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**Thin films of doped and undoped oxides,
properties and photocatalytic application**

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Dedication

Dedication

I dedicate this thesis:

To my husband and my dear parents.

To my sisters and my brothers.

To my paternal uncle.

***To all my colleagues and
everyone helped me.***

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List of Abbreviations

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TiO₂: Titanium dioxide.

ZnO : Zinc oxide.

CeO₂ : Cerium dioxide.

RE : Rare-earth.

Er : Erbium.

Sol-gel : Solution-gelation.

XRD : X-ray diffraction.

SEM : Scanning electron microscopy.

MB : Methylene blue.

PLD : Pulsed laser deposition.

CVD : Chemical vapor deposition.

FM: Frank-Vander Merwe.

VW: Volmer-Weber.

SK: Stransky-Krastanov.

LED: Light emitting diode.

MOCVD: Metal-organic chemical vapor deposition.

PECVD: Plasma-enhanced chemical vapor deposition.

PVD: Physical vapor deposition.

E-beam: Electron-beam.

DC: Direct cathodic.

RF: Radio frequency.

Ar: Argon.

Å: Angstrom.

MOVPE: Metal-organic vapor phase epitaxy.

OMVPE: Organometallic vapor phase epitaxy.

ALCVD: Atomic layer chemical vapor deposition.

List of abbreviation

ALE: Atomic layer epitaxy.

CBE: Chemical beam epitaxy.

UV: Ultraviolet.

a, b, c : lattice parametrs.

n: Density of electron.

μ: Electron mobility.

ρ: Resistivity.

σ: Conductivity.

CB : Conduction band.

VB : Valence band.

m₀ : mass of electron.

Sb : Antimony.

EZO : Er doper ZnO.

Zn_i : Zinc interstitial.

VO : Oxygen vacancies.

PL: Photoluminescence.

AZO: Al doped ZnO.

ITO: Indium oxide.

TCOs: Transparent conducting oxides.

E_g: Band gap energy.

h⁺/e⁻: electron-hole pair.

•OH: Hydroxyl radical.

H⁺: Hydroxyl radical.

H₂O₂: Peroxide.

CO₂: Carbon dioxide.

H₂O: Water.

M_nX_n: Metal salt.

List of abbreviation

M (OR)_n: Metal alkoxide.

C_nH_{2n+1}: Alkyl.

pH: Potential of hydrogen.

M-O-M: Metalloxane.

M: Molaire (mol/l).

Zn (C₂H₃O₂)₂, 2H₂O: Zinc acetate dihydrate.

C₂H₆O: Ethanol.

MEA: Mono Ethanol Amine.

C₂H₇NO: Mono Ethanol Amine.

ErCl₃, 6H₂O: Erbium (III) chloride hexahydrate.

La (NO₃)₃, 6H₂O: Nitrate Lanthanum hexahydrate.

Mg (CH₃COO)₂, 4H₂O: Magnesium acetate tetrahydrate.

Al (CH₃COO)₂: Aluminium acetate.

θ: The diffraction angle.

λ: The wavelength of the X-ray beam.

d_{hkl}: The distance of lattice planes.

hkl: Miller indices.

J.C.P.D.S: Joint Committee on Powder Diffraction Standards.

D: The crystallite size.

FWHM: Full Width at Half Maximum.

β: The width at half height.

δ: Dislocation density.

EDX: Energy dispersive X-ray spectroscopy.

EDS: Energy dispersive spectroscopy.

FTIR: Fourier transforme infrared.

IR : Infrared.

UV-Vis: Ultraviolet-Visible.

List of abbreviation

I: Intensity of light.

I₀: Incident light.

A: Absorbance.

T: Transmittance.

I_t: Intensity of transmitted light.

R: Reflectance.

I_r: Intensity of reflected light.

d: Thickness of layer.

α : The absorption coefficient.

h: Planck's constant.

ν : Photon frequency.

h ν : Photon energy.

He-Cd: Light source.

AC: Alternating current.

Z*(ω) : The complex impedance.

Re : Real part.

Im : Imaginary part.

C₁₆H₈N₃ClS : Methylene blue.

C₀ : The initial concentration of MB.

C_t : The concentration of MB after time t of irradiation.

EDTA : Ethylene di-amine tetra acetate.

IPA : Isopropanol.

n : Refractive Index.

NIR : Near-infrared.

NBE : Near-band-edge.

Z : The complex impedance.

R_s : Series resistance.

List of abbreviation

R_p : Parallel resistance.

CPE-T : constant phase element parameter.

CPE-P : constant phase element parameter.

X : The amplitude of the process.

E : The end point.

K : Pseudo rate constant.

LSPR : Localized surface plasmon resonance.

R² : Correlation coefficient.

AgNO₃ : Silver nitrate.

ASCA : Ascorbic acid.

V : unit cell volume.

ε : lattice strain.

SiO₂ : Silicium dioxyde.

Z : atomic number.

DRS : Diffuse reflectance spectroscopy.

I_{photo} : photo current.

I_{dark} : dark current.

k: constant rate.

ROS : Reactive oxygen species.

General Introduction

General Introduction

General Introduction

Titanium dioxide (TiO_2), zinc oxide (ZnO), cerium dioxide (CeO_2), and other semiconductors have received significant research interest among the wide variety of semiconductors available because of their exceptional characteristics and effectiveness in environmentally focused pollutant treatment techniques [1]. ZnO has been chosen as one of the most promising possibilities out of all of them because of its great optical transparency in the visible and near-infrared spectrum, as well as its vast exciton binding energy of 60 meV at ambient temperature and its wide band gap of 3.37 eV. Additionally, it has good thermal and chemical stability, is affordable, rich in resources, has a high radiation endurance, is non-toxic, biocompatible, easy to dope, and has excellent mechanical-electrical coupling qualities [2]. ZnO is a promising material for electronic or optoelectronic applications like gas sensors, solar cells (anti-reflecting coating and transparent conducting materials) [3], thin-film transistors, light emitting diodes, photodetectors and photocatalysis [2, 4]. Additionally, it is essential to modify ZnO 's performance through doping in order to accomplish these applications and enhance its characteristics [5]. However, in some applications, its effectiveness is restricted by the visible region's low absorption and the charge carriers' fast recombination [6]. Doping with rare-earth metals has been seen as an attractive option to these restrictions because it improves the material's visual spectroscopic characteristics and photocatalytic performances [7, 1]. It will require researchers to modify its electronic structure in order to alter its optical and electrical characteristics, which will improve several kinds of applications, including optoelectronic, electronic, spintronic, photocatalytic, and others [8]. For optoelectronic devices, doping with rare-earth (RE) elements specifically, erbium (Er) has been investigated as an excellent optical material [1]. As an effective approach to improve the functional characteristics of ZnO [9].

Many research investigations have been conducted on doping ZnO with elements like lithium (Li) in an effort to improve its properties. It has been shown that Li doping may alter defect states in the ZnO lattice, enhance photoluminescence, and produce p-type conductivity [10]. Co-doping with other elements, such as aluminum (Al), lanthanum (La), and magnesium (Mg), has synergistic effects that improve performance even more. For example, La improves crystallinity and decreases defect states [11], Al increases optical transparency and electrical conductivity [12], and Mg enables bandgap engineering [13]. Co-doping's effects on magnetic

General Introduction

and ferroelectric characteristics have also been investigated recently, expanding the use of ZnO-based materials in memory and multiferroic devices [14, 15].

The structural, electronic, and optical characteristics of ZnO thin films can be altered by variations in material composition, concentration, thickness, annealing temperature, and other factors. These modifications lead to variations in surface morphology, particle size, crystalline structure orientation, and defect concentration [16].

In order to obtain the major different properties of manufactured thin films, samples were analysed using X-ray diffraction (XRD) to investigate structural properties such as the crystalline quality and nature of the layers, the grain size, dislocation density, and the strain. The surface morphology was characterised by using the scanning electron microscopy (SEM). The UV-visible spectrophotometer was also used to analyse the optical characteristics such as the spectrum of the transmittance, reflectance and the optical gap energy also to measure the absorbance of the methylene blue (MB) after the irradiation for the photocatalytic activity.

Up to now, a several methods are used to prepare ZnO thin films including spray pyrolysis, sputtering, sol-gel dip-coating, spin coating, pulsed laser deposition (PLD), chemical vapor deposition (CVD) [17], electron beam deposition, electrochemical method and co-precipitation method [18]. We chose the sol gel dip-coating method for this study because it is easy to use, can be produced on a large scale, has a low fabrication temperature [19-23], and is an economical way to create consistent, high-quality thin films [24]. Because it allows for exact control over doping levels, surface morphology, and film thickness, it is a desirable option for creating our thin films. Recent studies have shown that dip-coated Er-ZnO films have better surface homogeneity, optical performance, and crystallinity [25, 26].

The aim of this work was to use the Sol Gel “Dip Coating” method to deposit undoped and doped and co-doped ZnO thin films under extremely controlled preparation conditions. To understand the manner in which ZnO thin films grow, how doping and co-doping affects their characteristics, and how to generate the best ZnO thin films that can be employed as a photocatalyst to remove organic pollutants with the greatest rate of photodegradation. A number of methods were used to examine the structural, morphological, optical, and electrical characteristics of the generated ZnO films.

General Introduction

This thesis consists of four chapters, and it is organized as follows:

In the begin, a general introduction.

- ✚ The first Chapter is provided an overview of thin films, including their applications, growth modes, and various elaboration techniques. Additionally, it talks about zinc oxide (ZnO), its properties, doping, as well as its main applications in technological fields.
- ✚ The second chapter presents a general description of the growth process of ZnO thin films via Sol gel “dip coating” technique, the experimental details of the elaboration of films and a brief review of the different characterization technique and the equipment employed to characterize zinc oxide are also given.
- ✚ The third chapter studies the effect of Er-doped zinc oxide thin films obtained by the sol-gel dip-coating method on structural, microstructural, optical, electrical and photocatalysis properties for the degradation of methylene blue under UV light and sunlight irradiation. Where the aim is for finding out the effect of doping rate on the ZnO characteristics.
- ✚ The fourth chapter presents the effect of doping and co-doping zinc oxide thin film obtained by the sol-gel dip-coating method on structural, microstructural, optical, electrical, UV photodetector and photocatalysis properties for the degradation of methylene blue under UV light and sunlight irradiation.

at the end, a general conclusion summarizes the main results obtained in this thesis and some perspectives for future research.

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Chapter I

***Background of ZnO thin films,
properties, growth techniques, and their
application***

Chapter I. Background of ZnO thin films, properties, growth techniques and their applications

I. Introduction

In recent years, oxide-based thin films especially ZnO, which possesses exceptional properties have attracted a lot of attention because of their possible uses in solar cells, optoelectronics, piezoelectric devices, and catalysis.

We will give a brief background to thin films in this chapter, including their growth modes, deposition methods, and applications. A description of zinc oxide (ZnO), its characteristics, and doping is also provided.

I.1. Thin films

I.1.1. Definition

A thin layer of a particular substance is often deposited on a substrate, which is a support. Although these thin films are usually layers 10 to 100 nanometers thick, one of its dimensions (thickness) could significantly decrease to the scale of nanometers “nm” and up to a few micrometers “ μm ” [1]. The thin film's first property is its quasi-two dimensionality. Most of the physical characteristics is disturbed as a result of this trait (Figure I.1) [2]. The role and characteristics of boundaries which are usually ignored for bulk materials, but are crucial in the case of thin layers are the primary distinction between matter in the solid state and matter in the thin layer state.

The two-dimensional topological effect becomes increasingly critical as the thickness decreases. However, the dimensionality issue becomes negligible and the material regains its recognized solid properties if the thickness beyond a certain threshold [3]. Additionally, the properties of the thin layer films may be influenced by those of the substrate they are standing on. A thin film of the same substance and thickness, for instance, may exhibit notably different physical characteristics depending on how it is placed on a semiconducting monocrystalline silicon substrate or an amorphous insulating substrate like glass [4]. The main reasons for the interest in thin films are the low cost of materials compared to their physical characteristics and the ease of use of the technologies used to produce them. These thin films are made from a wide range of materials. Let's mention metals, alloys, polymers, intermetallic compounds, and refractory compounds (oxides, nitrides, and carbides) [5].

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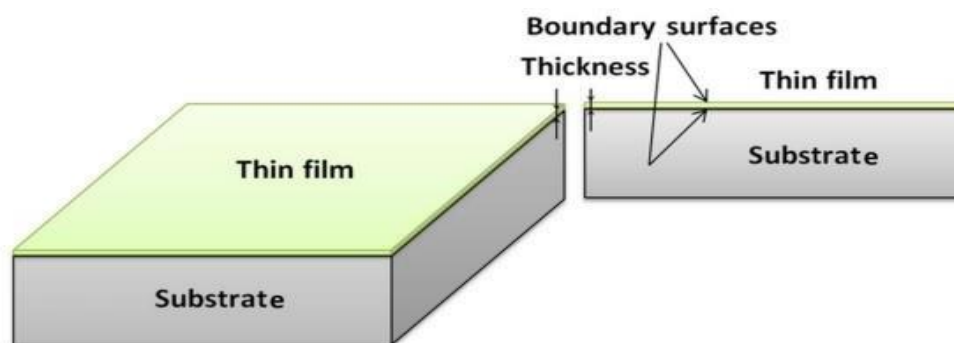


Figure I.1. Schematic of thin film deposited on a substrate.

I.1.2. Thin films growth

I.1.2.1. Thin films growth modes

The evaporation of source materials through the irradiation of energetic species or photons, thermal evaporation, or chemical decomposition are the methods used to deposit thin films on a substrate. There are three primary processes in any thin-film deposition procedure [6]:

- a) The production of the appropriate ionic, molecular, atomic species.
- b) Transport of these species to the substrate.
- c) Condensation on the same substrate is done either directly or via a chemical or electrochemical reaction in order to form the solid deposit. This stage often goes through three phases (Figure I.2) [7]:
 - (i) Nucleation is the formation of small nuclei that are statistically distributed over the surface of the substrate.
 - (ii) Growth of the nuclei and formation of larger islands, which often have the shape of small crystals (crystallites).
 - (iii) Coalescence of the islands (crystallites) and formation of a more or less connected network containing empty channels.

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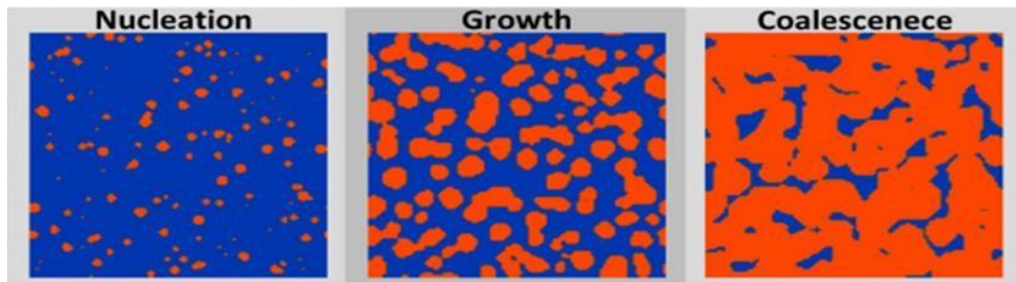


Figure I.2. Thin film formation modes: growth and coalescence [8].

I.1.2.2. Thin films growth mechanisms

Depending on the interaction between the substrate and the deposited atoms, three different nucleation modes can be observed during the formation of thin films (Figure I.3) [9].

- ✚ **Frank-Van der Merwe mechanism (FM):** Commonly called as the "layer-by-layer" growth mechanism this process involves covering the entire substrate with a monoatomic layer. As such, it is a two-dimensional layer-by-layer construction of the thin layer of matter. The finding that the atom layers are more strongly attached to the substrate than to one another suggests that it is accurate [10].
- ✚ **Volmer-Weber mechanism (VW):** Instead of being two-dimensional, the growth mechanism is three-dimensional. In fact, the expansion of islands along the vertical z direction and in the plane direction x and y is correlated with this growth style. In the end, these islands may combine to create a dense layer of atoms inside a film that is firmly connected to one another instead of the substrate [11, 12].
- ✚ **Stransky-Krastanov mechanism (SK):** is a case that is in between FM and VW. Initially, the growth is 2D to build the first layers, but it tends to become 3D with the formation of 3D islands as the atoms-substrate interaction energy steadily lowers [13].

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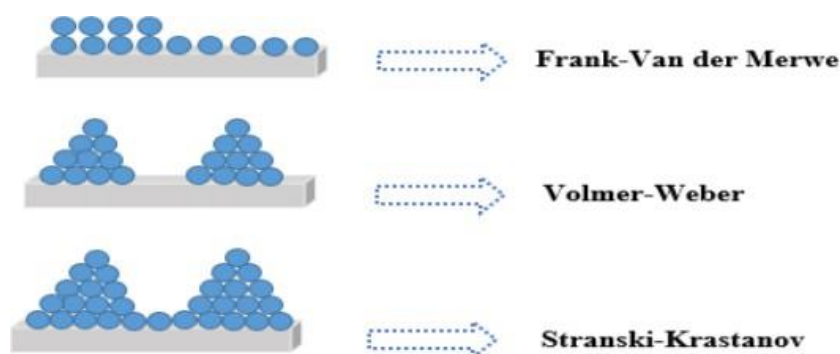


Figure I.3. Schematic representation of different growth thin films mechanisms [10].

I.1.3. Applications of thin films

There are many applications in many different fields as a result of the use of thin film processing methods. There are so many uses for thin layers that we are hard to list them all due to development. Each day, new research in this area is being conducted [14].

- ✚ Microelectronics: diode, transistor, LED lamps, solar cells.
- ✚ Optics: Thin layer technology is used mainly for two types of applications, on the one hand, reflective layers and on the other hand to the contrary anti-reflection layers.
- ✚ Decoration: Another aspect of thin film technology is its use in the luxury industry for decorative applications such as eyewear and jewelry.
- ✚ Chemistry: corrosion resistance, gas sensors, catalytic coatings, protective layers.
- ✚ Magnetic: information storage (computer memory), hard drive read heads.

I.1.4. Thin films deposition techniques

The particles of the coating material must move through a conducting medium while in close proximity to the substrate in order to form a thin layer film on a solid substrate. Atoms, molecules, ions, and molecular fragments are examples of particles. The medium of transport could be solid, liquid, gaseous, or even vacuum [15]. There are two basic groups of ways for creating thin layers, either physical methods or chemical methods. The chemical methods split into solution deposits and vapor phase deposits, which include combined, spray pyrolysis, electrochemical deposition, and sol-gel procedures. Deposition techniques including evaporation, laser ablation, molecular beam epitaxy, and pulsed-laser deposition are examples

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of physical approaches (Figure I.4) [13]. The creation of thin films in a repeatable, controlled, and predictable way is the goal of any deposition process [16].

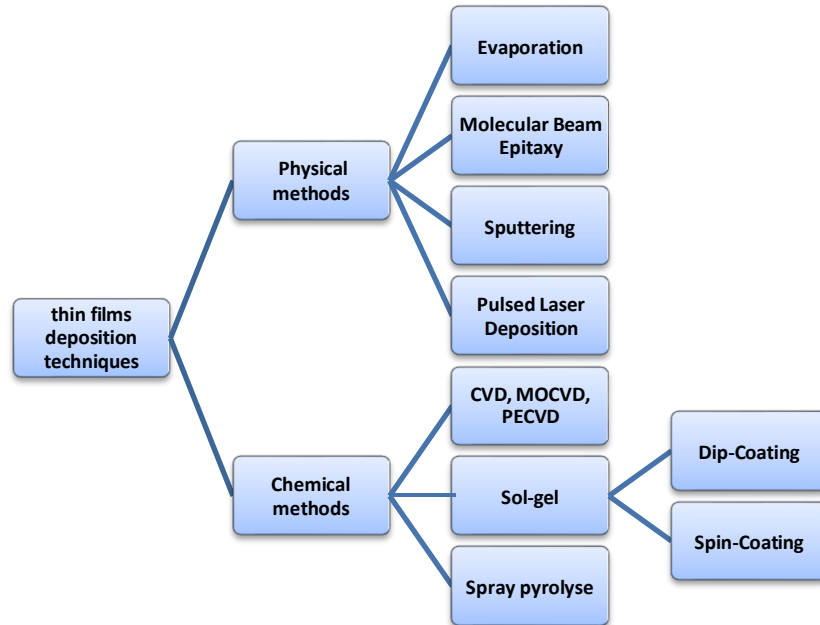


Figure I.4. Thin films deposition techniques.

I.1.4.1. Physical techniques

I.1.4.1.1. Physical Vapor Deposition

The process of creating a vapor flux and then condensing it into a thin layer on a substrate in a vacuum chamber is known as physical vapor deposition, or PVD [17]. The two main PVD production procedures are sputtering, which is a no-heat process, and thermal evaporation, which is accomplished by resistively heating or by employing an electron beam heating method [18]. The term PVD encompasses several techniques, including [19]:

- vacuum evaporation deposition, the material is vaporized using resistive heating and then permitted to move onto a substrate.
- Electron beam vapor deposition: the sample material is bombarded by a high-energy electron beam, which causes vaporization.
- Sputtering: this process vaporizes the material using a plasma discharge.

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- Pulsed laser deposition: the material evaporates as a result of a high-energy laser pulse.

I.1.4.1.2. Vacuum Evaporation

One of the most popular techniques for depositing functional films onto a variety of substrates is vacuum evaporation (Figure I.5). Through the use of a vacuum, vapor particles have the ability to drop directly onto the substrate, where they condense to form a functional coating. The evaporation of a functional substance and the condensation on the substrate are the two fundamental steps in the vacuum evaporation process. In high-vacuum evaporation, the coating materials are heated, gasified, and evaporated using electrical heating or electron beam heating. After the coating material's vapor reaches the substrate's surface and cools gradually, a high-quality thin film layer is eventually created. The purpose of vacuum is to keep the evaporating particles from mixing with the background gas or other undesirable particles. Functional materials that evaporate deposit onto the substrate's surface. Thermal vacuum evaporation has been successfully used to produce a variety of high-quality ZnO thin films [20, 22].

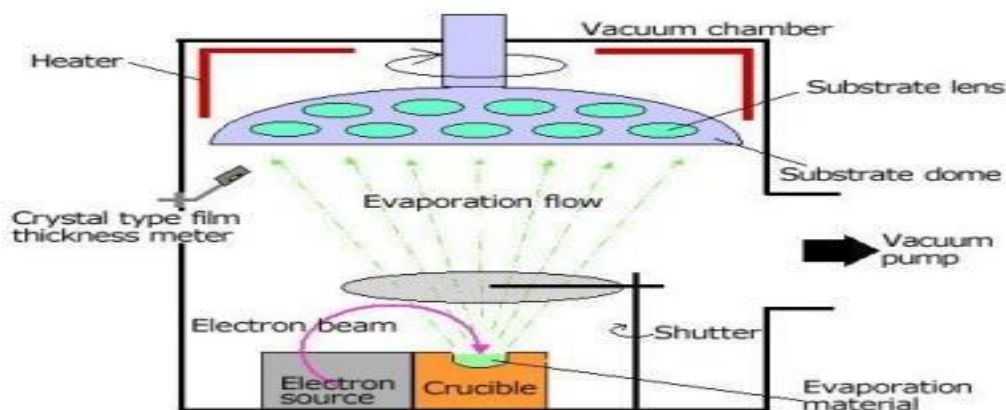


Figure I.5. Schematic of a vacuum evaporation with E-beam heating [23].

I.1.4.1.3. Molecular Beam Epitaxy

Epitaxy is a composite of the two Greek words "taxi" (arrangement) and "epi" (on). It is described as the development of a monocrystalline layer on a monocrystalline substrate known as the epitaxial layer [24]. One technique for creating thin films with excellent crystalline quality and extremely low roughness at low temperatures and at very high vacuums ($<10^{-10}$ Torr) is molecular beam epitaxy. The method's fundamental concept (Figure

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I.6) is based on the way atomic or molecule fluxes react with a monocrystalline substrate that has been heated to a suitable temperature [25].

The growth process of the molecular beam epitaxy can be summarized in the following steps [26]:

- 1) Deposition of atoms onto the surface of the substrate.
- 2) Nucleation process (creation of di-atomic islands).
- 3) Growth of islands by coalescence.
- 4) Formation of a layer by coalescence of islands.

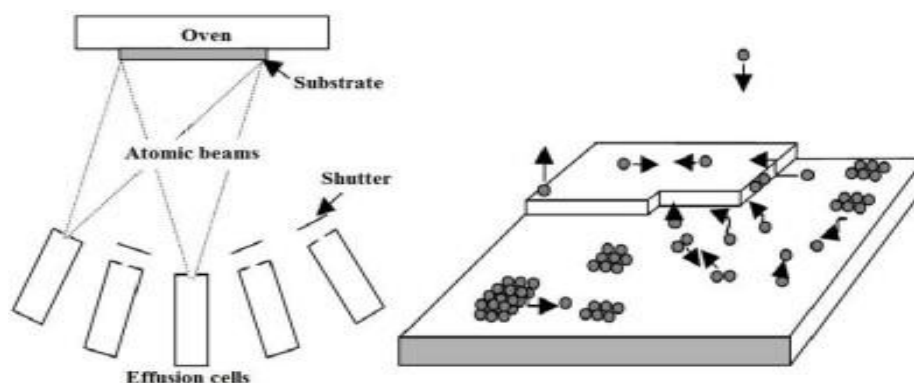


Figure I.6. The principle of Molecular Beam Epitaxy [26].

I.1.4.1.4. Sputtering

Because of its low cost, ease of use, large area, and low deposition temperature, sputter deposition a physical vapor deposition (PVD) technique is one of the most widely used growth methods for thin film deposition [27, 28]. Metals, ceramics, refractory materials, and dielectrics can all be deposited using the sputtering technique. This technique's basic idea is to bombard the material to be deposited (the target) with neutral gas ions, usually argon. The bombardment atoms are then broke away from the target and deposit on the substrate in front of the target [29]. In order to achieve a glow discharge in the remaining gas within the evacuated chamber, the basic version of the sputtering system comprises a metallic anode and cathode [28]. Additionally, film deposition requires an applied voltage of several KeV and a pressure greater than 0.01 mbar. In order to liberate molecules with higher kinetic energy

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from the cathode, the sputtering process relies on the ions produced from the discharge bombarding the molecules in the cathode. To optimize momentum transfer, the bombardment ions' atomic weight should be close to that of the target material. These molecules impact the anode or substrate while traveling in straight lines [28]. The diagram of the sputtering system is shown in Figure I.7.

Sputtering is referred to as simple if the discharge's environment (gas) is chemically neutral. Sputtering is considered reactive, though, if it contains active gases like nitrogen N_2 or oxygen O_2 . Depending on how the plasma is created or whether the target is conductive or insulating, there are two types of cathodic sputtering: direct cathodic sputtering (DC), which is only used when conductive materials are being sputtered, and sputtering radiofrequency (RF), which enables the spraying of either conductive or insulating materials. Numerous factors, including base vacuum, sputter gas pressure during deposition, sputter power, target and substrate temperature, etc., influence the deposition process. The magnetron device has been utilized to improve sputtering efficiency and reduce its disadvantages [29].

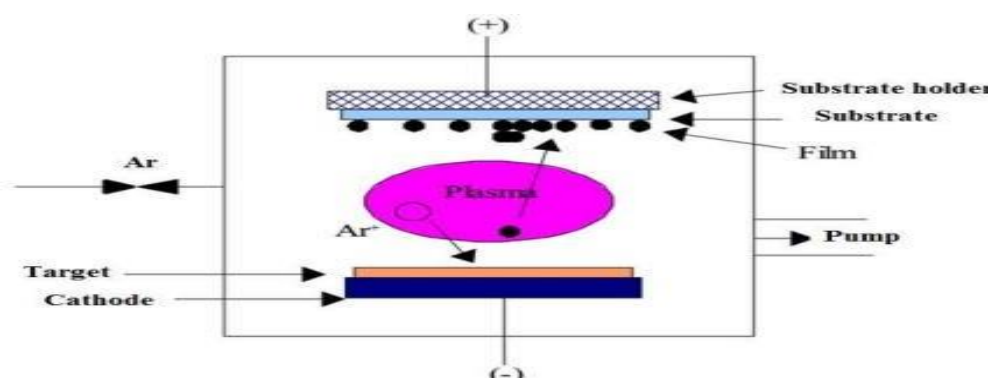


Figure I.7. The principle operating of the sputtering [30].

I.1.4.1.5. Laser Ablation

A highly powerful pulsed laser beam irradiates the target and ejects micron-sized particles during laser ablation, often referred to as pulsed laser deposition (PLD). The high intensity laser pulse ejects these particles from targets, which are thought to significantly impair the formed films' optical properties [31]. The energy of a laser pulse that is absorbed by a target is initially used for electronic excitation and subsequently transformed into mechanical, chemical, and thermal forms of energy, which leads to exfoliation, plasma formation, evaporation, and ablation [32]. Several energy species, such as atoms, molecules, electrons,

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ions, clusters, particles, and molten globules, are present in the plume that is created as the ejected material expands into the surrounding vacuum. In the end, these various species form a thin layer that condenses onto a substrate [17].

Figure I.8 displays a basic schematic of a typical PLD procedure in which a pulsed laser is directed at a target of the material to be deposited. Each laser pulse vaporizes or ablates just a small amount of the material, producing a plasma plume, when the laser energy density is high enough. A strongly forward-directed plume of the ablated material is released from the target. The material flux for film growth is supplied by the ablation plume [33].

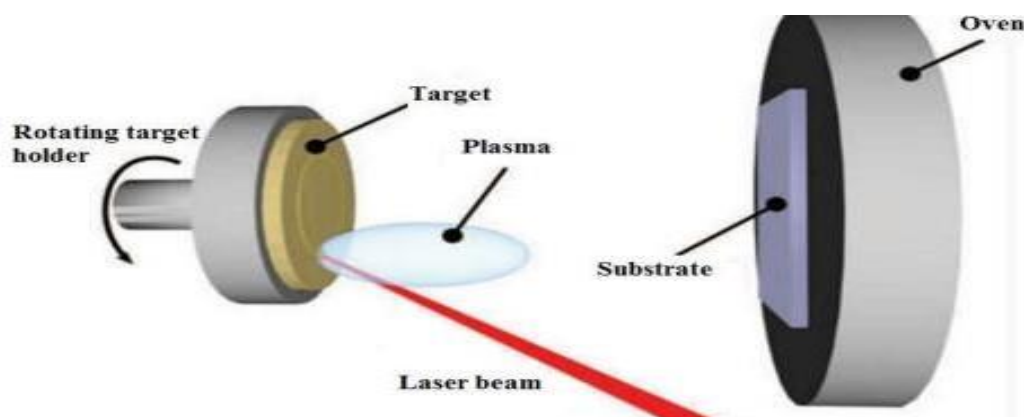


Figure I.8. Schematic of a typical Pulsed Laser Deposition process [34].

I.1.4.2. Chemical techniques

I.1.4.2.1. Chemical Vapor Deposition

The previously stated physical methods of producing thin films are very expensive and can require a lot of material target, even though they provide good quality and functionalized features. Chemical Vapor Deposition (CVD) is an extremely old method of processing [35]. It involves creating materials in the form of thin layers on a heated substrate by chemically reacting gaseous precursors [36].

It is employed for depositing controlled-structured thin and thick films with thicknesses ranging from Angstroms " $\text{\AA}$ " to fractions of a millimeter "mm" onto a heated surface. Because the film can grow in any direction depending on the gas precursor's achievement, this technique enables deposition on complex surfaces, which will be more beneficial in industries [37].

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Precursors determine the film composition in these techniques, and stoichiometry can be attained by regulating the precursors and deposition rate. It doesn't need a high vacuum and can permit element co-deposition. Thin films are grown using CVD methods under typical atmospheric conditions [38, 39]. Figure I.9 a typical CVD procedure consists of four essential steps:

1. A thermal activation of the chemical precursors to form a vapor.
2. This vapor is then transported through a heated chamber where the substrate is located.
3. In this chamber, the desired gas phase reactions occur and the reactants are deposited onto the substrate surface resulting in film formation.
4. Volatile by products are desorbed from the film and removed from the chamber through convection.

There are a wide range of techniques that fall under the CVD category [33]:

- Metal-organic chemical vapor deposition (MOCVD) is a specific type of CVD that utilizes metal-organic precursors.
- Metal-organic vapor phase epitaxy (MOVPE) or organometallic vapor phase epitaxy (OMVPE) is an MOCVD process that produces single crystal films on single crystal substrates from metal-organic precursors.
- Plasma-assisted or plasma-enhanced CVD (PECVD) is a technique in which electrical energy rather than thermal energy is used to initiate homogeneous reactions for the production of chemically active ions and radicals that can participate in heterogeneous reactions, which, in turn, lead to layer formation on the substrate.
- Atomic layer chemical vapor deposition (ALCVD), sometimes called atomic layer epitaxy (ALE), is a modification of the CVD process in which gaseous precursors are introduced sequentially to the substrate surface and the reactor is purged with an inert gas or evacuated between the precursor pulses.
- Chemical beam epitaxy (CBE) is high vacuum CVD technique that uses volatile metal-organic precursors and gaseous co-precursors.

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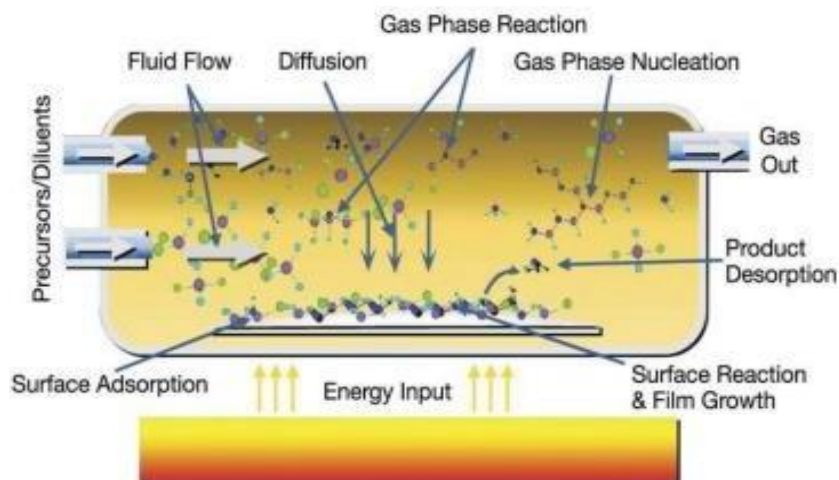


Figure I.9. The principle CVD process [37].

I.1.4.2.2. Spray Pyrolysis

A deposition method called spray pyrolysis is used to create ceramic coatings, powders, and both thick and thin layers [40]. A sprayer (nozzle) is used to spray small drops of the precursor solution which contains the material to be deposited onto a heated substrate, as illustrated in Figure I.10. In order to create the appropriate layer, the substrate's temperature causes the chemical interactions between the compounds and permits the solvents to evaporate [29].

The parameters that influence the properties of the thin layers prepared by spray pyrolysis are [41, 43]:

- The temperature of the substrate.
- The precursor solution (the type of solvent, the viscosity of the solution, the concentration of the compound in the solution).
- The distance between the nozzle and the substrate.
- The carrier gas and the rate at which the aerosol passes through.
- The size and opening time of the nozzle.
- The number of sprays.

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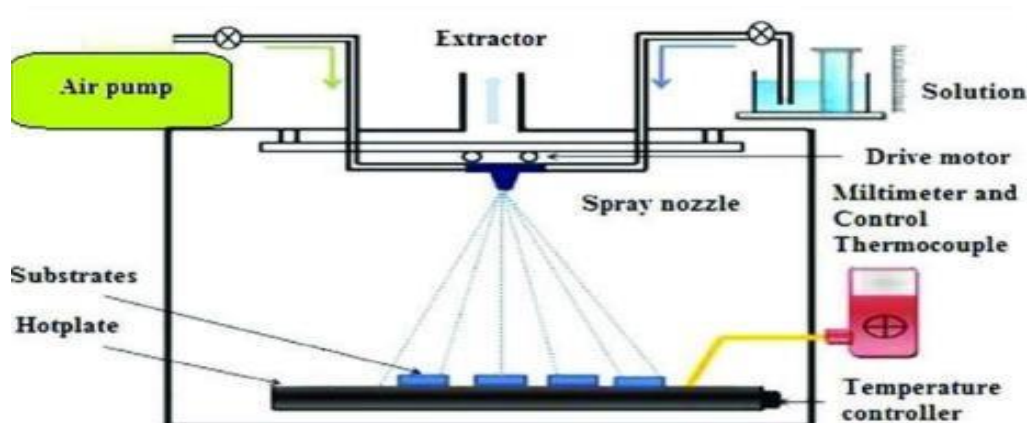


Figure I.10. Schematic of spray pyrolysis technique [29].

I.1.4.2.3. Sol-gel

A wide range of materials, including ceramics, powders, fibers, and thin films, are generated using the sol-gel (solution-gelation) approach, which is especially well adapted for creating coatings such thin oxide layers [44, 45]. A hydrolysis and condensation reaction occurs at low temperatures. The fundamental idea behind the sol-gel process is that a liquid-phase solution based on precursors undergoes a sequence of chemical events, including low-temperature polymerization, to become a solid. Pulling, centrifugation, drying, and annealing are the steps in the cycle, which can be carried out several times to produce a finished film with multiple layers [13].

In the field of research, the thin layers prepared by the sol-gel process are widely known and is used in various applications. The most used techniques are dip-coating and spin-coating [29].

I.1.4.2.3.1. Dip-Coating

This technique only involves dipping the substrate in the “sol” containing solution, pulling at an identified withdrawal rate while maintaining regulated pressure and temperature, and then letting it drain (Figure I.11). The liquid will flow onto the substrate throughout the ascent. A homogeneous, porous layer covers the substrate at the end of the flow. With this method, deposits on both substrate surfaces can be created in a single process. The films' thicknesses range from a few micrometers to 100 nm [13].

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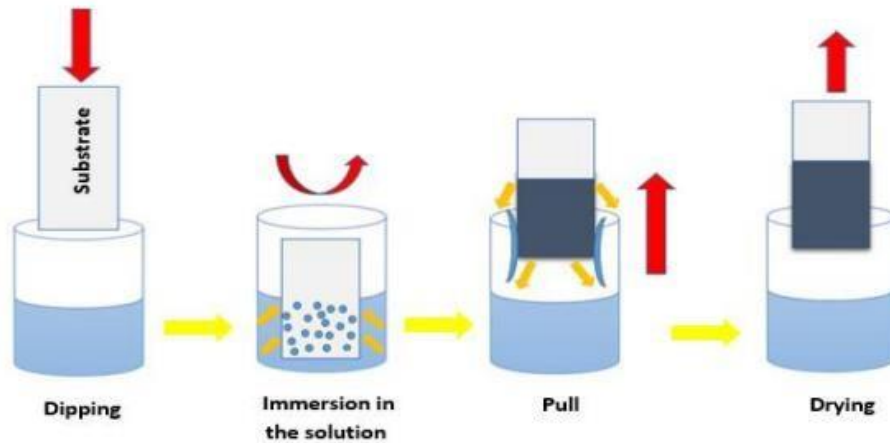


Figure I.11. The principle of thin films deposited by dip-coating method [10].

I.1.4.2.3.2. Spin-Coating

The "spin-coating" technique consists in producing, by centrifugation [10], a drop of solution is placed in the middle of a substrate that is fixed to a horizontal rotating support. Through centrifugation, the spinning distributes the solution until a homogeneous film is produced [13]. For small investments, it has the benefit of being simple to execute and producing excellent results on flat substrates in small areas (a few cm^2). Figure I.12 illustrates the four primary phases that make up this approach [29].

1. The extra solution (a few drops) is deposited on the substrate's surface.
2. **Acceleration:** this is the start of the rotation, and because centrifugal force allows solid particles of different densities to be separated in a liquid solution, its forces cause the solution to flow evenly over the sample and move the liquid away from the center towards the outside of the substrate.
3. **The rotation at a consistent speed:** this enables the uniform lowering of the layer's thickness and the ejection of excess sol in the form of droplets.
4. **Evaporation:** the more volatile solvents evaporate first during this phase, which causes the substrate to rotate at a steady speed and reduces the thickness of the deposited film [46, 47].

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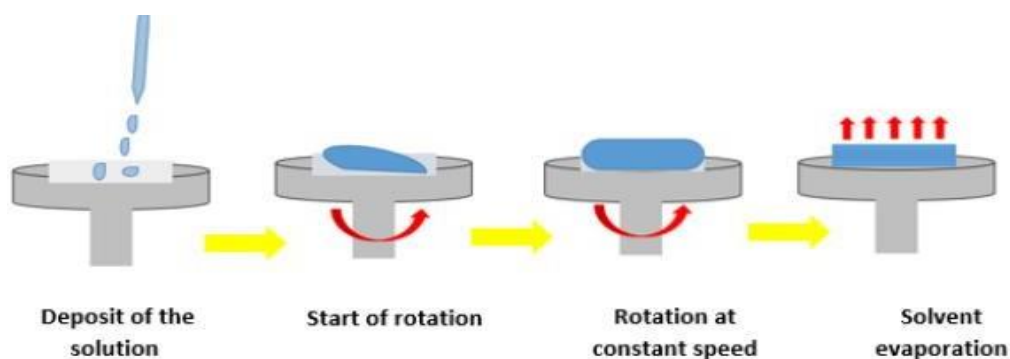


Figure I.12. Schematic representation of spin-coating principle [10].

I.2. Zinc oxide (ZnO) thin films

I.2.1. Definition

Zinc oxide (ZnO) is a nontoxic, cheaper and abundant on the earth's crust, inorganic compound belongs to the family of II–VI compound [37] has emerged as a promising material for research because of its properties, which include a high free energy of exciton binding (60 meV), and a wide direct band gap of 3.37 eV that makes it transparent to visible light [13]. This makes it a very attractive material for use in advanced optoelectronic devices [48, 49]. Good mechanical and thermal stability, a high optical gain (300 cm^{-1}), and a high cohesion energy of 1.89 eV [50]. Zinc oxide has attracted intensive research effort for its versatile applications and it exhibits many unique interesting properties [51, 53]. By reason of its optical, semiconducting, ultraviolet (UV) light-emitters, varistors, transparent high-power electronics, surface acoustic wave devices, piezoelectric transducers, gas sensors, and its use as a window material for solar cells, displays [54, 55], and catalytic properties.

I.2.2. Properties of ZnO

I.2.2.1. Structural properties

ZnO is found in the natural state under the name of Zincite, is one of II-VI compound semiconductors. It has crystal structure of rock salt (B1) (cubic symmetry) (Figure I.13a), zinc blend (B3) (Figure I.13b) or hexagonal wurtzite (B4) (Figure I.13c) [56].

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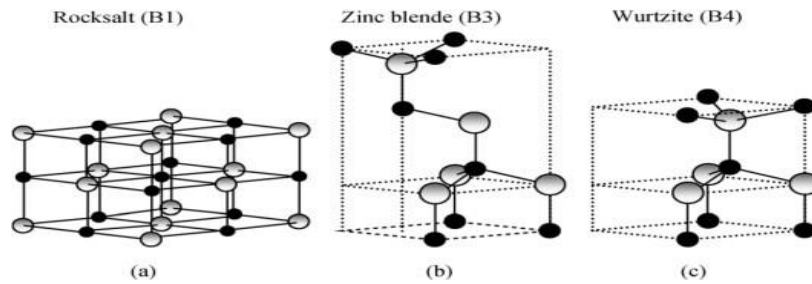


Figure I.13. Crystal structures of ZnO [57].

With the lattice parameters of $a = b = 3.2496 \text{ \AA}$, $c = 5.2042 \text{ \AA}$ and $\beta = 120^\circ$, ZnO crystals most frequently stabilize in the wurtzite structure with a hexagonal unit cell (space group P6₃mc) under ambient conditions. This structure has a ratio of $c/a = 1.601$, which is nearly identical to that of an ideal compact hexagonal structure ($c/a = 1.633$) (Figure I.14). In contrast, the zinc blende structure can only be stable on substrates with a cubic structure. In both of these configurations, the unit cell forms a tetrahedron with five atoms: four oxygen atoms (anions) surround one zinc atom (a cation), and vice versa. These Zn-O connections are covalent as well as ionic. However, only at high pressures (10^{-15} GPa) do the crystals display the rock salt phase. The ZnO wurtzite phase has a polar hexagonal axis known as the c-axis (0002) that is parallel to the z-axis and the other is the nonpolar plane includes (1120) and the (1010) [13].

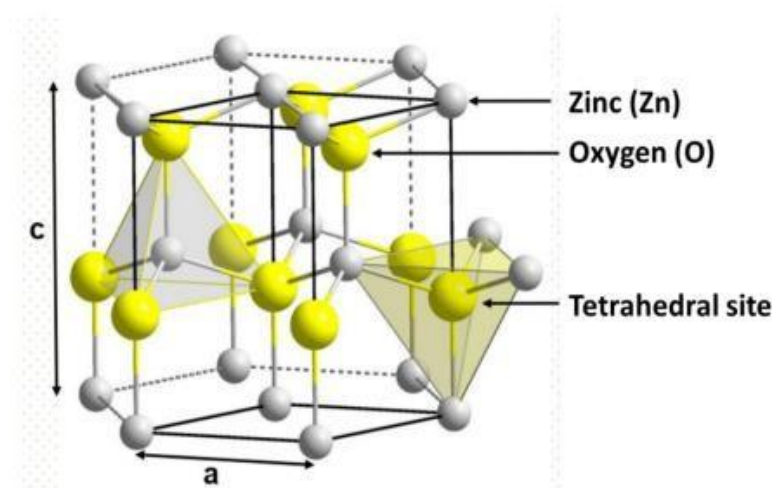


Figure I.14. Elementary crystal lattice of the wurtzite structure of ZnO [58].

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Various physical properties of the hexagonal structure of zinc oxide are summarized in Table I.1.

Table I.1. Physical properties of the zinc oxide in the wurtzite form [33]

Properties	Parameters value at 300K
Crystalline structure	Wurtzite
Lattice parameters	a=3.2496 Å c=5.2042Å
Refractive index	2.008-2.029
Band gap energy	3.37 eV, direct
Intrinsic carrier concentration	$<10^{-10} \text{ cm}^{-3}$
Exciton binding energy	60 meV
Melting point	1975°C
Density	5.606 g/cm ³

I.2.2.2. Optical properties

The majority of ZnO films' uses certainly relate to their optical characteristics; the key characteristics that determine the crystal's optical characteristics are optical constants like the dielectric constant, refractive index, extinction coefficient, and absorption coefficient [37]. According to the research findings, the thickness, optical gap, surface roughness, doping, crystalline quality of the film and deposition technique constitute a few of the elements that affect its optical properties [59].

The speed at which light travels through a substance as compared to through a vacuum is indicated by the material's refractive index [37].

The absorption loss as the wave travels through the sample is shown by the extinction coefficient, an imaginary part of the refractive index. Optical constants can be used to measure the material's band gap and provide information about how radiation passes through the sample and reflects off it [37].

Many decades ago, Optical properties of ZnO based thin films were widely studied [37]. ZnO has band gap energy of 3.37 eV at ambient temperature, which corresponds to an absorption

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threshold of about 380 nm in the near ultraviolet [60]. This band gap value is very significant for optics, especially for opto-electronic applications. More than 90% of visible light passes through this material due to its wide gap when the crystalline quality is high enough. With effective radiative recombination and a significant exciton energy of 60 meV [37]. ZnO's transparency to light in the visible and near ultraviolet–visible wavelength range is widely known [37], Its absorption coefficient and refractive index depend on the elaboration conditions between 1.90 and 2.20, while in its massive form, it has a refractive index of 2 [61].

Different experimental methods, including optical absorption, transmission, reflection, photo-reflection, spectroscopic ellipsometry, photoluminescence, etc., have been used to study the optical transitions in ZnO. In actuality, ZnO exhibits both intrinsic and extrinsic optical transitions. Extrinsic transitions are associated with dopants, impurities, or native defects in the ZnO lattice, which result in the formation of distinct energy levels inside the band gap, whereas intrinsic transitions occur between electrons from the conduction band and holes in the valence band, including excitonic effects brought on by coulomb interactions. As a result, they affect the emission process as well as optical absorption [37].

I.2.2.3. Electrical properties

At room temperature, zinc oxide, an II-VI semiconductor, has a large direct band gap of 3.3 eV. Zinc oxide is typically regarded as an n-type semiconductor. Some of ZnO's electrical characteristics are shown in Table I.2. Hall Effect measurements are used to determine the electrical characteristics of ZnO thin films, including mobility, charge carrier concentration, and electrical resistivity. The conduction band's electron density (n) and mobility (μ) determine an n-type thin film's electrical resistivity (ρ) [29]:

$$\sigma = \frac{1}{\rho} = e n \mu_n \dots\dots\dots I.1$$

σ : conductivity. n : the density of electrons. μ_n : electron mobility.

Zinc oxide's electrical resistivity can be altered by doping, adding additional zinc atoms to the interstitial position, or forming oxygen vacancies. These zinc interstitials and oxygen vacancies act as electron donors, decreasing the material's electrical resistivity [62].

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Interstitial hydrogen is another shallow donor defect that could be the cause of free electrons [63].

It is crucial to note that the preparation conditions, especially heat treatments, and the deposition technique affect the electrical resistivity of zinc oxide. Zinc atoms can be readily substituted with Group III elements (Al, Ga, In, and B) and Group IV elements (Si, Ge, and Zr) to produce n-type ZnO, or oxygen atoms can be substituted with a group element VII (F, Cl) to produce p-type ZnO doped with group I elements (Li, Na, and K). It should be noted, however, that type p is more difficult to find instead of type n [64, 65].

ZnO is a semiconductor of the $A^{VI}B^{II}$ group. The electronic configurations of the oxygen and zinc atoms are as follows [66, 67]:

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

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

Table I.2. Some electrical properties of ZnO [29].

Properties	Value
Nature of the band gap	Direct
Band gap at 300K	3.34 ± 0.02
Conductivity	n et (p)
Electrical conductivity	$10^{-6}-10^2 (\Omega.cm)^{-1}$
Charge carrier density	$10^{15}-10^{21} cm^{-3}$
Density of states in CB	$3.71 \cdot 10^{18} cm^{-3}$
Density of states in VB	$1.16 \cdot 10^{19} cm^{-3}$
Electron mobility	$0.2-200 cm^2/V.s$
Holes mobility	$5-50 cm^2/V.s$
The effective mass of electrons	$0.28 m_0$
The effective mass of holes	$0.60 m_0$
Thermal velocity of electrons	$2.2 \cdot 10^7 cm.s^{-1}$
Thermal velocity of holes	$1.5 \cdot 10^7 cm.s^{-1}$

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I.2.2.4. Luminescence properties

After being excited by a light wave (photoluminescence) or an electron bombardment (cathodoluminescence) with energy greater than or equal to the material gap, luminescence is the process of carrying a material back to its energy equilibrium. The absorption of this energy results in a “electron – hole” pair known as an exciton. The exciton may be donor or acceptor, free, or coupled to a neutral or ionized impurity [68].

Because of the recombination of an electron-hole pair formed after the absorption of energy higher than the gap, zinc oxide generates two forms of luminescence. The first type is excitonic. The energy of the gap less the exciton's binding energy, which is predicted to be 60 meV in ZnO, is the energy released as a UV photon. Therefore, at room temperature, the measured wavelength is roughly 380 nm. Strong UV luminescence is promised since the exciton's binding energy is significantly higher than kT at room temperature [13].

The second luminescence is for its part correlated with the existence of structural defects, impurities, dopants, which will cause energy levels in the gap more or less close to the valence and conduction bands [13].

There are two kinds of defects in ZnO (Figure I.15). These defects, which are intrinsic to the ZnO film and include oxygen vacancies or Zn interstitial, are known to as "deep" defects. They produce luminescence in the visible spectrum and have energy levels that are a few hundred meV or a few eV away from the valence band (VB) and conduction bands (CB) [69]. The second-called “shallow” defects, which are “doping” defects, are located a few tens of meV away from VB and CB. They will produce bound excitons and eventually induce discrete energy levels in the ZnO wurtzite gap, which will have a significant impact on the material's optoelectronic properties. Low trapping energy excitons at shallow defects result in a characteristic emission that is energetically very close to that of free excitons and only visible at low temperatures [70].

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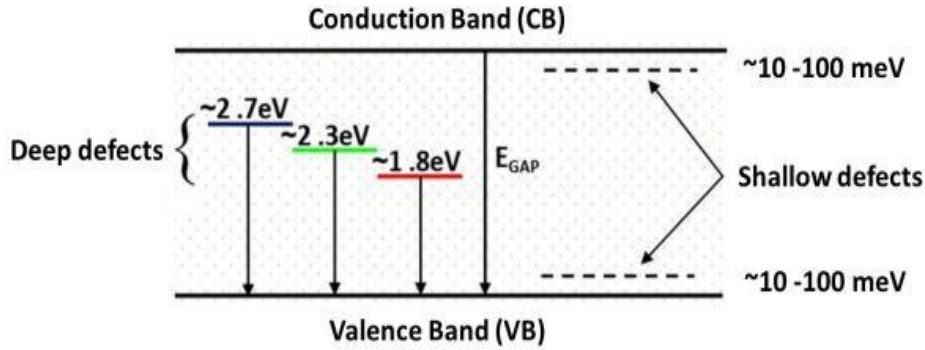


Figure I.15. Implantation in the forbidden band of deep and shallow defects [13].

I.2.3. Doping ZnO

To realize any type of device technology, it is important to have control over the concentration of intentionally introduced impurities, called dopants [33], doping is the introducing of impurities into an extremely pure semiconductor with the aim of enhancing the physical characteristics [71], and as a result, it may be a suitable and efficient method of regulating the optical luminescence, electrical conductivity, and photocatalytic activities [72]. The kind of dopant, its valence state, and where it is located in the lattice structure (interstitial or substitution) could all have an impact on these properties [73]. The ideal doping candidate should be sufficiently low in ionization energy, have a high solubility, and be relatively stable inside the crystal lattice.

There is a wide selective element doping which can offers a method for controlling and tailoring ZnO properties. Doping in ZnO can be classified into two types [74]:

❖ n-type doping

To significantly alter their electrical characteristics, n-type doping in ZnO can be achieved by replacing Zn with group III elements as aluminum (Al), gallium (Ga), and indium (In) [37]. By substituting group VII elements such as fluorine (F), chlorine (Cl), bromine (Br), and iodine (I) for O, n-type its conductivity can also be achieved in ZnO [37]. ZnO n-type doped films with a high electron concentration ($\sim 10^{17}$ - 10^{21} cm^{-3}) and low resistivity ($\sim 10^{-4}\text{ }\Omega\cdot\text{cm}$) have been reported by many researchers [37].

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❖ P-type doping

ZnO may be doped with acceptor impurities such as group I elements, such as lithium (Li) and sodium (Na), group V elements, such as nitrogen (N), phosphorus (P), antimony (Sb), and bismuth (Bi) [37], and group IB elements, such as copper (Cu) and silver (Ag) [37], in order to achieve p-type conductivity, which is much more difficult to achieve than n-type conductivity. Realizing p-type conductivity in ZnO has a very bad success rate. Another major concern is the reproducibility, stability, and reliability of p-type doping. Therefore, ZnO's commercialization for optoelectronic applications is limited by its low p-type conductivity [37].

I.2.3.1. Erbium doping ZnO

Doped with Erbium (Er) ZnO, as a photocatalyst, is important in the UV light-induced degradation of synthetic dyes. Among the several metal oxides, ZnO has attracted a lot of attention because of its many unique characteristics, including its large binding exciton binding energy, piezoelectricity, high surface to volume ratio, and wide band gap. To improve functionality and surface area [75]. In recent years, semiconductors doped with trivalent rare earth (RE^{3+}) ions have attracted significant interest in research and are technologically important substances in optoelectronic devices. Er doped ZnO (EZO) has been extensively studied and is expected to be one of the most promising materials for ZnO-based optoelectronic devices due to the 1.54 μm photoemission caused by Er intra-4f shell transition [76]. This emission makes such Er-doped semiconductors suitable candidates for light wave communication devices such as light-emitting diodes, laser diodes [77]. Some researchers have modified ZnO by doping it with rare earth elements (Er, Eu, Yb,...) that can induce changes in the luminescence properties of ZnO. Undoped ZnO is known to contain a high concentration of intrinsic defects, including zinc interstitials (Zn_i) and oxygen vacancies (VO). Because of its low formation energy, the VO is mostly found in ZnO. Numerous investigations on ZnO's photoluminescence (PL) reveal that the green emission originates from VO, which may be greatly impacted by prepared conditions, post-annealing, and dopant incorporation [76].

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I.2.3.2. Lithium doping ZnO

Because of its fundamental donor defects, which include zinc interstitials and oxygen vacancies, ZnO naturally displays n-type conduction. However, because of its strong self-compensation and limited dopant solubility, ZnO has difficulty to produce high-quality, repeatable p-type material [78]. By doping ZnO with V group elements as Sb, P, N, and As, several groups have been able to create p-type material. Theoretically, their acceptor levels are deep and have low limits of solubility. On the other hand, doping with elements that belong to the I group, such as Na, K, and Li, should theoretically result in reduced acceptor levels. Since the covalent bond length of Li-O (0.201 nm) is only a bit greater than that of Zn-O (0.197 nm), Li seems to be the most promising of the aforementioned dopants for doping ZnO. Furthermore, Li is regarded as one of the best choices because of its shallow acceptor levels and similar atomic radius to that of Zn and O. Lithium ion migration is also accelerated by the shorter binding energy of longer Li-O bonds. As a result, Li may readily replace Zn sites to create Li Zn acceptors, and ZnO's electrical conductivity can be greatly adjusted with the right amount of Li doping. Li interstitials, which function as donors, are created when Li ions are sufficiently mobile within a ZnO lattice [79]. According to Ardyanian et al., deep acceptor level growth suggests that p-type conduction is not significantly enhanced by this. Although ZnO photoluminescence has been examined in great detail, the impact of Li doping on ZnO photoluminescence has received less attention. Defect levels inside the material band gap are typically created in conjunction with the introduction of doping atoms into the semiconductor network [80]. The potential for Li to function as a p-type dopant and the finding of ferroelectricity in II–VI semiconductors are the two main reasons for interest in Li as a dopant in ZnO [78].

I.2.3.3. Aluminium doping ZnO

ZnO can be modified by doping it with a wide range of ions to satisfy the requirements of various application domains [81]. Recently, Ga, In, and Al have been identified as the best dopants to suppress the electron-hole recombination process and improve its spectroscopic characteristics in the visible region [82], their electrical and optical properties of ZnO films [81]. Therefore, doping of low valent metal such as Al into ZnO (AZO) improves the photocatalytic activity of ZnO by introducing impurity level into the band gap which constrain the recombination of charge carrier. Because of its availability, low cost, and low

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doping ionic radius, aluminum is the most commonly utilized [82]. Compared to Sn doped, indium oxide (ITO) films, Al doped ZnO (AZO) thin films have garnered greater interest because of their low cost, non-toxicity, high stability under hydrogen plasma, wide band gap semiconducting property, and good optical transmission in the visible wavelength region (400–700 nm) . Furthermore, it is possible to produce AZO films at a very low temperature (300°C). The optical and electrical characteristics of Al-doped ZnO films have been the subject of several investigations published in the literature [83]. Zi-Qiang Xu et al. have reported Al doped ZnO thin film as a UV detector under the illumination of 350 nm radiation [84].

I.2.3.4. Magnesium doping ZnO

ZnO can be doped with group II elements like Mg to improve its electrical and optical properties. Additionally, because Mg^{2+} (0.057nm) and Zn^{2+} (0.060 nm) have similar ionic radii, it is easy to incorporate Mg^{2+} ions into the zinc oxide lattice. This improves ZnO's crystallinity without altering the wurtzite structure. Additionally, the properties of these nanostructures depend on factors like surface morphology, particle size, orientation, crystalline structure, and concentrations of intrinsic and extrinsic defects, all of which can be altered by Mg doping [85]. Since Mg has a similar ionic radius and can extend the absorption wavelength from UV-A (320–400 nm) to UV-B (280–320 nm) and UV-C (200–280 nm) regions, Mg-doped ZnO has attracted a lot of interest to increase its photocatalytic activity [86]. For a greater enhancement of electrical and optical properties, the Zn:MgO films doped with other elements including Na and Al have been widely studied for solar cell applications [85].

I.2.3.5. Lanthanum doping ZnO

The physical, optical, chemical and photocatalytic properties of ZnO can be enhanced with doping elements such as transition elements and rare earth. Numerous scientific studies have focused on rare-earth-doped ZnO, with results confirming that the physico-chemical properties and transmission performance of ZnO in the visible region are enhanced by rare-earth doping. This is explained by the energy transfer between ZnO and the dopant ions, as the transition between the 4f levels make these rare earth excellent luminescence centers. La is one of the rare earth elements that works well for doping ZnO. Transparent conducting

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oxides (TCOs), and ZnO in particular, are perfect host matrices for RE ions because of their fundamental transparency and photoluminescence. One of the most soluble REs, lanthanum can significantly improve the quality of ZnO by increasing oxygen vacancies and, as a result, giving higher polar face stability. M.A. Lahmer et al. recently confirmed this conclusion. Additionally, Lanthanum doping enhances ZnO's photoluminescence activity, according to Sridevi et al.. Additionally, Xu et al. enhance the optoelectronic characteristics of La-doped ZnO films, where La causes a decrease in resistivity and an increase in transmittance [87].

I.2.3.6. Co-doping ZnO (Li:Mg, Li:Al, Li:La)

Doping ZnO with selective elements is thought to be an efficient method of modifying or tailoring its physical and chemical properties for particular applications. It is well known that the hexagonal wurtzite structure of ZnO contains large voids that can accommodate doping ions, even those with larger ionic radii than Zn^{2+} [88]. Since the introduction of alkali metals causes a defect in the lattice due to the charge difference between the alkali metal ion and the host metal ion, the doping of alkali metals in semiconductors is extensively researched. Lithium is used for doping among alkali metals because it has p-type characteristics and also helps to change the optical characteristics of ZnO [89]. Additionally, co-doping ZnO can be effective for improving optical characteristics, attaining p-type conduction, and increasing the dopant solubility. Li^+ ions are specifically recognized to increase the luminescence intensity [88]. Li co-doping has been shown to be effective in improving the electrical and optical characteristics of Al-doped ZnO and Mg-doped ZnO films by Nian et al., and Fujihara et al., respectively. Caglar et al., discovered that Li doping increases the crystallinity of ZnO films [90].

I.2.4. Application of ZnO thin films

Zinc oxide can be called a multifunctional material thanks to its unique physical and chemical properties [33]. Our society uses it extensively, and it plays a significant role in the production of many industrial products, including paints, cosmetics, medications, plastics, batteries, electrical equipment, rubber, textiles, and floor coverings. Solar cells, gas sensors, spintronic devices, photo-detectors, acoustic devices, lasers, transparent electrodes for luminescent devices, and photocatalytic applications are a few examples of the various applications for ZnO [13]. ZnO films are an essential component of many industrial manufacturing procedures

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because they can be doped with a range of elements in the intended target to obtain such desired and possible characteristics. ZnO devices are going to become more exotic and functional as we reach a new era [37].

I.2.4.1. Photovoltaic application

ZnO's ability to grow in a wide range of nanostructured morphologies and be deposited using a variety of methods, many of which are inexpensive, are two of its most attractive properties. Consequently, ZnO has a wide range of uses, especially in optoelectronic devices like solar cells. Where, several types of photovoltaic cells have been produced by combining ZnO with semiconductors [33].

Noting out that because native point defects in zinc oxide are inefficient donors, ZnO is extremely resistive in its undoped condition. However, substitutional doping with Al, In, or Ga can result in respectable impurity doping efficiencies [91].

Light-trapping and/or antireflection coatings and contacts are the simplest uses of ZnO-based materials in photovoltaic systems. Doping with group III elements is common for applications such as transparent interactions in solar cells. Whereas, doped ZnO electrodes are often utilized both as contacts and to enhance light trapping in thin film solar cells via textured electrode surface. For inorganic solar cells, the majority of ZnO-based electrode research has been published [92].

I.2.4.2. Solar cells

The photovoltaic effect, which uses sunlight to generate electricity, has been identified as a viable solution to the growing demand for energy while simultaneously focusing on the issue of carbon dioxide emissions from the combustion of fossil fuels. One of the more attractive developments for utilizing photons from sunlight to generate electricity is thin-film solar cells. Unlike batteries or fuel cells, solar cells do not utilize chemical reactions or require fuel to produce electric power, and, unlike electric generators, they do not have any moving parts [37].

The fundamental construction of solar cells is the same whether they are found in a calculator, a satellite, or a central power station. An optical coating, also known as an antireflection layer, allows light to enter the device by reducing the amount of light loss through reflection. This

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layer efficiently traps light that occurs on the solar cell by encouraging its transfer to the layers below that convert energy. The top junction layer, the absorber layer, which forms the device's center, and the back junction layer are the three energy-conversion layers that exist below the antireflection layer. To complete an electric circuit, two more electrical contact layers are required to transport the electric current to an external load and back into the cell. Silicon is used to make a great deal of solar cells, and as the materials change from amorphous (non-crystalline) to polycrystalline to crystalline (single crystal) silicon forms, the efficiency and cost of solar cells are increasing. Recent studies have focused on using a range of novel, inexpensive materials, including zinc oxide (ZnO). One material of great interest for use in inexpensive photovoltaics is ZnO [37].

ZnO-based materials are most commonly used in thin film solar cells as light-trapping and/or antireflection coatings and contacts. Doping with group III elements is common for applications such as transparent interactions in solar cells. On the other hand, doped ZnO electrodes are frequently employed in thin film solar cells as contacts and to improve light trapping through textured electrode surfaces [37].

I.2.4.3. Light-emitting diodes (LEDs)

Wideband gap semiconductor-based light-emitting diodes (LEDs) have garnered a lot of interest in the past decade because of their prospective optoelectronic uses in displays, mobile appliances, lighting, and automobiles [93]. ZnO is a particularly attractive choice for the fabrication of blue and UV LEDs, which require that the junction devices give high electron and hole concentration in the active region. This is due to its broad bandgap and significant exciton-binding energy at room temperature. Since ZnO is inexpensive and easily available, it offers a cost advantage over GaN, which attracts even more to the idea of fabricating ZnO-based optical systems. Interest in ZnO-based devices was encouraged by the commercial success of GaN-based optoelectronic and electrical devices [94].

On the other hand, the realization of ZnO-based LEDs is limited by the absence of stable and repeatable p type ZnO. Another strategy was proposed: n-type ZnO thin film formed over various p-type materials such as Si, GaN, zinc telluride, copper (I) oxide, and GaAs. There have been reports of several ZnO-based heterojunction and homojunction light emitters in the visible and ultraviolet (red, blue, green, or white) spectrums [37].

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I.2.4.4. Photocatalytic application

Environmental pollution caused by toxic chemicals released by industries has become of a major concern; and to tackle this issue several techniques have been explored. Heterogeneous photocatalysis by irradiating semiconductors surfaces is one of those effective techniques employed in the degradation of soluble organic contaminants in waters. The photocatalysis process is based on electron-hole pairs generation produced in a semiconductor. This process can be summarized mainly in five steps [95]:

- a) Under irradiation of semiconductor with photon energy greater than its band gap energy (E_g), electron-hole pairs (h^+ / e^-) are generated;
- b) The water molecules adhering to the semiconductor surface react with the holes (h^+) forming hydroxyl radicals such as ($\bullet OH$) and H^+ ;
- c) The generated electron (e^-) in the conduction band react with the dissolved oxygen molecules to produce superoxide ($O_2^{\bullet -}$) radicals;
- d) The super oxide products react with H_2O to form the peroxide H_2O_2 molecules that produce in turn hydroxyl radicals $\bullet OH$;
- e) These free radicals, especially hydroxyl radical ($\bullet OH$), are powerful oxidizers capable of decomposing pollutants into CO_2 and H_2O .

Since electron holes can recombine during the photocatalytic process and have a short existence, various methods can be used to prevent this from occurring and improve the photocatalytic efficiency. This includes doping with rare earth elements (La, Er, Yb, Y, and Ge) and different metals (Cr, Ni, Co, Fe, and Mn). Li-doped ZnO might enhance the crystalline quality of ZnO films, according to the findings of F. Boudjouan et al. [96].

I.3. Conclusion

Oxide-based thin films, particularly ZnO, continue to be a material of great interest due to their unique properties and broad applicability across various advanced technologies. Understanding their growth mechanisms and deposition methods is essential for optimizing their performance in devices such as solar cells, optoelectronics, and piezoelectric systems. Furthermore, tailoring ZnO's characteristics through doping opens up even more possibilities for enhancing its functionality. Continued research and development in this field promise to drive significant advancements in both fundamental science and practical applications.

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Chapter II

Experimental part and Characterization techniques

Chapter II. Experimental part and characterization techniques

II. Introduction

The first chapter present the characteristics, applications, and several deposition methods of zinc oxide semiconductors. This chapter focuses on the sol-gel dip-coating method that was utilized in this research to generate the films of undoped, doped, and co-doped ZnO. The experimental techniques and characterisation methods used for this study will be discussed in order to make it clear how the results will be presented; this task will be addressed in the next chapter.

II.1. Sol-gel method

There are two main categories for producing thin films; physical and chemical methods. In our research we have used the sol-gel dip-coating method for the elaboration of our films.

II.1.1. Definition

The process known as “sol-gel” involves a transition from a liquid “sol” (colloidal solution) to a “gel” phase. Typically, precursors are inorganic metal salts or metal organic compounds like metal alkoxide. After the precursors complete a process of hydrolysis and condensation reactions, a colloidal suspension, or “sol” is formed. The sol particles come up to form a continuous liquid phase, or gel [1]. The sol-gel process is usually explained as a result of three reactions: hydrolysis, alcohol condensation, and water condensation. Alcohol is frequently utilized as a co-solvent due to the immiscibility of water and alkoxides. The sol-gel process is defined by the following two steps [2]:

- **Sol:** a stable suspension of colloidal solid particles or polymers in a liquid.
- **Gel:** a stable expansion, porous, three-dimensional, continuous solid network surrounding a continuous liquid phase [3]. The gel is referred to as colloidal if the solid network contains colloidal particles [4].

The Figure II.1 represents a schematic of several stages involved in the synthesis of materials using the sol-gel technique [5].

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Figure II.1. Main steps of the growth of thin films by sol-gel method [6].

II.1.2. The precursor

The precursor is the main material that allows the chemical reaction to occur in the sol-gel process. Metal salts with the general formula M_nX_n (chlorides, nitrates, oxychlorides) and metal alkoxide compounds with the formula $M(OR)_n$, where M is a metal atom of valence n and R is an alkyl chain with the formula (C_nH_{2n+1}) , are the two main groups of precursors [5].

II.1.3. Sol-gel synthesis routes: There are two routes of sol-gel synthesis which are [7]:

II.1.3.1. Inorganic or colloidal route:

Obtained by dissolving metal salts (acetates, chlorides, nitrates, and oxychlorides) in an aqueous solution, which results in an easy change in pH that may be assured by the addition of a complexing agent. While its low cost, this route is still rarely utilized since it is hard to control. However, this is the supported way of obtaining ceramic materials [5]. It involves two steps:

- Variation in the pH of the solution: the decrease in pH leads to the formation of protonated species (powders) and the increase in pH lead to denser species (films).
- Polycondensation with the elimination of water molecules [8].

II.1.3.2. Metal-organic or polymeric route:

generated from metal alkoxides with the formula $M(OR)_n$, in which R is an organic alkyl group C_nH_{2n+1} in organic solutions and M is a metal (Cu, Al, Ag, etc.) or a metalloid (Si, for example). Although the particle size may be easily controlled using this method, it is a little

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expensive [5]. In order to generate glasses and ceramics with several components, the main advantage of using organic precursors is that they allow a homogenous and intimate molecular mixture of various precursors [9].

II.1.4. Reaction mechanism

Initially, metal alkoxides are dissolved in an organic solvent, usually alcohol. The sol-gel transition, also known as solidification, is initiated by an inorganic polymerization mechanism that involves two distinct reactions. The processes of hydrolysis and condensation of alkoxides are very interesting to researchers [10].

II.1.4.1. Hydrolysis

It is a reaction between a molecule of water and an alkoxide, allowing the releasing of a molecule of alcohol in three stages:

1. The fixing of a molecule of water on the metal atom M.
2. Transfer of proton from the water molecule.
3. The departure of an R-OH group carried out by a balanced reaction process.

In a neutral condition, the reaction is written [11, 12]:



This reaction can be influenced by the following parameters:

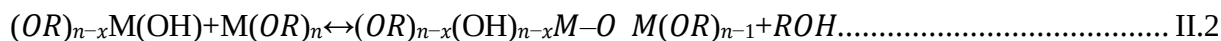
- The catalyst: acidic or basic.
- The nature of the solvent.
- The amount of water relative to the alkoxide ($[\text{H}_2\text{O}] / [\text{alkoxide}]$).
- The temperature.

II.1.4.2. Condensation

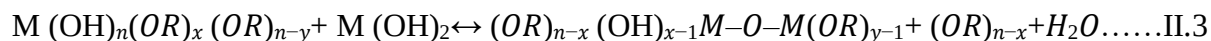
Usually, the precursors must hydrolyze at least partially in order for condensation happens. A much better nucleophilic hydroxyl group is produced by this hydrolysis instead of to the alkoxide group. As a result, the hydroxyl group undergoes a nucleophilic substitution reaction that is analogous to hydrolysis. A brief increase in the metal's coordination will result in the formation of a “metalloxane” (M-O-M) bridge. Oxolation and alcoxolation are two competitive processes [3].

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- **Alcoxolation:** This reaction takes place between two metal alkoxides, only one of which has been partially hydrolyzed. Its reaction mechanism is similar to that of hydrolysis.



- **Oxolation:** This mechanism occurs between two partially hydrolyzed alkoxides. The mechanism remains the same, except that the leaving group is a water molecule.



The solution cannot be used to deposit thin layers in most metal alkoxides because the hydrolysis processes cause particles of insoluble hydroxides and oxides to condense fast. Either the humidified environment or the additions of water in the form of an alcoholic solution causes hydrolysis to take place in order avoid this condensation of non-hydrolyzed solutions [13].

Since the mechanism of the condensation reaction is related to that of the hydrolysis reaction, the variables which affect the hydrolysis also affect the mechanism and kinetics of the condensation process, and as a result, the properties of the gel that is produced [14].

II.1.5. Dip-coating method

In order to produce a film with a uniform thickness, the substrate is immersed in the “sol” solution and then withdrawn under controlled and uniform conditions. In general the procedure may be divided into three essential steps [14]:

1. **Immersion & dwell time:** the substrate is dipped in the precursor solution at a constant speed and followed by a certain dwell time to allow sufficient interaction time of the substrate with the solution.
2. **Deposition:** the substrate is pulled upwards at a constant speed (film deposition: Excess liquid will drain from the surface).
3. **Evaporation:** the solvent evaporates by hot drying to form the thin films which can also be treated by annealing at a high temperature to improve their crystallization.

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Figure II.2. Holmarc's sol gel dip-coating method.

II.1.6. Advantages and disadvantages of sol gel process

The advantages of the sol-gel process [14]:

- The possibility for low-temperature oxide thin-layer deposition.
- The ability to deposit on large substrates.
- High purity and homogeneity thin film.
- It permits for multi-layers coatings.
- Deposition of thin layers on both sides of the substrate (dip-coating).

The disadvantages of the sol-gel process [14]:

- The very high cost of some precursors.
- The risks that substances cause to human health.
- Prolonged processing time.
- Some solutions made via the sol-gel technique have a very brief lifespan, and the process can be difficult to recreate.

II.2. Experimental part

II.2.1. preparation devices

II.2.1.1. Choice of substrates

Because the substrate often leads to stress to develop in the deposited film, it is important for the growth of thin films in terms of the lattice and thermal mismatch between it and the film.

Chapter II. Experimental part and characterization techniques

The ZnO film's optical, electrical, and crystalline properties are all impacted by the substrate choice [15].

In this study, our undoped, doped, and co-doped ZnO thin films were deposited on glass substrate (Figure II.3), was chosen for three reasons: economics, to perform a good optical characterization of our films, and to minimize the stresses.



Figure II.3. Glass substrate.

II.2.1.2. Cleaning substrates

The cleaning of the substrate is an essential step prior the deposition of thin films. This process is necessary used to remove all traces contaminants that would otherwise affect the properties of the film. Cleaning is the process of removing impurities without causing damage to the substrate. The substrate surface cleaning process was carried out at the Structures, Properties and Inter-Atomic Interaction Laboratory (LASPI²A) of Abbes Laghrour University-Khenchela- using an ultrasonic bath of the "BAKU 3060" type is shown in Figure II.4. The common cleaning procedures are as follows:

- ✚ Cutting of the substrates.
- ✚ Cleaning in an acetone bath in an ultrasonic bath for 10 min.
- ✚ Rinsing with distilled water for 10min.
- ✚ Ultrasonic bathing with methanol for 10 min.
- ✚ Rinsing with distilled water for 10 min.
- ✚ Ultrasonic bathing with ethanol for 10 min.
- ✚ Using joseph paper to dry samples.



Figure II.4. Ultrasonic bath “BAKU 3060”.

II.2.1.3. Preparation of thin films

In this work, a sol-gel dip-coating method was employed to deposit thin films of the undoped, doped, and co-doped ZnO onto a glass substrate. To create a 0.4 M solution, the zinc acetate dihydrate $[\text{Zn}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 2\text{H}_2\text{O}]$ (from LOBA CHEMIE) with molar mass $219.4986 \text{ g.mol}^{-1}$ precursor was dissolved in pure ethanol ($\text{C}_2\text{H}_6\text{O}$) with a purity of 99.9%, the mixture was stirred at room temperature for 15 min using a magnetic agitator. Then we have added a few drops of monoethanolamine (MEA) ($\text{C}_2\text{H}_7\text{NO}$) as stabilized to achieve a homogeneous solution. Subsequently, the solution was stirred at a temperature of 60°C for 2 hours. Finally the sol was aged for 24h at room temperature under atmospheric pressure. In order to investigate the impact of doping rates using Erbium (III) chloride hexahydrate ($\text{ErCl}_3 \cdot 6\text{H}_2\text{O}$) with different ratio molar: 2%, 5%, 7%, 10%, 15% and co-doping impact using different precursors with same ratio molar (1%): Nitrate Lanthanum hexahydrate $[\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}]$, Magnesium acetate tetrahydrate $[\text{Mg}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}]$ and Aluminium acetate $[\text{Al}(\text{CH}_3\text{COO})_2]$ on the thin layers of ZnO.

II.2.1.4. Deposition of thin films

After the preparation of the ZnO sol, the dopants were added before 15 min of the deposition of our thin films. The substrate was cleaned, dried and then placed in the support of the Holmarc's dip-coater equipment at the Structures, Properties and Inter-Atomic Interaction Laboratory (LASPI²A) of Abbes Laghrour University-Khenchela-, this process is very simple was carried out at room temperature, the substrate was dipped in the coating solution and remains in the solution for a while then it is removed from the solution withdrawal speed of 0.4mm/s . After each coating layer, the sample was dried at 400°C for 10 min in a hot plate “ClatRonic” type to evaporate the solvent and the residual organic. This process was repeated

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10 times. Finally, the as coated films were subsequently annealed in the “PROtherm” furnace at 500°C for 2 hours to transform from the amorphous to polycrystalline state.

II.3. Characterization techniques

II.3.1. X-ray diffraction technique

X-ray diffraction is one of the most important techniques for the determination of structural properties. It is a simple and non-destructive analysis technique, Widely used for determining lattice parameters, the inter-particle distance of the planes, preferred orientation of the crystal, phase composition (qualitatively and quantitatively), grain sizes, lattice strain and residual stress etc. [16]. In our work, the structural properties of our samples were studied by X-ray diffractometer (Rigaku MiniFlex 600) with CuK α radiation has a wavelength of 1.5418Å in the range of $20^\circ < 2\theta < 80^\circ$.



Figure II.5. Rigaku type MiniFlex 600 X-ray diffractometer.

II.3.1.1. Principle of X-ray diffraction technique

The crystal structure of materials in the form of bulk, powder, or thin films may be determined by X-ray diffraction. It depends on how X-rays and the crystal lattice interact [17]. The term “X-rays” describes a kind of electromagnetic radiation with wavelengths between 0.01 and 10 nm. This method's basic idea is to expose the sample to a monochromatic X-ray beam with a wavelength of λ , which creates a source of diffracting radiation. A detector then recovers these diffracted photons in the form of intensities. This method is used to identify known structures or sometimes to detect and characterize new structures for catalytic purposes [18]. It is based on the Bragg law, which provides the relationship between the diffraction angle θ , the wavelength λ of the X-rays, and the distance

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d_{hkl} between the crystallographic planes [14]:
 $2.d.\sin\theta=n.\lambda$II.4

With d representing the interplanar distance of the crystal lattice, λ is the wavelength of the incident beam which is (1.5418Å) for CuK α line, n is an integer that represents the order of the reflection and θ represents the angle of incidence of the X-rays with respect to the surface of the sample [4].

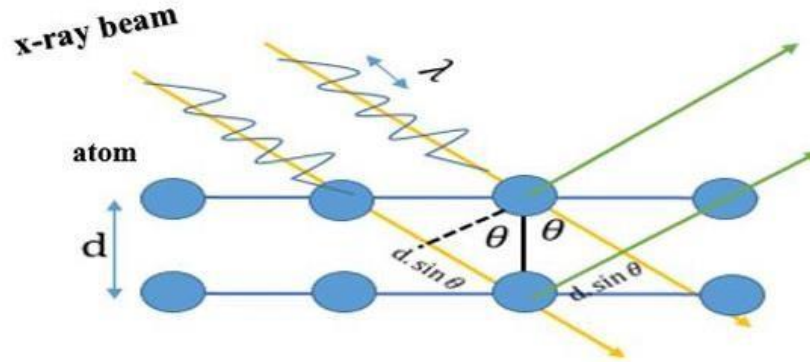


Figure II.6. The principle of Bragg's law [4].

II.3.1.2. Determination of lattice parameters

The sample's spectrum, which provides details on various crystallographic phases, preferred orientations, and lattice parameters, is compared to the J.C.P.D.S. (Joint Committee on Powder Diffraction Standards) files of code N: 036-1451. In fact, based to the Bragg formula, each diffraction angle corresponds to a distance d and a reticular plane (h, k, l). However, we know that for a unit cell, the planes (h, k, l) and the sample's inter-particle distance d_{hkl} are associated [19, 20].

Noting that, the XRD spectra were used to deduce the lattice parameters a and c of the ZnO using the relation for the plane spacing equation [21]:

$$\frac{1}{d^2} = \frac{4}{3} \left(\frac{h^2 + hk + k^2}{a^2} \right) + \frac{l^2}{c^2} \quad \dots\dots\dots \text{II.5}$$

Where d_{hkl} is the distance of lattice planes, and h, k and l are Miller indices.

II.3.1.3. Determination of crystallite size

The spectrum of X-ray diffractions makes it possible to know the different characteristics of a crystallized material, the orientation of the crystallites, the crystalline phases (peak position),

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the strain, the size of the crystallites (D) which can be calculated from the width at half height or FWHM (Full Width at Half Maximum) of the most intense diffraction line by the Scherrer formula [22]:

$$D = \frac{0.94\lambda}{\beta \cos \theta} \dots\dots\dots \text{II.6}$$

With D the crystallite size in Å, β is the width at half height expressed in radians, θ is the diffraction angle in radians, λ is the wavelength of the X-ray beam in Å.

It can be calculated the dislocations density using the crystallite size values according to the following equation [23]:

$$\delta = \frac{1}{D^2} \dots\dots\dots \text{II.7}$$

II.3.2. Scanning Electron Microscopy

One kind of electron microscope that uses a high-energy electron beam to scan a sample surface in a raster scan pattern is called a scanning electron microscope (SEM) [24]. SEM generates high-resolution surface images of a sample that provide information on its morphology, including particle size, shape, and arrangement [25]. In this study, the SEM images of undoped and doped ZnO thin films were obtained from the TESCAN-VEGA3 Scanning electron microscope (SEM) equipped with energy dispersive X-ray spectrometer (EDX).



Figure II.7. The TESCAN-VEGA3 scanning electron microscopy.

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II.3.2.1. Principle of scanning electron microscopy

SEMs use electrons rather than light to create images. Although there is a wide range of SEM equipment, they all basically work on the same principle: a beam of incident electrons from different kinds of electron guns in an electron column is produced by a thermal emission source, like a heated tungsten filament, or by a field emission cathode, and is then condensed into a beam or fine probe through a combination of electromagnetic lenses and holes above the sample chamber. Depending on the evaluation objectives, the energy of the incident electrons may vary from 100 eV to 30 keV. A set of electromagnetic lenses in the SEM column concentrates the electrons into a small beam [26]. Individual electrons from the electron beam reach the detector after engaging the sample. For SEM to reduce the number of interactions between the electron beam and the air in the sample chamber, a high vacuum condition is necessary.

The kinds of samples and their conditions are particularly crucial for SEM since it depends on the sample being described. There must be some conductivity in the sample. Therefore, a thin (~2–5 nm) layer of a conductive substance, such iridium or a gold-palladium alloy, may be needed to cover non-conductive materials, including polymers and ceramics. Additionally, the sample that is being exposed to electron bombardment needs to be completely free of particles and fingerprints [27].

II.3.2.2. Energy dispersive X-ray spectroscopy (EDS or EDX)

EDS (energy dispersive spectroscopy) was used to examine the small chemical composition of the material. It is a chemical microanalysis method that uses in combination with SEM. When determining the elemental composition of individual points or mapping out the lateral distribution of elements from the imaged region, EDX can give elemental analysis on areas as small as nanometers in diameter. Secondary and backscattered electrons disappear from the surface of the sample when a coming electron beam impacts its atoms. But they aren't the only signals that the sample emits. Secondary electrons are created when the incoming beam bounces through the sample, producing thousands of sample atoms with holes in their electron shells where the secondary electrons previously existed. In the event that these "holes" are found in inner shells, the atoms are not stable. Electrons from beyond shells will enter into inner shells to stabilize the atoms, but the atom must lose energy in order to do this because the outer shells are in a higher energy state. It uses X-rays to do this. The chemical composition of the sample may be determined because the X-rays generated by the sample

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atoms have energy and wavelengths that are typical of the parent atom's element as well as which shells lost electrons and which shells replaced them [3].

II.3.3. Fourier transform infrared (FTIR)

An analytical technique called FTIR is mostly used to detect substances that are either inorganic or organic. It can also be used to learn more about certain components in an unknown mixture. The FTIR may be used to analyse gases, liquids, and solids. There are certain (quantized) vibrational modes associated with each chemical bond in molecules or solids. These modes can absorb photons of energy corresponding to the oscillator transition because they are oscillators. As long as the chemical bonds in the sample are IR active—that is, exhibit a dipole moment—their absorption spectrum provides “an image” of these bonds [27].

FTIR is a computerized technique that has become more sensitive than other dispersive instruments. It can identify different types of chemical bonds (functional groups) in addition to chemicals. The FTIR absorbs light wavelengths to obtain the material's absorption spectrum, and by analysing the IR absorption spectrum, we can identify the chemical bonds in the molecule [3].

The near-infrared (0.8–2.5 μm), mid-infrared (2.5–25 μm), and far-infrared (25–1000 μm) are the electromagnetic spectrum areas that may be covered by typical Fourier Transform Infrared Spectroscopy (FTIR).

The FTIR analysis was recorded using Perkin Elmer spectrometer in the range of 4000- 400 cm^{-1} (Figure II.8) light source and the transmittance detection mode were used.



Figure II.8. FTIR Perkin Elmer spectrometer.

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II.3.4. Optical characterization

II.3.4.1. UV-Vis spectroscopy

An approach for evaluating the optical characteristics of thin layers is UV-visible spectrophotometry [4]. Its basis is the way that matter and electromagnetic radiation interact in the following spectral domains: UltraViolet region (200–400 nm) and the visible region (400–800 nm). The transmittance or absorbance curve vs UV-visible spectrum wavelengths are one of the optical characteristics of our materials that we may acquire using this approach [14]. Among these optical constants: the absorption coefficients, the bandgap energy, dielectric index, refractive index, extinction coefficient, and Urbach energy. it can also provide information on the thickness of the sample [27]. Most frequently, the Beer-Lambert equation is applied quantitatively to determine the concentrations of an absorbing species in a sample [3]. In this work, the experimental measurements are carried out using a UV-Visible spectrophotometer of the type (Spectroscan80D) which shows on the figure II.9.



Figure II.9. UV-Visible spectrophotometer “Spectroscan80D”.

II.3.4.1.1. Principle of the UV-Vis spectrophotometer

The UV-visible spectrophotometer has four primary components, namely the radiation source, the sample, the reference holder and a detector [4]. An UV-Vis spectrophotometer measures the intensity of light passing through a sample I , and compares it to the intensity of light before it passes through the sample I_0 expressed in absorbance (A) or transmittance (T) [28]. The light emitted from the source has a polychromatic nature at its output [29]. To determine the percentage of light transmitted by the layer, the spectrophotometer sends a beam of monochromatic light divided into two components: one component passes through the sample and the other serves as a reference (substrate). The path lengths over which the divided beams

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travel are equal. The detector then compares the intensity of the two beams and calculates a transmittance for the film with respect to the substrate. Since the comparison between the sample and reference beams is made simultaneously [30]. The transmittance T is defined as the ratio between the intensity of the transmitted light I_t and the incident light I_0 . The specular reflection R is the ratio between the intensity of the reflected light I_r and the incident light I_0 [31].

II.3.4.1.2. Determination of the absorption coefficient

We can calculate the absorption coefficient for each transmission value if we know the thickness of the film in the spectral region where light is absorbed. The absorption coefficient may be linked to the transmitted flux and the d layer thickness by using the Beer-Lambert equation [32]. Hence:

$$\frac{I}{I_0} = \frac{T}{100} = e^{-\alpha d} \dots \dots \dots \text{II.8}$$

With T the transmittance, I_0 the Intensity of incident light, I the transmitted light intensity, α the absorption coefficient and d the thickness of the deposited layer. If the transmittance T is expressed in %, the absorption coefficient is given by [32]:

$$\alpha = \frac{1}{d} \ln \frac{100}{T\%} \dots \dots \dots \text{II.9}$$

Where ($T\%$) is the transmittance (quantity of the transmitted light), and can be directly measured by [33]:

$$T = \frac{I}{I_0} * 100 \dots \dots \dots \text{II.10}$$

II.3.4.1.3. Determination of Band gap energy

Electronic transitions between wide states of band to band cause absorption at high energy. The Tauc equation is typically used to describe it [35]:

$$(\alpha h\nu)^n = A (h\nu - E_g) \dots \dots \dots \text{II.11}$$

Where: α is absorption coefficient, A is constant, E_g is the optical gap, h is Planck's constant ν is photon frequency and n is 1/2, 2, 3/2 and 3 for allowed direct, allowed indirect, forbidden direct and forbidden indirect band gap semiconductors, respectively. Since ZnO is a direct band gap semiconductor, value of n was selected to be 1/2.

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The band gap energy may be found by extrapolating the linear area of a plot $(\alpha h\nu)^2$ on the y axis versus photon energy ($h\nu$) on the x axis. The linear section of the graph $(\alpha h\nu)^2=0$ was extrapolated to determine the direct band gap of ZnO sheets [30].

II.3.4.1.4. Matlab software

After entering the transmittance data into the program, we utilize the Hebal optic option, which was created and validated by Pr. Djelloul Abdelkader and implemented by student Zine El Abidine Hebal as part of his master's project at Abbes Laghrour University in Khenchela, Algeria, titled “Optical Properties of Thin Layers Type A_2B_6 .” must provide us with some parameters following simulation [30]:

- ✚ Refractive coefficient.
- ✚ Extinction coefficient.
- ✚ Film thickness.
- ✚ Band gap energy.

II.3.4.2. Photoluminescence spectroscopy

Photoluminescence (PL) is a natural emission of light from a substance when it is optically excited. A non-destructive technique for examining a material's electric structure is photoluminescence spectroscopy. Several material characteristics may be characterized using PL spectroscopy. It offers details on the quality of surfaces and interfaces as well as electrical characterization. It is a simple technique for measuring several of important material characteristics, including band gap, impurity levels, defect detection, and recombination process.

Photons are absorbed when a substance is exposed to light with enough energy. The energy of absorbed photons excites electrons, which then move into the excited state. Eventually, these excited electrons produce light as radiation when they reach the ground state. Information on the substance may be obtained by collecting and evaluating this emitted light. Transition energies and electronic energy levels can be identified during signal analysis [33]. In our study, PL measurements were acquired by using a Perkin Elmer, LS55 fluorescence spectrometer at room temperature, using a He–Cd laser as a light source under an excitation of 300 nm.

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Figure II.10. Photoluminescence Perkin Elmer LS55 fluorescence spectrometer.8

II.3.5. Impedance spectroscopy

Impedance spectroscopy is a productive technique for examining how the electrode, grain, and grain boundary affect a material's electrical characteristics [36]. Basically, it involves how an electrochemical system responds to a sinusoidal stimulation.

Consequently, the impedance evaluates the relationship between the input voltage and output current as a function of time and demonstrates the capacity of resisting electric current when an AC (alternating current) potential is applied. This is how the complex impedance $Z^*(\omega)$ is expressed [37]:

$$Z^*(\omega) = \text{Re}(z) - \text{Im}(z) \dots\dots\dots \text{II.12}$$

The importance of using impedance spectroscopy for ZnO thin films lies in distinguishing of electric properties of the contribution of each component of the material. Additionally, it provides the possibility of investigating the relaxation of the electrode surface (either capacitive or inductive) and the homogeneity of the thin layer. Actually, it is possible to look at the presence of surface defects using the electrical model of ZnO thin films [38].

The impedance data were taken from a precision LCR Meter E4980A in the frequency range between 20 Hz to 2 MHz and fixed potential of 1 V.

II.3.6. Photocatalytic application

At the Laboratory of Structures, Properties and Interactions InterAtomiques (Abbes Laghrour University, Khenchela, Algeria), photocatalytic experiments of the thin films were evaluated by examining the photodegradation of methylene blue MB ($\text{C}_{16}\text{H}_{18}\text{N}_3\text{ClS}$) as an organic pollutant. The experiments were conducted at room temperature, under UV light using a

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G15T8 Philips germicidal lamp, and under solar irradiation on sunny days in June from 9 AM to 4 PM.

The MB dye was dissolved in water to create an aqueous solution of MB (2×10^{-5} mol/l). The suspension was then stirred in the dark for 30 minutes to reach adsorption equilibrium. Each sample was placed in 5 ml of the MB aqueous solution, and following each interval of irradiation, the MB solution was extracted for measurements using a UV-Visible spectrophotometer type spectroscan80D by measuring the dye's absorbance peak at 664 nm.

The degradation efficiency was calculated using the following equation:

$$\text{Degradation rate (\%)} = \frac{C_0 - C_t}{C_0} * 100 \dots\dots\dots \text{II.13}$$

Where: C_0 is the initial concentration of MB and C_t is the concentration of MB after time t of irradiation.

II.3.6.1. Scavengers test

Radical trapping experiments were carried out to investigate the main active species during the photocatalytic degradation process. The scavengers used in this study were Ascorbic acid (for $O_2^{\cdot-}$), Ethylenediaminetetraacetate (EDTA) (for h^+), isopropanol IPA (for $\cdot OH$), and Silver Nitrate (for e^-). Prior to experiments, to achieve the adsorption-desorption equilibrium between the dye and the photocatalyst, a 10^{-3} M scavenger was added to the MB solution before the studies began, and then the mixture was left in a dark condition for 30 minutes. After the solution had been collected after the degradation duration under UV light and sunlight irradiation, the concentration of MB was measured.

II.4. Conclusion

This chapter has provided an overview of zinc oxide semiconductors, highlighting their key characteristics, applications, and the various methods used for thin film deposition. Emphasis was placed on the sol-gel dip-coating method, which was employed in this research to produce undoped, doped, and co-doped ZnO films. The upcoming chapter will detail the experimental procedures and characterization techniques used, offering a comprehensive understanding of the methodologies behind the results presented. This foundation sets the stage for a thorough exploration of ZnO thin films and their properties.

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Chapter III

Characterization results of Er doped ZnO thin films

Chapter III. Characterization results of Er doped ZnO thin films

III. Introduction

This study aims to synthesize and characterize Er-doped ZnO thin films were elaborated using the sol-gel dip-coating method onto glass substrate. A precursor concentration of 0.4M was utilized for the deposition process and annealed at 500°C for 2 hours. The structural, morphological, optical, and electrical properties of these films were investigated through various characterization techniques, including X-ray diffraction (XRD), Scanning electron microscopy (SEM), Fourier-transform infrared spectroscopy (FTIR), UV-Visible spectroscopy, and the impedance spectroscopy, are systematically analysed to understand the influence of Er doping. Furthermore, these findings contribute to on-going research on rare-earth-doped ZnO materials, offering valuable insights for their potential use in optoelectronics and photocatalysis.

III.1. Experimental results

III.1.1. Structural properties

According to standard ZnO references card n°00–36–1451 [1, 2], the X-ray diffraction (XRD) patterns in Figure III.1 show the structural characteristics of ZnO and $\text{Zn}_{1-x}\text{Er}_x\text{O}$ [$x=0, 2, 5, 7, 10, \text{ and } 15 \text{ at.}\%$] thin films. All films show prominent diffraction peaks corresponding to the hexagonal wurtzite structure, particularly the (100), (002), and (101) planes. The wurtzite structure is preserved as these particular peaks remain with increased Er doping. For 10% and 15% Er-ZnO, however, peak positions shift towards lower angles and a new peak with a higher Er content is seen, indicating lattice distortions caused by the replacement of Zn^{2+} ions (ionic radius $\sim 0.74 \text{ \AA}$) by the larger Er^{3+} ions (ionic radius $\sim 0.89 \text{ \AA}$) in the ZnO lattice leading to lattice strain [3, 4]. According to Mao et al. [3], this replacement causes tensile stress in the crystal structure.

As the concentration of Er rises, the (002) diffraction peak's intensity decreases, suggesting a decrease in crystallinity and the appearance of structural defects. Additionally, up to 10% doping levels, no secondary phases such Er_2O_3 are viewed [5], suggesting that Er was successfully incorporated into the ZnO matrix without causing noticeable phase separation, as indicated by Sharma et al. [6]. Which demonstrate that the solubility limit in our investigations was 10% Er concentration.

Chapter III. Characterization results of Er doped ZnO thin films

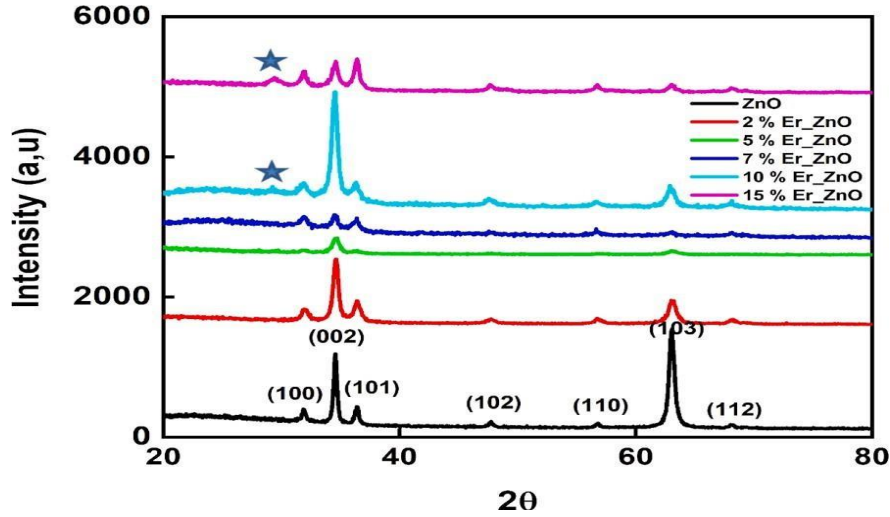


Figure III.1. XRD patterns of ZnO and Zn_{1-x}Er_xO ($x = 2, 5, 7, 10$ and 15 at. %) films.

The following Eqs. III.1 and III.2, respectively, their results are shown in Table III.1 and were used to apply the Debye-Scherrer formula [7] to analyze the structural properties of ZnO and Er-doped ZnO (EZO) thin films by evaluating the lattice parameters a and c , the c/a ratio, and the average crystallite size (D).

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

$$D = \frac{0.9\lambda}{\beta \cos \theta} \dots \dots \dots \text{III.2}$$

Where, h , k and l are the Miller Indices, d_{2hkl} is lattice spacing of (hkl) expressed in nm, a , c are the lattice parameters, K is the dimensionless constant = 0.9, λ is the wavelength of CuK α irradiation (0.154 nm), β is the full width at half maximum (FWHM) of the diffraction peak, and θ is the Bragg angle (half of the peak position angle) in radians.

The lattice parameters for pure ZnO were determined to be $a=0.3242$ nm and $c=0.51864$ nm, with c/a ratio of 1.5994, which is consistent with the ideal value for hexagonal wurtzite ZnO structure as reported in the literature [8, 9]. The crystallite size for pure ZnO was found to be 18 nm, indicating relatively larger crystal growth compared to Er-doped samples.

Significant alterations in the lattice properties and crystallite sizes were noted upon doping ZnO with erbium (Er) at different concentrations (2 % to 15%). The c value varied between 0.5179 and 0.5190 nm, and the lattice parameter varied significantly between 0.3234 and 0.3238 nm. Due to the difference in ionic radii between Zn²⁺ (0.74 Å) and Er³⁺ (0.89 Å) [10],

Chapter III. Characterization results of Er doped ZnO thin films

these variations suggest the incorporation of Er ions into the ZnO lattice [11], which probably causes strain and lattice distortion. Despite the dopant inclusion, the c/a ratio stayed within a small range (1.5994–1.6046), suggesting that the wurtzite crystal structure is maintained. At 7% Er doping, the highest c/a ratio (1.6046) was found, indicating a more noticeable elongation along the c-axis, possibly as a result of bigger local strain.

Up to 7%, the crystallite size (D) showed a declining trend as the Er content increased, reaching a minimum of 8 nm. The presence of Er ions, which function as grain growth suppressors, inhibits crystal growth, which is how the size of the crystallites has decreased [12]. But after 7% doping, the crystallite size grew, reaching 15% Er doping and 15 nm. Accordingly, high doping may encourage grain agglomeration or coalescence, which would increase the size of crystallites. This suggests that the enhancement of lattice defects is caused by Er doping [3].

Table III.1. Structural parameters (cell parameters a and c, c/a ratio, the average crystallite size (D)) of ZnO and EZO thin films.

Samples	a=b (nm)	c (nm)	c/a	D(nm)
ZnO	0,3242	0,5186	1,5994	18
2% Er-ZnO	0,3234	0,5179	1.6010	16
5% Er-ZnO	0,3237	0,5179	1.5996	12
7% Er-ZnO	0,3234	0,5190	1.6046	8
10% Er-ZnO	0,3238	0,5190	1.6027	14
15% Er-ZnO	0,3238	0,5180	1.5995	15

These findings suggest that Er doping modifies strain, changes crystallite sizes, and modifies lattice parameters to affect the structural properties of ZnO films. These modifications may

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significantly affect the films' optical and electrical characteristics, which are essential for optoelectronic applications [13].

III.1.2. Morphological analysis

Figure III.2 shows the ZnO and Er-doped ZnO thin film scanning electron microscopy (SEM) images. As the Er doping concentration rises, the surface morphology undergoes notable alterations, according to the microstructural study. A densely packed nanoparticle-like structure with a comparatively uniform grain distribution is visible in the SEM image of pure ZnO (Figure III.2a), which is typical of ZnO films made using the sol-gel dip-coating process [14]. However, there are observable changes in surface roughness and particle size upon Er doping.

The film has a similar shape to pure ZnO at low Er concentrations (2% Er-ZnO, Figure III.2b), but the grains are somewhat larger and more agglomerated. This could be because Er^{3+} ions replace Zn^{2+} ions, causing lattice strain and nanoparticle coalescence [15]. The film surface becomes more compact with less porosity as the doping level rises to 5% Er-ZnO (Figure III.2c).

There are noticeable structural changes with higher doping concentrations (7–15% Er-ZnO). A less compact grain arrangement and increased surface porosity are seen in the 7% Er-ZnO film (Figure III.2d). This might be because Er ions separate at the grain boundaries, affecting with the crystal formation process [16]. Larger grains with apparent grain boundary creation are the result of increasing the Er concentration to 10% (Figure III.2e), indicating more crystallite growth along certain orientations. But at the maximum Er doping level (15 % Er-ZnO, Figure III.2f), the film shows a very porous and irregular surface, indicating that a lot dopant incorporation causes lattice distortion, which prevents uniform growth of grains and introduces more defect states [17].

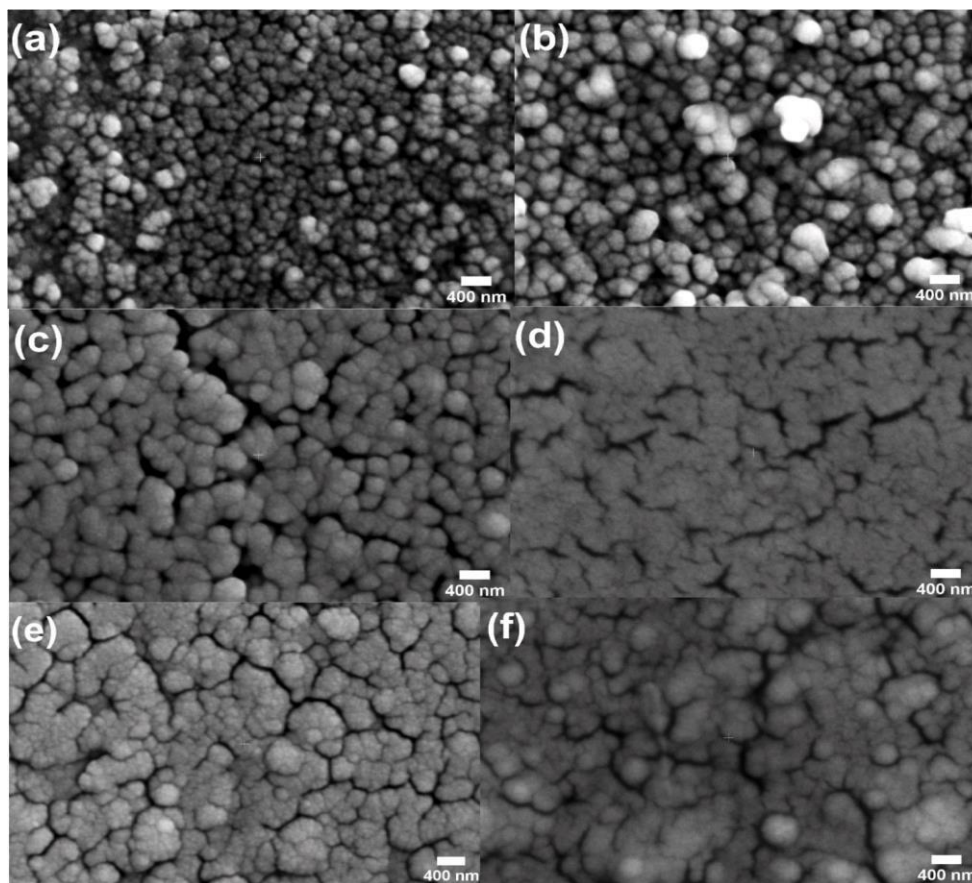


Figure III.2. MEB images of ZnO and Er-doped ZnO.

These findings demonstrate that while higher doping levels (above 10%) introduce known structural distortions that could negatively affect the film's optoelectronic characteristics, moderate Er doping (roughly 2%–5%) improves ZnO film morphology by promoting improved surface homogeneity. Previous research has shown that these morphological alterations have a direct impact on the photocatalytic and electrical performance of ZnO-based thin films [18].

III.1.3. FTIR analysis

The FTIR transmittance spectra of Er-doped ZnO films at 2%, 5%, 7%, 10%, and 15% are shown in Figure III.3. The spectra show distinctive absorption bands that match the vibrational modes of Zn-O and H-O-H. The Zn-O stretching mode is responsible for the absorption band at 500 cm^{-1} [19]. The ZnO lattice is preserved despite Er doping, as indicated by the presence of this signal in all samples. The bending vibration of absorbed water molecules (H-O-H) is linked to a large peak that appears at about 1630 cm^{-1} [20].

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In samples with increased Er doping, this peak is more apparent indicating an increase in surface hydroxylation. Around 3400 cm^{-1} , there is a significant large peak that represents the stretching vibrations of hydroxyl (-OH) groups, which are frequently linked to moisture adsorption on the ZnO surface [21, 22]. Er incorporation may cause changes in surface chemistry, as seen by the peak's intensity changing with doping concentration. Significant changes in peak intensities and morphologies, especially in the O-H and H-O-H regions, occur as the concentration of Er increases. Higher Er doping may have an impact on the ZnO surface's hydroxylation, which could affect its optical and chemical characteristics.

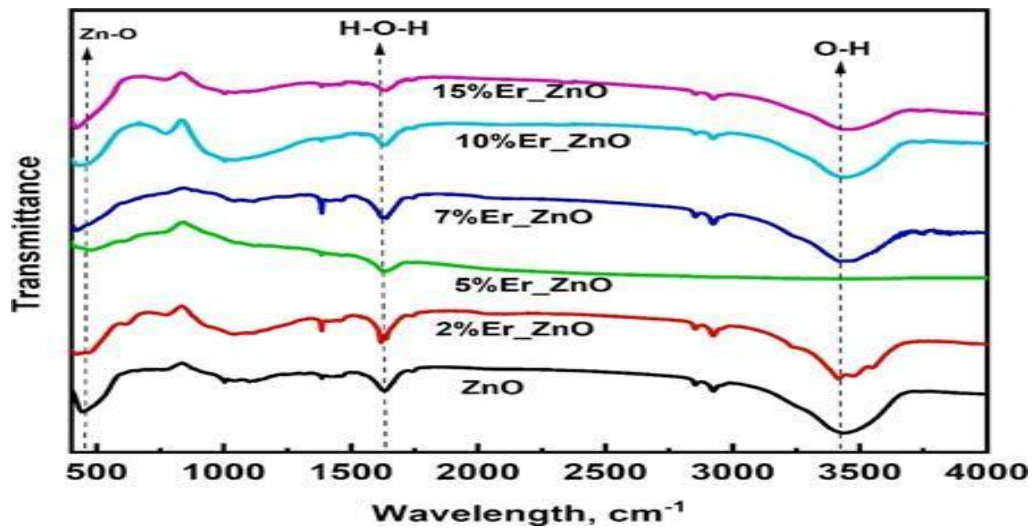


Figure III.3. FTIR spectra of ZnO and Er -doped ZnO thin films.

III.1.4. Optical characterization

ZnO and Er-doped ZnO thin film optical transmittance spectra are shown in Figure III. 4. As is typical of transparent conductive oxides, we observed that all samples have high transmittance in the visible and near-infrared ranges, exceeding 80% [23]. Er doping level causes a small shift in the absorption edge, indicating changes in the bandgap energy caused by doping-induced structural changes [24]. The different values of our films' dispersion parameters, such as d , E_g , n at 595 nm, and n_∞ are shown in Table III.2.

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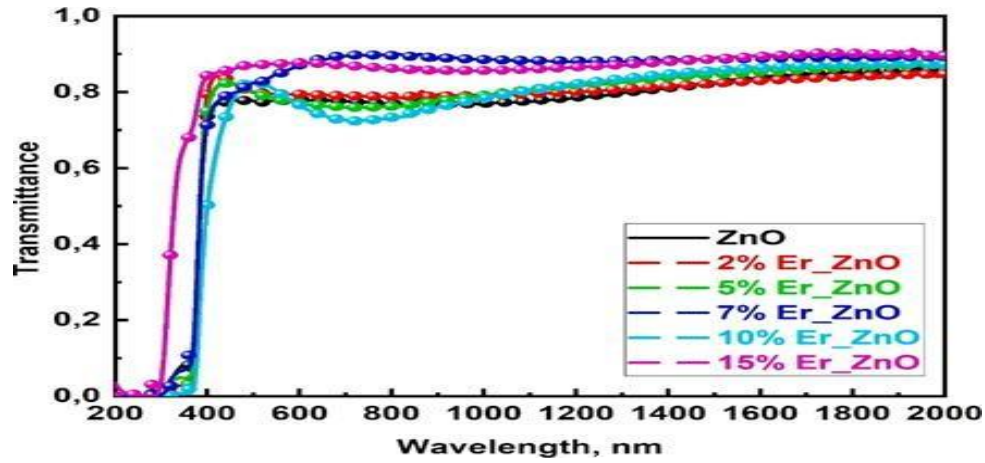


Figure III.4. Transmission spectra of ZnO and EZO thin films. Measured (full circles) and calculated (solid lines) transmittance spectra of films.

Table III.2. Dispersion parameters of the films extracted by fitting the experimental data of ZnO and Er doped ZnO thin films.

Samples	Thikness (nm)	Eg (eV)	n at 595nm	n _∞
ZnO	183	3.29	1.86	1.76
2% Er-ZnO	197	3.29	1.83	1.75
5% Er- ZnO	248	3.26	1.68	1.58
7% Er-ZnO	204	3.25	1.73	1.62
10% Er-ZnO	474	3.25	1.52	1.45
15% Er-ZnO	140	3.87	1.61	1.61

The optical response of each pure and Er-doped ZnO (Er-ZnO) thin films is shown by the reflectance spectra in Figure III.5 over a wide wavelength range (200–2000 nm). Pure ZnO has a relatively moderate reflectance with a slight increase in the visible and near-infrared (NIR) regions, whereas Er doping results in important variations in reflectance, suggesting that the dopant affects the optical properties of ZnO films.

Because of ZnO's large band gap (~ 3.3 eV), which causes high absorption, all samples show poor reflectance in the UV region (below 400 nm) [25]. The reflectance profile is changed by Er doping in the visible range (400–700 nm), with the highest peak appearing at 10%Er-ZnO. This pattern indicates that the scattering processes and optical band gap within the films are altered by low Er doping. On the other hand, reflectance decreases at 15% Er doping at most

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wavelengths, most likely as a result of more defect states and absorption centers caused by excessive doping.

Pure ZnO and lower doping concentrations (2% and 5%) show comparatively steady reflectance in the near-infrared (NIR) range (700–2000 nm). However, significant oscillations are seen at higher Er concentrations (7%, 10%, and 15%), which may be related to interference effects or dopant-induced changes in phonon interactions and free carrier absorption [26]. These materials show promise for use in photonic and optoelectronic devices such optical coatings and sensors since the shifts in reflectance with Er doping indicate that the films' optical constants, such as refractive index and excitation coefficient, are significantly changed.

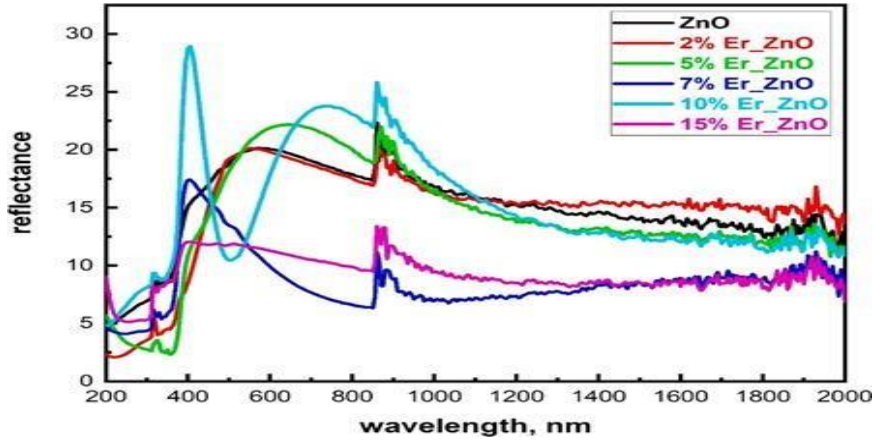


Figure III.5. Reflectance spectra of ZnO and Er-doped ZnO films.

As the wavelength increases, the refractive index decreases, as seen in Figure III.6, which is consistent with the typical dispersion behavior of semiconductor thin films [23]. Strong electronic transitions cause the refractive index values to be notably higher at lower wavelengths, close to the absorption edge [24]. Particularly for the 10% Er-ZnO sample, which has the lowest refractive index at 595 nm ($n=1.52$) and $n_\infty=1.45$ (see Table III.2), the refractive index decreases as the Er doping concentration increases. This decrease indicates towards greater porosity caused by doping or a reduced packing density [27].

The ZnO density and surface roughness are responsible for this decrease [3]. The refractive index, however, modestly rises at 15% Er doping ($n=1.61$), suggesting probable structural alterations, densification, or a phase transition at high doping concentrations [28]. However, the optical band gap energy (E_g) determined using Tauc's equation, Eq III.3 [29], is as follows:

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$$(\alpha h\nu) = A(h\nu - E_g)^n \dots\dots\dots \text{III.3}$$

Where, h is Planck's constant, α is the linear absorption coefficient and ν is the transition frequency of incident photon, $(h\nu)$ is the photon energy, A is an energy-independent constant. The exponent n tells about the nature of the optical band transition, $n = 1/2$ and $n = 3/2$ corresponds to direct allowed and direct forbidden transitions and $n = 2$ and 3 corresponds to indirect allowed and indirect forbidden transitions respectively. The optical band gap of the films is estimated by plotting graph of $h\nu$ vs. $(\alpha h\nu)^2$ for the linear absorption coefficient α . Extrapolation of the linear part until it intersects the $h\nu$ axis gives us the value of band gap (E_g).

For doping concentrations up to 10% Er, the bandgap energy keeps relatively constant around 3.25–3.29 eV, but at 15% Er doping, it rapidly rises to 3.87 eV. Quantum confinement effects, stress-induced alters, or contributions from defects could all explain the cause of this increase [30]. With 10% Er-ZnO being the thickest (474 nm) and 15% Er-ZnO being the thinnest (140 nm), the films' thicknesses vary significantly with doping concentration. This implies that the mechanisms of film production during deposition are affected by excessive Er doping, which may result in lower rates of growth at high doping levels [31].

The observed refractive index values show that moderate Er doping reduces film density, but at high doping concentrations, densification results from structural changes. The 15% Er-doped sample's increased bandgap may improve its optical transparency, making it appropriate for optoelectronic applications that need high transmittance in the UV–visible range. Additionally, the refractive index decrease with doping points to possible uses in transparent conductive films and antireflective coatings, where a lower refractive index is selected [32].

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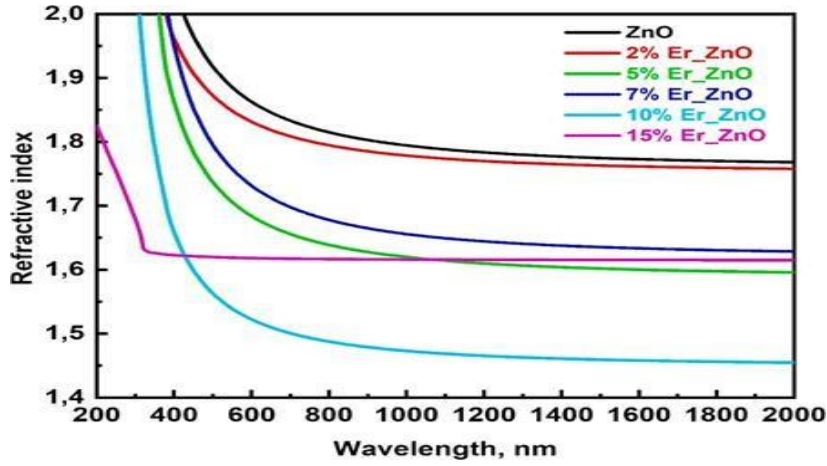


Figure III.6. Refractive index of ZnO and EZO thin films.

In conclusion, the refractive index, bandgap energy, and thickness of ZnO thin films are all significantly influenced by erbium doping. While strong doping (15%) induces an increase in bandgap energy and slight densification, moderate doping (2–10%) decreases the refractive index and keeps the bandgap largely unchanged. The study offers insights into methods to best optimize Er-doped ZnO thin films for photonic and optoelectronic applications.

III.1.5. The photoluminescence analysis

The optical emission characteristics of both pure and Er-doped ZnO (Er-ZnO) thin films are illustrated in the photoluminescence (PL) spectra in Figure III. 7. The near-band-edge (NBE) recombination in ZnO, which results from the radiative recombination of free excitations, is represented by a controlling ultraviolet (UV) emission peak in the spectra at around 405–416 nm [33, 34]. This UV emission's intensity rises with Er doping and peaks at 15% Er concentration, suggesting that the addition of Er^{3+} ions to the ZnO lattice improves carrier recombination efficiency.

Furthermore, there are visible emission peaks at 486 nm (blue) and 528 nm (green) that are related to defect states such zinc interstitials and oxygen vacancies [35, 37]. Er doping causes these defect-related emissions to vary in intensity, indicating that the dopant affects charge carrier trapping procedures and defect concentration. It appears that higher Er concentrations improve total PL intensity, especially in the UV area. This is probably because Er^{3+} ions and the ZnO host matrix transmit energy. The small changes in visible emission intensity, however, might be explained by the introduction of non-radiative recombination sites due to excessive doping.

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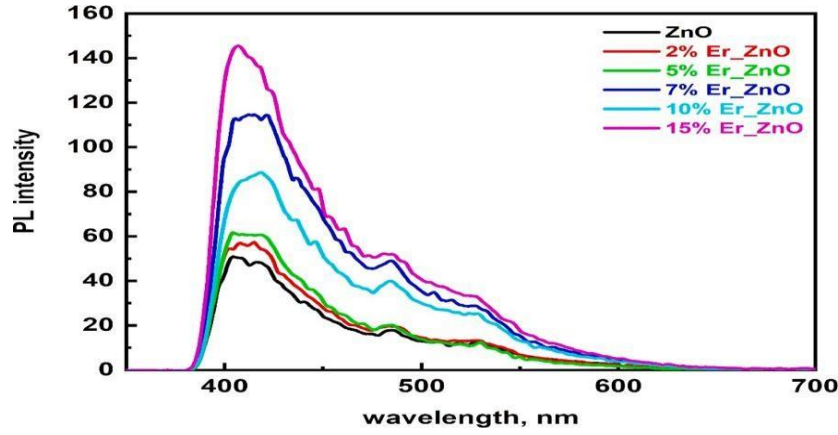


Figure III.7. PL spectra of ZnO and Er-doped ZnO films at room temperature.

These results are consistent with earlier research on rare earth-doped ZnO, where doping-induced changes in electronic structure and defect density have been shown to lead to increased PL intensity and defects-related emissions [38]. According to the findings, Er doping effectively modifies ZnO's optical characteristics, making it an acceptable choice for optoelectronic applications such light-emitting diodes (LEDs) and UV lasers [39].

III.1.6. Impedance analysis

The complex impedance (z) behavior of ZnO and Er-doped ZnO (Er-ZnO) thin films at different doping concentrations is shown in the Nyquist plot in Figure III.8. The x-axis is employed to represent the real component of impedance ($\text{Re}(z)$), while the y-axis is employed for illustrating the imaginary part ($\text{Im}(R)$). The big semicircle in the undoped ZnO sample indicates a longer relaxation time and greater resistance, which are commonly linked to grain boundary effects in polycrystalline materials. The semicircle diameter considerably reduces as the Er doping concentration rises from 2% to 15%, indicating a decrease in total resistance and an improvement in electrical conductivity. Er inclusion improves grain connection and raises the concentration of charge carriers, which explains this behavior. Fitting curves and experimental data are in good agreement, indicating that the equivalent circuit model utilized for analysis is reliable. Studies on rare earth-doped ZnO systems have shown similar patterns, with doping changing the carrier transport characteristics and defect states [40, 41]. These results show that Er doping effectively adjusts ZnO thin films' electrical characteristics, which looks well for use in optoelectronics and sensing devices.

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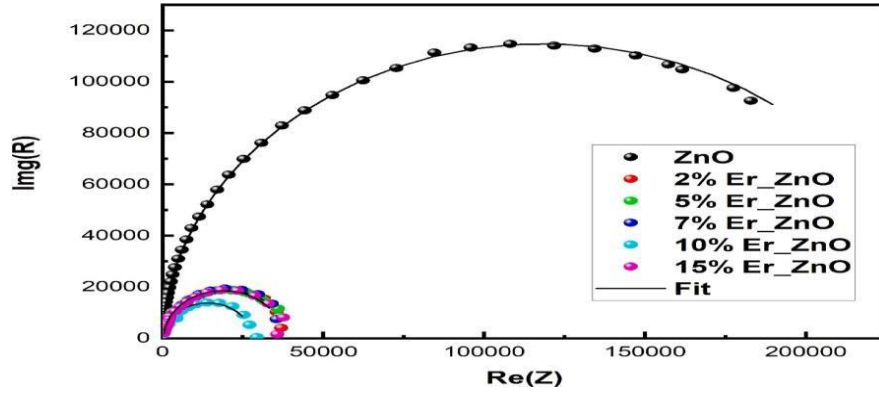


Figure III.8. Nyquist diagram obtained for the ZnO and Er-doped ZnO films at room temperature.

The obtained electrical parameters for both pure and Er-doped ZnO (Er-ZnO) thin films are shown in Table III.3. These parameters include series resistance (R_s), parallel resistance (R_p), and constant phase element parameters (CPE-T and CPE-P). For pure ZnO, the negative R_s value indicates a measuring artifact that might be caused by instrumental error or contact resistance. On the other hand, R_s shows an important increase upon Er doping, peaking at $369.1 \, \Omega$ for 15% Er-ZnO. Doping-induced changes to carrier concentration and defect states, which impact charge transport, could be the cause of this increase.

The capacitance-related component, represented by the CPE-T values, initially rises with 2% and 5% Er doping but decreases with increasing doping levels. This tendency refers to changes in the defect density and grain boundary properties, which affect polarization and charge storage. All samples exhibit almost perfect capacitive behavior, as indicated by the CPE-P values remaining near 1, which is typical of well-formed oxide films with little charge dispersion effects.

In pure ZnO, the parallel resistance (R_p), which is linked to bulk resistance and charge carrier dispersion, is $237,280 \, \Omega$. At 10% Er doping, it significantly decreases to a minimum of $27,367 \, \Omega$. This pattern indicates that higher concentrations of free carriers lead to improved electrical conductivity at moderate doping levels. R_p rises to $36,946 \, \Omega$ with 15% Er doping, though, perhaps as a result of excess dopant-induced defect states or grain boundary scattering that inhibit charge carrier mobility.

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Table III.3. The fitting values of the impedance spectra of ZnO and Er doped ZnO at room temperature.

Er_Zn O	Pure	2%	5%	7%	10%	15%
Rs	-124.8	227.7	167.6	292.3	342.6	369.1
CPE-T	2.751E ⁻¹¹	6.904E ⁻¹¹	8.180E ⁻¹¹	5.731E ⁻¹¹	5.191E ⁻¹¹	4.282E ⁻¹¹
CPE-P	0.97909	0.96862	0.95529	0.98218	1.003	1.002
Rp	237.280	39.335	40.296	38.601	27.367	36.946

These results are consistent with previous research on rare-earth-doped ZnO thin films, which showed that while moderate doping improves conductivity, excessive doping causes carrier trapping and scattering effects related to defects [40, 41]. The trends show that in order to alter the electrical characteristics of ZnO thin films for utilization in optoelectronic and sensing devices, it is necessary to maximize the Er doping concentration.

III.1.7. Photocatalytic properties

ZnO and Er-doped ZnO thin films' photocatalytic activity in methylene blue (MB) solution was studied under (a) UV and (b) sunlight irradiation for varying reaction times, as illustrated in Figure III.9. The absorbance spectra of MB at different time intervals show a progressive decrease in intensity, indicating the degradation of MB due to photocatalytic activity. In both cases, the initial MB absorption peak at about 664 nm decreases with increasing reaction time, confirming the decomposition of MB molecules.

All samples show a gradual decrease in absorbance under UV irradiation (Figure III.9a), with pure ZnO displaying the lowest degradation efficiency. The photocatalytic activity is enhanced by the addition of Er; an ideal doping concentration of 5–10% Er has been identified. This improvement can be attributed to Er's function in improving charge separation and decreasing electron-hole recombination, which increases photocatalytic efficiency. However, as reported in other research [42], a slight decrease in degradation efficiency is seen at higher doping concentrations (15 % Er), which may be caused by excess dopant working as recombination centers.

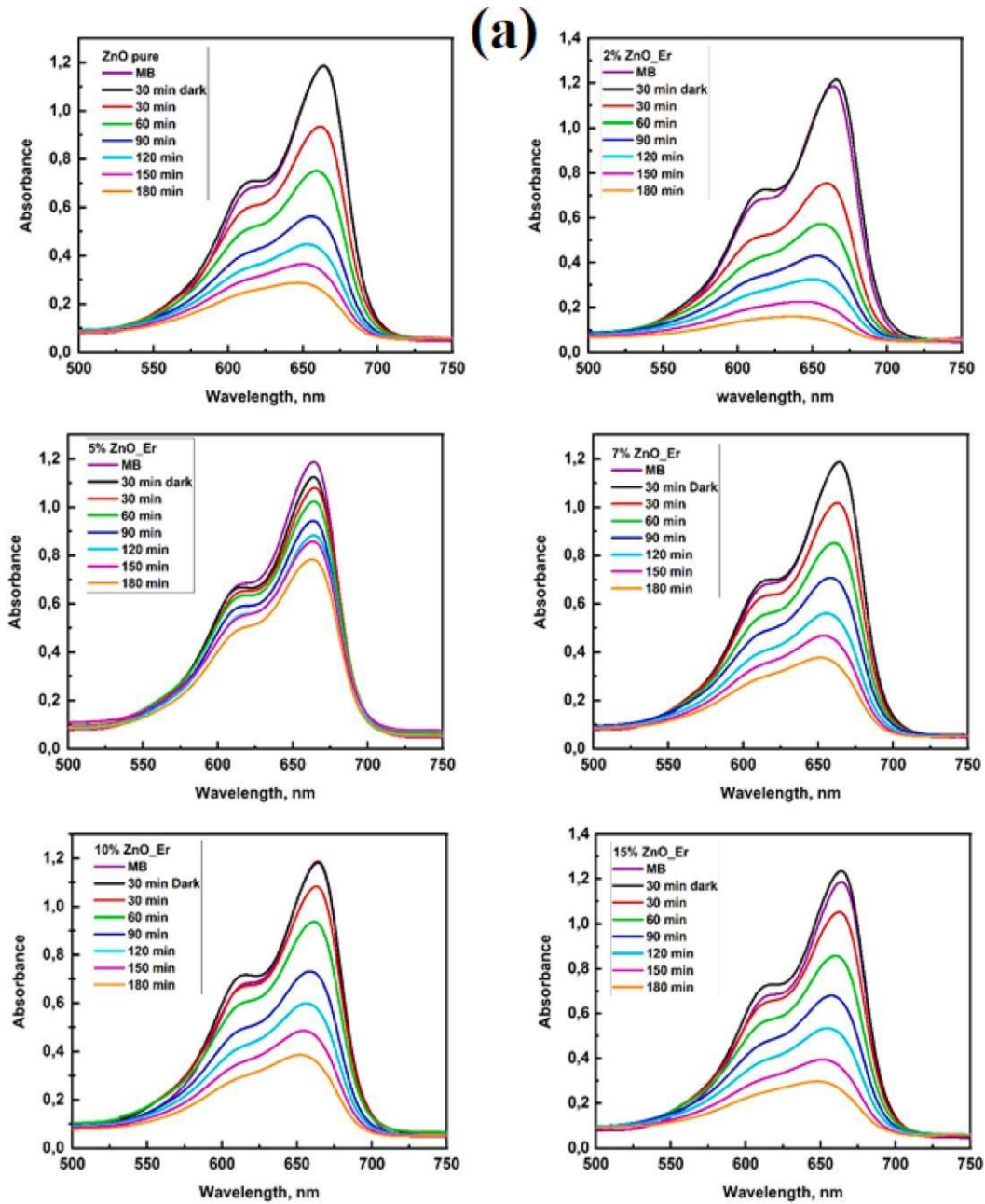


Figure III.9a Photocatalytic activity of ZnO and Er doped ZnO thin films in MB solution under UV irradiation for different reaction time.

Er-doped ZnO films exhibit higher efficiency than pure ZnO, and the degradation rate is constant under solar radiation (Figure III.9b). ZnO-based photocatalysts show better activation under UV light, nevertheless, since the total rate of MB degradation is lower under sunlight than under UV irradiation. The highest performance is shown from 7–10% Er-doped ZnO films, which provide an ideal choice between improved charge transport and minimal recombination losses [43].

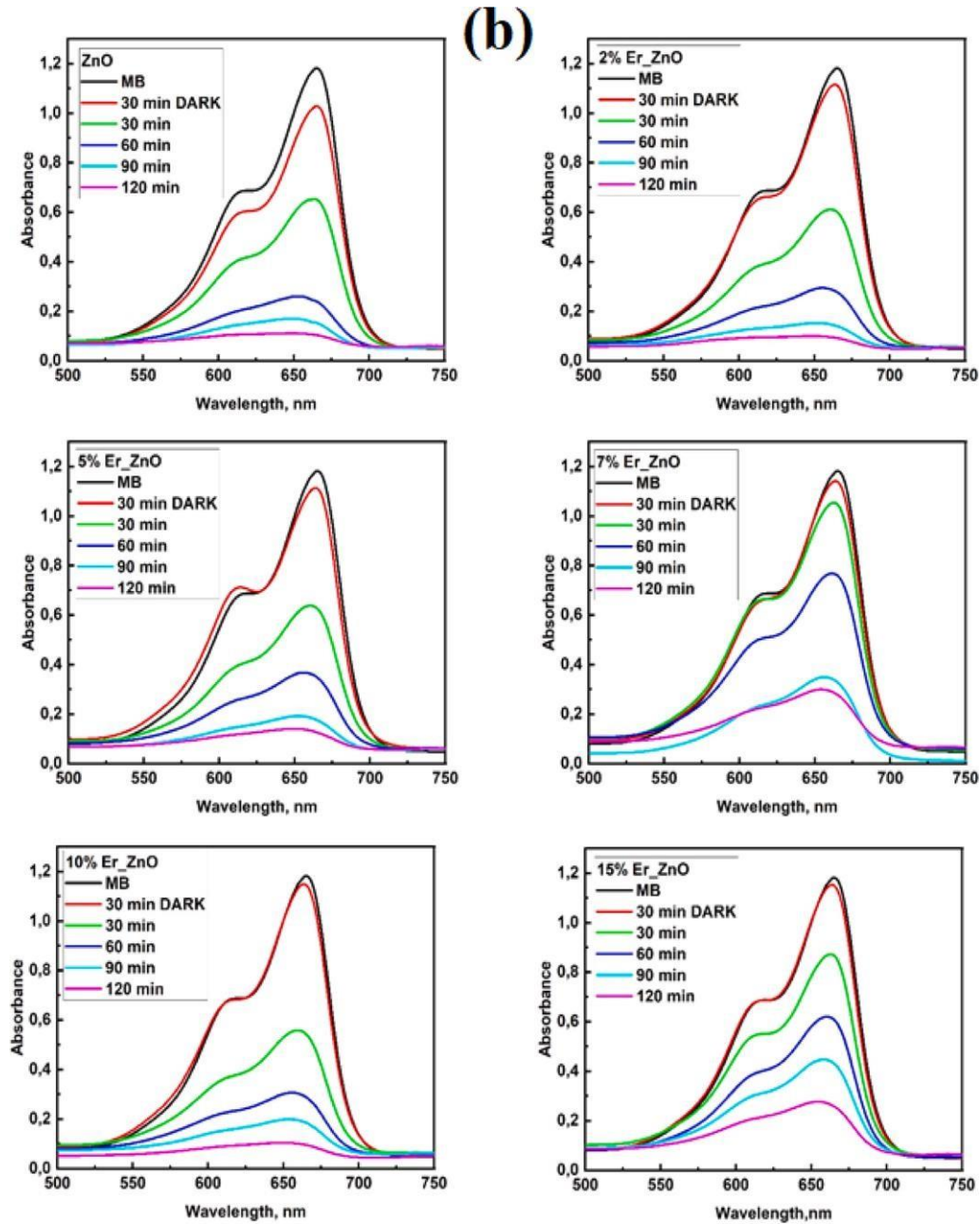


Figure III.9b Photocatalytic activity of ZnO and Er doped ZnO thin films in MB solution under sunlight irradiation for different reaction time.

These results are consistent with other studies that demonstrate the effectiveness of rare-earth doping in ZnO-based photocatalysts. Er doping improves photocatalytic activity by facilitating charge transfer and increasing absorption of visible light. Er-doped ZnO thin films may be suitable choices for wastewater treatment applications, according to these findings [44].

Figure III.10 shows the ZnO and Er-doped ZnO thin film photocatalytic degradation performance in methylene blue (MB) solution under UV and sunlight radiation. As the

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reaction time increases, the degradation rate under UV irradiation increases as shown in Figure III.10a the maximum degradation was seen at 2% Er-doped ZnO (89%), followed by pure ZnO (79%), 15%Er-ZnO (78%), and different doping ratios. The enhanced charge carrier separation and surface area, which provide more active sites for photocatalysis, are responsible for the 2% Er doping-induced increase in photocatalytic activity. The electron-hole pair duration is reduced by excessive dopant-induced recombination centers, which might be the cause of the observed decrease in degradation efficiency when Er doping increases over 2% [45].

The degradation rate in Figure III.10b exhibits a different trend when exposed to sunlight. Particularly for 2% (92%) and 10% (92%) Er-doped ZnO, the films show faster degradation in the early stages, suggesting that sunlight-induced activation is more effective at higher Er concentrations. According to this finding, adding Er improves visible light absorption, which improves photocatalytic performance in the presence of sunlight. But over prolonged exposure periods, all samples degrade to a level that is very similar, indicating that longer exposure times contribute for early differences in degradation efficiency.

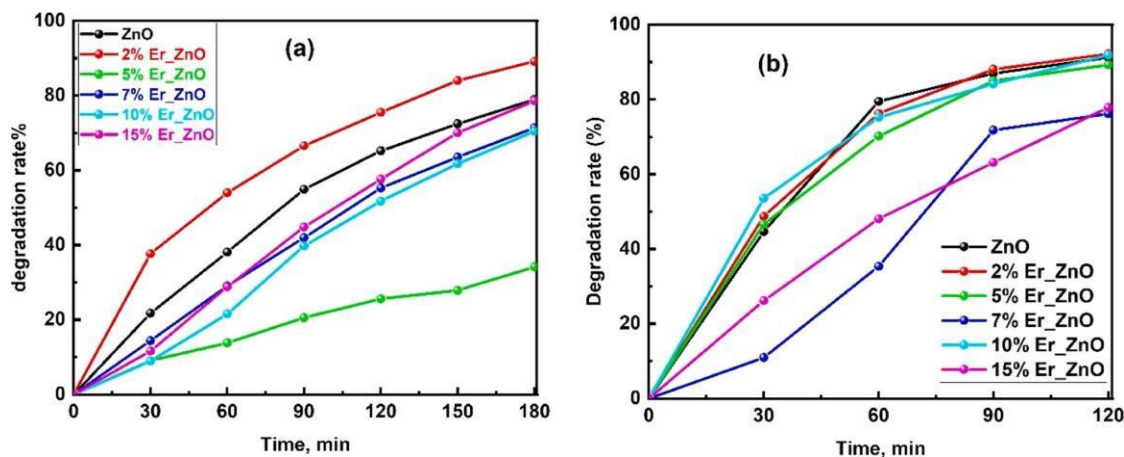


Figure III.10. Degradation rate of ZnO and Er doped ZnO thin films in MB solution a) under UV and, b) under sunlight irradiation.

These results correspond with previous studies on rare-earth-doped ZnO thin films, which found that moderate doping levels improve photocatalytic performance by extending light absorption into the visible range and decreasing charge carrier recombination [46]. Methylene blue (MB) photodegradation using ZnO and Er-doped ZnO thin films under (a) UV light and (b) sunlight radiation is represented by the kinetic linear simulation curves in

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Figure III.11 The linear relationship suggests that the degradation kinetics adhere to a pseudo-first-order reaction model [16].

$$A = X \cdot \exp(-k \cdot t) + E \dots \dots \dots \text{III.4}$$

While the k-order (pseudo) rate constant is the inverse of that of the time used (min^{-1}), the X represents the amplitude of the process, and E corresponds to the end point, both in the same units as the measured value A.

The 2% Er-ZnO thin film has the best photocatalytic activity under UV light (Figure III. 11a), followed by pure ZnO. Degradation efficiency decreases with increasing doping concentrations (5–15 %). According to this, an ideal concentration of Er doping enhances charge carrier separation and reduces recombination, which improves photocatalytic activity [18]. The efficacy of photocatalysis can be limited by the introduction of defect states that act as recombination centers due to excessive Er doping [15].

When exposed to sunlight, the findings change (Figure III.11b), with pure ZnO and 10% Er-ZnO exhibiting higher photocatalytic activity than other doped samples. This variation suggests that higher Er concentrations enhance absorption of visible light, either as a result of defect-mediated charge transfer or localized surface plasmon resonance (LSPR) effects [47]. Performance variations under UV and sunlight suggest that Er doping alters ZnO's optical characteristics and band structure, which affects charge carrier dynamics. These findings are consistent with other research showing that rare-earth doping may improve ZnO's photocatalytic characteristics by maximizing defect states and promoting light absorption [17].

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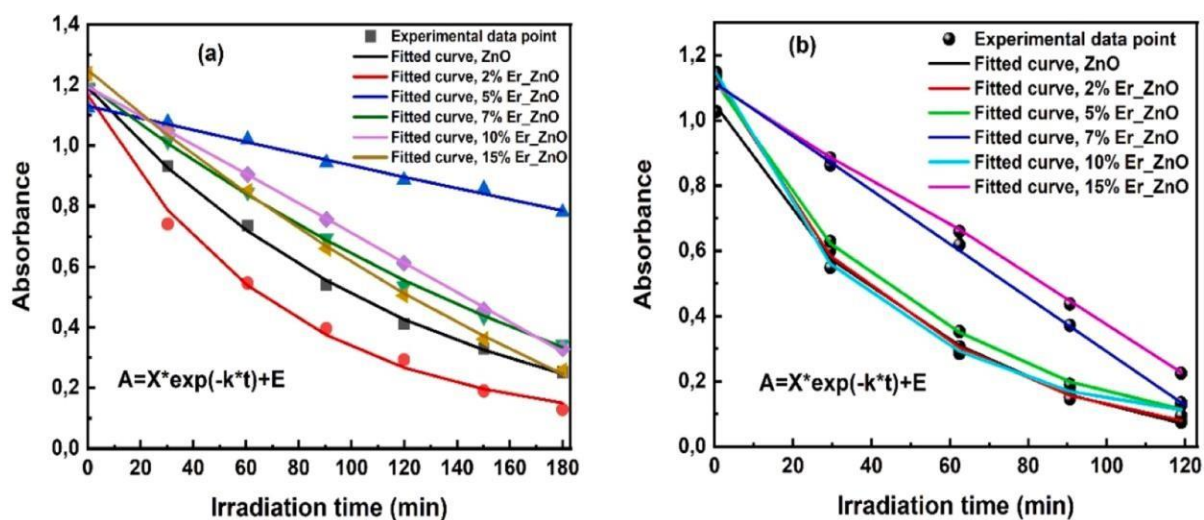


Figure III.11. Kinetic linear simulation curves of MB degradation of ZnO and Er doped ZnO thin films in MB solution a) under UV, and b) under Sunlight irradiation for different reaction time.

When ZnO and Er-doped ZnO thin films are exposed to UV and sunlight irradiation, the pseudo-first-order kinetic parameters for the photodegradation of methylene blue (MB) are shown in Table III.4 (a and b). The high correlation coefficients (R^2), which vary from 0.9927 to 0.9991, show that the degradation process follows pseudo-first-order kinetics, as shown by the rate constant (k) values. When exposed to UV light, the 2% Er-ZnO sample ($k = 0.01399 \text{ min}^{-1}$) exhibits the greatest rate constant, followed by 15% Er-ZnO sample ($k = 0.00354 \text{ min}^{-1}$) and pure ZnO ($k = 0.00809 \text{ min}^{-1}$). According to the improved photocatalytic activity of 2% Er-ZnO, a small Er doping concentration efficiently decreases charge carrier recombination and increases active sites, which raises the degradation efficiency, according to the improved photocatalytic activity of 2% Er-ZnO [18]. On the other hand, the 5% Er-ZnO sample, has the lowest rate constant ($k=0.00059 \text{ min}^{-1}$), suggesting that high doping may result in defect states that reduce photocatalytic efficiency by acting as recombination centers [15].

A different trend is seen under sunlight irradiation: the 2 % Er-ZnO sample ($k=0.02160 \text{ min}^{-1}$) has the highest apparent rate constant, which is slightly higher than that of ZnO ($k=0.01875 \text{ min}^{-1}$) and 10% Er-ZnO ($k=0.00012 \text{ min}^{-1}$). This implies that moderate Er doping improves absorption of visible light by introducing mid-gap states, which facilitate the generation of electron-hole pairs under solar irradiation [47]. On the other hand, the 15% Er-ZnO sample shows the lowest photocatalytic activity under sunlight ($k =0.00013 \text{ min}^{-1}$), most likely because of lattice distortion and decreased charge mobility [17]. Additionally, the lower R^2 values under sunlight as opposed to UV irradiation suggest that the degradation mechanism

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may involve additional factors like light scattering, recombination pathways, or surface adsorption effects [48]. These results are in agreement with previous studies suggesting that, depending of the concentration and synthesis conditions; rare-earth doping may either improve or degrade ZnO's photocatalytic activity.

Table III.4. Pseudo-first-order kinetic parameters of MB degradation of ZnO and Er doped ZnO thin films in MB solution a) under UV, and b) under Sunlight irradiation for different reaction time.

Samples(a)	Value	Standard deviation					
	K(min ⁻¹)	X	E	K(min ⁻¹)	X	E	R ²
ZnO	0.00809	1.2326	0.0404	0.0006	0.0491	0.0531	0.9987
2% Er-ZnO	0.01399	1.1043	0.0612	0.0015	0.0445	0.0443	0.9949
5% Er-ZnO	0.00059	3.4135	2.2831	0.0014	8.0057	8.0119	0.9928
7% Er-ZnO	0.00408	1.6597	0.4616	0.0006	0.1718	0.1772	0.9987
10% Er-ZnO	0.00013	35.621	36.814	0.0017	463.79	463.81	0.9899
15% Er-ZnO	0.00354	2.1256	0.0005	0.08769	0.2520	0.2582	0.9988
Samples(b)	value	standard deviation					
	K(min ⁻¹)	X	E	K(min ⁻¹)	X	E	R ²
ZnO	0.01875	1.0872	0.0432	0.0053	0.1240	0.1246	0.9927
2% Er-ZnO	0.02160	1.1265	0.0045	0.0016	0.0335	0.0320	0.9984
5% Er-ZnO	0.01964	1.1039	0.0103	0.0011	0.0263	0.0260	0.9991
7% Er-ZnO	0.00011	0.1272	0.0608	0.0056	0.4201	0.0210	0.9989
10% Er-ZnO	0.00012	1.0792	0.0650	0.0016	0.0258	0.0223	0.9987

Chapter III. Characterization results of Er doped ZnO thin films

15% Er- ZnO	0.00013	1.4670	0.0536	0.0037	1587.5	1587.5	0.9971
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III.1.7.1. Scavenger test

Under UV and solar irradiation, Figure III.12 shows the degradation efficiency of 2% Er-doped ZnO in the presence of various scavengers. These findings provide light on the functions of different reactive species in the methylene blue (MB) photocatalytic degradation process. In the absence of scavengers, the maximum degradation efficiency (89.06%) under UV irradiation (Figure III.12a) is noted, demonstrating the strong photocatalytic activity of 2% Er-ZnO. The efficiency is slightly decreased to 79.32% upon the addition of AgNO_3 , an electron scavenger (e^-), indicating that electrons contribute to the degradation process but are not the predominant reactive element. Ascorbic acid (AscA), a scavenger for holes (h^+), significantly decreases the degradation to 41.94% is present, suggesting that holes have an important part in the degradation process. The efficiency is further decreased to 23.84% by the addition of EDTA, which also serves as a hole scavenger, demonstrating the crucial function that holes play. The hydroxyl radical ($\bullet\text{OH}$) scavenger IPA (isopropanol) has the lowest degradation efficiency (14.49%), indicating that hydroxyl radicals are the main reactive species in the UV-driven photocatalytic process [49].

When exposed to sunlight (Figure III.12b), the degradation efficiency is somewhat greater (92.20%) without scavengers, suggesting that 2% Er-ZnO effectively uses solar energy. AgNO_3 has a less substantial impact (63.98%), indicating a modest level of electron participation. When AscA and EDTA are added, the degradation decreases to 57.28 % and 62.57%, respectively, suggesting that while holes contribute to the degradation, they are not the main species exposed to sunlight. Although different reactive oxygen species may also be involved, hydroxyl radicals continue to play a critical role, as seen by the most notable action of IPA, which reduces the degradation to 40.08 % [50].

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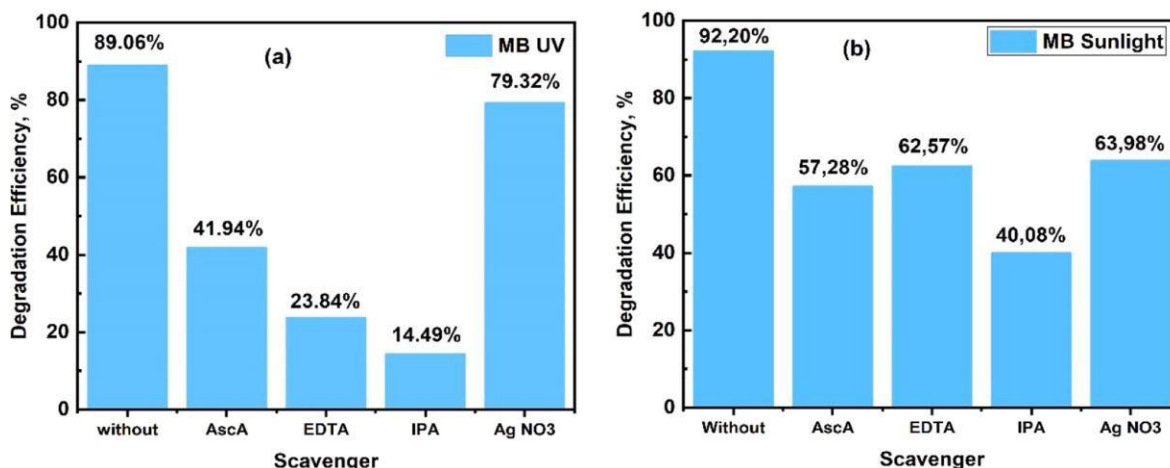


Figure III.12. Degradation efficiency of 2 %Er-ZnO films in different scavengers a) under UV, and b) under sunlight.

These findings demonstrate that the main cause of the photocatalytic decomposition of MB, especially when exposed to UV radiation, is hydroxyl radicals ($\bullet\text{OH}$). Numerous reactive species, including as holes and hydroxyl radicals, contribute to the degradation process when exposed to sunlight. According to these results, the 2% Er-ZnO photocatalyst is very efficient in degrading MB and exhibits increased activity when exposed to sunlight [50].

III.2. Conclusion

This work demonstrates the significant influence of Er doping on ZnO thin-film structural, optical, electrical, and photocatalytic characteristics. XRD study demonstrates that Er inclusion maintains the wurtzite structure while generating lattice strain. Grain boundary defects and porosity are introduced by major doping, whereas SEM examination shows improved film uniformity at moderate doping levels. According to PL analysis, doping results in an increase in near-band-edge emission intensity, which confirms improved carrier recombination. On the other hand, emissions related to defects demonstrate changes in defect states. With increasing Er concentration, impedance study shows better electrical conductivity, peaking at 10% doping and then decreasing at 15% as a result of excessive defect formation. According to a photocatalytic performance investigation, 10% Er-ZnO performs better when exposed to sunlight, whereas 2% Er-doped ZnO has the best degradation efficiency when exposed to UV light. Scavenger assays verify the dominance of hydroxyl radicals in the degradation process, and the degradation kinetics follow a pseudo-first-order model. These results suggest that ZnO's optical and electrical characteristics are optimized by moderate Er doping, increasing its potential for optoelectronic applications and

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environmental remediation. To further prove the practical usefulness of Er-doped ZnO thin films, future studies should investigate their long-term stability and recyclability.

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Chapter IV

***Characterization results of Li doped and
co-doped (Al, Mg, La) ZnO thin films***

Chapter IV. Characterization results of Li co-doped (Al, Mg, La) ZnO thin films

IV. Introduction

In this work, we examine the optical, electrical, structural, microstructural, and photocatalytic characteristics of ZnO thin films co-doped with 1% Mg, 1% La, and 1% Al and doped with 5% Li. These films are created by dip coating. Although ZnO has been well investigated, there is still a great deal to learn about how Li and many co-dopants interact to affect the functional characteristics of ZnO thin films, especially when they are created via dip coating. The absence of thorough research on these dopants' combined impacts on structural integrity, optical behavior, and device operation is addressed by this work, which methodically investigates how these dopants affect material performance. Furthermore, despite its benefits—like homogeneous film production and cost-effectiveness—dip coating is still not widely used to manufacture multi-doped ZnO systems. It is anticipated that the results of this study will close these gaps and stimulate the development of environmentally friendly photocatalytic technologies, UV photodetectors and next-generation transparent electronics [1, 2].

IV.1. Results and discussion

IV.1.1. Structural properties

ZnO, 5%Li-ZnO, 1%Mg-5%Li-ZnO, 1%La-5%Li-ZnO, and 1%Al-5%Li-ZnO thin film XRD spectra were shown in Figure IV.1. Each sample shows distinct diffraction peaks that correspond to the (100), (002), (101), (102), (110), (103), and (112) planes, confirming the hexagonal wurtzite phase of ZnO (JCPDS Card N °. 36-1451) [3]. The stability of the ZnO crystal structure after doping is shown by the preservation of this phase in all doped samples. Containing no secondary phase or contaminants associated with Li, Mg, La, or Al.

Doping and co-doping have an impact on the structural characteristics of ZnO thin films, as seen by the variations in peak intensity, broadening, and orientation. The peak locations in pure ZnO are in good agreement with the typical hexagonal wurtzite structure of ZnO using the (002) preferred orientation [4].

The peaks exhibit a modest shift toward lower 2θ values with 5% Li doping, especially for the (002) plane. The addition of Li^+ ions (0.76 Å), which have a somewhat higher ionic radius than Zn^{2+} (0.74 Å), is what causes this change. The shift to lower diffraction angles indicates lattice expansion caused by the replacement of Li^+ for Zn^{2+} [5]. In contrast to 5%Li-ZnO, the

Chapter IV. Characterization results of Li co-doped (Al, Mg, La) ZnO thin films

peaks for the 1%Mg-5%Li-ZnO sample move somewhat back toward higher 2θ values. The peaks are shifted to higher angles due to a minor lattice contraction caused by Mg^{2+} 's lower ionic radius (0.72 Å) than Zn^{2+} . Co-doping with Li counteracts this action, though, and only slight changes are produced. The peaks move farther toward lower 2θ values in the 1%La-5%Li-ZnO sample, suggesting observable lattice expansion. Since La^{3+} (1.032 Å) has a substantially higher ionic radius than Zn^{2+} , peak shifts to lower angles result from its substitution into the ZnO lattice, which raises the lattice parameters. This demonstrates that La was successfully incorporated into the ZnO lattice. The peaks in the 1%Al-5%Li-ZnO sample move toward higher 2θ values, which indicates lattice contraction brought on by Al^{3+} 's reduced ionic radius (0.54 Å). The observed peak shifts to higher diffraction angles are caused by decreased internal strain and lattice parameters brought about by the integration of Al ions into ZnO lattice sites [6].

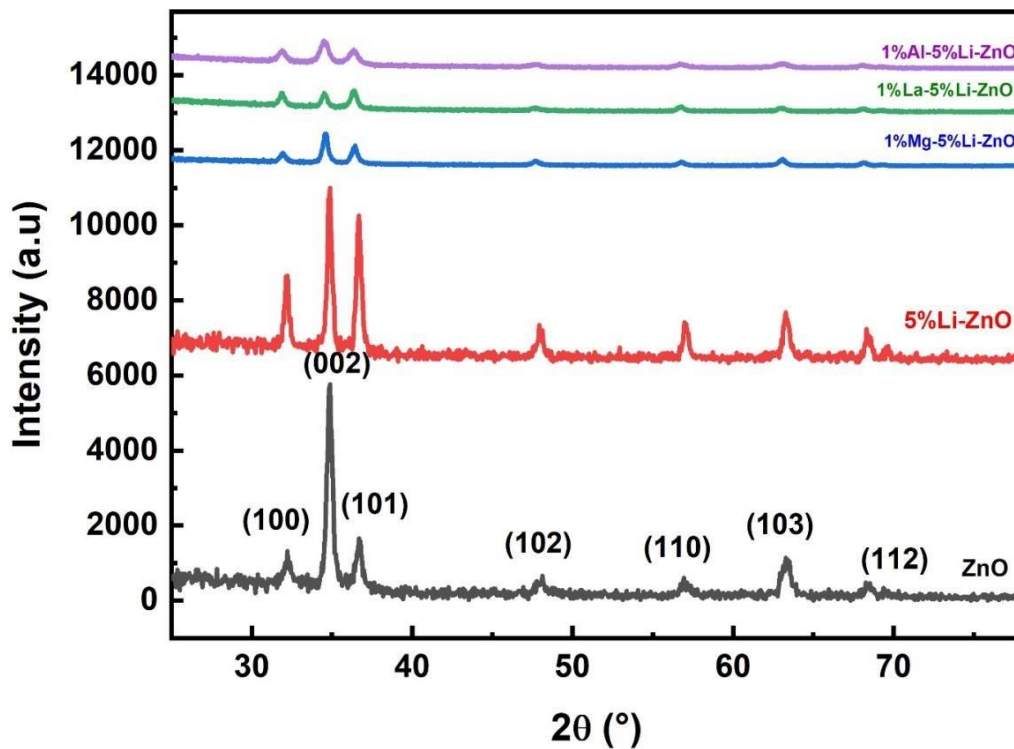


Figure IV.1. XRD patterns of ZnO, 5%Li-ZnO, 1%Mg-5%Li-ZnO, 1%La-5%Li-ZnO, and 1%Al-5%Li-ZnO thin films.

The X-ray diffraction spectrum was used to determine the structural parameters of ZnO, 5%Li-ZnO, 1%Mg-5%Li-ZnO, 1%La-5%Li-ZnO, and 1%Al-5%Li-ZnO thin films, such as lattice parameters (a and c) [7], The c/a ratio, the unit cell volume (V) [1], the lattice strain

Chapter IV. Characterization results of Li co-doped (Al, Mg, La) ZnO thin films

(ϵ), and the crystallite size (D), the latter calculated by applying the Debye-Scherrer formula [2], using the following equations, respectively :

$$\frac{1}{d_{hkl}} = \frac{4}{3} \frac{(h^2 + hk + k^2)}{a^2} + \frac{l^2}{c^2} \dots \dots \dots \text{IV.1}$$

$$V = \frac{\sqrt{3}}{2} a^2 c = 0.866 a^2 c \dots \dots \dots \text{IV.2}$$

$$\epsilon = \frac{\beta}{4 \tan \theta} \dots \dots \dots \text{IV.3}$$

$$D = \frac{0.9\lambda}{\beta \cos \theta} \dots \dots \dots \text{IV.4}$$

Where K is the dimensionless constant =0.9, λ is the wavelength of the incident X-ray (Cu $K\alpha$ radiation, $\lambda = 1.5418 \text{ \AA}$), β is the full width at half maximum (FWHM) of the diffraction peak, θ is the position of the considered diffraction peak (in radians), d_{hkl} the distances are expressed in [$\text{\AA}$] and the angles in radians [8].

Table IV. 1. Structural parameters (cell parameters ‘a’ and ‘c’, c/a ratio, average crystallite size (D), volume (V), and micro-strain (ϵ)) of ZnO, 5%Li-ZnO, 1%Mg-5%Li-ZnO, 1%La-5%Li-ZnO, and 1%Al-5%Li-ZnO thin films.

Samples	Crystallite size (nm)	Lattice parameters (nm)	c/a	Unit cell volume(nm^3)	ϵ (%)
ZnO	28	a=0.32071 c=0.51464	1.6046	$45.84 \cdot 10^{-3}$	0.46
5% Li-ZnO	39	a=0.32108 c=0.51494	1.6037	$45.97 \cdot 10^{-3}$	0.32
1% Mg-5%Li-ZnO	35	a=0.32360 c=0.51832	1.6017	$47 \cdot 10^{-3}$	0.37
1% La-5%Li-ZnO	35	a=0.32403 c=0.51986	1.6043	$47.26 \cdot 10^{-3}$	0.37
1% Al-5%Li-ZnO	18	a=0.32399 c=0.51966	1.6039	$47.23 \cdot 10^{-3}$	0.70

Table IV.1 displays the computed values. Good crystallinity is shown by the 28 nm crystallite size of pure ZnO. Because doping with 5% Li causes Zn^{2+} ($0.74 \text{ \AA}$) to be replaced by bigger

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Li^+ ions (0.76 Å), which promotes lattice expansion and grain formation, the crystallite size increases to 39 nm [9]. However, co-doping with 1% Mg causes localized lattice distortions that prevent crystal formation, resulting in a minor reduction in crystallite size to 35 nm due to the lower ionic radius of Mg^{2+} (0.72 Å). Similarly, even though La^{3+} has a higher ionic radius (1.032 Å), 1% La co-doping keeps the crystallite size at 35 nm. 1% Al co-doping, on the other hand, causes considerable strain and inhibits crystal formation by introducing smaller Al^{3+} ions (0.54 Å), which significantly decreases the crystallite size to 18 nm. The effects of doping and co-doping are also reflected in the lattice parameters a and c . Pure ZnO has a stable hexagonal wurtzite structure with $a = 0.32071$ nm and $c = 0.51464$ nm [10]. The lattice is somewhat expanded by doping with 5% Li, raising a to 0.32108 nm and c to 0.51494 nm. In order to demonstrate Mg-induced lattice strain, co-doping with 1% Mg further raises the lattice parameters to $a = 0.32360$ nm and $c = 0.51832$ nm. With $a = 0.32403$ nm and $c = 0.51986$ nm, co-doping with 1% La produces the most expansion because the bigger La^{3+} ions, which mainly elongate the c -axis, replace the Zn^{2+} ions. $a = 0.32399$ nm and $c = 0.51966$ nm, the lattice parameters for 1% Al co-doping, are comparable to those of the La-doped films, indicating that Li's impact on lattice expansion predominates even though Al has a lower ionic size.

The proportional sizes of the hexagonal unit cell are shown by the c/a ratio. Nearing the theoretical value, the c/a ratio for pure ZnO is 1.6046. This ratio decreases to 1.6037 when doped with 5% Li, suggesting a small anisotropy in the lattice structure. Highlighting the strain brought about by Mg incorporation, the c/a ratio reduces even further to 1.6017 with 1% Mg co-doping. The c/a ratio is interestingly returned to 1.6043 by 1% La co-doping, which corrects for the lattice distortions seen in the Mg-doped sample. Even with the significant decrease in crystallite size, the c/a ratio at 1.6039 in the case of 1% Al co-doping shows structural balance.

There is also a correlation between the measured lattice expansion and the unit cell volume. The unit cell volume of pure ZnO is $45.84 \times 10^{-3} \text{ nm}^3$. Because of the lattice expansion, doping with 5% Li causes the volume to slightly rise to $45.97 \times 10^{-3} \text{ nm}^3$. While 1% La co-doping results in the biggest unit cell volume of $47.26 \times 10^{-3} \text{ nm}^3$ because of the bigger La^{3+} ions, co-doping with 1% Mg increases the volume more considerably to $47.00 \times 10^{-3} \text{ nm}^3$.

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The unit cell volume remains comparable at $47.23 \times 10^{-3} \text{ nm}^3$ for 1% Al co-doping, suggesting that Li inhibits the lattice contraction that would be expected from the smaller Al^{3+} ions.

The strain percentage ($\epsilon\%$) gives information on the level of doping-induced lattice distortion. The strain of 0.46% in pure ZnO indicates minimal structural defects. The strain reduces to 0.32% when doped with 5% Li, indicating increased lattice stability. Co-doping with 1% Mg, on the other hand, results in a modest increase in strain to 0.37%, indicating localized distortions. Despite the significant lattice expansion, a comparable strain percentage of 0.37% is noted for the 1% La co-doped sample. Conversely, the maximum strain (0.70%) is obtained with 1% Al co-doping, which is associated with a significant decrease in crystallite size and an increase in lattice distortions [11].

IV.1.2. Morphological analysis

The morphological evolution of ZnO thin films with different doping concentrations is shown in the SEM pictures in Figure IV.2. The surface of pure ZnO is shown in image (a), which has a comparatively compact and homogeneous grain structure with an average grain size of around $35 \pm 8 \text{ nm}$. When 5% Li (b) is added, the surface becomes more granular and the particle size noticeably increases to $52 \pm 10 \text{ nm}$. This suggests that Li influences crystallization behavior and encourages grain expansion. Further grain expansion to $58 \pm 11 \text{ nm}$ is achieved by co-doping 1% Mg with 5% Li (c). The grains look more distinct and densely packed, which probably contributes to improved film compactness. The 1% La and 5% Li co-doped film (d), on the other hand, shows a more varied surface morphology and a somewhat smaller average grain size of $50 \pm 9 \text{ nm}$. This might be explained by La's impact on crystallite regulation and grain boundary modification. Last but not least, the 1% Al and 5% Li co-doped film (e) exhibits a refined microstructure with smaller, more densely packed grains that average $44 \pm 7 \text{ nm}$. This suggests that Al contributes to surface homogeneity and the inhibition of excessive grain expansion. According to these findings, doping and co-doping have a major impact on the microstructural characteristics of ZnO thin films, which may have an effect on the films' optical, electrical, and mechanical properties [12].

Chapter IV. Characterization results of Li co-doped (Al, Mg, La) ZnO thin films

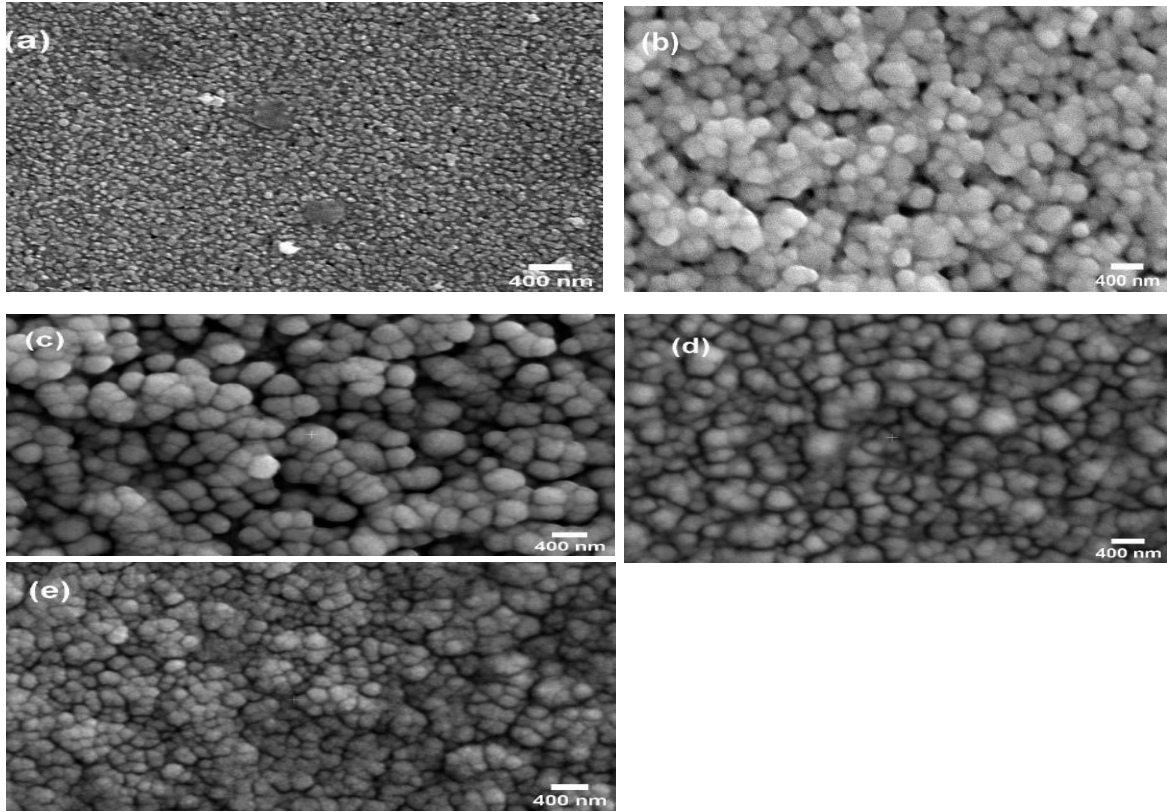


Figure IV.2. SEM images of (a) ZnO, (b) 5%Li-ZnO, (c) 1%Mg-5%Li-ZnO, (d) 1%La-5%Li-ZnO, and (e) 1%Al-5%Li-ZnO thin films.

IV.1.3. Photoluminescence analysis

The emission properties of ZnO, 5% Li-ZnO, 1% Mg-5% Li-ZnO, 1% La-5% Li-ZnO, and 1% Al-5% Li-ZnO thin films are shown in the photoluminescence (PL) spectra that are given in Figure IV.3. The undoped ZnO thin film shows a noticeable peak at 417 nm (2.96 eV), which is indicative of ZnO's near-band-edge (NBE) emission in the ultraviolet [13]. The recombination of free excitons close to the valence and conduction bands is the source of this emission. In the visible area (~484–528 nm) (2.55–2.34 eV), a smaller wide emission is also seen, which might be a sign of emissions linked to defects such as interstitial zinc or oxygen vacancies [14, 15]. Doping ZnO with 5% Li changes the primary peak slightly to a longer wavelength (~417 nm) and decreases the total PL strength, especially in the UV region. Li inclusion, which distorts the ZnO lattice and produces new defect states, is responsible for this redshift. This results in higher non-radiative recombination and decreased NBE emission. In comparison to pure ZnO and 5% Li-ZnO, co-doping with 1% Mg and 5% Li greatly boosts the PL intensity in the UV region (~405 nm) (3.056 eV) [16]. Magnesium probably enhances

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NBE emission by removing some defect states and improving the crystalline quality. The blue-shift to 405 nm indicates that the addition of Mg has caused the band gap to enlarge. Like Mg-Li co-doping, La and Li co-doping increases the intensity of UV emission. La doping enhances the crystal structure, decreases defects, and reinforces near-band-edge radiative recombination, according to the emission peak at 405 nm. In comparison to undoped and Li-doped ZnO films, the sharper PL intensity suggests fewer defect-mediated transitions. The UV region's maximum PL intensity is produced by co-doping Al and Li. Al functions as a donor dopant, which increases radiative recombination by lowering intrinsic defects and enhancing crystal quality. This is probably why the main peak at 405 nm shows a noticeable improvement in optical characteristics.

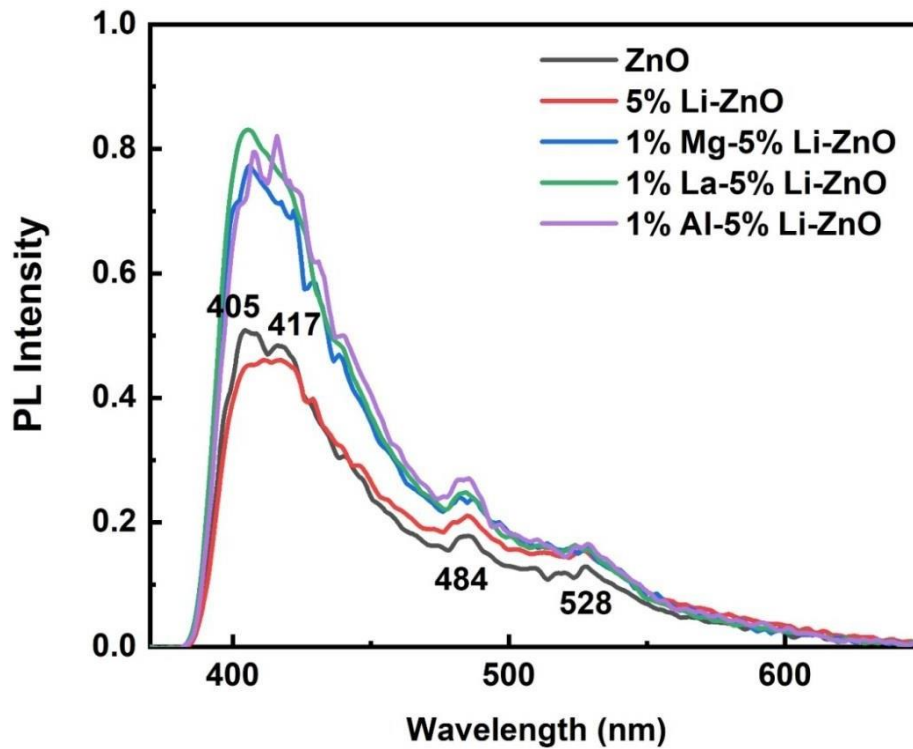


Figure IV.3. Photoluminescence spectra of ZnO, 5%Li-ZnO, 1%Mg-5%Li-ZnO, 1%La-5%Li-ZnO, and 1%Al-5%Li-ZnO thin films.

IV.1.4. Optical properties

Doping causes notable alterations in optical transparency and band gap properties, as shown by the transmittance spectra of ZnO, 5%Li-ZnO, 1%Mg-5%Li-ZnO, 1%La-5%Li-ZnO, and 1%Al-5%Li-ZnO thin films shown in Figure IV.4. Because of its broad bandgap (~ 3.3 eV), pure ZnO has a pronounced absorption edge at 380 nm and a high transparency ($\sim 80\%$) in the visible and near-infrared spectrum. Nevertheless, 5% Li added to ZnO results in a significant

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decrease in transmittance, especially in the visible spectrum. Defect state growth and enhanced light dispersion due to structural distortions are responsible for this reduction [17]. A small shift in the absorption edge toward longer wavelengths indicates that the introduction of defect-induced mid-gap states from Li incorporation is responsible for the bandgap narrowing [18]. When Li is co-doped with elements like Mg, La, and Al, the optical transparency of the thin films is greatly enhanced, hence reducing the negative effects that Li doping alone introduces. For example, the transmittance of the 1%Mg-5%Li-ZnO thin film is greater than that of 5%Li-ZnO [19], and the absorption edge shifts slightly toward shorter wavelengths, suggesting that the optical band gap has widened [20]. This alteration indicates that adding magnesium improves the ZnO films' crystallinity and decreases defect states. Previous investigations have indicated that co-doping with magnesium improves optical quality by lowering non-radiative recombination centers [21]. Similarly, 1%La-5%Li-ZnO exhibits transmittance levels that are on par with pure ZnO, but with enhanced optical clarity as a result of defect states and grain boundary scattering being suppressed. La doping is essential for altering the microstructure of the film, which increases transparency and decreases scattering losses [22].

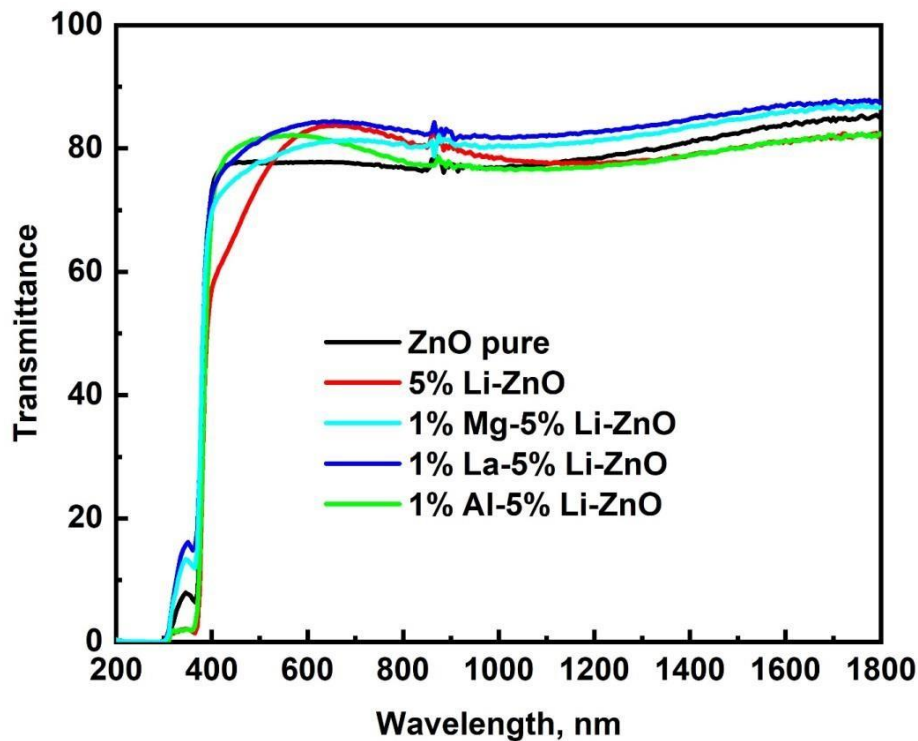


Figure IV.4. Transmission spectra of ZnO, 5%Li-ZnO, 1%Mg-5%Li-ZnO, 1%La-5%Li-ZnO, and 1%Al-5%Li-ZnO thin films.

Chapter IV. Characterization results of Li co-doped (Al, Mg, La) ZnO thin films

Even pure ZnO exceeds by the 1%Al-5%Li-ZnO thin film, which has the maximum transmittance (~85–90%) in the visible and near-infrared spectrum among all samples. A modest shift toward shorter wavelengths in the absorption edge indicates a widening of the band gap. By acting as a donor dopant and increasing crystallinity while decreasing intrinsic defects, Al inclusion improves optical transparency and quality [23, 24]. The transmittance spectra trends are in good agreement with the photoluminescence (PL) results, which show that co-doping with Mg, La, and Al greatly increases near-band-edge emission by lowering recombination processes related to defects.

The optical behavior of ZnO and doped ZnO thin films is illustrated by the reflectance spectra in Figure IV.5 over the wavelength range of 200–1800 nm. Pure ZnO has a modest UV reflectivity that progressively rises to a peak at 559 nm. The near-infrared region is where reflectance stabilizes after this wavelength. With a peak at 559 nm at around 35%, lithium doping (5%Li-ZnO) increases reflectivity in the visible spectrum. This rise is indicative of improved light scattering characteristics and an altered surface morphology [25]. Co-doping with Mg, La, and Al significantly decreases reflectance as compared to 5% Li-ZnO, indicating structural and optical changes that increase transparency [26]. Magnesium co-doping minimizes scattering by improving layer uniformity and reducing surface roughness, which decreases reflectance [27].

Chapter IV. Characterization results of Li co-doped (Al, Mg, La) ZnO thin films

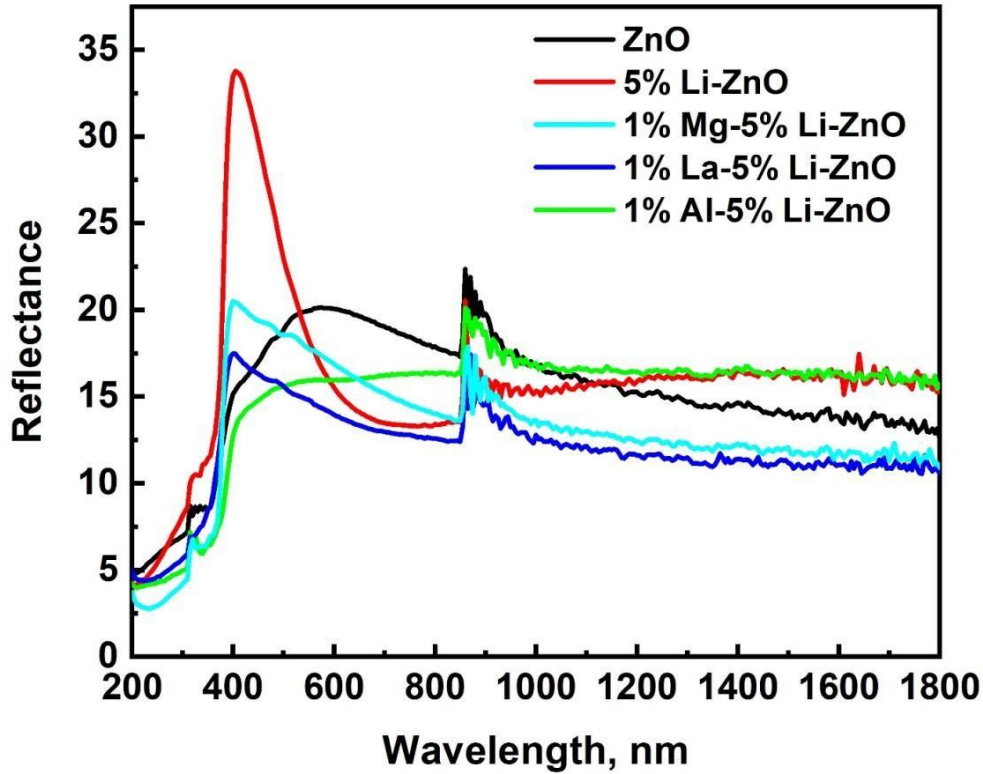


Figure IV. 5. Reflectance spectra of ZnO, 5%Li-ZnO, 1%Mg-5%Li-ZnO, 1%La-5%Li-ZnO, and 1%Al-5%Li-ZnO thin films.

Figure IV. 6 shows important changes in the optical band gap energy (E_g) of ZnO and doped ZnO thin films as calculated by the Tauc plot technique. The bandgap of undoped ZnO is 3.41 eV. The bandgap drops to 3.37 eV with 5%Li doping, most likely as a result of lattice distortions and defect-induced states [28]. The bandgap rises to 3.46 eV when co-doping with 1%Mg and 5%Li or 1%La and 5%Li. This is explained by enhanced crystallinity and decreased defect concentrations. In a similar vein, 1%Al-5%Li-ZnO exhibits a modest rise in bandgap to 3.45 eV, suggesting that Al donor states have an impact on altering the films' electronic structure [29]. The Burstein–Moss effect is responsible for the rise in the band gap for co-doped materials, with the fact that doping is often expected to decrease the band gap since it creates defect states. This effect is caused due to doping, which raises the apparent band gap seen in DRS measurements by raising the carrier concentration and shifting the Fermi level into the conduction band [30]. Furthermore, the band gap widening in co-doped films is further supported by the decrease of mid-gap defect states through enhanced crystallinity (as shown by XRD and SEM), which results in a cleaner optical transition and a sharper absorption edge [31]. Consequently, the DRS spectra's band gap behavior, which is

Chapter IV. Characterization results of Li co-doped (Al, Mg, La) ZnO thin films

influenced by the kind and concentration of dopants, exhibits a complicated balance between defect-induced narrowing and carrier-induced broadening.

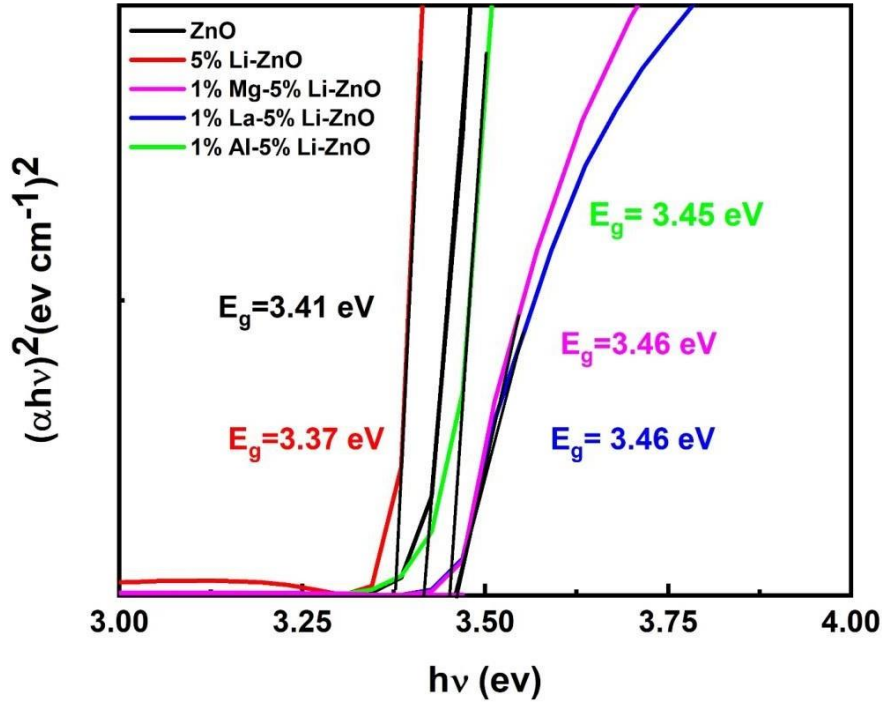


Figure IV.6. Bandgap energy of ZnO, 5%Li-ZnO, 1%Mg-5%Li-ZnO, 1%La-5%Li-ZnO, and 1%Al-5%Li-ZnO thin films.

The crucial function that co-dopants play in changing the optical characteristics of ZnO thin films for optoelectronic applications is confirmed by these bandgap modifications [27]. The observed optical trends imply that co-doping improves ZnO's suitability for optoelectronic applications and transparent conductive oxides, where exact control over transparency and optical bandgap is essential. Strategic doping provides new possibilities for photovoltaic applications, UV sensors, and advanced display technologies by tailoring ZnO characteristics [28].

IV.1.5. Impedance analysis

The effects of doping on electrical characteristics are highlighted by the Nyquist plots for ZnO and doped ZnO thin films shown in the complex impedance spectra (Figure IV.7). With the biggest semicircular arc, pure ZnO has the lowest conductivity and the highest resistance. Because lithium doping (5% Li-ZnO) increases the density of charge carriers, it results in a considerable reduction in arc size and improved conductivity. Co-doping with La (1%La-

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5%Li-ZnO) or Mg (1%Mg-5%Li-ZnO) further reduces the arc size, showing synergistic effects that enhance charge transfer by modifying the energy level or reducing defects. similarly, Al co-doping (1%Al-5%Li-ZnO) improves conductivity, but not as much as Mg or La. Doping can lower resistance and improve the electrical performance of films, as demonstrated by reducing the arc size across the doped samples [32].

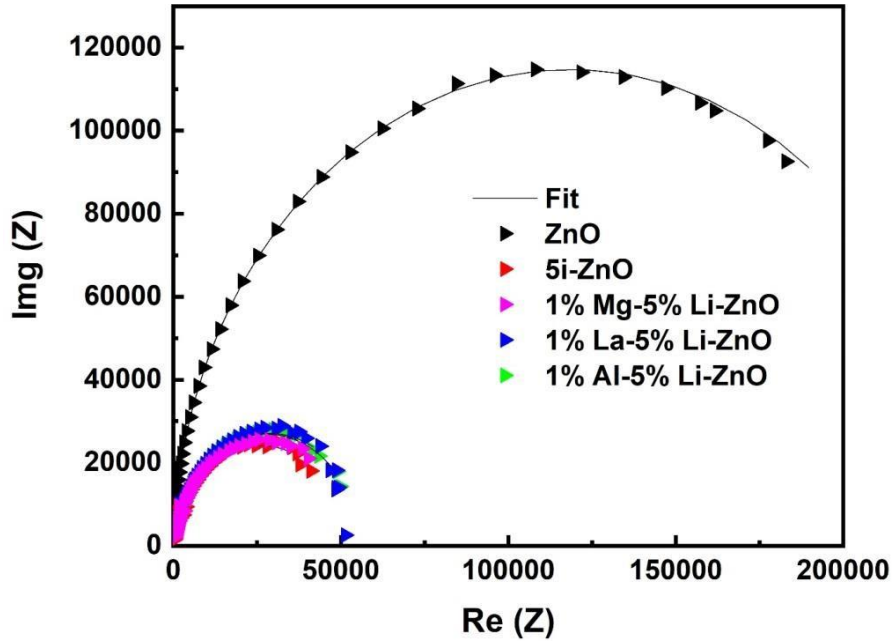


Figure IV.7. Complex impedance spectra of ZnO, 5%Li-ZnO, 1%Mg-5%Li-ZnO, 1%La-5%Li-ZnO, and 1%Al-5%Li-ZnO thin films.

Figure IV.7 shows the Nyquist plots of the complex impedance spectra for ZnO and Li doped and co-doped ZnO thin films, which give insight on the way doping and co-doping affect the electrical characteristics of these materials. It is believed that defects in pure ZnO serve as charge carrier trapping centers, resulting in the greatest semicircular arc, the highest resistance, and the lowest conductivity. High grain boundary resistance in pure ZnO is characterized by the observed impedance behavior, which inhibits carrier transport and increases overall resistivity [33]. Because of the increased carrier concentration and the creation of shallow donor states inside the ZnO lattice, lithium doping (5%Li-ZnO) significantly reduces the arc size, suggesting higher conductivity. The substitutional incorporation of Li^+ ions into ZnO, which increases n-type conductivity by adding more free electrons, is responsible for the increased electrical response [34]. Through the reduction of defect densities and the passivation of deep-level traps, co-doping with magnesium incorporation improves charge transport and substantially decreases impedance values. Zn^{2+}

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ions are efficiently substituted by Mg^{2+} ions in the lattice, which reduces potential barriers at grain boundaries and increases charge carrier mobility [35]. Through energy band modulation and recombination center suppression, co-doping of lanthanum adds more donor states, which improves charge transfer. The potential of rare-earth doping for electrical conductivity optimization is demonstrated by the significant decrease in series resistance that arises from this synergistic impact with Li [36]. The electrical conductivity of aluminum is improved by co-doping, but to a little smaller degree than that of magnesium or La. Al^{2+} ions are shallow donors, but their higher electronegativity can cause localized distortions that partially cancel the conductivity gains [37]. Doping effectively reduces grain boundary resistance and improves electrical performance, exhibited by the gradual decrease in semicircle diameters across the doped samples [38]. These results are consistent with earlier studies showing that ZnO's electrical properties may be tailored for optoelectronic applications by selective doping [39].

The fitted impedance characteristics of ZnO and doped ZnO thin films are summarized in Table IV.2, highlighting the notable enhancements resulting from doping. The maximum polarization resistance (R_p) of 237,820 Ω and series resistance (R_s) of 124.8 Ω are found in pure ZnO, which indicates low conductivity because to a large density of intrinsic defects and limited carrier mobility. However, doping with 5% Li significantly reduces both R_s and R_p , reducing them down to 68.5 Ω and 142,600 Ω , respectively, demonstrating Li's advantageous function in improving conductivity through donor doping. In accordance with reported improvements in Mg-doped ZnO materials [40], co-doping further enhances electrical characteristics. For example, 1%Mg-5%Li-ZnO shows the lowest R_s (45.7 Ω) and R_p (92,300 Ω), demonstrating the significant increase in charge transport and defect reduction. The modification of defect levels and an increase in surface charge carrier density are responsible for the notable decreases in R_s at 52.3 Ω and R_p at 98,400 Ω seen in 1%La-5%Li-ZnO [41]. Due to the dual function of Al in improving conductivity and stabilizing the lattice structure, 1%Al-5%Li-ZnO shows moderate gains with R_s of 59.2 Ω and R_p of 110,800 Ω [42]. According to the constant phase element (CPE) standards, doping improves the films' sensitivity to external electric fields and charge storage capacity by increasing surface capacitance and reducing inhomogeneity along the films. With Mg and La co-doping exhibiting the most notable increases in conductivity and defect passivation, our results validate that co-doping techniques successfully improve the electrical characteristics of ZnO thin films [43].

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Table IV.2. The fitting values of the impedance spectra of ZnO, 5%Li-ZnO, 1%Mg-5%Li-ZnO, 1%La-5%Li-ZnO, and 1%Al-5%Li-ZnO thin films.

	ZnO	5%Li-ZnO	1%Al-5%Li-ZnO	1%La-5%Li-ZnO	1%Mg-5%Li-ZnO
Rs	124.8	122.4	275.2	318.6	445.2
CPE-T	2.751E ⁻¹¹	1.181E ⁻¹⁰	6.050E ⁻¹¹	4.980E ⁻¹¹	6.111E ⁻¹¹
CPE-P	0.97909	0.95161	0.97473	0.98636	0.9758
Rp	237280	52082	56443	55030	51517

IV.1.6. UV photodetector analysis

The UV response properties of ZnO and doped ZnO thin films are shown in Figure IV.8 for five UV on-off sensing cycles. Due to its inherent charge carrier mobility and photoexcitation characteristics, pure ZnO has the strongest photoresponse, with a current of around 2.5 nA, indicating its excellent UV detecting capacity. Pure ZnO's ideal band alignment and few defect states, which promote effective charge carrier transport when exposed to UV light, are responsible for this high sensitivity. Under UV exposure, the 5% Li-ZnO thin film shows improved stability and repeatability while exhibiting a slightly lower peak current (~1.8 nA). This implies that if Li doping slightly decreases overall carrier mobility because of lattice distortion effects, it produces shallow donor states that improve the separation of photo-generated carriers. However, co-doped samples with current levels below 0.2 nA show significantly reduced UV photoresponses, such as 1%Mg-5%Li-ZnO, 1%La-5%Li-ZnO, and 1%Al-5%Li-ZnO. Effective charge carrier transport is restricted by the rise of recombination sites and increasing structural disorder, which may be the cause of this performance decrease. The 1%Al-5%Li-ZnO film exhibits the lowest UV response among the co-doped samples, most likely as a result of deep-level trap states that prefer recombination over charge transfer. Similar results have been shown in the literature, where enhanced grain boundary scattering caused by excessive Al incorporation in ZnO matrices could affect carrier mobility [44]. These findings imply that co-doping causes trade-offs in structural and electrical characteristics, whereas Li doping somewhat improves the UV sensitivity.

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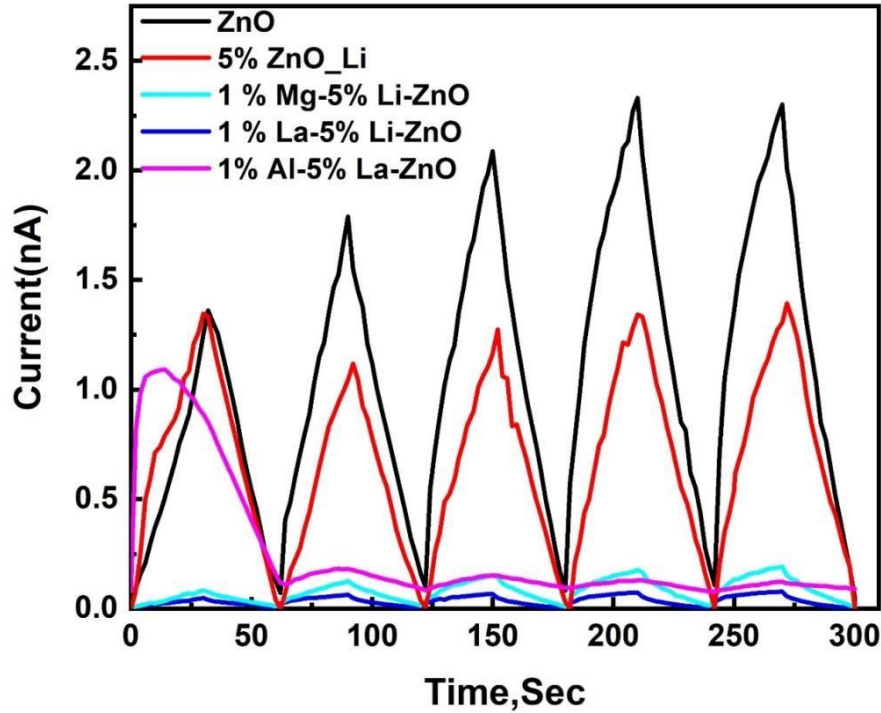


Figure IV.8. UV response during 5 UV on–off sensing cycles for ZnO, 5%Li-ZnO, 1%Mg-5%Li-ZnO, 1%La-5%Li-ZnO, and 1%Al-5%Li-ZnO thin films.

The I-V curves of ZnO and doped ZnO thin films under UV and dark illumination conditions are shown in Figure IV.9. In order to demonstrate effective charge production and transport, pure ZnO shows a modest dark current but an important rise when exposed to UV light. Improved sensitivity is demonstrated by lithium-doped ZnO (5%Li-ZnO), which exhibits a reduction in dark current due to less intrinsic defect states while maintaining a significant UV response. On the other hand, co-doping with La (1%La-5%Li-ZnO) and Mg (1%Mg-5%Li-ZnO) increases the dark current while decreasing the UV response, suggesting that these dopants improve electrical conductivity at the expense of photoconductivity. On the other hand, Al co-doping produces a balanced effect that indicates an ideal balance between charge carrier dynamics and control of defects. This is demonstrated by enhance UV response and moderate dark current.

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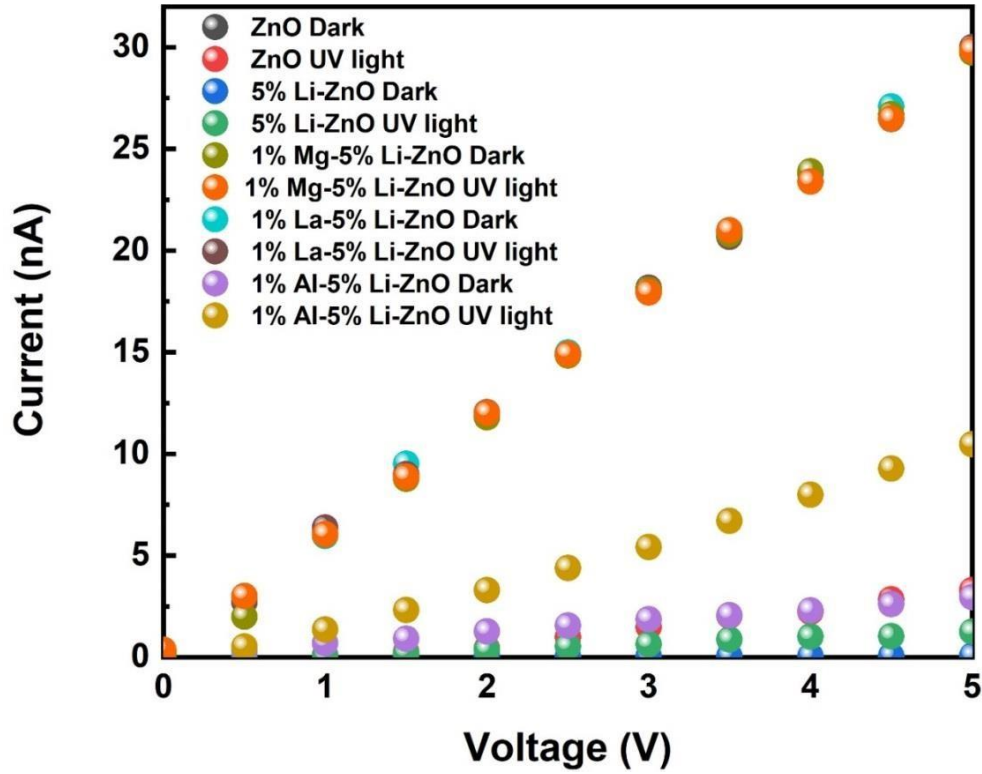


Figure IV.9. The I-V curves of ZnO, 5%Li-ZnO, 1%Mg-5%Li-ZnO, 1%La-5%Li-ZnO, and 1%Al-5%Li-ZnO samples measured in the dark and under UV illumination.

The photocurrent (I_{photo}) and dark current (I_{dark}) values, along with the calculated sensitivity at 5 V, are summarized in Table IV.3. Due of higher defect states that affect recombination rates, Li doping reduces sensitivity to 15.62, whereas pure ZnO has the maximum sensitivity of 65.8. Due to the dominance of bulk conductivity over photogenerated carrier contributions, co-doped samples—especially those containing Mg and La—display significantly higher dark current values (29.73–29.85 nA), which reduces sensitivity. Al co-doping strikes the ideal equilibrium, providing modest dark current and improved photoresponse, indicating its potential for use in photodetector applications.

Table IV. 3. The results exhibited the parameters of the ZnO, 5%Li-ZnO, 1%Mg-5%Li-ZnO, 1%La-5%Li-ZnO, and 1%Al-5%Li-ZnO samples at 5 V.

Samples	I_{dark} (nA)	I_{photo} (nA)	Sensitivity
ZnO	0.05	3.29	65.8
5%Li-ZnO	0.08	1.25	15.62
1%Mg-5%Li-ZnO	29.73	29.85	1.00
1%La-5%Li-ZnO	29.85	30.01	1.00
1%Al-5%Li-ZnO	2.95	10.47	3.54

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IV.1.7. Photocatalytic activity

The photocatalytic degradation activities of ZnO-based thin films in methylene blue (MB) solution under UV light irradiation at various time intervals are seen in Figure IV.10. After 180 minutes, the decomposition efficiency of pristine zinc oxide is approximately 60%, indicating moderate activity. Photogenerated electron-hole pairs recombine rapidly, which is the reason for the lack of performance. When 5% Li is introduced, the photocatalytic activity has significantly increased, and during the same duration, degradation surpasses 80%. Localized defect states and oxygen vacancies, which promote effective charge separation and prolong carrier lifetimes, are likely the reason for this improvement [45].

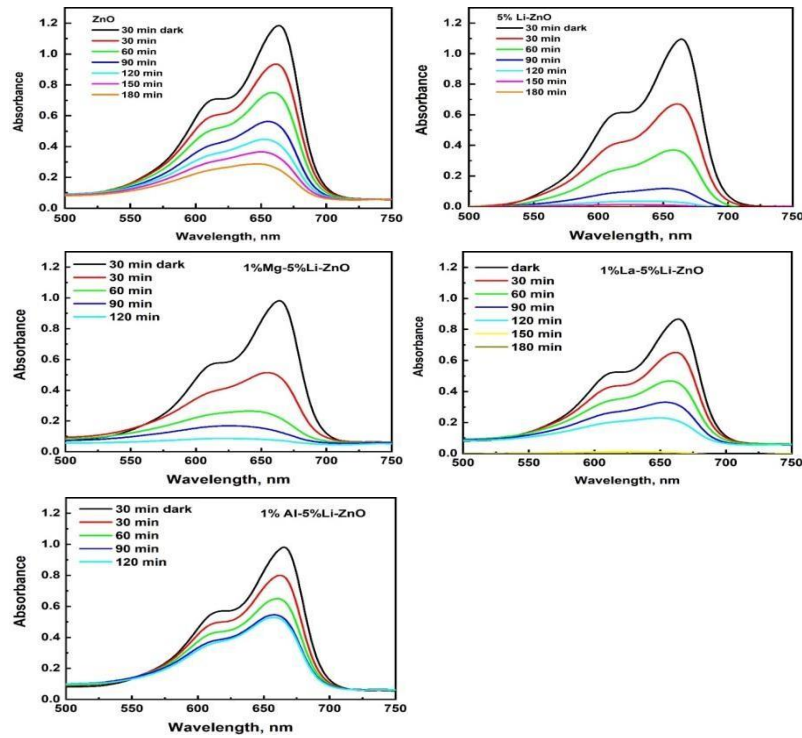


Figure IV. 10. Photocatalytic activity of ZnO, 5%Li-ZnO, 1%Mg-5%Li-ZnO, 1%La-5%Li-ZnO, and 1%Al-5%Li-ZnO thin films in MB solution under UV irradiation for different reaction time.

The photocatalytic reaction is further enhanced by co-doping with other elements. The 1%La-5%Li-ZnO thin film had the greatest degrading efficiency, reaching about 100% in 120 minutes. The synergistic action of La and Li is responsible for this greater activity; La introduces surface defect states and modifies the electronic structure resulting in enhanced active site density and improved charge dynamics. This observation is consistent with earlier

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research on ZnO catalysts doped with La [46]. The 1%Mg–5%Li–ZnO film exhibits high activity as well, with degradation rates close to 95%. Differences in ionic radii and defect interactions, which impact the mobility and recombination behavior of charge carriers, might be the cause of the slightly decreased efficiency when compared to La doping.

On the other hand, the 1%Al–5%Li–ZnO thin film shows only little enhancement. It performs better than undoped ZnO, but not as well as samples that are co-doped with La and Mg. As can be seen in Figure IV.11, its degradation efficiency notably reaches a peak at around 56% after 120 minutes of irradiation, after which no more activity is seen. This saturation behavior is most likely caused by Al dopants that encourage charge recombination deactivating active surface sites or forming mid-gap states. Similar effects of photocatalytic stagnation have been seen in other systems and are usually attributed to reactive intermediate degradation or surface fouling [47].

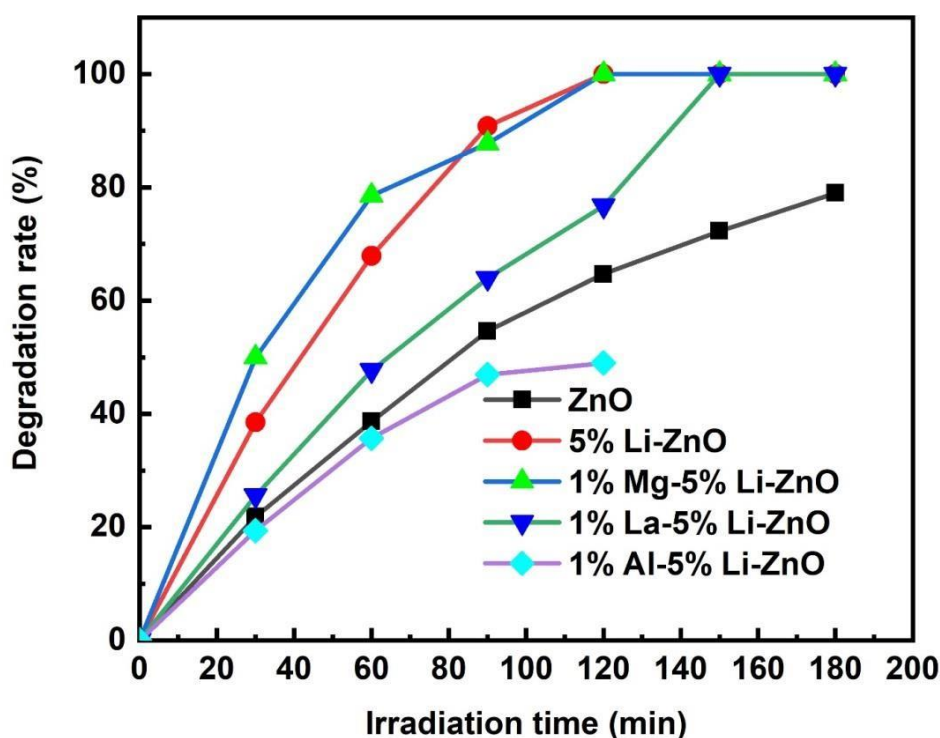


Figure IV. 11. Degradation rate of ZnO, 5%Li-ZnO, 1%Mg-5%Li-ZnO, 1%La-5%Li-ZnO, and 1%Al-5%Li-ZnO thin films in MB solution.

A dark blank test was performed to confirm that the deterioration was caused by photocatalysis and not by dye instability or physical adsorption. In the absence of UV irradiation, the absorbance spectra of MB for all films were essentially constant during 180 minutes, as shown in Figure IV.11. This demonstrates that deterioration does not take place in

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the absence of light and that actual photocatalytic reactions are responsible for the effects seen under UV light. The chemical stability of MB dye in non-irradiated settings was confirmed by El-Shamy et al. [48] with similar findings.

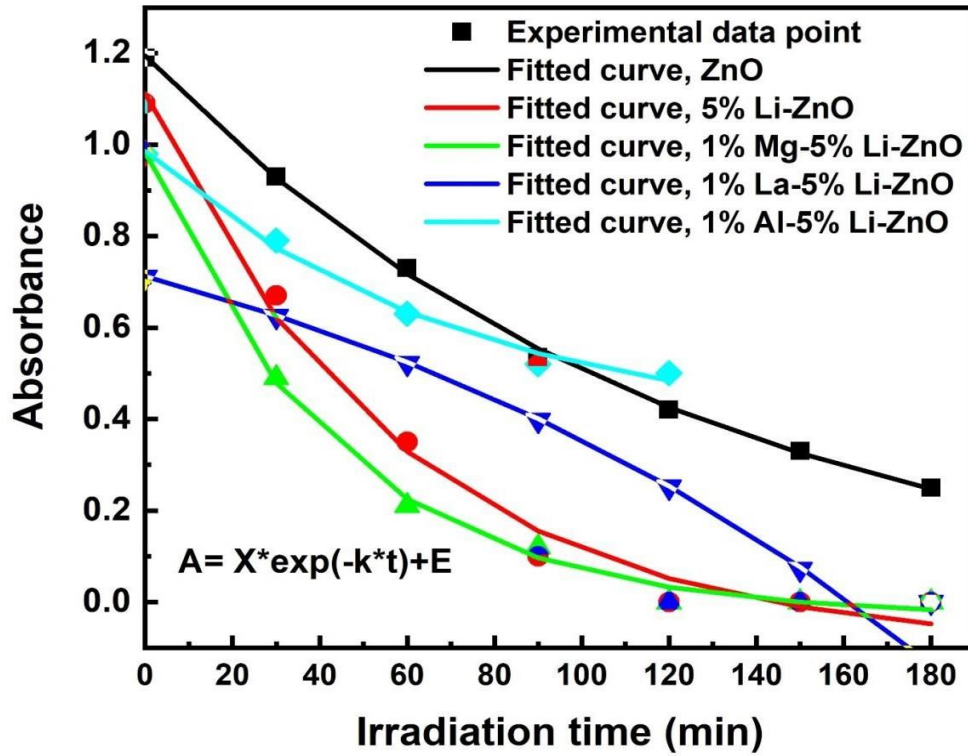


Figure IV. 12. Degradation kinetics of MB aqueous solutions by ZnO, 5%Li-ZnO, 1%Mg-5%Li-ZnO, 1%La-5%Li-ZnO, and 1%Al-5%Li-ZnO films.

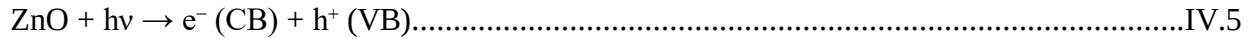
Pseudo-first-order kinetics were used to further investigate the photocatalytic degradation rates, as seen in Figure IV.12 and summarized in Table IV.4. The 1%Mg–5%Li–ZnO sample had the greatest rate constant ($k = 0.02284 \text{ min}^{-1}$), whereas pristine ZnO had the lowest ($k = 0.00819 \text{ min}^{-1}$). Doping and co-doping's effects on recombination suppression and charge separation efficiency are evident in these patterns. High correlation coefficients ($R^2 = 0.99$) were shown by all doped samples, confirming the validity of the experimental findings and showing an excellent fit with the kinetic model.

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Table IV. 4. Pseudo-first-order kinetic parameters of MB degradation.

Samples	Value			Standard deviation			R ²
	K(min ⁻¹)	X	E	K(min ⁻¹)	X	E	
ZnO	0.00819	1.22693	-0.03312	0.00046	0.03350	0.0362	0.9993
5% Li-ZnO	0.01726	1.21286	-0.10142	0.00238	0.06175	0.0540	0.9894
1%Mg-5%Li-ZnO	0.02284	1.01587	-0.03299	0.00144	0.02452	0.0171	0.9972
1%La-5% Li-ZnO	-0,00606	-0,42823	1,140492	0,00601	0,70211	0,7704	0.8989
1%Al-5% Li-ZnO	0.0142	0.61339	0.372479	0.00308	0.06115	0.0643	0.9930

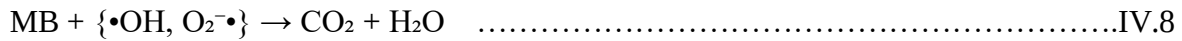
The usual photocatalytic process of ZnO under UV light can account for the increased photocatalytic activity of these coatings. Electrons (e⁻) are stimulated from the valence band (VB) to the conduction band (CB) upon absorption of photons with energy larger than the band gap, leaving holes (h⁺) in the VB Eq (IV.5):



Superoxide radicals are created when the photogenerated electrons degrade into molecular oxygen adsorbed on the film surface Eq (IV.6), and hydroxyl radicals are created if the holes oxidize water or hydroxyl groups Eq (IV.7):



The decomposition of MB into non-toxic end products depends mainly on these reactive oxygen species (ROS), which include $\cdot\text{OH}$ and $\text{O}_2^{\cdot-}$ Eq(IV.8):



By producing electronic defect levels that trap charge carriers, decrease recombination rates, and increase ROS formation, dopants like Li, La, and Mg improve this process. Current research by Iqbal et al. [49] and Zahid et al. [50] supports this process by showing that doping may alter the band structure and improve the efficiency of charge separation in ZnO systems. Significantly, the 1%La–5%Li–ZnO film in this study degraded MB almost completely in 120 minutes, which is in good comparison to other advanced ZnO composites that contain rare

Chapter IV. Characterization results of Li co-doped (Al, Mg, La) ZnO thin films

earth or carbon elements [51, 52]. This highlights the value of co-doping techniques in photocatalytic water treatment.

IV. 2. Conclusion

The comprehensive analysis of ZnO and Li-co-doped ZnO thin films with additional dopants (Mg, La, and Al) demonstrates significant enhancements in structural, optical, electrical, and photodetector properties. Among the studied samples, the 1%Al-5%Li-ZnO film exhibits superior crystallinity, highest optical transmittance (92%), and the widest bandgap (3.46 eV), indicating its strong potential for transparent optoelectronic applications. Meanwhile, the 1%La-5%Li-ZnO film shows remarkable electrical conductivity and outstanding UV photodetector performance, with the highest photoresponsivity and fastest response time. These findings confirm that both La and Al co-doping strategies significantly improve the multifunctional performance of ZnO films, making them promising candidates for advanced optoelectronic and UV photodetection applications.

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General Conclusion

General Conclusion

General Conclusion

This thesis has presented a comprehensive investigation into the effects of rare-earth and co-doping strategies on the structural, optical, electrical, photocatalytic, and photodetector properties of ZnO thin films synthesized via the sol-gel dip-coating method. The study primarily focused on the incorporation of erbium (Er) as a rare-earth dopant and lithium (Li) co-doped with secondary elements such as magnesium (Mg), lanthanum (La), and aluminum (Al) to enhance the multifunctional performance of ZnO.

The experimental results demonstrate that Er doping significantly modifies the microstructure of ZnO by inducing lattice strain and influencing defect states. Moderate Er concentrations (2–5%) improve film uniformity, optical emission near the band edge, and electrical conductivity, while excessive doping leads to the formation of secondary phases, porosity, and reduced performance. Photocatalytic testing confirmed the efficacy of 2% Er-ZnO under UV light and sunlight, following pseudo-first-order degradation kinetics dominated by hydroxyl radicals.

Meanwhile, Li-based co-doping—particularly with Al and La—resulted in considerable improvements in crystallinity, optical transparency, electrical conductivity, and UV photodetection capabilities. The 1%Al–5%Li–ZnO film achieved the highest optical transmittance and widest bandgap, making it suitable for transparent optoelectronic devices. In contrast, 1%La–5%Li–ZnO exhibited exceptional electrical conductivity and UV photoresponse, positioning it as a strong candidate for efficient photodetectors.

Overall, the findings of this work highlight the critical role of dopant type and concentration in tailoring the physical and functional properties of ZnO thin films. By optimizing these parameters, it is possible to develop materials with targeted performance characteristics for advanced applications in optoelectronics, environmental remediation, and UV sensing. Future research should focus on long-term stability, recyclability, and device integration to further advance the practical deployment of these doped ZnO materials.

Perspective

Perspective

Perspective

Doping zinc oxide (ZnO) with lithium (Li) has emerged as a promising strategy to tailor and enhance its intrinsic properties, particularly for applications in photocatalysis. By introducing lithium ions into the ZnO lattice at varying concentrations, typically ranging from low (1–3%) to moderate levels (5–10%), significant modifications in structural, optical, and electronic properties can be achieved. Lithium ions, due to their small ionic radius and unique valence state, can effectively substitute zinc sites or occupy interstitial positions within the ZnO crystal structure, leading to changes in carrier concentration, defect density, and bandgap energy. These modifications often result in improved charge carrier separation and mobility, which are critical factors in enhancing photocatalytic efficiency. Additionally, Li doping has been reported to induce shifts in the absorption edge of ZnO, extending its photoresponse towards the visible light region and thus broadening the spectrum of usable solar energy. The concentration of lithium plays a crucial role; optimal doping levels promote defect passivation and reduce electron-hole recombination, while excessive doping may lead to the formation of secondary phases or increased defect sites that can act as recombination centers, adversely affecting performance. Overall, lithium-doped ZnO demonstrates a notable improvement in photocatalytic degradation of organic pollutants, making it a highly efficient and cost-effective material for environmental remediation and solar-driven catalytic processes. Future research focusing on fine-tuning lithium concentrations and understanding the doping mechanisms at the atomic level will further unlock the potential of Li-doped ZnO in advanced photocatalytic applications.

Abstract

Abstract

This thesis focuses on the detailed investigation of the structural, optical, electrical, photocatalytic, and photodetector properties of doped ZnO thin films synthesized using the sol-gel dip-coating method. Two doping strategies were studied: erbium (Er) doping and lithium (Li) co-doping combined with secondary elements such as Mg, La, and Al.

X-ray diffraction (XRD) confirmed the hexagonal wurtzite structure for all films. At higher Er concentrations (10% and above), a secondary Er-rich phase appeared, indicating the solubility limit of Er in the ZnO lattice. Scanning electron microscopy (SEM) showed that moderate Er doping (2–5%) improved film uniformity, while excessive doping led to porosity and defects. Photoluminescence (PL) results revealed enhanced near-band-edge emission with increasing Er content, and electrical measurements showed improved conductivity up to 10% Er doping. Photocatalytic tests using methylene blue demonstrated that 2% Er-doped ZnO performed best under UV light and sunlight irradiation.

In the co-doped films, 1%Al–5%Li–ZnO exhibited the highest transmittance (92%) and the widest optical bandgap (3.46 eV). Meanwhile, 1%La–5%Li–ZnO showed the best electrical conductivity and excellent UV photodetector performance, with high photoresponsivity and a fast response time.

Overall, Er doping mainly enhances the optical and photocatalytic properties of ZnO, while Li-based co-doping with La or Al significantly improves electrical and UV detection performance. These results highlight the great potential of doped ZnO thin films for applications in optoelectronics, UV photodetectors, and environmental remediation.

Keywords: sol-gel, dip coating, photoluminescence, impedance spectroscopy, photocatalysis, scavenger experiments, doping, co-doping.

Résumé

Résumé

Cette thèse porte sur l'étude approfondie des propriétés structurales, optiques, électriques, photocatalytiques et photodéetectrices des films minces de ZnO dopés, synthétisés par la méthode sol-gel suivie du dépôt par trempage. Deux stratégies de dopage ont été explorées : le dopage au erbium (Er) et le codopage au lithium (Li) combiné à des éléments secondaires tels que le Mg, le La et l'Al.

Les analyses par diffraction des rayons X (XRD) ont confirmé la structure wurtzite hexagonale pour tous les films. À des concentrations élevées en Er (10 % et plus), une phase secondaire riche en Er est apparue, indiquant la limite de solubilité de l'Er dans la matrice ZnO. La microscopie électronique à balayage (MEB) a montré qu'un dopage modéré en Er (2–5 %) améliore l'uniformité des films, tandis qu'un dopage excessif provoque une porosité et des défauts. Les mesures de photoluminescence (PL) ont révélé une émission renforcée près du bord de bande avec l'augmentation du taux d'Er, et les mesures électriques ont montré une meilleure conductivité jusqu'à 10 % d'Er. Les tests photocatalytiques sur le bleu de méthylène ont montré que le film dopé à 2 % d'Er est le plus efficace sous lumière UV et sous lumière solaire.

Dans les films codopés, le film 1 %Al–5 %Li–ZnO présente la plus forte transmittance (92 %) et le plus large gap optique (3,46 eV). Le film 1 %La–5 %Li–ZnO, quant à lui, présente la meilleure conductivité électrique ainsi qu'une excellente performance en photodétection UV, avec une photo-réponse élevée et un temps de réponse rapide.

En résumé, le dopage à l'Er améliore principalement les propriétés optiques et photocatalytiques du ZnO, tandis que le codopage au Li avec La ou Al améliore les propriétés électriques et la détection UV. Ces résultats mettent en évidence le fort potentiel des films minces de ZnO dopés pour des applications dans l'optoélectronique, les photodéetecteurs UV et la dépollution environnementale.

Les mots clés :

revêtement par immersion, sol-gel, photoluminescence, spectroscopie d'impédance, photocatalyse, expériences de piégeage, dopage, co-dopage.

الملخص

الملخص

تهدف هذه الأطروحة إلى دراسة الخصائص البنيوية والبصرية والكهربائية والظوئية التحفيزية والكشف الضوئي لأغشية ZnO الرقيقة المطعمة، والمحضرة باستخدام طريقة السول-جيل مع تقنية الطلاء بالغمر. تم اعتماد استراتيجيتين للتطعيم: تطعيم بأيونات الإيريبيوم (Er) وتطعيم مشترك بالليثيوم (Li) مع عناصر إضافية مثل المغنيسيوم (Mg)، اللانثانوم (La)، والألمنيوم (Al).

أظهرت تحاليل حيود الأشعة السينية (XRD) أن جميع الأغشية تمتلك بنية وورزيت سداسية. ومع ارتفاع تركيز الإيريبيوم (10% فأكثر)، ظهرت طور ثانوي غني بالإيريبيوم، مما يشير إلى حد النوبانية داخل مصفوفة ZnO.

أظهرت صور المجهر الإلكتروني الماسح (SEM) أن التطعيم المتوسط بـ 2-5% Er (يحسن من انتظام السطح، في حين أن التركيزات العالية تؤدي إلى زيادة في المسامية وعيوب في الحبيبات. أظهرت قياسات الفلورة (PL) تحسناً في الانبعاث القريب من حافة النطاق مع زيادة تركيز الإيريبيوم، بينما أظهرت القياسات الكهربائية تحسناً في التوصيلية حتى تركيز 10%. أظهرت التجارب التحفيزية باستخدام صبغة الميثيلين الأزرق أن ZnO المطعم بـ 2% Er هو الأكثر كفاءة تحت الأشعة فوق البنفسجية و تحت ضوء الشمس.

أما بالنسبة للأغشية المطعمة بـ Li مع عناصر إضافية، فقد أظهر ZnO-5%Li-1%Al أعلى نسبة نفاذية للضوء (92%) وأوسع فجوة طاقوية (eV3.46)، بينما أظهر ZnO-5%Li-1%La أفضل توصيل كهربائي وأداءً ممتازاً في الكشف عن الأشعة فوق البنفسجية، مع استجابة ضوئية عالية وزمن استجابة سريع.

في الختام، يُظهر تطعيم ZnO بالإيريبيوم تحسناً في الخصائص البصرية والظوئية التحفيزية، في حين أن التطعيم المشترك بـ Li مع La أو Al يعزز الأداء الكهربائي وقدرات الكشف الضوئي. وتؤكد هذه النتائج الإمكانيات الكبيرة لأغشية ZnO المطعمة في تطبيقات الإلكترونيات الضوئية وكواشف الأشعة فوق البنفسجية ومعالجة التلوث البيئي.

الكلمات المفتاحية:

طلاء الغمس بالمحلول-تجلط، التالف الضوئي، مطيافية المعاوقة، التحفيز الضوئي، تجارب الكاسح، التطعيم، التطعيم المشترك