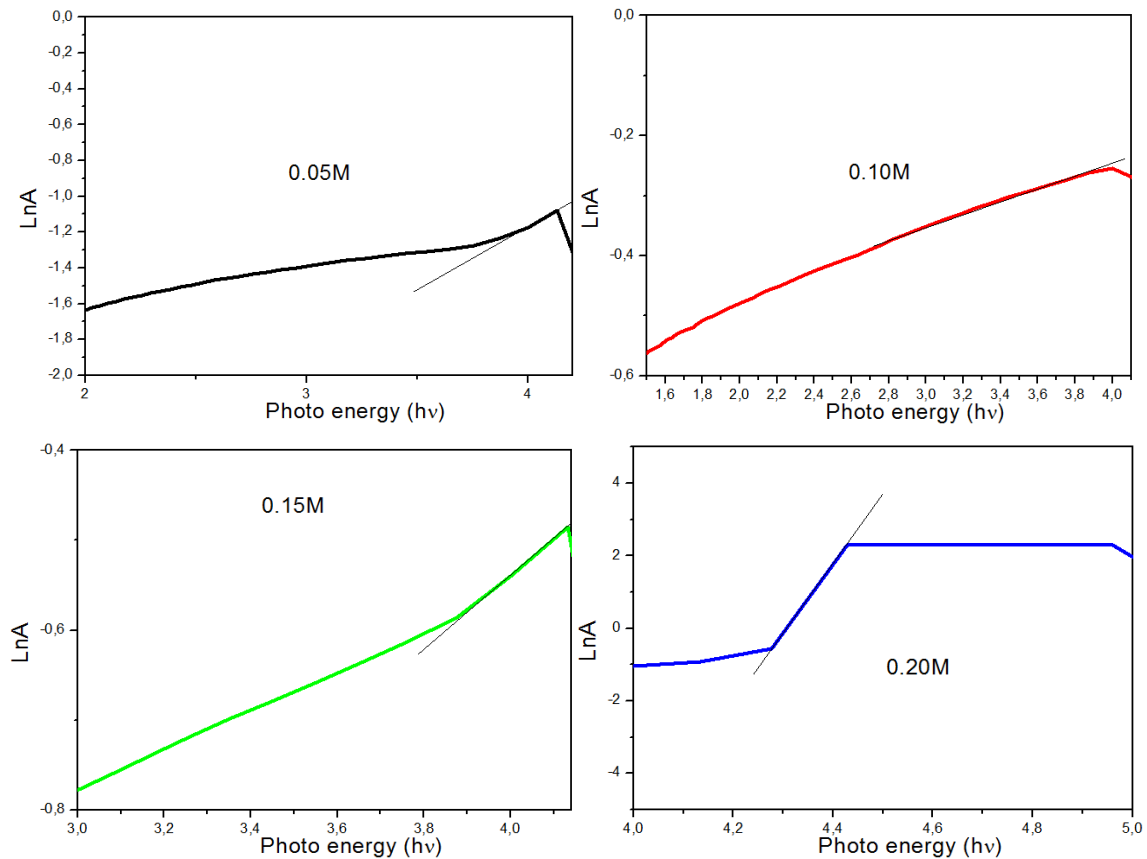


Figure III.4: Plot of $(\text{Ln}a)$ versus $(h\nu)$ of MgO thin film for different molarities.

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The Table III.2 below gives as the values of E_g and E_u at different concentrations of molarities to MgO solution. In the other hand, Figure III.5 shows the variation of optical band gap and Urbach energy of MgO thin films as a function molarity. As can be seen, that the band gap energy E_g and Urbach energy E_u are dependent to the change in MgO 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 thin films decreased slowly with increassating the MgO molarity, 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.

| Molarity (mol.l ⁻¹) | Optical gap energy E_g (eV). | Urbach energy E_u (meV). |
|---------------------------------|--------------------------------|----------------------------|
| 0.05 | 4.77 | 519 |
| 0.10 | 4.48 | 465 |
| 0.15 | 4.42 | 420 |
| 0.20 | 4.28 | 375 |

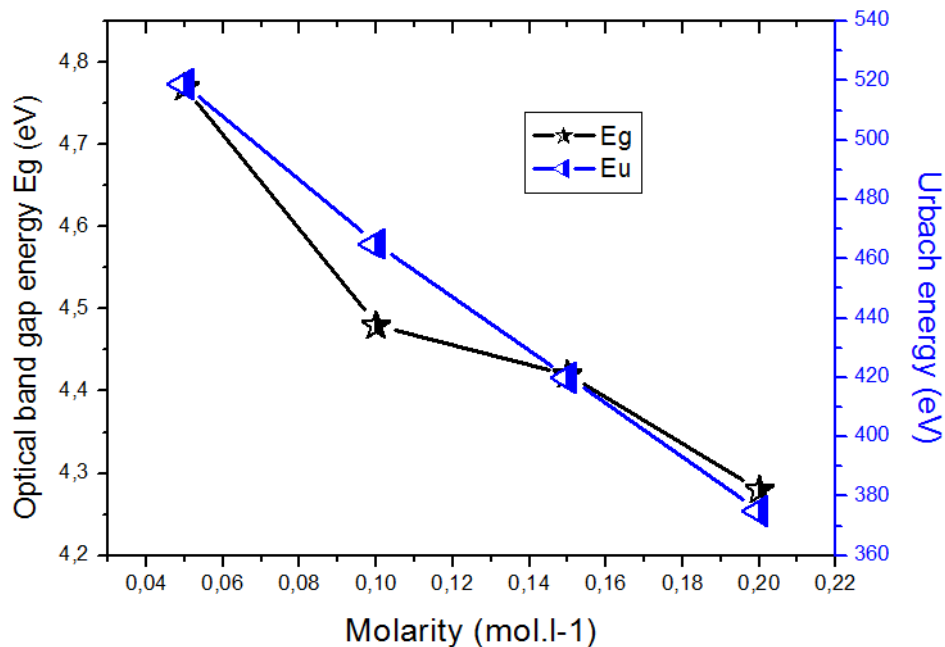


Figure III.5: The variation of optical band gap and Urbache energy of MgO thin films as a function molarity.

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III.3: Molarity effect on Electrical properties of MgO thin films:

The four-point probe is required to measure the sheet resistance of the films. Since negligible contact and spreading resistance are associated with the voltage probes, the sheet resistance (R_{sh}) can be estimated, when the film thickness less than the spacing between the probes, using the following relation [12,13]:

$$R_{sh} = \frac{\pi}{\ln(2)} * \frac{V}{I} \quad (\text{III.7})$$

where I is the applied current and V is the measurement voltage.

Table III.3 and Figure III.6 gives the R_{sh} values of MgO thin films as a function of concentration molarity. As can be seen that the R_{sh} was found decreases with increasing the concentration molarity. The decrease of the resistance can be explain by the increase in the films thickness of the deposited MgO thin films with molarity.

Table III.3 The electrical resistance of of MgO thin films with different molarities.

| Molarity (mol.l ⁻¹) | 0.05 | 0.10 | 0.15 | 0.20 |
|--------------------------------------|--------|--------|--------|--------|
| I (A)*10 ⁻⁶ | 0.5 | 0.5 | 0.5 | 0.5 |
| V ₁ (V) | 0.0712 | 0.0542 | 0.0473 | 0.0325 |
| V ₂ (V) | 0.0290 | 0.0473 | 0.0277 | 0.398 |
| V ₃ (V) | 0.0640 | 0.0521 | 0.0455 | 0.217 |
| R _{sh} (Ω) *10 ⁷ | 2.18 | 2.11 | 1.87 | 1.68 |

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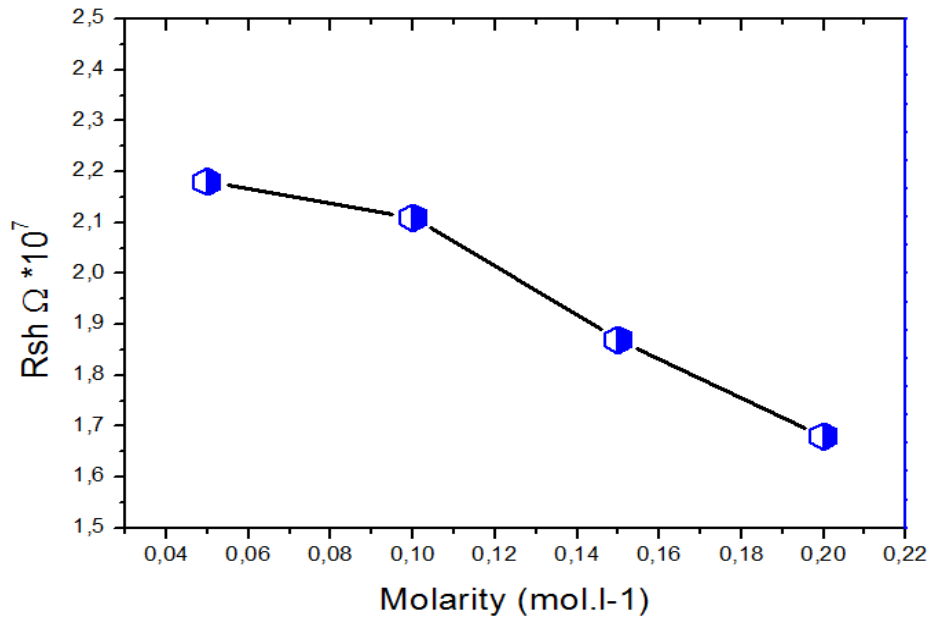


Figure III.6 The electrical resistivity variations with different molarities of MgO thin films.

III.4. Conclusion:

In this study Magnesium Oxide thin films were deposited on galas substrate by pneumatic technique. The effects of concentration molarity (0.05; 0.1; 0.15 and 0.2M) were successfully investigated. The high transmission was found in the deposited MgO thin film with lowest molarity. The transmittance of MgO thin films decreases rapidly as the wavelength increases in the range of (300-400) nm, and then increases slowly at higher wavelengths. The band gap of MgO thin films decreases as the molarity increases and the band gap values range between 4.8-4.3 eV. The Urbach energy values range between 375-519 meV. The electrical resistance of our films in the order $2 \cdot 10^7 \Omega$.

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General Conclusion

General Conclusion

In conclusion, highly transparent conductive MgO thin films have been deposited on glass substrate by spray pneumatic method. The influence of solution molarity on optical and electrical properties was investigated.

At high solution molarity exhibit an average optical transparency about 60 %, in the visible range for the lowest solution molarity. The shift of optical transmittance towards higher wavelength can be showed by the increase of band gap energy from 3.975 to 3.980 eV with decreasing of solution molarity of 0.5 to 0.2 mol/l. The Urbach energy changes with the optical band gap of films reaching the minimum value of 375 eV at 0.05 mol/l.

The transparent MgO thin films become conducting to have a optimal value of the electrical resistance of our films in the order $2 \times 10^7 \Omega$.

The best estimated optical and electrical characterisation MgO thin films are achieved in prepared MgO thin films with 0.1M.

Abstract

In this work, Magnesium Oxide (MgO) thin films were deposited on galas substrate (350°C) by pneumatic technique. The effects of concentration molarity in the rang (0.05; 0.1; 0.15 and 0.2M) were successfully investigated. The high optical transmission was found in the deposited MgO thin film with lowest molarity it is 60%. The transmittance of MgO thin films decreases rapidly as the wavelength increases in the range of (300-400) nm, and then increases slowly at higher wavelengths. The band gap of MgO thin films decreases as the molarity increases and the band gap values range between 4.8-4.3 eV. The Urbach energy values range between 375-519 meV. The electrical resistance of our films in the order $2 \times 10^7 \Omega$.

Keywords

.....

ملخص

في هذا العمل ، تم ترسيب الأغشية الرقيقة بأكسيد المغنيسيوم (MgO) على ركيزة زجاج (350 درجة مئوية) بواسطة تقنية تعمل بالهواء المضغوط. تم التحقيق بنجاح في آثار تركيز التركيز في المدى (0.05 ؛ 0.1 ؛ 0.15 ؛ 0.2 M) تم العثور على ناقل حركة بصري عالي في الأغشية الرقيقة MgO المودعة بأقل نسبة من 60٪. تقل سرعة نفاذية الأغشية الرقيقة MgO بسرعة مع زيادة طول الموجة في حدود (300-400) نانومتر ، ثم يزداد ببطء عند أطوال موجية أعلى. تتناقص فجوة الشريط في الأغشية الرقيقة لـ MgO مع زيادة الشراة وتتراوح قيم فجوة النطاق بين 4.3-4.8 فولت. تتراوح قيم الطاقة Urbach بين 375- 519 meV. المقاومة الكهربائية لأفلامنا بالترتيب $2 \times 10^7 \Omega$.

الكلمات الدالة :