



People's Democratic Republic of Algeria
Ministry of Higher Education and Scientific Research
UNIVERSITY OF ABBES LAGROUR KHENCHELA
Faculty of Sciences and Technology
Department of Mater Sciences



Order N°:

Serial N°:

THESIS

For obtaining the Doctorate Degree in Physics
Specialty: Materials Physics and its Applications

Presented by:

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Entitled

***Preparation and Characterization of Metal Oxide
Thin Films for Photocatalytic Environmental
Remediation***

Publicly defended on: 16/ 02 / 2026

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Academic Year: 2025-2026

Dedication

When one task gets simpler,

it is due to the completion of all challenging tasks.

I dedicate this thesis to my parents, my extended family,

and all those who have provided their support.

I greatly appreciate your kindness

Hayet

Acknowledgements

With utmost reverence, invoking the Name of Allah, the Most Compassionate, the Most Merciful, I embark on this expression of deep gratitude to Allah, the Almighty, the wellspring of sustenance and enlightenment. Without His guidance, blessings, and mercy, the completion of this work would not have been possible.

First and foremost, I would like to express my deepest gratitude to my thesis supervisor, Professor **Djelloul Abdelkader**, Head of the Laboratory of Structures, Properties and Interatomic Interactions (LASPI2A) at Abbes Laghrour University, Khenchela, Algeria, for his invaluable guidance, constant support, and insightful advice throughout the course of this work. His scientific expertise, patience, and encouragement have not only shaped this research but have also played a vital role in my academic and personal development. It has been a great honor and privilege to work under his supervision, and I am truly indebted to him for his trust and continuous motivation.

I would also like to extend my sincere gratitude to Professor Sabrina Iaiche, Professor at Abbes Laghrour University, Khenchela, Algeria, for having supervised me during the past five years. I could not have been more fortunate. I warmly thank her for her availability, valuable assistance, and wise advice. I am deeply grateful for her pedagogy, patience, and the fruitful discussions we had throughout the realization of this work. She introduced me to research in the field of semiconductor devices and ensured continuous guidance during the progress of my studies. May she find here the testimony of my profound gratitude and the assurance of my highest consideration.

I am also sincerely thankful to the honorable members of the jury: **Professor A. Chala** (University of Khenchela, President), Professor Djelloul Abdelkader (University of Khenchela, Supervisor), **MCAS. Iaiche** (University of Khenchela, Co-Supervisor), Professor **L. Remache** (University of Oum El Bouaghi, Examiner), and Professor **S. Roguai** (University of Khenchela, Examiner) for accepting to evaluate this thesis and for devoting their valuable time and expertise. Their constructive feedback and suggestions have been of great importance in improving the quality of this work.

Acknowledgements

I would also like to extend my appreciation to all my professors at Abbes Laghrour University and beyond, who have enriched my academic and research journey with their knowledge, inspiration, and valuable courses that provided the foundation for this study.

My heartfelt thanks go to my family, especially my beloved parents, whose unconditional love, sacrifices, and prayers have always been the cornerstone of my life. Their encouragement, patience, and unwavering belief in me have been my greatest source of strength and motivation. Without their constant support, none of this would have been possible. I am equally grateful to my brothers and sisters for their understanding, encouragement, and for always being by my side in times of need.

I would also like to express my gratitude to my colleagues, fellow researchers, and friends, who have provided a stimulating and supportive environment throughout the years. Their cooperation, stimulating discussions, and shared experiences inside and outside the laboratory have made this journey both productive and enjoyable.

Finally, I am deeply grateful to everyone who, in one way or another, contributed to the realization of this work. Each word of encouragement, every piece of advice, and every helping hand has left a lasting impact on me, and I will carry this gratitude with me in all my future endeavors.

الملخص

تهدف هذه الدراسة إلى تحضير أغشية رقيقة من الأكاسيد المعدنية باستخدام تقنية الغمس بطريقة السول-جيل، ودراسة فعاليتها في التحفيز الضوئي لمختلف المذيبات (الإيثانول-الميثانول) على ركيزة زجاجية، مع تطبيقات في التحفيز الضوئي والكشف الضوئي على التوالي. قمنا بدراسة الخصائص البنيوية والمورفولوجية والضوئية والكهربائية لهذه الأغشية باستخدام عدة تقنيات. حيث أظهرت مخططات حيود الأشعة السينية أن جميع الأغشية متعددة البلورات وتتكون من بنية وورترزيت سداسية كما أظهرت الأغشية الرقيقة من أكسيد الزنك المطعمة بالمغنيزيوم والمحضرة باستخدام مذيب الإيثانول توجهًا مفضلًا على طول (002)، وقد بينت معادلة شيرر أن أحجام البلورات تتراوح بين 22.82 و 36.07 نانومتر. وخضعت الطبقات المكونة من أغشية أكسيد الزنك المطعمة بالصوديوم والمغنيزيوم لتحليل مورفولوجي باستخدام المجهر الإلكتروني الماسح حيث كشف عن أسطح كثيفة، متجانسة وملساء وأكد تحليل الطيفي للطاقة المشتتة عن وجود قمم مرتبطة بعناصر الزنك والأكسجين والمغنيزيوم والصوديوم، وبذلك تم التحقق من تركيب الأغشية الرقيقة. وقد أظهرت هذه الأغشية شفافية ضوئية تقارب 90% في المجال المرئي، بينما تراوحت فجوة الطاقة المباشرة بين 3.22 و 3.38 إلكترون فولت في حين أن التحليل الطيفي بالأشعة تحت الحمراء أكد وجود أكسيد الزنك والدمج الفعال للمغنيزيوم والصوديوم، وهو ما يتوافق مع نتائج حيود الأشعة السينية أظهر تحليل الضوء المنبعث بشكل أساسي قمم انبعاث. كما أشارت نتائج التحفيز الضوئي أن دمج المغنيزيوم والصوديوم في أكسيد الزنك يزيد من كفاءة التحفيز الضوئي. حيث لوحظ التحلل الأمثل لمركب الميثيل الأزرق تحت إشعاع الأشعة فوق البنفسجية يصل إلى 99.91% بعد ساعتين، باستخدام طبقات رقيقة من أكسيد الزنك التي تم تحضيرها باستعمال مذيب الميثانول والمضاف إليها 9% من المغنيزيوم.

يؤدي ادراج المغنيزيوم والصوديوم الى رفع مستويات التوصيل الكهربائي مقارنة بالفضة العنصرية.

الكلمات المفتاحية: أغشية رقيقة، ZnO، تقنية الغمس بطريقة السول-جيل، التطعيم، المغنيزيوم، الصوديوم، التحفيز الضوئي، الكاشف الضوئي

Abstract

This research aims to fabricate metal oxide thin films using the sol-gel dip coating method and to examine their effectiveness in the photocatalytic degradation of various solvent (ethanol-methanol) on a glass substrate, with applications in photocatalysis and photodetection, respectively. We examined the structural, morphological, optical, and electrical characteristics of these films using various methods. X-ray diffraction patterns demonstrate that all films are polycrystalline and consist of a hexagonal wurtzite structure. The Mg-doped ZnO thin films, produced using ethanol solvent, have a preferential orientation along (002), with Scherer's formula indicating crystallite sizes between 22.82 and 36.07 nm. layers composed of thin layers of Na-doped ZnO and Mg-doped ZnO thin films were subjected to morphological analysis by scanning electron microscopy (SEM), revealing surfaces that were dense, homogeneous, and smooth. The EDS analysis identified peaks associated with the elements zinc, oxygen, magnesium, and sodium. Consequently, the composition of the thin films is validated, with the optical transparency of ZnO films approximating 90% within the visible spectrum, owing to their exceptional crystalline quality. The direct band gap varied from 3.22 to 3.38 eV, whereas FT-IR spectra confirm the presence of ZnO and the effective incorporation of magnesium and sodium, corroborating the XRD findings. The analysis of photoluminescence mostly showed emission peaks. The outcomes of photocatalysis have shown that the incorporation of magnesium (Mg) and sodium (Na) into zinc oxide augments photocatalytic efficiency. The best degradation of the dye methyl blue under UV irradiation attains 99.91% after 2 hours, using thin layers of ZnO synthesized with methanol solvent and doped with 9% Mg. The inclusion of doping increases electrical conductivity levels. Magnesium and sodium doping provide enhanced structural and electrical characteristics relative to elemental silver.

Keywords: Thin films, ZnO, sol-gel dip coating, Doping, magnesium, sodium, Photocatalysis, Photodetector.

Résumé

Cette recherche vise à fabriquer des films minces d'oxyde métallique en utilisant la méthode de revêtement par immersion sol-gel et à examiner leur efficacité dans la dégradation photo catalytique de divers solvants (éthanol-méthanol) sur un substrat de verre, avec des applications en photocatalyse et en photodétection, respectivement. Nous avons examiné les caractéristiques structurales, morphologiques, optiques et électriques de ces films en utilisant diverses méthodes. Les diagrammes de diffraction des rayons X démontrent que tous les films sont polycristallins et consistent en une structure wurtzite hexagonale. Les films minces de ZnO dopé au Mg, produits en utilisant un solvant à l'éthanol, ont une orientation préférentielle le long (002), avec la formule de Scherer indiquant des tailles de cristallites comprises entre 22,82 et 36,07 nm. Couches composées de fines couches de ZnO dopé au Na et de films minces de ZnO dopé au Mg ont été soumises à une analyse morphologique par microscopie électronique à balayage (MEB), révélant des surfaces denses, homogènes et lisses. L'analyse EDS a identifié des pics associés aux éléments zinc, oxygène, magnésium et sodium. Par conséquent, la composition des couches minces est validée, avec une transparence optique de ZnO d'environ 90% dans le spectre visible, en raison de leur qualité cristalline exceptionnelle. L'écart de bande direct variait de 3,22 à 3,38 eV, tandis que les spectres FT-IR confirment la présence de ZnO et l'incorporation efficace de magnésium et de sodium, corroborant les résultats des DRX. L'analyse de la photoluminescence a principalement montré des pics d'émission. Les résultats de la photocatalyse ont montré que l'incorporation de magnésium (Mg) et de sodium (Na) dans l'oxyde de zinc augmente l'efficacité photo catalytique. La meilleure dégradation du colorant bleu de méthyle sous irradiation UV atteint 99,91% après 2 heures, en utilisant des couches minces de ZnO synthétisé avec un solvant méthanol et dopé avec 9% Mg. L'inclusion du dopage augmente les niveaux de conductivité électrique. Le dopage au magnésium et au sodium fournit des caractéristiques structurales et électriques améliorées par rapport à l'argent élémentaire.

Mots-clés : Films minces, ZnO, revêtement par immersion sol-gel, dopage, magnésium, sodium, photocatalyse, photodétecteur.

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List of abbreviations and symbols

➤ α	— Absorption coefficient
➤ AO7	— Acid Orange 7 (Orange II dye)
➤ % at.	— Atomic percentage
➤ C_0	— Initial concentration of dye (mg/L)
➤ C_t	— Concentration of dye at time t
➤ D	— Degradation efficiency
➤ DRX	— X-ray diffraction
➤ EDS/EDX	— Energy Dispersive X-ray Spectroscopy
➤ Eg	— Optical band gap energy (eV)
➤ FE-SEM	— Field Emission Scanning Electron Microscopy
➤ FTIR	— Fourier Transform Infrared Spectroscopy
➤ $h\nu$	— Photon energy
➤ KC	— Adsorption coefficient
➤ kr	— Reaction rate constant
➤ L-H	— Langmuir–Hinshelwood model
➤ MB	— Methylene Blue
➤ MEA	— Monoethanolamine
➤ MO	— Methyl Orange
➤ MZO	— Magnesium-doped Zinc Oxide
➤ n	— Refractive index
➤ n_∞	— Infinite-wavelength refractive index
➤ NBE	— Near Band Edge
➤ NZO	— Sodium-doped Zinc Oxide
➤ PL	— Photoluminescence
➤ S	— Seebeck coefficient ($\mu\text{V/K}$)
➤ SEM	— Scanning Electron Microscopy
➤ TCO	— Transparent Conductive Oxide
➤ ΔT	— Temperature difference (K)
➤ ΔV	— Output voltage (V)
➤ UV	— Ultraviolet
➤ UV-Vis	— Ultraviolet-Visible Spectrophotometry

List of abbreviations and symbols

- XRD — X-ray Diffraction
- ZnO — Zinc Oxide
- λ — Wavelength (nm)

General Introduction

General Introduction

Water scarcity has become one of the most pressing global issues, exacerbated by climate change, prolonged droughts, and population growth, which together increase pressure on freshwater resources and amplify the impact of pollution [1,2]. A sustainable solution to this challenge lies in wastewater treatment and reuse, ensuring both water availability and environmental protection [3].

Among the various treatment methods, photocatalysis has emerged as a promising technology due to its effectiveness in water purification, degradation of hazardous substances, and potential applications in clean energy generation [4]. As an advanced oxidation process, photocatalysis employs light irradiation to degrade toxic organic compounds, microorganisms, and environmental contaminants into harmless byproducts [5–7].

In this context, semiconductors play a central role. Although insulating under normal conditions, many semiconductors exhibit photocatalytic activity when irradiated with light, enabling a wide range of applications including piezoelectric transducers [9], gas sensors [10], transparent electrodes in photovoltaic cells [11], and optoelectronic devices. Their dual characteristics—high optical transparency and good electrical conductivity across the visible spectrum [12]—make wide band-gap semiconductors such as TiO_2 [13], Fe_2O_3 , ZnO , ZnS [14,15], CuO [16], CdS [17], and SnO_2 [18] attractive candidates for photocatalytic degradation of toxic dyes [19].

Among them, zinc oxide (ZnO) stands out for its unique properties: a direct band gap of 3.37 eV, a high exciton binding energy (60 meV at room temperature), and intrinsic n-type conductivity originating from oxygen vacancies and zinc interstitials [20,21]. ZnO also exhibits high optical transmittance ($T \geq 90\%$) and a refractive index of 1.8–1.9, with a hexagonal wurtzite structure where Zn occupies half of the tetrahedral sites [22]. These properties have enabled its use in light-emitting diodes (LEDs), laser diodes, solar cells, surface acoustic wave devices, thin-film transistors, photodetectors, and photocatalysis [23–30].

Organic dyes such as rhodamine B, methyl orange, and methylene blue (MB) are of particular concern due to their high solubility, complex structures, and resistance to degradation by conventional chemical, biological, or photolytic treatments [31–33]. This has

increased interest in photocatalytic approaches, which offer cost-effectiveness, sustainability, and environmental compatibility [32].

ZnO can be synthesized in various morphologies, including nanowires, nanotubes, and thin films, through vapor-phase, liquid-phase, and solid-state techniques such as atomic layer deposition [36], chemical vapor deposition [40], sputtering [39], microwave-assisted methods [41], spray pyrolysis [42], and the sol-gel dip-coating process [38,43]. Among these, sol-gel dip coating is particularly advantageous due to its simplicity, low cost, energy efficiency, and ability to produce c-axis-oriented ZnO thin films at relatively low temperatures [44]. It also allows fine control over composition and microstructure.

The properties of ZnO can be further enhanced through metal-ion doping, which modifies its electrical, structural, and optical characteristics. Dopants such as Mg, Cd, Al, Fe, Co, and Ag introduce donor or acceptor levels within the band gap, improving conductivity and photocatalytic performance [4,21]. Magnesium doping is especially effective, as the similar ionic radius of Mg^{2+} to Zn^{2+} enables substitution in the ZnO lattice with minimal mismatch, thereby improving photocatalytic efficiency by generating oxygen vacancies [45–47]. Sodium doping, on the other hand, can act as a shallow acceptor, enhancing p-type conductivity and making ZnO suitable for p–n junction devices [48–50].

It is also important to note that the choice of solvent in sol-gel synthesis influences the viscosity, polarity, and solubility of precursors, thereby affecting the morphology, crystallinity, and optical properties of ZnO thin films [18,51,52]. Thus, optimizing both the dopant concentration and the solvent system is critical for achieving high-performance ZnO-based materials.

The present work focuses on the preparation of ZnO thin films on glass substrates via the sol-gel dip-coating method, using different solvents and incorporating Mg and Na dopants at concentrations of 3%, 5%, 7%, and 9%. The goal is to improve the structural, morphological, optical, and electrical properties of ZnO thin films and evaluate their photocatalytic efficiency in degrading dyes such as methylene blue and orange II under UV and solar irradiation.

This thesis is structured as follows:

- ✚ Chapter I provides a comprehensive literature review on ZnO, including its structural, optical, and electrical properties, applications, and characterization

methods such as XRD, UV-Vis spectroscopy, FTIR, photoluminescence, and FE-SEM.

- ✚ Chapter II details the thin-film deposition techniques and the experimental methodology for synthesizing ZnO, $\text{Zn}_{1-x}\text{Mg}_x\text{O}$, and $\text{Zn}_{1-x}\text{Na}_x\text{O}$ thin films using the sol-gel dip-coating process.
- ✚ Chapter III presents and discusses the experimental results, focusing on the effect of solvents, Mg doping, and photocatalytic performance of ZnO thin films under UV and solar light.
- ✚ Chapter IV examines the impact of Na doping on the structural, optical, and electrical properties of ZnO thin films, with emphasis on their performance in photodetection and photocatalysis.

Finally, the Conclusion summarizes the key findings, highlights the contributions of this work, and suggests future research directions.

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Chapter I:

*Properties of zinc oxide,
photocatalytic behavior, and
characterizations
methodologies*

I. Introduction

Pollution has been pervasive for ages and poses a significant threat to human existence. Consequently, individuals have resorted to devising techniques to mitigate this issue by employing transparent conductive oxides, which have gained popularity and prevalence owing to their varied features and affordability, enabling their application across multiple domains. The process involves the incorporation of photocatalytic elements. This chapter will examine the process, emphasizing the characteristics of zinc oxide and its applications. To elucidate the methodology for obtaining findings, we shall examine the instruments employed to describe thin films.

. I.1 Overview of transparent conducting oxides

In 1907, approximately a century ago. Thermal Conductivity Observations (TCO) have been utilized in various applications for three to four decades [1]. The initial transparent conductive oxide thin film was documented by Badeker, it comprises the nonmetal component, B, which consists of oxygen. When combined with various metals or metal alloys, A results in compound semiconductors exhibiting distinct optoelectronic properties. The opto-electrical characteristics can be modified through doping with metals, metalloids, or nonmetals. Therefore, metals may constitute the compound semiconductor itself, A, or serve as a dopant, D [2].

I.1.1 categories of metallic oxides

Metal oxides can be categorized into two categories, n-type and p-type metal oxides, based on whether conduction is facilitated by electrons or holes.

➤ n-type and p-type metal oxides

To enhance the characteristics of transparent conducting oxides, we employ doping with two primary families of metal oxides.

(Table I.1) lists several principal metals utilized for n-type and p-type doping.

p-type oxides (hole conduction). They are recognized for their relative instability owing to their propensity to readily exchange oxygen from their lattice with the atmosphere. P-type oxides are utilized in specific applications, including high-temperature oxygen sensors.

n-type oxides, which facilitate electron conduction. These materials are predominantly

utilized in gas sensor applications due to their enhanced stability and good chemisorption characteristics [3,4,5].

Table I.1 Enumeration of metal oxides [3].

n-type metal oxides	P-type metal oxides
SnO ₂	NiO
WO ₃	PdO
ZnO	La ₂ O ₃
TiO ₂	TeO ₂
InO ₃	Ag ₂ O
Ta ₂ O ₃	BaTiO ₃

I.2 The Concept of Zinc oxide

Zinc oxide ZnO is a naturally occurring substance known as "zincite," but it may also be artificially manufactured in bulk quantities.

ZnO is a non-toxic binary compound of the II-VI group. It possesses a collection of attributes that enable its utilization across many applications. It exhibits transparency in the visible and near-infrared spectrum, possesses a high exciton binding energy of 60 meV, and features a broad direct bandgap of 3.3 eV. It may also be utilized in optoelectronics, cathodoluminescence, photoluminescence, electroluminescence, as a chemical sensor in thin films, or as a piezoelectric material [6].

I.2.1 Characteristics of Zinc Oxide

All transparent conductive oxides possess distinctive features that set them apart from one another. Zinc oxide possesses numerous features that make it the most prevalent and regularly used compound. This chapter will examine the qualities that have garnered notice.

I.2.1.1 Structural characteristics of ZnO

ZnO manifests in three crystalline forms, contingent upon the production conditions [7].

- The wurtzite (hexagonal) structure, which is stable under ambient conditions.
- The sphalerite (cubic face-centered) structure, which is unstable and manifests under elevated pressure.
- The Rock-Salt structure (NaCl), which manifests under extreme pressures.

Zinc oxide (ZnO), referred to as zincite in its native form, is typically encountered in various hues (ranging from orange to dark red) owing to impurities, although pyramidal crystals are exceedingly uncommon [8,9,10].

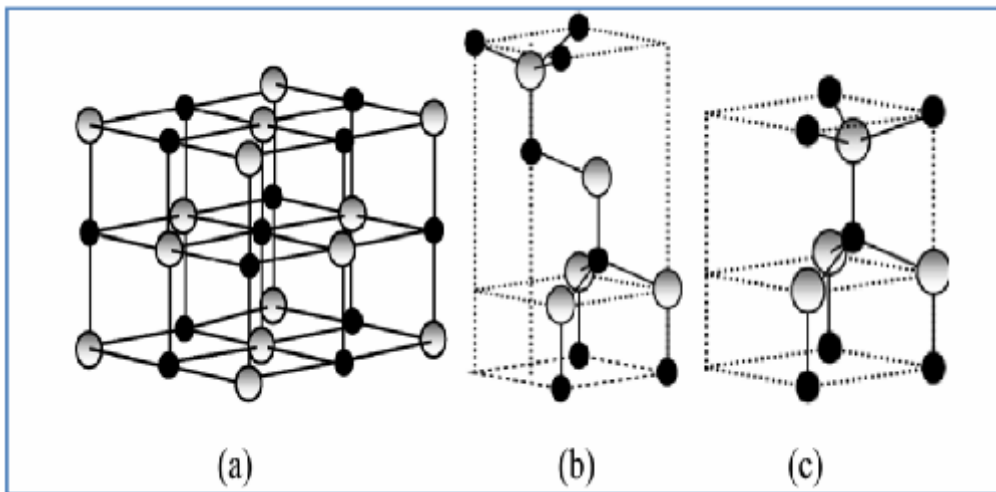


Fig1.1 ZnO crystal structures: (a) Cubic rocksalt. (b) Cubic zinc blende. (c) Hexagonal wurtzite (Zinc atoms in gray and oxygen in black) [11]

I.2.1.2 Electronic and optical characteristics

To fully comprehend the electrical and dynamic properties of materials, it is essential to grasp the Brillouin zone corresponding to their crystal structure [12,13].

The band structure of ZnO is associated with its crystallographic structure and the electronic configurations of oxygen ($1s^2 2s^2 2p^4$) and zinc ($1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2$), wherein the 2p states of oxygen comprise the valence band and the 4s states of zinc form the conduction band of the ZnO semiconductor. **Fig I.2** illustrates the separation of these two bands. This image illustrates the presence of a vacant band of roughly 3.37 eV at 300 K [14].

Zinc oxide is a semiconductor, a transparent substance with a bulk refractive index of 2, although its refractive index and absorption coefficient in thin film form fluctuate based on

manufacturing conditions. The refractive index ranges from 1.90 to 2.20. This material can transmit over 90% of visible light under conditions of adequate crystalline quality, owing to its substantial band gap. Doped ZnO is categorized as a transparent conductive oxide (TCO). [12,13]

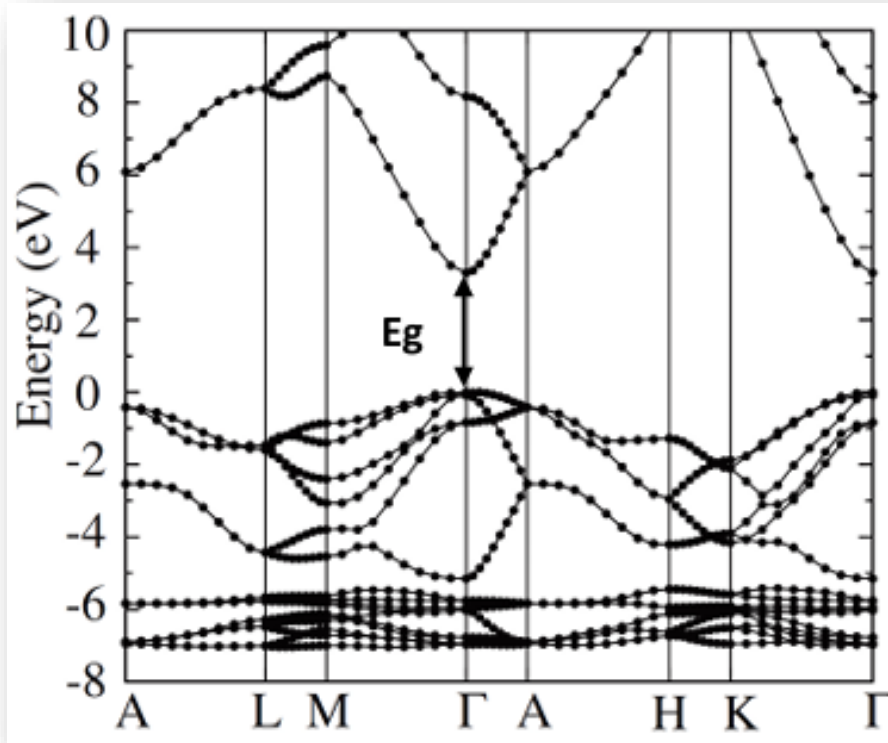


Fig I.2 shows the theoretical band diagram for ZnO in the Wurtzite structure.[15]

I.2.2 Selection of doping substances

Zinc oxide is noteworthy for numerous technical applications due to its distinct physical and chemical features, rendering it more appealing than other oxides. Numerous scholars have investigated the impact of doping ZnO thin films with various dopants [16].

This study employed magnesium nitrate hexahydrate and Sodium acetate dihydrate to dope zinc oxide, enhancing its characteristics for many applications.

Mg-doped ZnO thin films have been fabricated by several techniques, including radio frequency (rf) magnetron sputtering [17,18], whereas Arshad et al. [19] generated Mg-doped ZnO nanoparticles via a wet chemical process. It was observed that Mg doping suppressed

particle size growth, augmented the optical gap, and improved visible photoluminescence (PL) emission. Furthermore, Chebil et al. [20] indicated in their study on Mg-doped ZnO synthesized using sol-gel that the preferred orientation along the c-axis was absent in Zn: MgO thin films, whereas Mg doping resulted in an increase in crystallite size, optical bandgap, and surface roughness.

Numerous papers have shown the development of n-type ZnO on p-type substrates, including GaN, SiC, AlGaN, SrCu₂O₂, and Si. The majority of research on ZnO heterojunction diodes has been on p-GaN due to the comparable bandgap, a lattice constant discrepancy of 1.8%, and the same wurtzite crystal structure shared by ZnO and GaN.[21] theoretical investigations by Fan et al. [22] have demonstrated that sodium (Na), serve as superior p-type dopants for ZnO in comparison to group V elements, with Na substituting at zinc sites (Na-Zn) and forming shallow acceptor levels [23].

In our research, we modified both the minerals incorporated into zinc oxide, such as magnesium and sodium, and the solvents employed, utilizing various solvents like ethanol and methanol to fabricate ZnO thin films. We examined their distinctions, and this will be the focus of the subsequent chapters.

I.2.3 Utilizations of thin-film ZnO

The structural, optical, and electrical features of zinc oxide enable its utilization in diverse applications, including photocatalytic processes and photodetector. The subsequent chapters will extensively address these applications and their significance.

I.2.3.1 Photocatalyst

A catalyst is a material, typically a semiconductor, that accelerates the rate of a chemical reaction. Photocatalysis is the process that occurs at the catalyst when photons with energy that exceeds the band gap are absorbed. This results in the formation of electron-hole pairs in the semiconductor, also known as photoelectrons in the conduction band and photo holes in the valence band. These charge carriers have a finite lifespan. These particles may either regroup via multiple pathways or diffuse to the semiconductor surface due to the potential gradient induced by band curvature. The minimum energy of the conduction band establishes the reduction potential of the photoelectrons, whereas the maximum energy of the valence band dictates the oxidation capability of the photo-holes. Molecules are transported to the

interface zone concurrently, subsequently diffused, and ultimately chemisorbed onto an active site on the catalyst surface. Consequently, oxidation-reduction processes are viable. The adsorbed particle undergoes photoreduction if its potential exceeds that of the photoelectrons. Another possibility is that it may undergo photooxidation if its potential is found to be less than that of the photo holes [24].

➤ **Principle of heterogeneous photocatalysis**

Heterogeneous photocatalysis entails the irradiation of a semiconductor utilizing natural sunlight or artificial ultraviolet light. This material experiences photon excitation, with energy equivalent to or above its band gap energy, facilitating the transition of an electron from the valence band to the conduction band. The photogenerated electrons and holes in the semiconductor possess reducing and oxidizing capabilities, respectively, enabling them to interact with the species adsorbed on the photocatalyst's surface. Only a subset of these pairs will be used in the pollutant degrading methods, the remainder will recombine through trapping and will not contribute to pollution control [25].

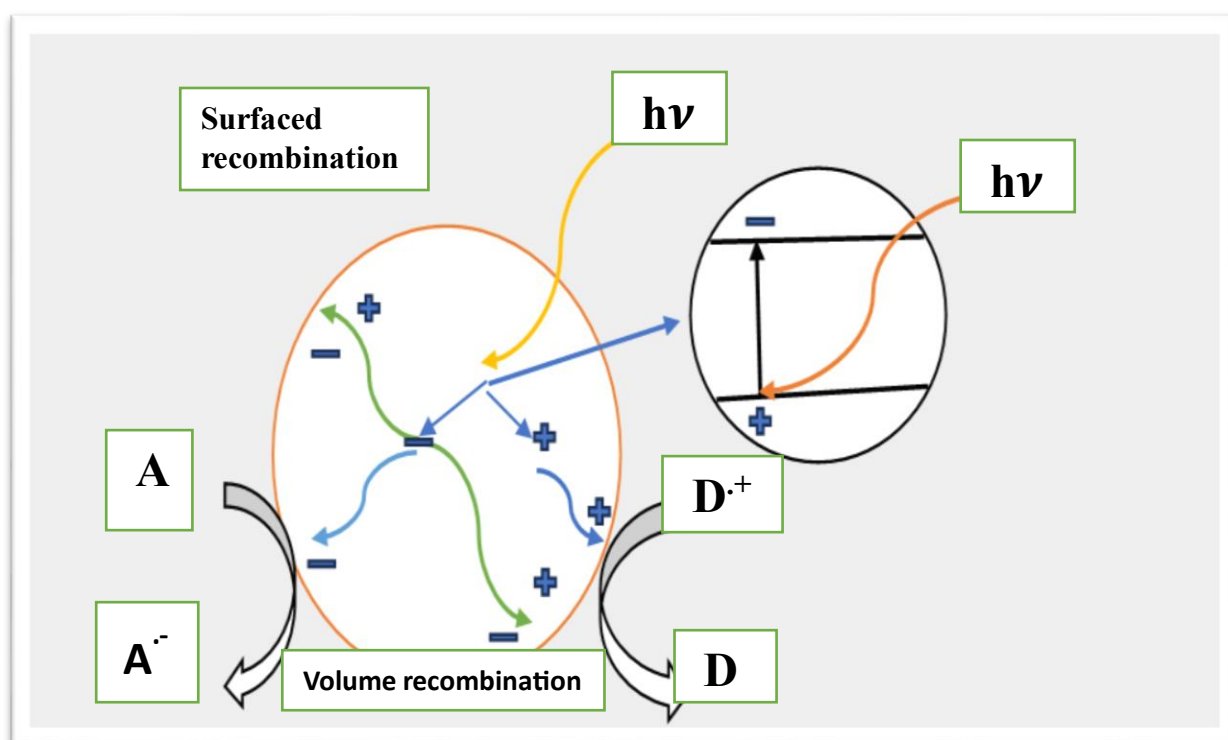


Fig I.3 Photocatalytic Schematic.

➤ **The photodegradation of MB and MO**

The solution's absorbance was assessed by measuring the UV-Vis spectrum within the wavelength range of 500–750 nm. The degradation efficiency (D) was established employing the subsequent equation:

$$D\% = \frac{C}{C_0} \times 100 = \frac{A_0 - A_t}{A_0} \times 100 \quad (I.1)$$

C_0 denotes the initial concentration of the MB and MO options, while C indicates the final amount of the two dyes in the solution [26]

➤ **Kinetics of photocatalytic reactions**

The Langmuir–Hinshelwood (L–H) kinetic model is predominantly employed to characterize the photocatalytic oxidation of diverse contaminants, especially pollutants [27,28].

The L–H model is associated with the initial concentration of contaminants through the following equation:

$$R = -\frac{dc}{dt} = krk\theta = \frac{krkC}{1+kC} \quad (I.2)$$

where R depicted the oxidation rate of the reactant, C denotes the concentration of the reactant, t indicates the length of light, kr signifies the noticed reaction rate constant, and KC refers to the adsorption coefficient of the reacting agent [29-30].

➤ **Factors influencing photocatalytic efficacy**

• **Impact of concentration of catalysts**

At low concentrations, the rate of photocatalytic degradation is linearly proportional to the catalyst quantity, subsequently becoming independent of the catalyst concentration [ZnO] [31,32]. The concentration of the catalyst is directly correlated with the concentration of electron-hole pairs, which affects the initial pace of the photocatalytic activity. Nonetheless, up to a certain threshold, the whole surface of the catalysts is illuminated. Exceeding this value, the surplus particles obstruct their neighbours, so restricting the effective transmission of light in the solution (the solution becomes opaque). In this instance, the rate of the process becomes independent of the catalyst's mass [33].

- **Impact of luminance**

Ollis and his colleagues [34] investigated the influence of illumination on the kinetics of the photocatalytic process in a colloidal medium, concluding that for low photon flux, degradation is directly proportional to light energy. For an increased flux, degradation is directly proportional to the square root of the energy.

This transition results from the preponderance of electron-hole pair recombination processes. At elevated light intensities, the deterioration rate becomes independent of photon flux, resulting in a transition to a mass transfer-dominated system [35].

It has been demonstrated that the reaction rate for all forms of photocatalytic reactions is related to the exposure energy [36].

- **Influence of the Solvent**

Alkoxides exhibit immiscibility in water, necessitating the combination of these precursors with water and, if required, a catalyst, all within a shared solvent. In such cases, it is advisable to employ the alcohol linked to the -OR ligand of the alkoxide to avert potential interactions among the various components that could modify the reaction kinetics. The initial solution is generally an alcoholic solution [37].

- **Soil Ph**

Considering the mechanisms underlying gelation, it is evident that pH significantly influences the progression of the reactions; specifically, H_3O^+ and OH^- ions exert disparate effects on the two reaction types: the H_3O^+ cation, drawn to oxygen, promotes the substitution of OR groups with OH^- (hydrolysis), whereas the OH^- anion, attracted to the electronegative metal M, enhances the formation of M-O-M bonds (condensation). An acidic atmosphere promotes hydrolysis, whereas a basic environment enhances condensation. Catalysis directly influences the morphology of the resultant substance. This component significantly affects the porosity of the final material, which consequently influences its physical qualities [38-39].

- **Impact of dyes MB and MO molecular architecture**

Additional research has examined the influence of the molecular architecture of pollutants on photocatalytic efficacy. Lachhab's team investigated the influence of dye chemical structures on their adsorption on titanium dioxide and, subsequently, on their photocatalytic degradation. Five structurally distinct dyes were chosen: Methyl Red, Orange G, Alizarin S,

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Congo Red, and Methylene Blue. The maximum adsorption constant was observed for Methyl Red, due to the carboxyl group replaced on the benzene rings [40].

The efficiencies of photodecomposition are significantly influenced by the molecular structures and functional groups of the contaminants [41]. Scientific research on the photocatalytic degradation of methylene blue and orange methylene in an aqueous zinc oxide suspension demonstrates that molecular structure significantly affects degradation. In identical experiments, varying percentages of pollutants were eliminated, with the degradation of blue methylene surpassing that of the yellow-orange pollutant, especially under sunlight exposure [42]

During our study, we altered the solvents, employing ethanol and methanol. We also modified the pollutants, employing methyl blue and orange yellow, in addition to the photocatalytic action. We subjected the samples to sunlight and ultraviolet radiation, and upon evaluating the percentage of pollutant degradation and the reaction rate.

I.2.3.2 Photodetectors

Photodetectors are utilized in numerous uses across various domains, including compact disc players, optical-fiber interactions, surveillance of rockets or intercontinental ballistic missiles, and remote sensing. They are semiconductor devices that receive optical signals and transform them into electrical signals. A generic photodetector functions similarly to a solar cell that produces electricity [43].



Fig I.4 *The Fundamentals of UV Photodetectors*

➤ **Analysis of Current and Voltage**

The current (I)-voltage (V) electrical measurement is a fundamental technique employed for characterizing p-n junctions. The current-voltage characteristic curves of solid-state devices are the superimposition of the I-V curve in the absence of light (dark) and in the presence of light. The tests solely indicate the electronic characteristics of the junctions, including threshold voltage, diode quality factor, reverse saturation current, and series resistance [44, 45].

➤ The photoconductivity gain (G), sensitivity (S), responsivity (R), and detectivity (D) were employed to evaluate the photoelectrical criteria for assessing the optoelectronic performance of ZnO thin films, derived using the following equations [46,47].

$$S = \frac{I_{ph}}{I_{dark}} \quad (I.3)$$

$$R = \frac{I_{ph}}{A_0 P_{opt}} \quad (I.4)$$

$$G = R \times \frac{hc}{e\lambda} \quad (I.5)$$

$$D = R \left(\frac{A_0}{2eI_{dark}} \right)^{1/2} \quad (I.6)$$

I.3 Characterization methodology

Following the examination of the structural, optical, and electrical properties of ZnO and the photocatalytic activity of thin films, we will now address the characterization methods employed to assess these attributes.

- We employed X-ray diffraction (XRD) to assess the crystal quality, structural characteristics, and lattice parameters.
- Field Emission Field Emission Scanning Electron Microscopy (FE-SEM) was employed to analyze the topography of the synthesized samples, along with the growth process and the size and morphology of the nanoparticles.
- To examine the optical properties, all produced films were evaluated utilizing a UV–Visible spectrophotometer. The transmittance (T) and refractive index (n) of several thin layers were measured in the range of 190–1100 nm
- to ascertain the chemical composition utilizing Fourier transform techniques (FTIR)
- to elucidate the optical properties of materials, using photoluminescence spectral analysis.

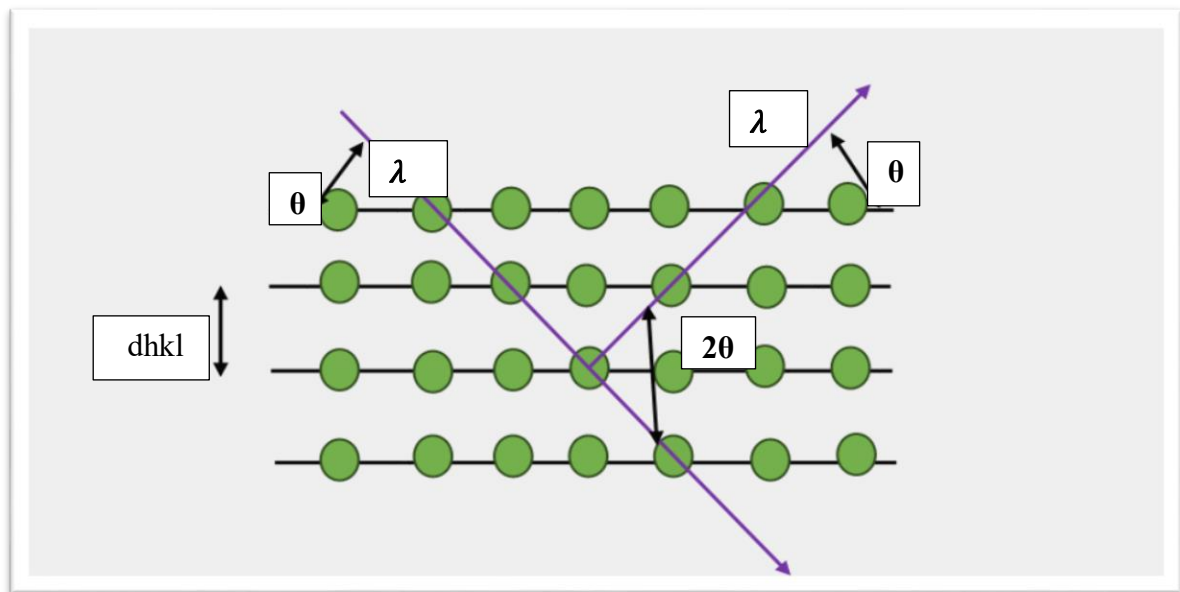
I.3.1 X-ray diffraction (XRD)

The structural analysis of the film samples was conducted using X-ray diffraction (XRD), employing a D8 ADVANCE system with Cu K α radiation ($\lambda = 1.54184 \text{ \AA}$) over the angular range of 20° to 80° .

It is a prevalent, non-destructive characterization method largely utilized for phase identification of crystalline materials, capable of producing a distinctive fingerprint of unit cell dimensions through Bragg reflections linked to crystal structures. The crystal structure can diffract X-rays because the interplanar spacing in a crystal lattice is comparable to the wavelength of X-rays. The high-energy X-ray can penetrate deeply into materials and can be diffracted by periodic atomic arrays. While diffracted X-rays can radiate in all directions, only those that adhere to Bragg's law are constructive and, therefore, detectable [48].

➤ Principle of X-ray Diffraction (XRD)

A monochromatic X-ray beam aimed at a polycrystalline material is partially reflected by the atomic planes of specific crystals. To quantify X-ray photon diffraction, the beam must strike the atomic planes at a specific angle. The reflected waves must be in phase to constructively interfere with one another for detection by the sensor [49].



FigI.5 crystal planes in Bragg's state

➤ **Assessment of lattice parameters**

In the hexagonal structure, the inter-reticular distance $d(hkl)$ is correlated with the parameters of the lattice a and c , as well as the Miller indices h , k , and l , via the equation that follows [50,51].

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

➤ **Measurement of grain size**

Scherrer's technique

The grain size of the numerous specimens was initially ascertained utilizing the X-ray diffraction spectra employing Scherrer's equation [52,53].

$$D = \frac{K\lambda}{\beta \cos \theta} \quad (I.8)$$

where D indicates the grain size in nanometers (nm), λ denotes the wavelength of the X-ray beam, θ is the diffraction angle, and β signifies the full width at half maximum (FWHM) measured in radians.

The dislocation density (δ) was derived using formulas [54,55].

$$\delta = \frac{1}{d^2} \quad (I.9)$$

The volume of the unit cell (V_{cell}) of the hexagonal ZnO structure was estimated applying these formulae [56,57]:

$$V_{cell} = \frac{\sqrt{3}}{2} a^2 c \quad (I.10)$$

X-ray density (ρ_{X-ray}) and specific surface area (S^*) were calculated utilizing the subsequent calculations [58, 59]:

$$\rho_{X-ray} = \frac{ZM}{V_{cell} Na} \quad (I.11)$$

$$S^* = \frac{6000}{\rho_{X-ray} D} \quad (I.12)$$

I.3.2 Field Emission Scanning Electron Microscopy (FE-SEM)

The surface morphology of the produced films was analyzed using FE-SEM (Thermo Scientific Quattro SEM). enabled the acquisition of cross-sectional images subsequent to the transverse sectioning of samples, allowing for the assessment of film thickness [60].

➤ **Fundamental tenet of (FESEM)**

This technique employs a highly focused electron beam that systematically scans the sample surface point by point. The interaction of the beam with the material results in the emission of backscattered electrons, secondary electrons, Auger electrons, X-rays, and photons from the sample surface. The magnitude of these signals is around a cubic micron ($\sim\mu\text{m}^3$), which is quite significant in comparison to the place of contact. The fundamental SEM image is generated from a combination of secondary and backscattered electron signals in differing ratios. The identification of secondary electrons facilitates topological surface imaging with little compositional sensitivity. In backscattered electron acquisition, imaging is contingent upon the atomic number (Z) of the atoms within the material [61,62].

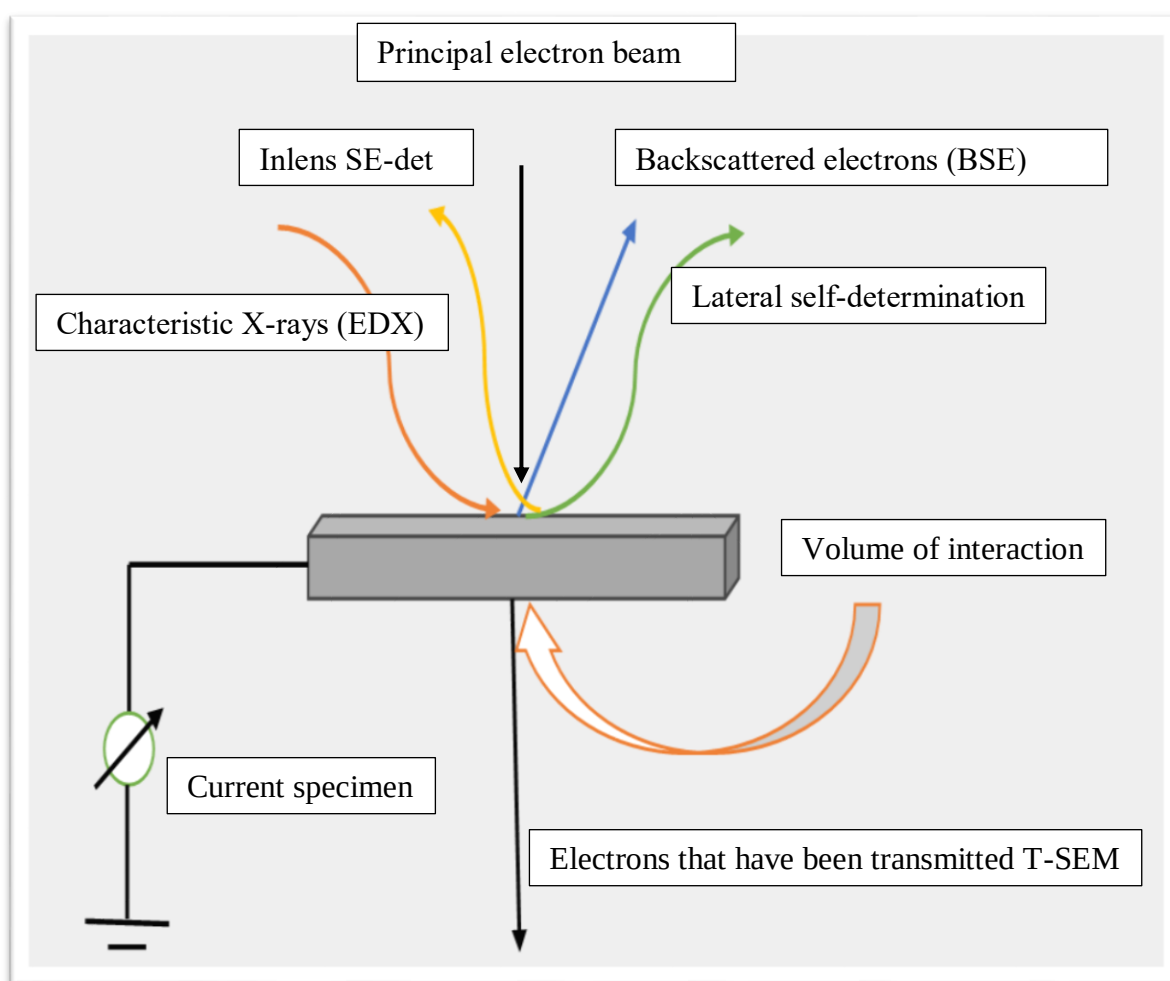


Fig I.6 Demonstration of electron-specimen relations in Scanning Electron Microscopy (SEM).

➤ **Energy dispersive X-ray spectroscopy (EDS or EDX)**

EDX is a chemical microanalysis method utilized alongside SEM. EDX offers elemental analysis of regions as little as one nanometer in diameter, facilitating the determination of elemental composition at specific spots or the mapping of lateral elemental distribution within the imaged area. When an incident electron beam interacts with the sample's atoms, secondary and backscattered electrons are released from the surface of the sample. Nonetheless, these are not the sole signals released from the sample. When the incident beam interacts with the sample, it generates secondary electrons, resulting in numerous sample atoms having vacancies in their electron shells where the secondary electrons were previously located. If these "holes" exist in inner shells, the atoms are in an unstable condition. To stabilize the atoms, electrons from outside shells will transition to inner shells; however, since the outer shells possess a

higher energy state, the atom must relinquish some energy to facilitate this process. It accomplishes this by X-rays. The X-rays released from the sample atoms possess characteristic energy and wavelength, indicative not only of the parent atom's element but also of the electron shells that lost and replaced electrons, so enabling the measurement of the sample's elemental makeup. An EDX spectrum indicates the element associated with each peak and the accompanying type of X-ray [63].

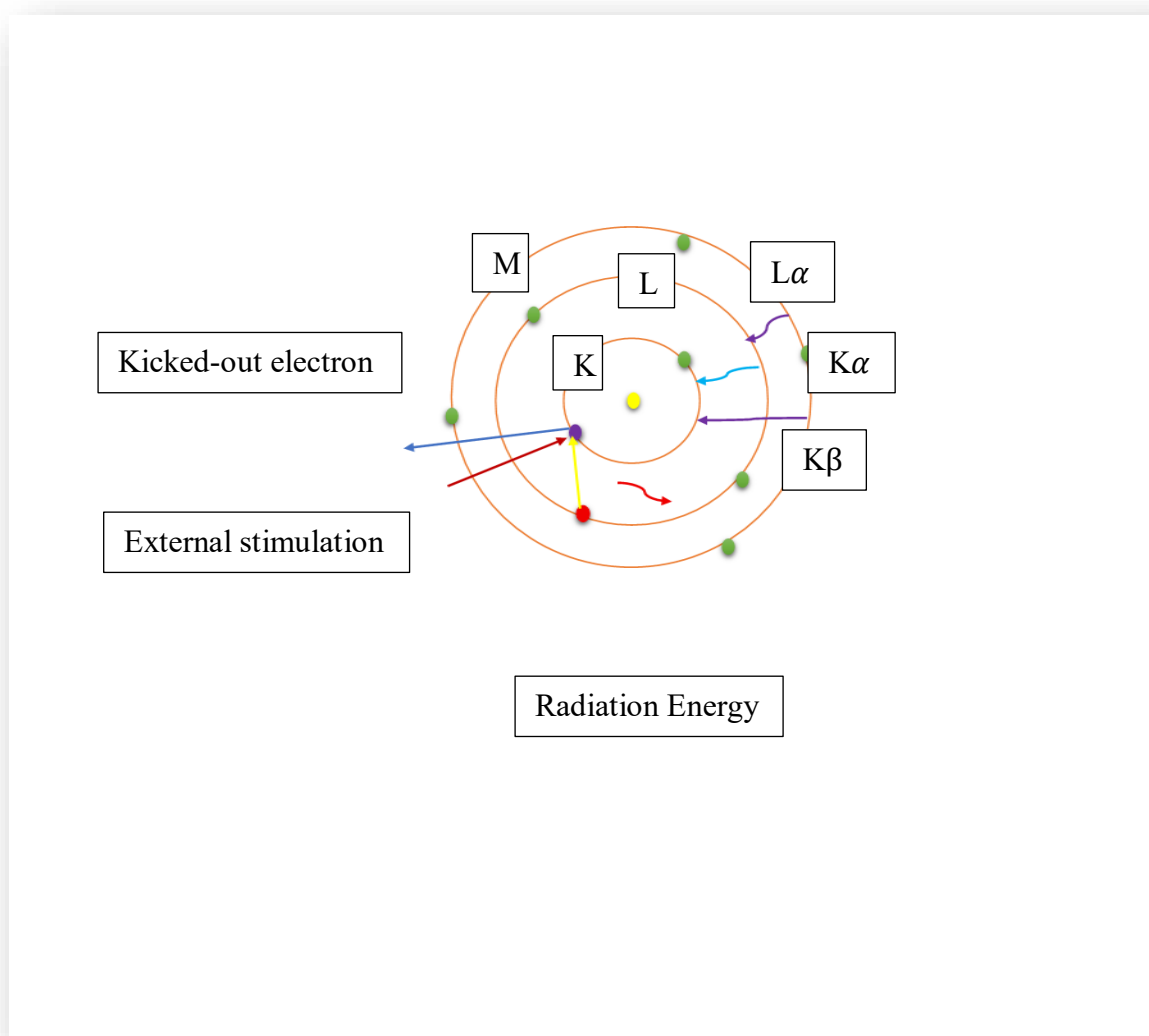


Fig I.7 Diagram of X-ray excitations in Energy Dispersive X-ray (EDX) analysis.

I.3.3 Ultraviolet-Visible Spectrophotometry

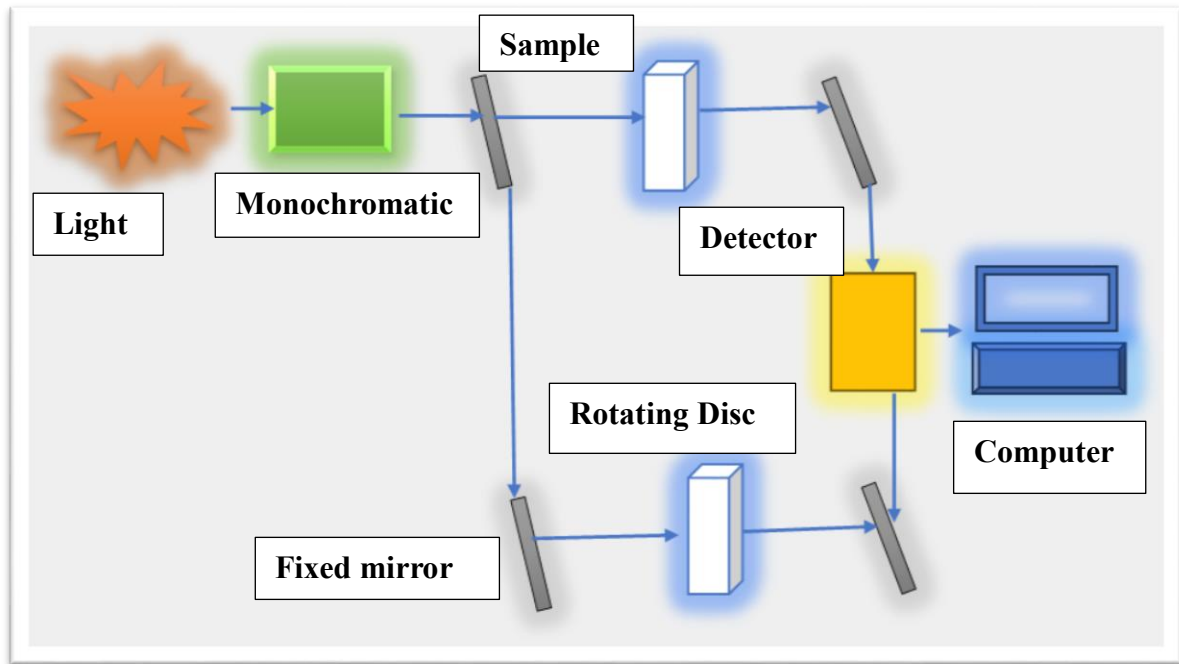
The fields of spectroscopy are often classified according to the wavelength range of the measurements performed.

The optical properties were assessed by quantifying the transmittance of the films. We utilized a spectrophotometer in our research. Perform a scan of the 80D spectrophotometer across the UV–Vis spectral range of 190–1100 nm.



FigI.8 Ultraviolet-Visible A spectrometer

It is a scientific technique for measuring the absorbance of a substance as a function of the wavelength of emitted electromagnetic radiation. whose operational principle is illustrated in **Fig I.9**, we successfully generated curves depicting the fluctuation of transmittance as a function of wavelength within the UV-Visible spectrum. Through the application of these curves. Optical attributes can be calculated, including the optical absorption threshold, absorption coefficient, and valence band tail width [8].



FigI.9 Schematic depiction of the spectrophotometer.

➤ **Assessing the band gap width**

In the spectral range of light absorption, and with knowledge of the layer thickness (d), we can ascertain the absorption coefficient of the layer as a function of wavelength in accordance with Beer-Lambert's equation [64,65,66].

$$T = e^{-\alpha d} \quad (\text{I.13})$$

$$\alpha = \frac{1}{d} \ln \left(\frac{100}{T} \right) \quad (\text{I.14})$$

The absorption coefficient α is articulated as a function of the optical gap (E_g) in accordance with Tauc's equation [8]

$$\alpha h\nu = A(h\nu - E_g)^n \quad (\text{I.15})$$

$h\nu$: photon energy of the incoming radiation (eV).

A : constant contingent upon electron-hole mobility

E_g : optical gap energy (eV),

$n = 2$ or $1/2$ corresponding to a direct or indirect gap transition, respectively [8]

I.3.4 Fourier Transform Infrared Spectrometry (FTIR)

In order to ascertain the chemical interactions and structure of ZnO thin films, Fourier-transform infrared (FTIR) spectroscopy was performed utilizing a Perkin-Elmer spectrometer at a resolution of 8 cm^{-1} , operating in transmitting mode over the spectral range of $400\text{--}4000\text{ cm}^{-1}$.



Fig I.10 *Fourier-transform infrared spectrum.*

The energy of photons released in this range is inadequate to facilitate electronic transitions within materials but can stimulate the excitation of chemical bonds between atoms. Consequently, incident infrared photons will be absorbed when their energy aligns with the excitation energy of an atomic bond in the material, which is influenced by the chemical environment of the bonds, the atomic mass, and the bond characteristics. Thus, a material with a specific chemical composition and structure will correlate to a distinct set of excitation modes, enabling the identification of its characteristic chemical bonds. The excitation modes can be computed via "group theory" and are enumerated in tables, so aiding in the identification of chemical bonds [67].

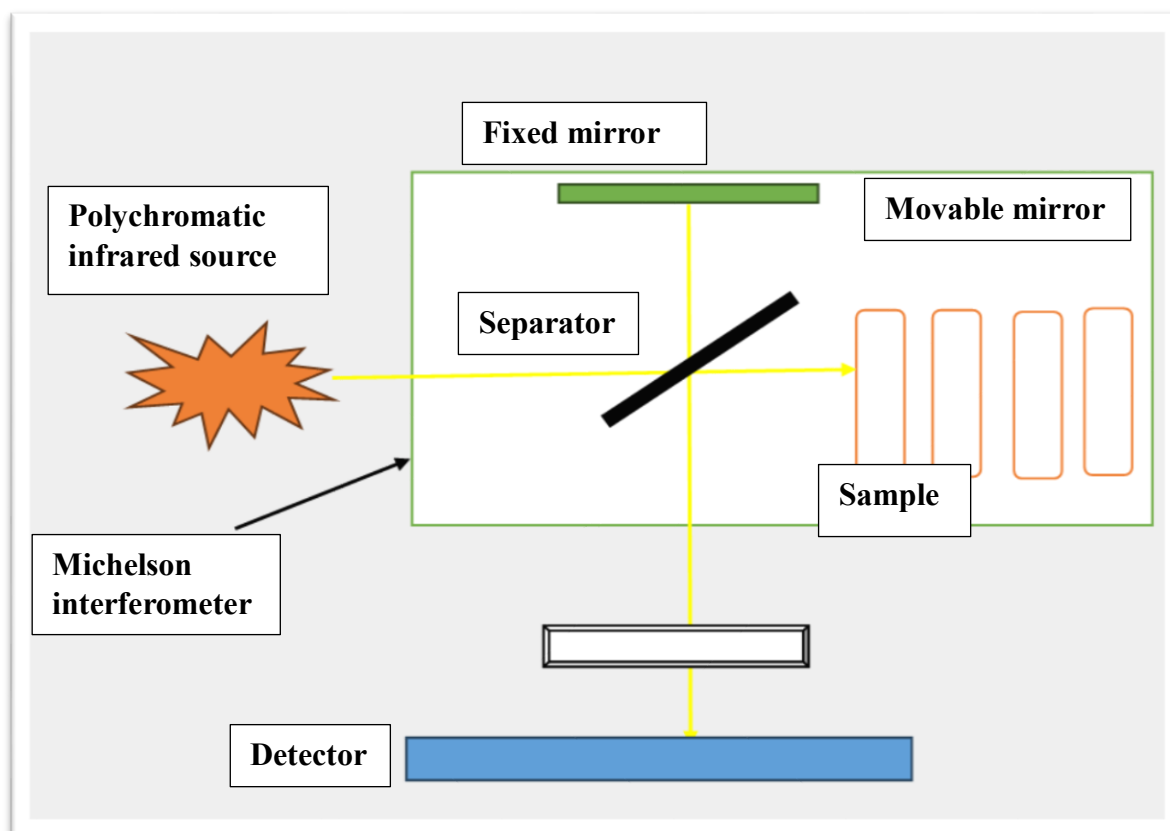


Fig I.11 The essential principles of infrared (IR) spectroscopy analysis are delineated as follows.

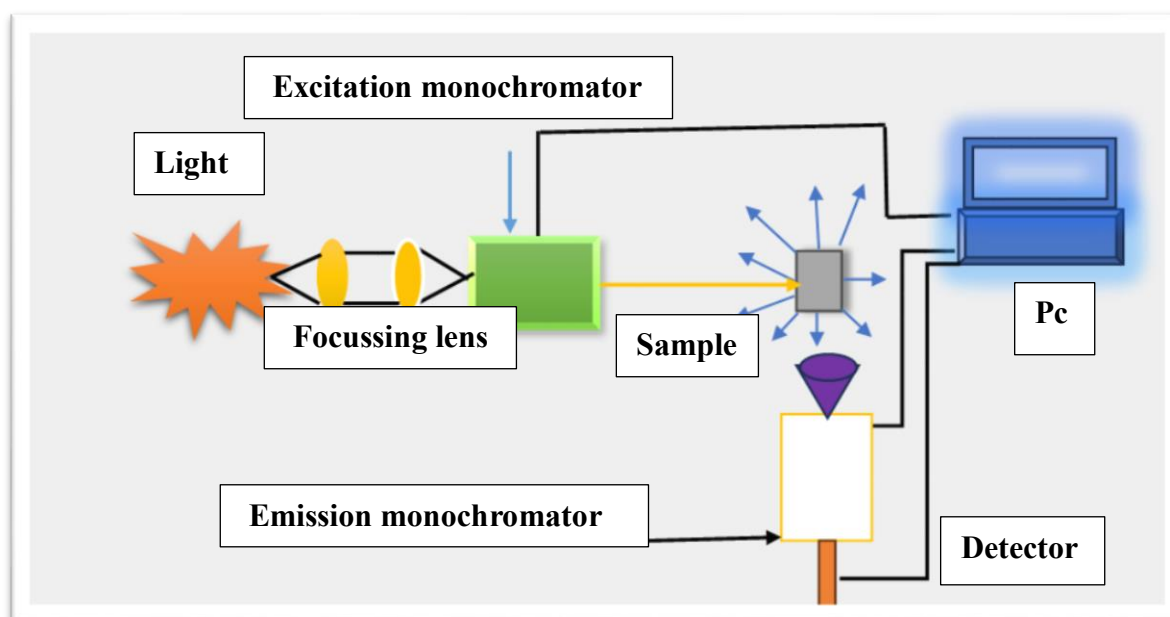
I.3.5 Photoluminescence spectroscopy

In this investigation, photoluminescence measurements were conducted using a PerkinElmer fluorescence spectrophotometer at room temperature, with an excitation wavelength of 300 nm.



Fig I.12 Photoluminescence Perkin Elmer spectrophotometer.

Photoluminescence (PL) refers to the spontaneous emission of light from a substance when subjected to optical excitation. Photoluminescence spectroscopy is a non-invasive technique for investigating the electronic structure of materials. Photoluminescence spectroscopy can be employed to characterize various material characteristics. It offers electrical characterization and insights into the condition of surfaces and interfaces. This approach directly measures essential material properties, including band gap, impurity levels, defect detection, and recombination mechanisms. **Fig I.13** illustrates the schematic diagram of the photoluminescence measurement apparatus. When high-energy light strikes a substance, photons are absorbed. Electrons are elevated to an excited state due to the energy of absorbed photons. Ultimately, these energized electrons return to the ground state by producing radiation in the form of light. The emitted light can be gathered and examined to obtain information regarding the substance. Upon examining the signals, transition energies and electronic energy levels can be ascertained [63].



FigI.13 A diagram illustrating components utilized for measuring photoluminescence spectra.

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Chapter I: Properties of zinc oxide, photocatalytic behavior, and characterizations methodologies

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Chapter II :

Deposition Techniques and Experimental Methodologies

II. Introduction

This chapter discusses the fundamental notion of thin films. We also discussed the methodology for fabricating these films, encompassing both physical and chemical techniques, particularly the sol-gel dip-coating method employed to produce thin films utilizing ZnO.

II.1 Thin Film Materials

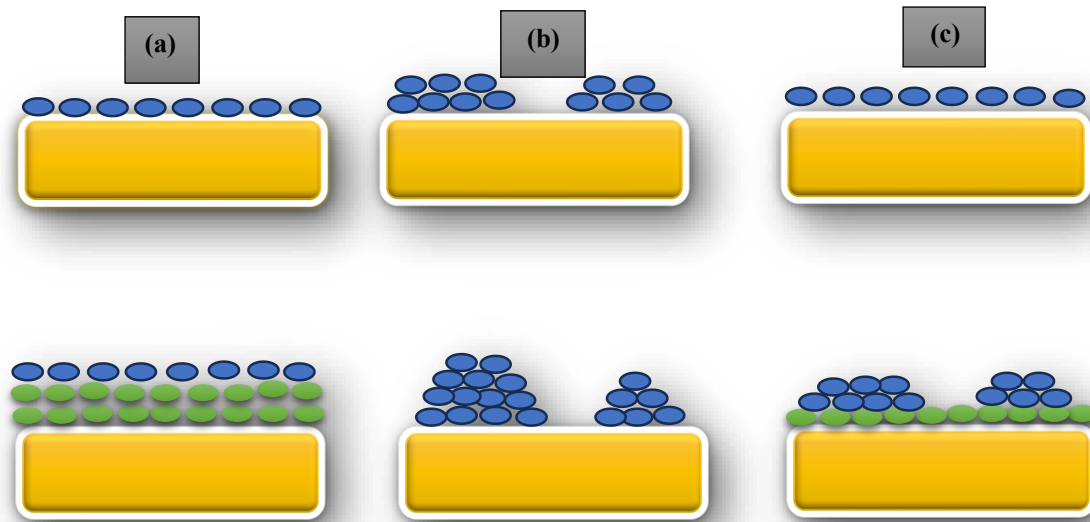
II.1.1 Concept of a thin film

A thin film is defined as a substance applied to a substrate, characterized by a significantly reduced dimension (thickness) measured in nanometers. It is hypothesized that the material in question will restore the recognized characteristics of the bulk substance. The substrate exerts a substantial influence on the structural properties of the overlying layer. A thin layer of identical material and thickness may exhibit markedly different physical properties based on whether it is deposited on an amorphous insulating substrate like glass or a monocrystalline silicon substrate [1]

II.1.2 Mechanism of growth for thin film creation

Multiple development modes exist:

- Bidimensional Growth (Frank Van-der-Merve) On one facet of a crystal, the atomic layers sequentially accumulate while the surface stays planar throughout the deposition process [2]
- Three-Dimensional Growth (Volmer-Weber) This entails the creation of islands composed of many atomic layers. In a state of thermodynamic equilibrium [3,4]
- Stranski- Krastanov mechanism (SK) The growth initiates in a manner akin to the Frank Van-der-Merve (2D) growth, but after few atomic layers, it transitions to three-dimensional development [5,6]

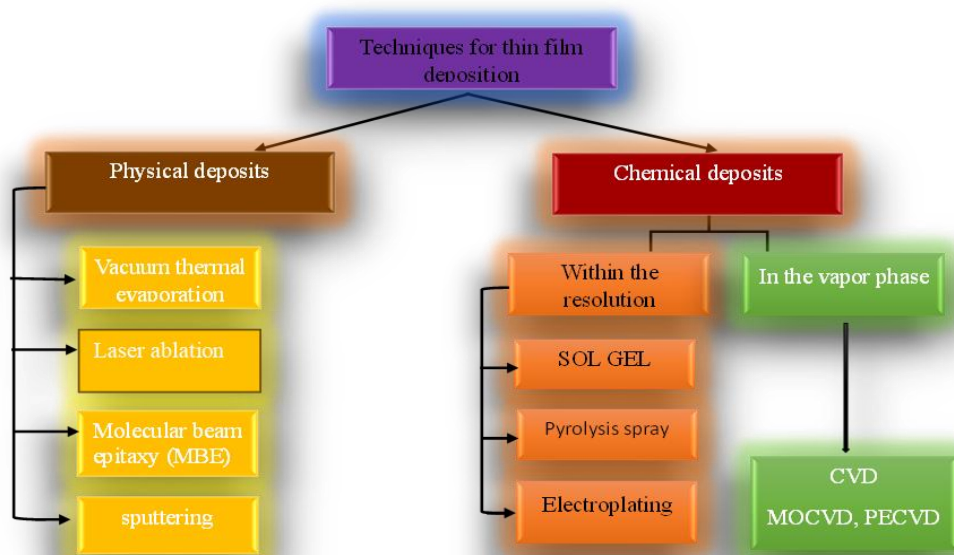


FigII.1 Illustration mechanisms of thin film.

(a) Frank Van-der-Meme (b) Volmer-Weber (c) Stranski- Krastanov mechanism (SK)

II.2 Thin-layer fabrication methodologies

A thin film can be produced using a pair of approaches: physical and chemical:



FigII.2 Schematic fabrication of thin layers.

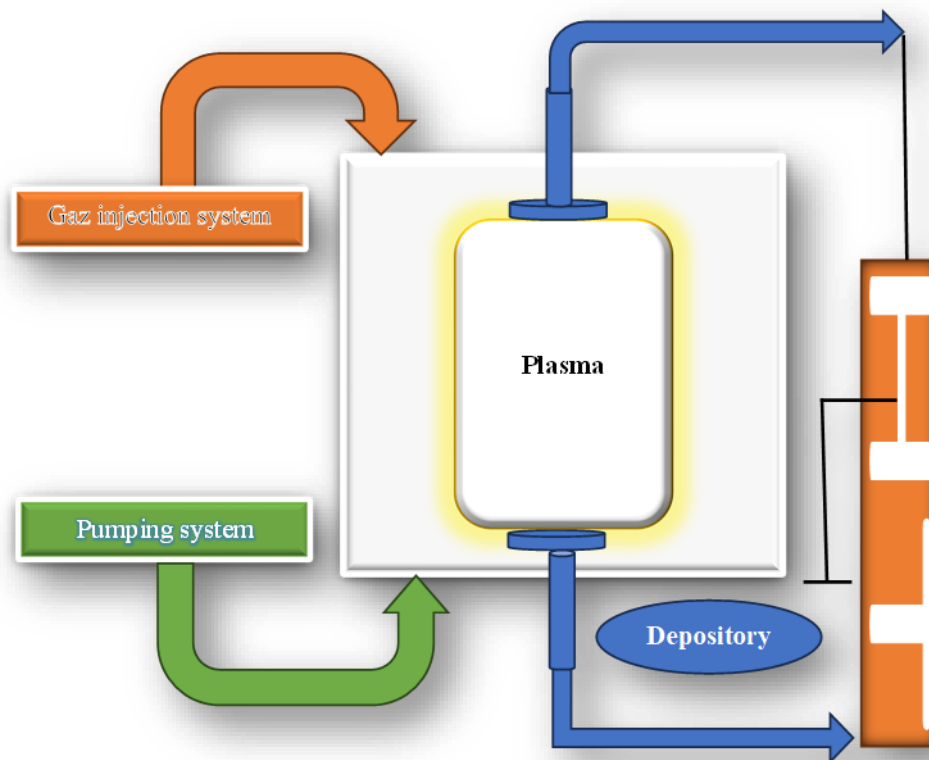
II.2.1 physical mechanisms

Numerous physical techniques are employed to fabricate thin films. We shall reference some of them: Sputtering, Laser ablation and Molecular beam epitaxy.

II.2.1.1 Sputtering

Fig II.2 depicts the sputtering framework, comprising four fundamental components:

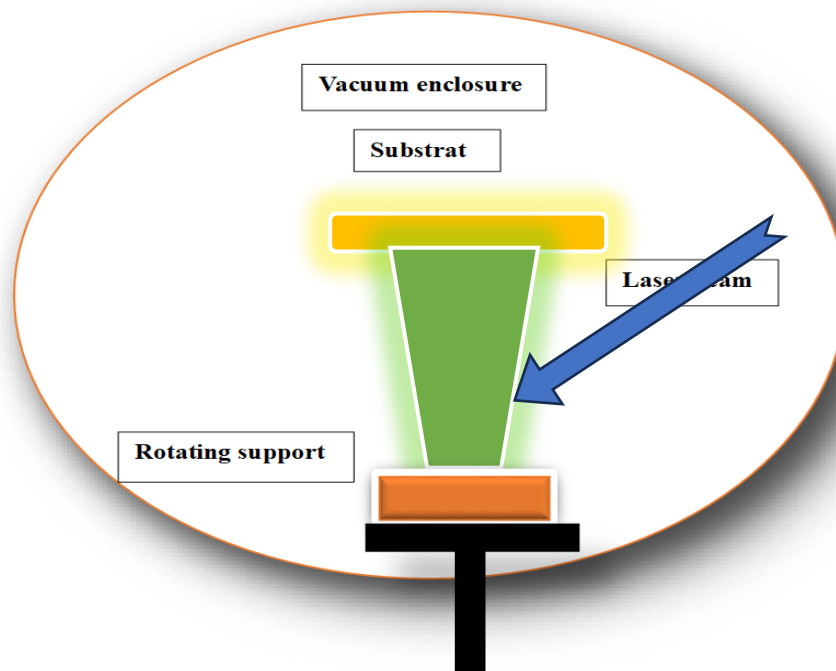
- A chamber designed for sputtering.
- A dual pumping apparatus designed to attain extremely low pressures and sustain a stable dynamic pressure during the deposition phase.
- A high-voltage generator (direct current or radio frequency).
- A gaseous injection apparatus [7].



FigII.3 schematic of cathodic sprayer.

II.2.1.2 Laser ablation

A concentrated, pulsed laser beam irradiates the target, subsequently transforming into thermal, chemical, and mechanical energy, leading to evaporation, ablation, plasma generation, and potential exfoliation. The expelled material spreads into the surrounding vacuum as a plume including several energetic species. These varied species ultimately aggregate onto a substrate as a thin coating [8].



*FigII.4*Graphical for laser ablation.

II.2.1.3 Molecular beam epitaxy

Silicon epitaxy employs a silicon source that is thermally activated by electron bombardment inside a vacuum environment. Growth occurs at low temperatures (400-800°C). It is mostly used for III-V compounds in microelectronic applications. There are two categories of epitaxy, each significant for distinct purposes. Homoepitaxy refers to instances when both the layer and substrate consist of same materials, such as the deposition of thin silicon (Si) layers on a silicon substrate. The second sort of epitaxy, heteroepitaxy, contrasts with the former, since it involves instances when the layer and substrate consist of dissimilar materials.

In comparison to the other approaches outlined, this method yields the most superior crystallized thin layers, achieving thicknesses as little as fractions of monolayers [9].

II.2.2 Section Chemical Approach

Subsequent to discussing physical methods, we transition to chemical methods, which are predominant globally owing to their characteristics, affordability, and rapid production of thin films.

II.2.2.1 Colloidal Technique

The process relies on a pre-prepared colloidal solution for formation. This is a dispersion of material in a liquid solvent, organized into granules known as micelles, which are aggregation of molecules in a colloidal solution, typically measuring between 2 and 200 nm in diameter.

Solvation refers to the intimate interaction between solvent molecules and solute molecules or ions. The stability of a colloidal solution arises from the equilibrium between attracting and repulsive forces acting on the particles. These interactions are contingent upon the temperature and pH of the solution [10].

II.2.2.2 Pyrolytic spray

A normal pneumatic system or an atomizer with an ultrasonic generator is used to disperse the substance's basic components into fine droplets. The jet impacts the heated substrate surface at a sufficiently elevated temperature to facilitate the decomposition of the solutes in the solution and to initiate processes that are likely to produce the desired material. At increased temperatures, volatile byproducts from the reactions will be swiftly eliminated, leaving just the chemicals to be deposited onto the substrate [11].

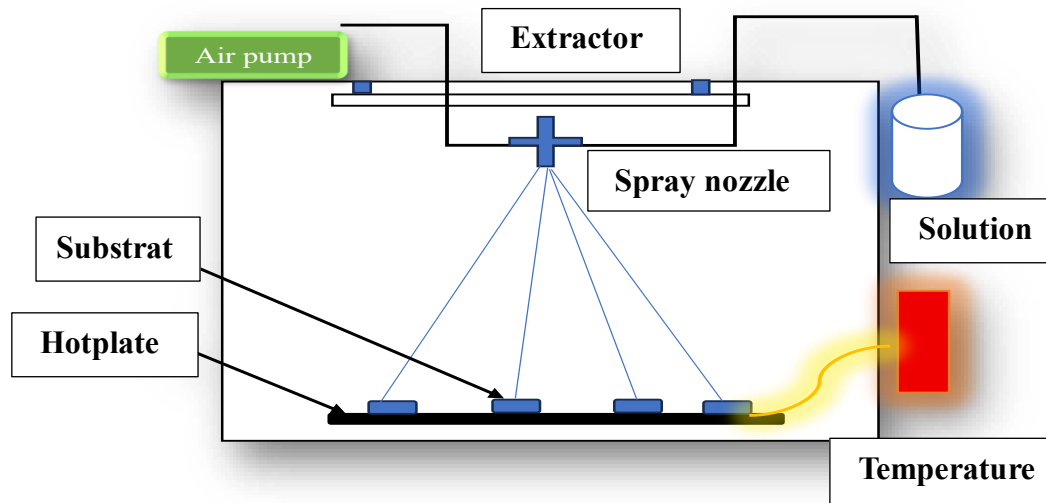


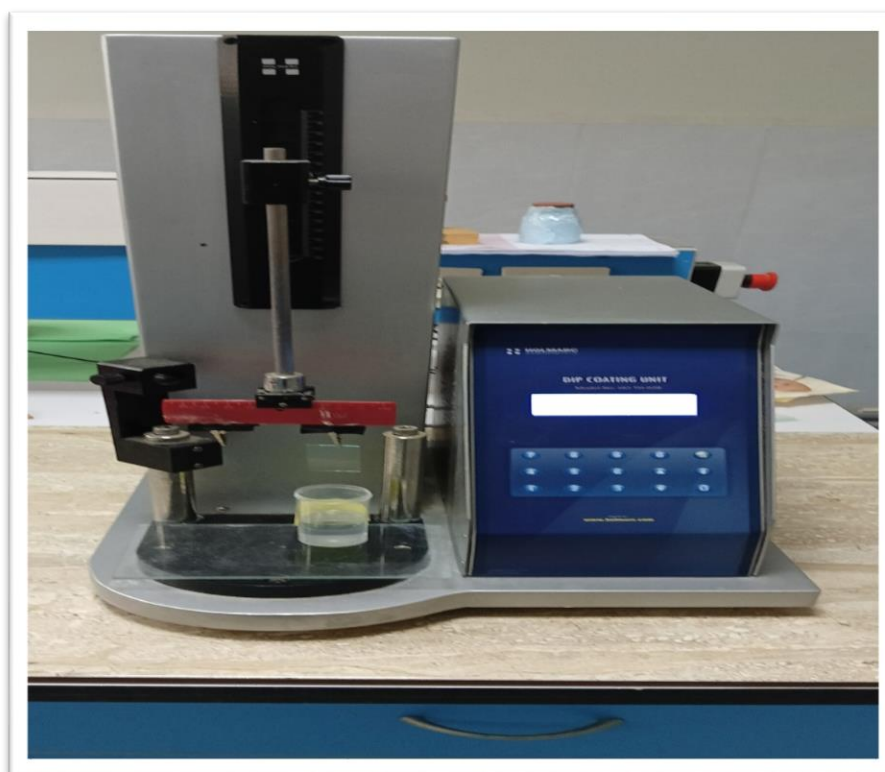
Fig II.5 Schematic of spray pyrolysis.

II.2.2.3 Sol-gel technique

Sol-Gel Technique The sol-gel method is a wet-chemical synthesis approach for the creation of oxide gels, glasses, and ceramics at low temperatures. It relies on the regulation of hydrolysis and condensation of alkoxide precursors. Roy and colleagues employed the sol-gel method to synthesis diverse novel ceramic oxide compositions exhibiting exceptional chemical homogeneity, incorporating elements such as Si, Al, and Zr, which standard ceramic powder methods could not achieve. Ceramic or glass materials can be fabricated in various forms, including fibers, thin films, porous aerogels, or monolithic bulk glasses. Since then, powders, fibers, thin films, and monolithic optical lenses have been produced from sol-gel glass [12].

II.3 The experimentation approach

We employed chemical techniques, notably the sol-gel dip -coating a method, to fabricate thin films. This results from its characteristics and accessibility, enabling rapid production of thin films. This chapter will provide a detailed discussion of this method.



FigII.6 Sol gel dip -coating technique.

II.3.1 The concept of sol-gel and its classifications

Solid particles are generated through the polymerization of metal oxide (M-O) or metal hydroxide (MOH) groups, resulting in interconnected M-O-M or M-OH-M bridges among metal atoms. The repeating unit consists of carbon atoms. In this context, metal atoms serve as the fundamental repeating unit. This colloidal suspension is referred to as a "sol." Gradually, the individual molecules adhere to one another, creating a three-dimensional network saturated with liquid, thereby producing a "gel." The resultant gel is subsequently cured—typically in a solvent—to enhance the network's strength. The subsequent sections of this chapter will elaborate on the crosslinking and drying processes. Process parameters, including precursor type, solvent, acid or base catalyst, temperature, and pressure, govern the desired characteristics of the finished gel antenna [13].

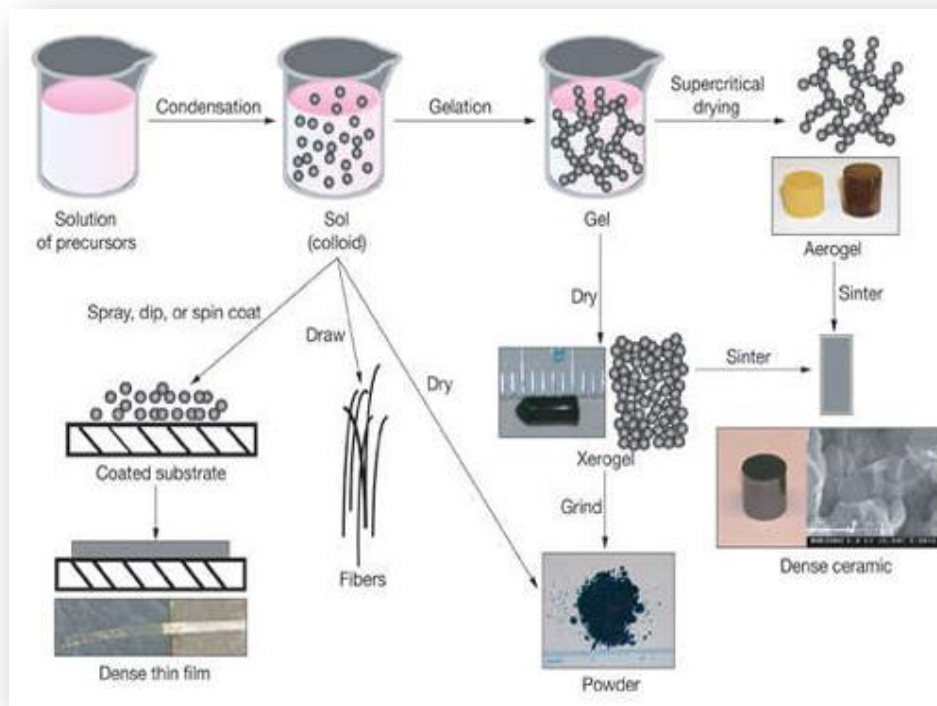


Fig II.7 Fabrication structures by sol-gel technique [13].

➤ Dip-coating

The dip-coating technique is a film deposition procedure in which the substrate to be coated is submerged in a liquid and subsequently removed at a precise pace under regulated temperature and ambient conditions [12,14].

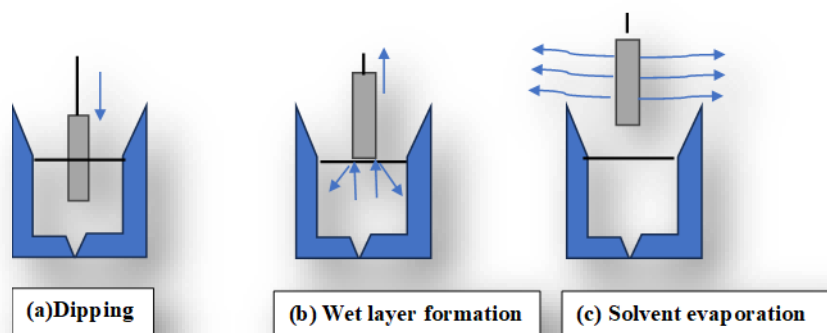


Fig II.8 Phases of the dip-coating procedure.

➤ Spin-coating

This technique involves centrifuging a solution applied in excess onto a substrate. It offers the benefit of straightforward implementation and yields excellent results on tiny, flat substrates [15].

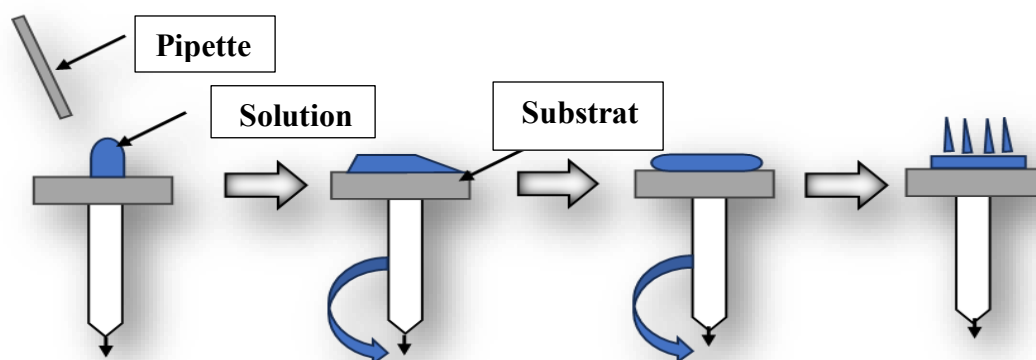


Fig II.9 The spin-coating technique.

II.3.2 Components of the research

Our research was conducted in the Laboratory of Structures, Properties, and Interatomic Interactions (LASPI2A) at Abbes Laghrour University, Khenchela, utilizing equipment for the preparation of zinc oxide solution. We employed an Ohaus-type electronic balance to ascertain the mass of the substances utilized in the investigation. We employed a magnetic stirrer to achieve homogeneity in the solution. ZnO thin films were produced using a sol-gel dip coating apparatus, as previously stated. We dried the samples at a temperature of 400°C; the final stage remaining is annealing. Consequently, we employed an annealing furnace model WISD-FHX-03, a muffled type, and established the temperature at 500°C to enhance the characteristics of ZnO thin films.

II.3.3 The precursors

The Forerunners represent the preliminary phase in this process:

- Zinc acetate dihydrate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$), Sigma – Aldrich, 99.9%
- Ethanol ($\text{C}_2\text{H}_5\text{OH}$), Sigma – Aldrich, 99.8% as the solvent.
- Methanol (CH_3OH), Sigma – Aldrich, 99.8% as the solvent.

- Monoethanolamine (MEA, Sigma – Aldrich,99%)
- Magnesium nitrate hexahydrate ($\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$)
- Sodium acetate dihydrate ($\text{C}_2\text{H}_7\text{NaO}_4$, Sigma-Aldrich,99%)

II.3.4 Selecting the type of substrate

The selection of substrate influences the crystalline quality, optical characteristics, and electrical properties of ZnO film. The substrate is crucial for the growth of thin films due to lattice and thermal mismatches, which often result in stress development in the deposited film [16]. In this study, our undoped and doped ZnO thin films were deposited on microscope slide glass substrates measuring 2.5×2.5 cm. The selection of glass as a substrate was based on three factors: cost considerations, the facilitation of effective optical characterization of our films, and the reduction of tensions. [17]

➤ substrate washing

The quality of the placed layers is contingent upon the surface condition and cleanliness of the substrate. Consequently, the cleaning of the substrate constitutes a pivotal step in the process of sample preparation. The following procedures are employed for the purpose of substrate cleaning: The cleaning process was conducted in distilled water using ultrasound for a duration of 15 minutes. Thereafter, the specimen was rinsed with distilled water. The cleaning procedure involved the utilization of methanol for a period of 5 minutes, followed by acetone for an additional 5 minutes. The final step involved drying the specimen using optical paper [18].



FigII.10 ultrasonic bath apparatus

II.3.5 Production of thin films

The creation of ZnO thin films required the formulation of solution. The solution (A and B) was formulated utilizing zinc acetate dihydrate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$) and magnesium nitrate hexahydrate ($\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) as precursors in the manufacture of ZnO: Mg. Ethanol ($\text{C}_2\text{H}_5\text{OH}$) and methanol (CH_3OH) were utilized as solvents, each separately. Solution (c) was formulated with sodium acetate dihydrate ($\text{C}_2\text{H}_7\text{NaO}_4$) as a precursor for the synthesis of ZnO: Na, with ethanol serving as the sole solvent. All components were synthesized at a concentration of 0.4 M with pure analytical-grade reagents.

The film was fabricated on a glass substrate by dip coating with several variations: pure ZnO, ZnO: Mg, and ZnO: Na. The substrate was purified with acetone, Methanol, and distilled water for five minutes each, as previously executed.

The experiment involved the separate combination of 0.02634g of Zinc acetate with 30 ml of ethanol and 30 ml of methanol in a glass beaker. Subsequently, the vessel is enveloped in aluminium foil to prevent the evaporation of solvents. The solution was subjected to magnetic stirring for a period of 2hours, with the objective of achieving a Homogenous mixture at room temperature.

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The atomic ratio of Mg: Zn were modified to produce five distinct films: undoped ZnO, 3%Mg: ZnO, 5%Mg: ZnO, 7%Mg: ZnO and 9%Mg: ZnO. It was determined that the molar ratio of MEA to Zinc acetate was sustained at 1:1 in order to ensure optimum stability. Subsequently, the samples were permitted to mature at ambient temperature for a period of 48 hours, with the objective of enhancing solvation and stability.

The dip-coating procedure entailed the submersion of the substrates in the formulated Mg-doped ZnO solutions, at 3000 rpm for 30 seconds. The coated substrates were subjected to a preheating process at a temperature of 400°C for a duration of 10 minutes, with this cycle being repeated 15 times to ensure uniform film thickness.

Conversely, thin films of ZnO including Sodium acetate dihydrate ($C_2H_3NaO_4$) were deposited by the aforementioned approach. In this study, we altered the concentration of sodium acetate dihydrate to examine its impact on the characteristics of ZnO.

➤ Photocatalytic assessment

Photocatalytic activity measurements were conducted in the Laboratory of Structures, Properties, and Interatomic Interactions (LASPI2A) at Abbes Laghrour University, Khenchela. The measurements involve assessing the degradation of an organic compound, typically a dye or pollutant, in the presence of the sample under analysis, which may be a photocatalyst, when exposed to UV or visible irradiation. This method, which is reasonably straightforward, is currently prevalent in the domain of nanomaterials. We utilized two pollutants, Methylene blue (MB) and methylene orange (MO), in our examples.

II.3.6 Dyes

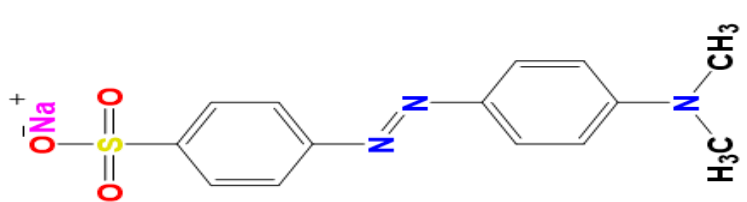
II.3.6.1 Meaning of dyes

Dyes have been used extensively in many applications for painting and dyeing purposes. In contrast, natural organic dyes were widely used, especially in the textile sector. The synthetic dye industry started in 1856 when English scientist W. H. Perkin found the first synthetic color, "mauve," while attempting to synthesize artificial quinine for malaria treatment (aniline, a basic dye). Perkin obtained a patent for his groundbreaking discovery and then initiated a manufacturing line, a progression that was promptly emulated by others. Recently, novel synthetic dyes have been introduced to the commercial market. The acceleration of this trend was enabled by Kekule's 1865 discovery of benzene's molecular structure. Consequently, by the dawn of the 20th century, synthetic dyes had almost entirely supplanted natural colors [19]

II.3.6.2 Orange II

Orange II (OII), often known as acid orange 7 (AO7), is a water-soluble anionic azo dye that is resistant to degradation. The composition of this dye includes a sulfonate (SO₃) and an azo group including aromatic rings within the molecule. Orange II, utilized in the plastics, textile (leather, decorating), printing (ink, paper), and pharmaceutical industries, is a hazardous dye in both its azo and hydrazine forms [20,21]. The physical and chemical characteristics of Orange-II are detailed in the subsequent **Table II.1**

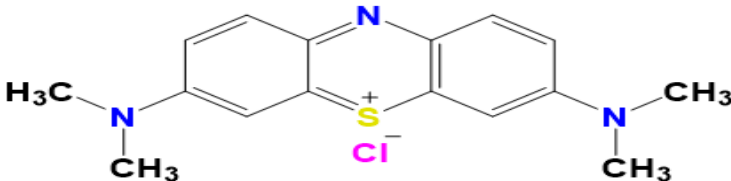
Table II.1 characteristics of Orange II [22].

Molecular architecture	
Molecular Weight(g/mole)	350.32
Melting point °C	164
solubility in water (g/l)	116
Synonyms	Orange Acid 7; 4-(2-hydroxy-1-naphthylazo) benzenesulfonic acid sodium salt; Sodium 4-[(2-hydroxy-1-naphthyl) azo benzenesulfonate]

II.3.6.3 Fundamental characteristics of methylene blue

Methylene blue is a phenothiazine [23] compound and a cationic dye [24] it appears as a dark green powder and in various hydrated forms: monohydrate, dihydrate, trihydrate, and pentahydrate [25], with trihydrate [26] being the most prevalent. It is frequently utilized as a model organic pollutant owing to its stable molecular configuration [27].

Table II.2 Characteristics of MB.[28]

Designation	Methylene blue, also known as tetramethylthionine chloride.Basic Blue 9 (C.I.)
Chemical designation	3,7-Bis(dimethylamino) phenazathionium chloride
Familial Unit	Fundamental dye
Unrefined formula	C ₁₆ H ₁₈ N ₃ ClS
Molar mass (mg/l)	319.86
Water solubility (g/l) at 20°C	40
Molecular architecture	

II.3.6.4 Hazards of organic contaminants.

The predominant classification of dyes is predicated on the chemical structures of synthetic dyes and the application techniques employed for various substrates (textiles, paper, leather, plastics, etc.). The buildup of organic debris in watercourses results in unpleasant tastes, bacterial growth, foul scents, and aberrant coloration. A color can be detected by the human eye at a concentration of 5×10^{-6} g/L [29]. In addition to their unattractive look, coloring chemicals can disrupt light transmission in water, thereby inhibiting photosynthesis in aquatic vegetation.

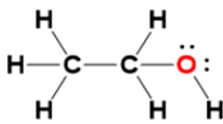
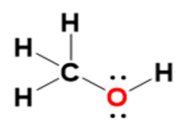
Synthetic organic dyes are substances that cannot be refined through normal biological degradation [30]. This endurance is intricately linked to their chemical composition.

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Ultimately, we not only altered the doping agents, such as Mg-doped ZnO and Na-doped ZnO thin films, and the pollutants, but also progressed to a significant aspect: modifying the solvents to investigate the properties of zinc in various solvents and attain improved outcomes in photocatalytic applications. This will be discussed in the subsequent chapters. **Table II.3** delineates certain properties of ethanol and methanol.

The following table delineates a comparison of the characteristics of the two solvents, ethanol and methanol.

TableII.3 Characteristics of both Solvents

Denomination	Ethanol	Methanol
Chemical formula	C ₂ H ₆ O	CH ₃ OH
Density	0.81 kg/l	0.7918 g/cm ³
State	Liquid	Liquid
Boiling point	78.37 °C	64.7 °C
Hue	Achromatic	Achromatic
Molar mass	46.068 g/mol	32.0419 ± 0.0014 g/mol
Structure		

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CHAPTER III

Structural, Optical, and Electrical Properties of ZnO:Mg Thin Films Fabricated by the Sol-Gel Immersion Deposition Technique

III.1 Introduction

In this chapter, we investigate the effect of Mg incorporation on the structural, optical, and electrical properties of ZnO thin films prepared by the sol-gel immersion deposition technique. ZnO is a wide band gap semiconductor with attractive properties for optoelectronic and photocatalytic applications; however, its performance is often limited by intrinsic defects and moderate conductivity [1-4]. Mg doping is introduced as an effective strategy to tune the band gap, improve crystallinity, and enhance the photoresponse of ZnO-based films [5-8].

The study focuses on the role of Mg concentration and solvent type in determining film quality and functional properties. Structural characterization provides insights into phase composition and grain size evolution with doping, while optical analysis highlights changes in band gap and absorption behavior. Electrical measurements under dark and UV illumination further reveal the influence of Mg incorporation on charge carrier dynamics. In addition, the photocatalytic activity of the films is evaluated through the degradation of methylene blue under both UV and sunlight irradiation.

The results presented in this chapter contribute to a better understanding of the relationship between processing conditions, Mg doping, and the resulting physical properties of ZnO thin films. These findings provide useful guidelines for optimizing ZnO:Mg materials for applications in optoelectronics, sensors, and environmental remediation.

III.2 Structural Analysis

Fig III.1 presents the XRD patterns of undoped and Mg-doped ZnO thin films synthesized using two different solvents: ethanol (**Fig III.1a**) and methanol (**Fig III.1b**). All films exhibit diffraction peaks that can be indexed to the hexagonal wurtzite structure of ZnO (JCPDS card No. 36-1451), confirming the successful growth of ZnO phase without detectable secondary phases such as MgO or other impurities within the detection limit of XRD. This indicates that Mg ions were successfully incorporated into the ZnO lattice rather than forming separate phases.

For the ethanol-based samples (**Fig III.1a**), the diffraction pattern is dominated by a strong (002) peak located around 34.4° , suggesting a preferential growth along the c-axis perpendicular to the substrate surface. With increasing Mg concentration, a slight shift of the (002) peak towards higher angles can be observed (inset), indicating lattice contraction due to the substitution of Zn^{2+} (ionic radius $0.74 \text{ \AA}$) by smaller Mg^{2+} ions ($0.65 \text{ \AA}$). This shift provides clear evidence of successful Mg incorporation into the ZnO crystal lattice. Additionally, the

relative intensity of the (002) reflection increases with doping, implying enhanced texturing and improved crystallinity along the c-axis direction.

In contrast, the methanol-based samples (**Fig III.1b**) display multiple reflections corresponding to (100), (002), (101), (102), (110), (103), and (112) planes. The presence of several diffraction peaks suggests a polycrystalline nature with no dominant orientation. Similar to the ethanol-based films, peak shifts towards higher 2θ values with increasing Mg concentration are also visible, confirming lattice distortion caused by Mg substitution. The improved peak intensities at higher doping levels (7% and 9% Mg) suggest better crystallinity compared to the undoped film.

The crystallite size (D) was estimated from the most intense peaks using the Debye–Scherrer equation, and a gradual reduction in size with increasing Mg concentration was observed. This reduction can be attributed to the distortion of the ZnO lattice and the inhibition of grain growth caused by Mg incorporation. Furthermore, the calculated lattice parameters (a and c) showed a slight decrease with doping, consistent with the smaller ionic radius of Mg^{2+} compared to Zn^{2+} .

Overall, the XRD analysis confirms that Mg doping significantly influences the structural properties of ZnO thin films. Ethanol-based films exhibited a strong c-axis orientation, while methanol-based films revealed a polycrystalline structure. In both cases, Mg incorporation led to peak shifts, reduced crystallite size, and modified lattice parameters, all of which are crucial for tuning the films' optical and electrical behavior discussed in the following sections.

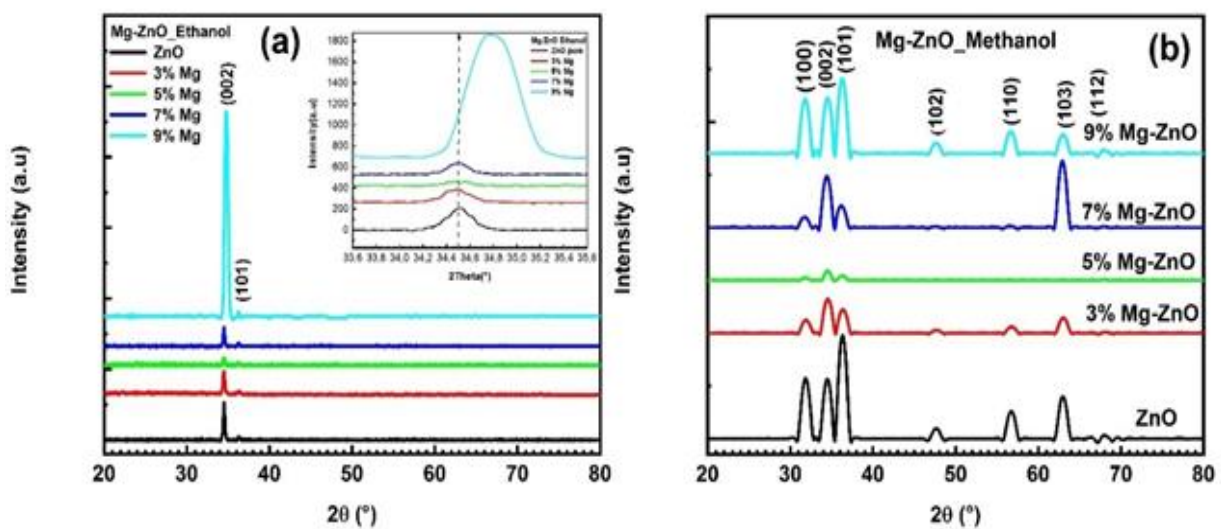


Fig III.1 XRD patterns of undoped and Mg-doped ZnO thin films using: (a) Ethanol and (b) Methanol solvents.

The structural parameters of the undoped and Mg-doped ZnO thin films were extracted from the XRD data and are summarized in **Tables III.1** and **III.2**. These include the interplanar spacing d , lattice constants a and c , lattice ratio (c/a), average grain size D , and dislocation density δ . The calculated values provide further insight into the effect of Mg incorporation and the solvent type (ethanol or methanol) on the crystallographic properties of the films.

Table III.1 *The comparison of inter planer distance, grain size, lattice constants, dislocation density and lattice ratio among Mg: ZnO films using Ethanol solvents.*

Samples	(hkl)	$2\theta(^{\circ})$	FWHM	$a(\text{\AA})$	$c(\text{\AA})$	c/a	$D \text{ (nm)}$	δ	$d(\text{hkl})$
Pure	002	34.467	0.5077	3.0022	5.2000	1.7320	17.1099	0.0034	2.6000
3% Mg	002	34.449	0.5082	3.0037	5.2026	1.7320	17.0919	0.0034	2.6013
5% Mg	002	34.460	0.4898	3.0027	5.2009	1.7320	17.7334	0.0031	2.6004
7% Mg	002	34.456	0.4621	3.0027	5.2016	1.7320	18.7988	0.0028	2.6008
9% Mg	002	34.793	0.3884	2.9749	5.1527	1.7320	22.3846	0.0019	2.5763

For the films prepared with ethanol as solvent (**Table III.1**), the results confirm that all samples crystallize predominantly in the hexagonal wurtzite structure with strong orientation along the (002) plane. The lattice constants a and c remain nearly unchanged for low Mg doping levels (3–7%), indicating that Mg is substitutionally incorporated into the ZnO lattice without significantly disturbing the structure. However, at higher Mg concentration (9%), a noticeable contraction of the lattice is observed, with the a -parameter decreasing from 3.0022 Å (undoped) to 2.9749 Å and the c -parameter reducing from 5.2000 Å to 5.1527 Å. This reduction is consistent with the smaller ionic radius of Mg^{2+} compared to Zn^{2+} , confirming successful substitution. The average crystallite size D increases with Mg content, from 17.1 nm in pure ZnO to 22.4 nm for 9% Mg-doping, while the dislocation density δ decreases accordingly. This suggests that Mg incorporation improves crystallinity and reduces lattice defects at higher concentrations.

Table III.2 The comparison of inter planer distance, grain size, lattice constants, dislocation density and lattice ratio among Mg ZnO films using Methanol solvents.

Samples	(hkl)	$2\theta(^{\circ})$	FWHM	a(Å)	c(Å)	c/a	D (nm)	Δ	d(hkl)
Pure	101	36.326	0.9980	2.8533	4.9421	1.7320	8.7496	0.0130	2.4710
3% Mg	002	34.511	0.7535	2.9985	5.1935	1.7320	11.529	0.0075	2.5967
5% Mg	002	34.507	0.6643	2.9987	5.1940	1.7320	13.078	0.0058	2.5970
7% Mg	103	62.966	0.4261	1.7031	2.9499	1.7320	22.829	0.0019	1.4749
9% Mg	101	36.311	0.7653	2.8544	4.9441	1.7320	11.409	0.0076	2.4720

On the other hand, the structural parameters of the films deposited with methanol as solvent (**Table III.2**) exhibit a more complex behavior due to the polycrystalline nature of the samples. Unlike ethanol-based films, which show a dominant (002) orientation, methanol-grown films reveal multiple preferred orientations depending on Mg content. For the undoped sample, the most intense peak corresponds to the (101) plane, with relatively small grain size (8.7 nm) and high dislocation density. Upon Mg doping, the main orientation shifts to the (002) plane for 3% and 5% Mg, accompanied by an increase in crystallite size (11.5–13.0 nm) and a decrease in dislocation density. Interestingly, at 7% Mg doping, the preferred orientation changes again to the (103) plane, leading to the largest crystallite size of 22.8 nm and the lowest dislocation density, indicating highly improved crystallinity. For 9% Mg, the orientation returns to the (101) plane with a smaller crystallite size (~11.4 nm), suggesting that excessive Mg concentration may disturb the lattice and deteriorate structural quality.

III.3 Morphological analysis

Fig III.2 shows the FE-SEM surface morphology of undoped and Mg-doped ZnO thin films prepared using ethanol as a solvent, with different Mg concentrations (0%, 3%, 5%, 7%, and 9%).

From the micrographs, the undoped ZnO film (**Fig. III.2a**) exhibits a uniform and densely packed granular morphology with relatively small grains, suggesting good nucleation and homogeneous growth. Upon the incorporation of Mg (**Fig. III.2b–e**), noticeable changes in the surface morphology can be observed. At 3% Mg doping (**Fig. III.2b**), the grains become slightly larger and better defined, indicating that Mg incorporation promotes grain growth and

improves crystallite boundaries. At 5% Mg doping (**Fig. III.2c**), the grains appear more compact and interconnected, which may enhance surface coverage and reduce voids.

However, further increasing Mg content to 7% (**Fig. III.2d**) leads to the formation of surface agglomerates and defects, indicating that excessive Mg incorporation disturbs the homogeneity of the ZnO matrix. This results in irregular grain distribution and localized clustering, which may negatively impact the film's uniformity. At 9% Mg doping (**Fig. III.2e**), the surface morphology becomes less compact, with a slight reduction in grain size compared to the lower doping concentrations, suggesting that high Mg content suppresses crystal growth and introduces surface stress.

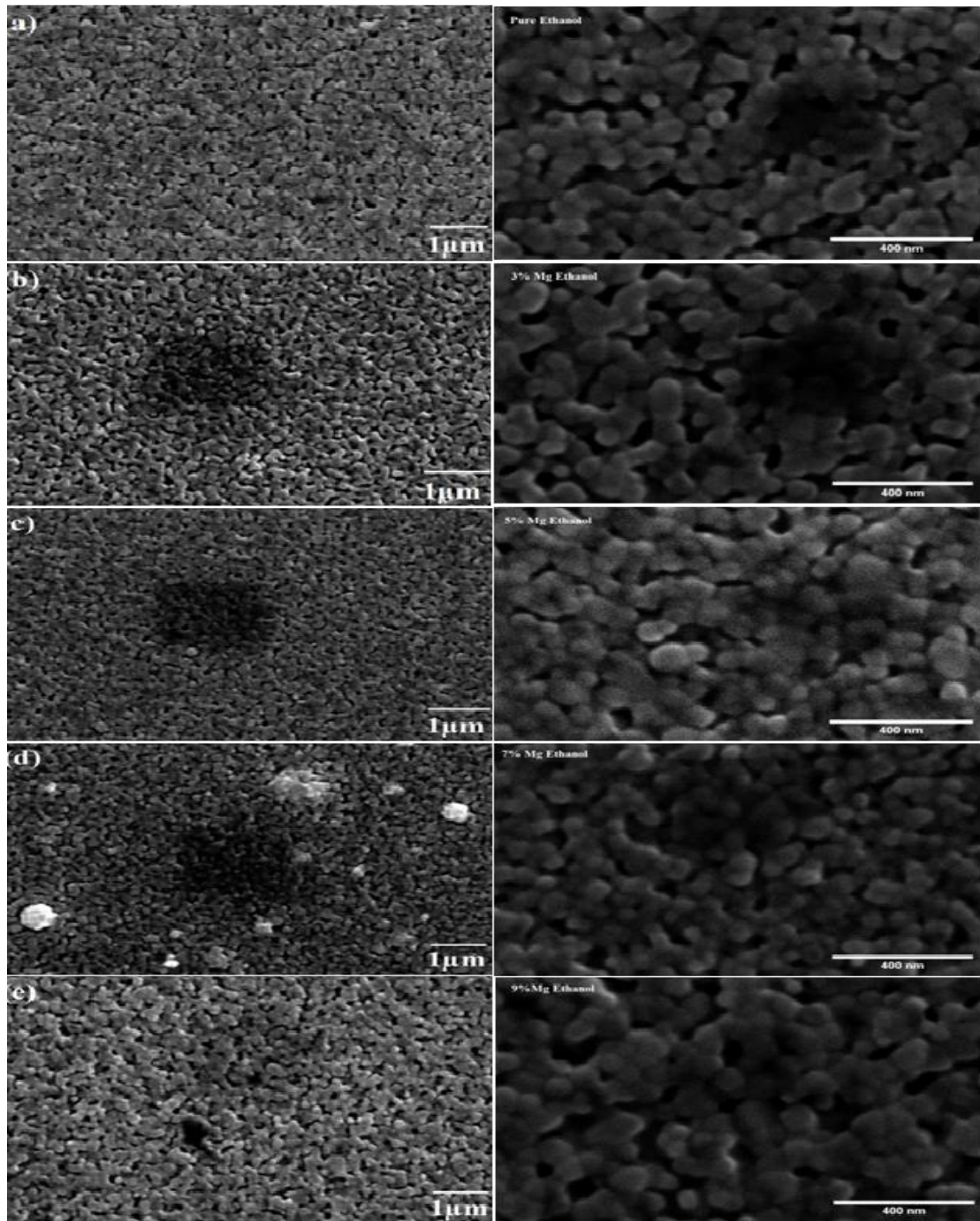


Fig III.2 FE-SEM image for undoped and doped ZnO as a function of Mg content using Ethanol solvent.

These morphological findings are further supported by the EDX compositional analysis summarized in **Table III.3**, which reports the elemental ratios of Zn, O, and Mg for both methanol and ethanol solvents. For the ethanol-based samples, the Zn/O ratio varies noticeably with doping concentration. For instance, the undoped ZnO shows a Zn-rich composition (Zn: 39.59 wt%, O: 30.38 wt%), whereas at 3% and 5% Mg doping, oxygen incorporation increases (38.95 wt% and 49.41 wt%, respectively), leading to improved stoichiometry. At higher doping levels (7% and 9%), the Mg content rises to 2.16–3.19 wt%, accompanied by fluctuations in the Zn/O ratio, which may explain the observed grain distortion and agglomeration in the FE-SEM images.

In contrast, the methanol-based films exhibit higher Zn content at lower Mg concentrations (65.56 wt% Zn at 3% Mg), while at 9% Mg doping, the Zn/O ratio decreases significantly (43.79 wt% Zn, 33.25 wt% O), indicating a destabilization of the ZnO lattice. This comparison shows that ethanol as a solvent provides better elemental balance and smoother Mg incorporation compared to methanol, resulting in more uniform morphology.

Table III.3 *The ratio of ZnO undoped and Mg-doped ZnO chemical components for both solvents.*

Weight. %						
Methanol				Ethanol		
Phases	Zn	O	Mg	Zn	O	Mg
Pure	51.12	30.76	0	39.59	30.38	0
3% Mg	65.56	22.97	1.45	26.01	38.95	1.99
5% Mg	60.35	27.25	0.48	6.30	49.41	1.96
7% Mg	68.79	22.64	1.43	32.19	35.06	2.16
9% Mg	43.79	33.25	1.69	30.88	35.11	3.19

Fig III.3 displays the EDX spectra of pristine ZnO and Mg-doped ZnO thin films prepared using ethanol as a solvent. The spectra clearly confirm the presence of zinc (Zn) and oxygen (O) as the main constituents of the films, with additional signals corresponding to magnesium (Mg) in the doped samples. A small Si peak is also visible, which originates from the glass substrate.

For the undoped ZnO film, only Zn and O peaks are observed, confirming the formation of ZnO without any impurity elements. The relatively strong Zn peak compared to O indicates a Zn-rich composition, consistent with the EDX quantification results in **Table III.3**.

Upon introducing 3% Mg doping, an additional Mg peak appears in the spectrum, verifying the successful substitution of Mg into the ZnO lattice. The relative intensity of the O peak also increases compared to undoped ZnO, suggesting improved stoichiometry.

At 5% Mg doping, the Mg peak becomes more pronounced, indicating a higher Mg incorporation within the ZnO host matrix. The Zn/O ratio decreases compared to the pristine sample, consistent with the higher oxygen content observed in the quantitative analysis.

With further increase to 7% Mg doping, the Mg signal is more evident, but the Zn peak intensity remains dominant. This suggests that while Mg is incorporated into the lattice, Zn is still the major constituent. The slight fluctuations in the O peak intensity reflect changes in oxygen incorporation with increasing dopant concentration.

Finally, in the case of 9% Mg doping, the Mg peak intensity is at its highest, confirming the maximum incorporation of Mg among the samples. However, the spectra also show a relative reduction in Zn peak intensity compared to lower doping concentrations, indicating that high Mg content modifies the elemental ratio and may lead to structural distortions, as seen in the FE-SEM results.

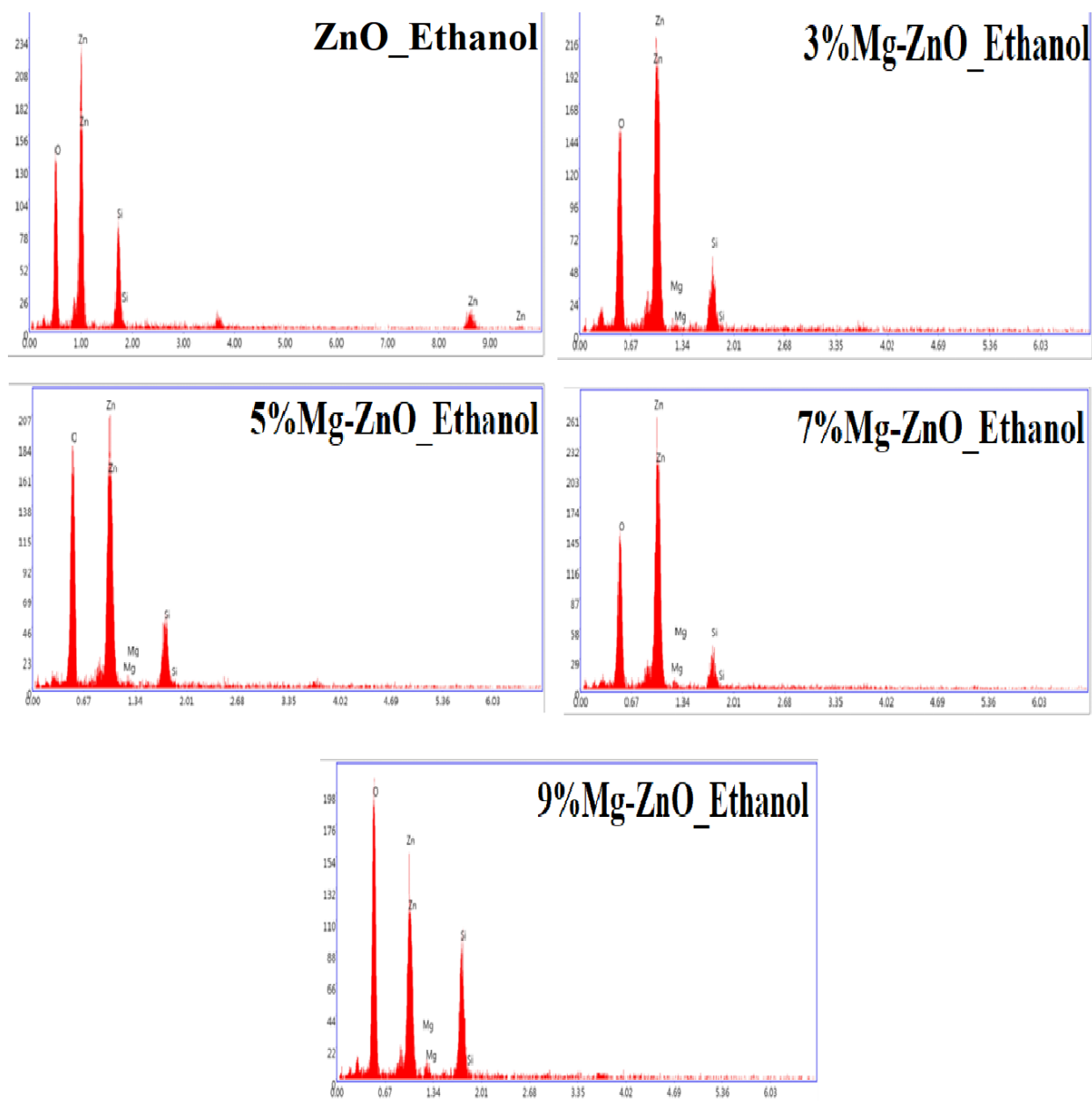


Fig III.3 EDX spectra of pristine ZnO and Mg-doped ZnO using Ethanol solvent.

Fig III.4 illustrates the FE-SEM images of pristine and Mg-doped ZnO thin films synthesized with methanol solvent at different Mg doping concentrations (0%, 3%, 5%, 7%, and 9%).

For the undoped ZnO film (**Fig. III.4a**), the surface shows a uniform granular morphology with compact and densely distributed grains, characteristic of typical nanostructured ZnO. The grains are relatively small but well interconnected, providing a smooth and continuous surface.

At 3% Mg doping (**Fig. III.4b**), the surface morphology changes significantly, with the appearance of irregular surface features and larger aggregated clusters. These surface disruptions suggest that methanol as a solvent, in combination with low Mg doping, induces rapid nucleation, which destabilizes the uniform growth of ZnO grains.

With 5% Mg doping (**Fig. III.4c**), the surface becomes more homogeneous compared to the 3% sample, with smaller and more compact grains, indicating partial recovery of uniform nucleation. This suggests that moderate Mg incorporation helps stabilize the ZnO matrix, leading to better grain packing.

At 7% Mg doping (**Fig. III.4d**), the grains become larger, rounder, and more distinct, with fewer voids between them. This indicates enhanced crystal growth and densification at this doping concentration, possibly due to improved stabilization of the Zn–O lattice with Mg substitution.

For the 9% Mg-doped ZnO film (**Fig. III.4e**), the grains remain relatively uniform but show signs of agglomeration and increased grain boundary roughness. This implies that excessive Mg incorporation induces lattice strain, leading to irregularities in the grain distribution and possible stress-induced defects.

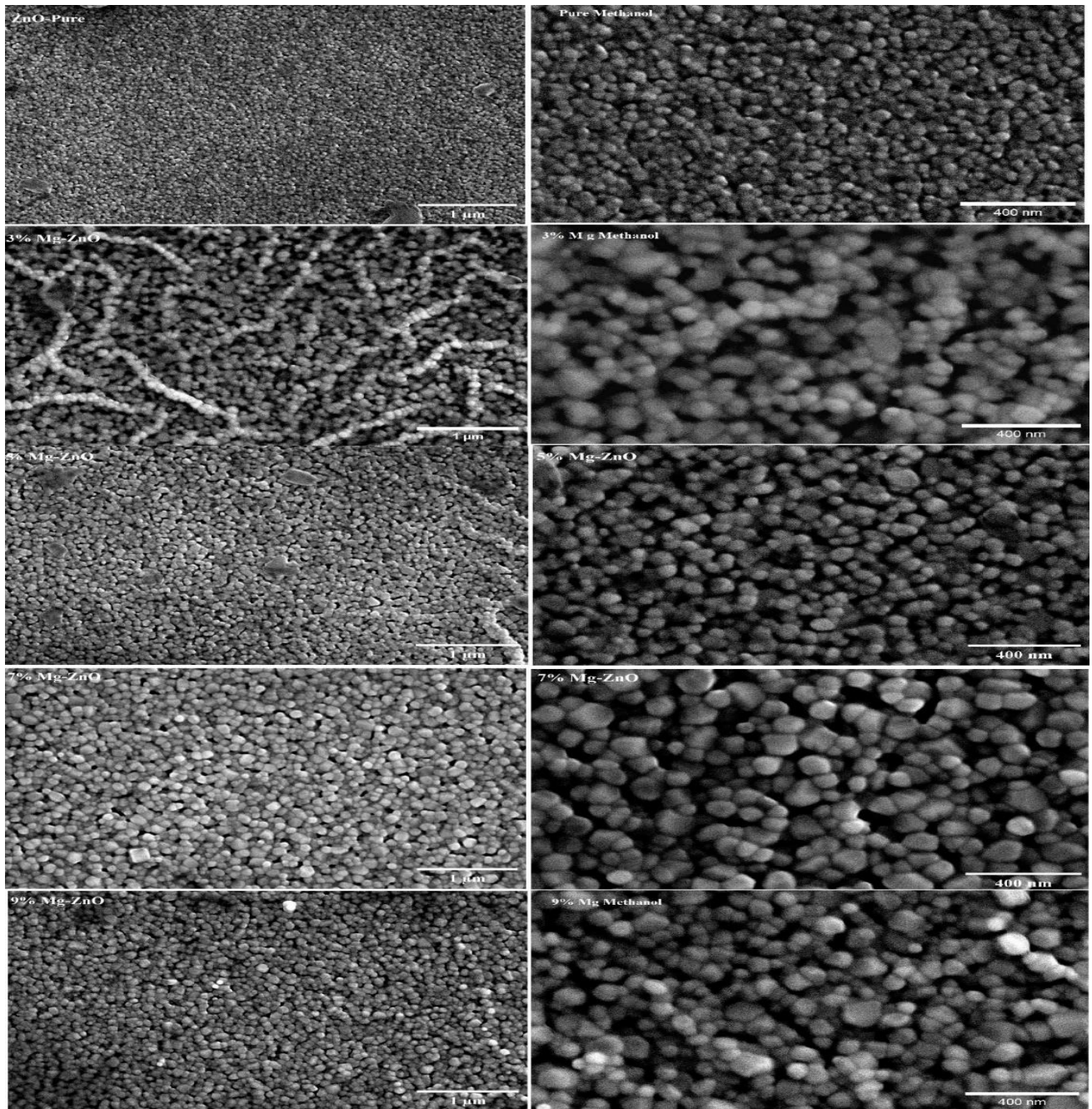


Fig III.4 FE-SEM image for undoped and doped ZnO as a function of Mg content using Methanol solvent.

The EDX spectra shown in Fig. III.5 represent the elemental composition of pristine ZnO and Mg-doped ZnO nanoparticles synthesized using methanol as a solvent. For the undoped ZnO spectrum, the characteristic peaks corresponding to zinc (Zn) and oxygen (O) are clearly observed, confirming the formation of ZnO. Additionally, a minor peak of (Si) is also detected, which can be attributed to the substrate or contamination during the measurement process.

Upon the introduction of magnesium (Mg) into the ZnO lattice, distinct Mg peaks appear in the spectra for all doping concentrations (3%, 5%, 7%, and 9% Mg-ZnO), indicating the successful incorporation of Mg into the ZnO matrix. The relative intensity of the Mg peaks increases with higher doping levels, consistent with the rise in Mg concentration. Meanwhile, the Zn and O peaks remain dominant across all samples, further confirming the preservation of the ZnO framework after doping.

A comparison among the spectra reveals that the elemental distribution remains similar, with O and Zn peaks as the main constituents, but the gradual increase of Mg signals demonstrates the substitution of Zn atoms by Mg. This substitution can induce modifications in the structural, electronic, and optical properties of ZnO, which is essential for tailoring material performance. The presence of Si in all spectra can again be linked to the underlying substrate or residual impurities, and it does not significantly affect the interpretation of Mg doping effects.

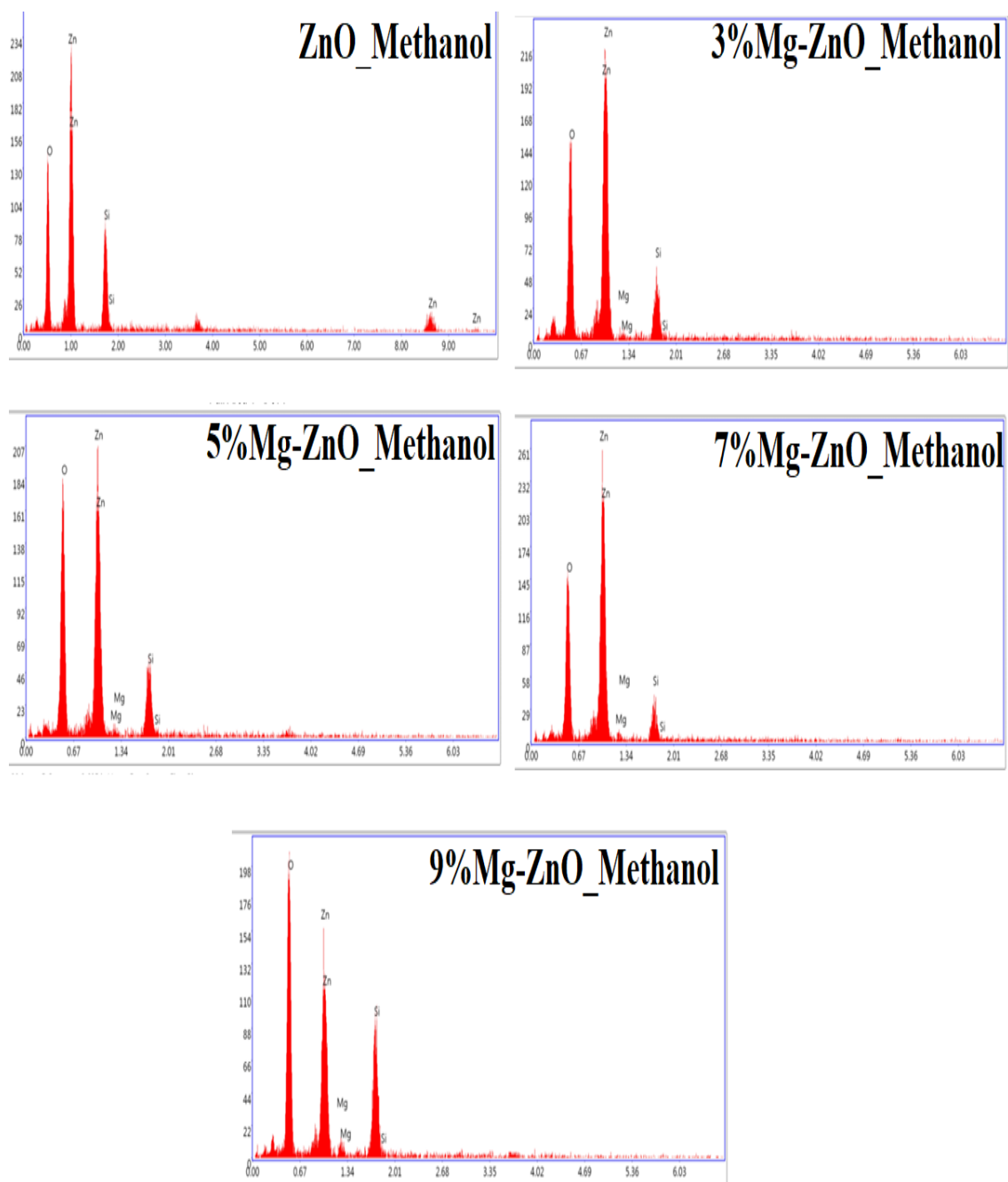


Fig III.5 EDX spectra of pristine ZnO and Mg-doped ZnO using Methanol solvent.

The histograms presented in **Fig. III.6** illustrate the particle size distribution of pristine ZnO and Mg-doped ZnO synthesized using two different solvents, ethanol and methanol. Each graph shows the variation in particle diameter along with the corresponding mean size, allowing a comparative evaluation of the effect of solvent and Mg doping concentration on particle growth.

For the pristine ZnO samples, a clear distinction is observed between the two solvents. ZnO synthesized in ethanol exhibits a mean particle diameter of 66.56 nm, whereas in methanol, the average size is significantly smaller at 49.59 nm. This indicates that methanol promotes the formation of finer ZnO nanoparticles compared to ethanol, likely due to differences in polarity, dielectric constant, and reaction kinetics between the two solvents.

Upon Mg doping, both solvents display an increase in particle size. For ethanol-based samples, the mean particle size evolves from 80.40 nm (3% Mg) to 83.27 nm (9% Mg). Similarly, in methanol-based samples, the size increases from 80.31 nm (3% Mg) to 85.52 nm (9% Mg). This trend confirms that the incorporation of Mg ions into the ZnO lattice enhances particle growth, which can be attributed to modifications in nucleation and growth dynamics induced by Mg.

Interestingly, intermediate doping concentrations reveal solvent-dependent variations. At 5% Mg, ethanol produces particles of mean size 69.81 nm, whereas methanol results in significantly larger particles averaging 91.62 nm. At 7% Mg, however, ethanol favors smaller particles (65.45 nm) compared to methanol (66.41 nm), though the difference is less pronounced. These results suggest that the interplay between solvent type and Mg concentration has a critical role in controlling the crystallization and aggregation behavior of ZnO nanoparticles.

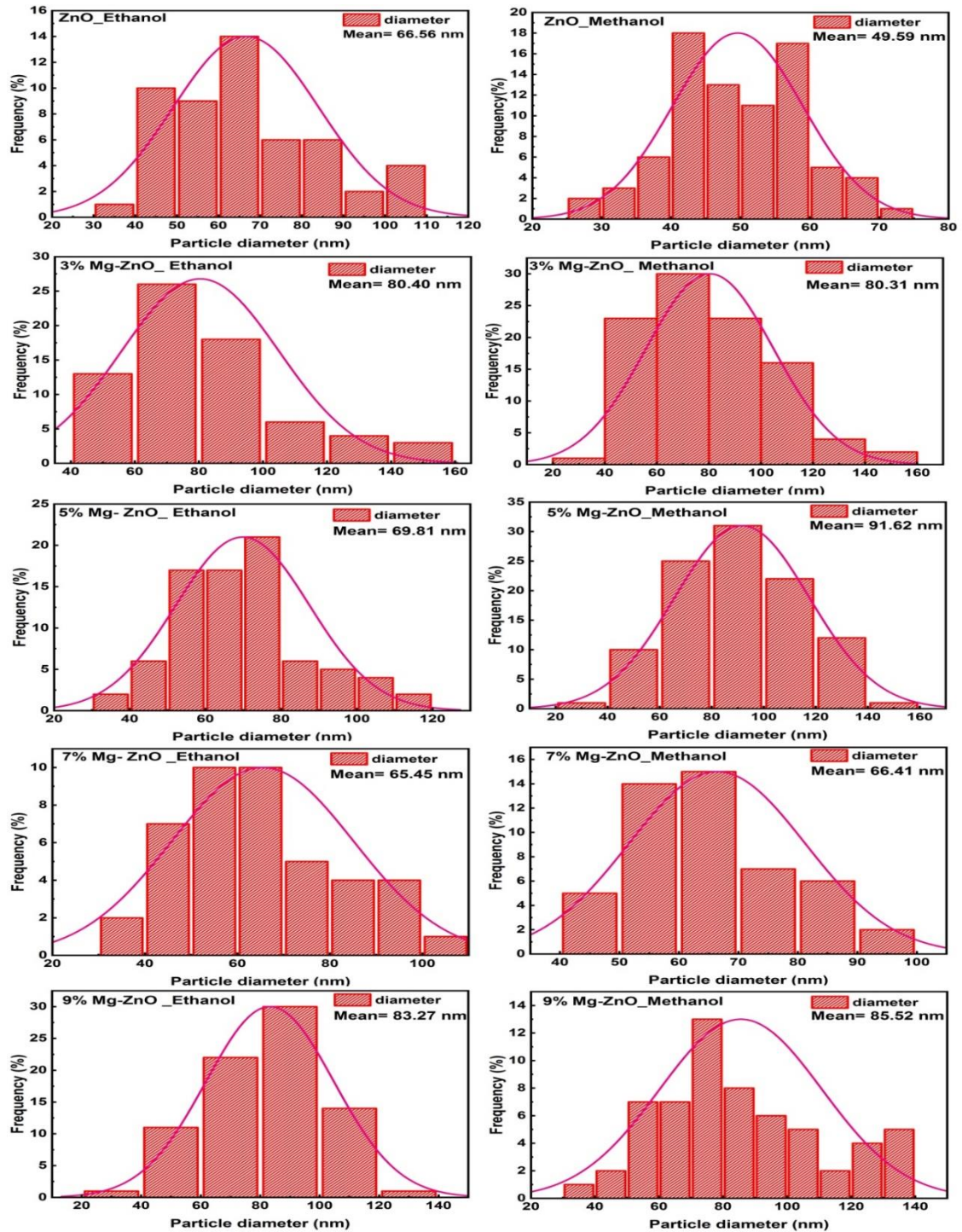


Fig III.6 Evolution of particle size of Zinc oxide-magnesium as function of particle number for both solvents (ethanol – methanol).

III.4 Fourier Transform Infrared (FTIR) Analysis

The FTIR spectra in Fig. III.7 show the vibrational characteristics of pristine ZnO and Mg-doped ZnO thin films deposited on glass substrates using ethanol (a) and methanol (b) as solvents. The observed absorption bands provide insight into the chemical bonds and functional groups present in the prepared thin films, as well as the effect of Mg incorporation.

In both spectra, a broad absorption band around 3440 cm^{-1} is clearly visible, which corresponds to the O–H stretching vibrations, indicating the presence of hydroxyl groups adsorbed on the film surface or residual water molecules. Additionally, the band observed near 1630 cm^{-1} is assigned to H–O–H bending vibrations, further confirming the presence of moisture in the samples. These features are common in oxide materials prepared via wet chemical routes.

The characteristic absorption peak of Zn–O stretching vibrations appears in the low-frequency region around 572 cm^{-1} for ethanol-based films and 532 cm^{-1} for methanol-based films. This shift suggests that the solvent type influences the bond environment within the ZnO lattice. Importantly, the Zn–O band remains prominent in all samples, confirming the formation of ZnO as the main phase even after Mg doping.

For ethanol-derived samples (a), an additional peak near 960 cm^{-1} can be observed, which may be attributed to residual organic species or C–O related vibrations arising from ethanol decomposition during the synthesis. This peak is absent in the methanol-based samples (b), highlighting solvent-dependent differences in the chemical environment of the films.

With increasing Mg content (3%–9%), no new peaks emerge, but slight shifts and intensity variations are observed in the Zn–O region, indicating that Mg ions are incorporated into the ZnO lattice without introducing new vibrational modes. This behavior supports the substitutional doping mechanism of Mg into Zn sites.

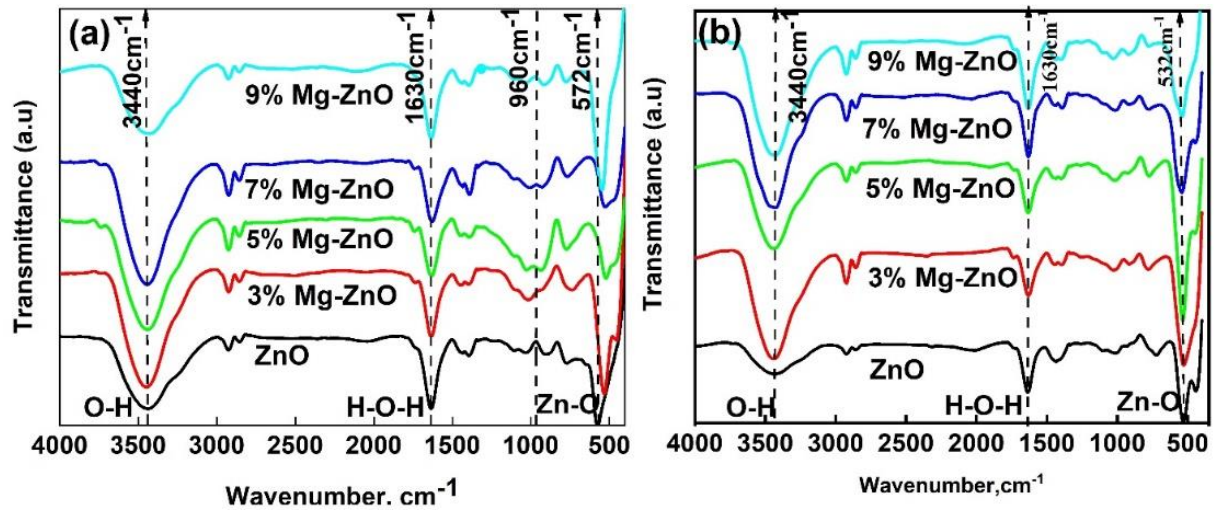


Fig III.7 FTIR spectra of undoped ZnO and Mg-doped ZnO thin films using: **(a)** Ethanol and **(b)** Methanol solvents deposited onto glass substrate.

III.5 Optical Propertie

Fig III.8 presents the optical transmittance spectra of ZnO and Mg-doped ZnO (MZO) thin films deposited on glass substrates at 500 °C, prepared using two different solvents: (a) ethanol and (b) methanol. In both cases, the films exhibit a sharp absorption edge in the UV region ($\approx 350\text{--}400\text{ nm}$), which is characteristic of ZnO-based semiconductors, confirming their direct wide bandgap nature. Beyond this edge, the transmittance significantly increases, reaching values above 75–85% in the visible and near-infrared regions, indicating good optical transparency of the films.

For the ethanol-based samples (**Fig III.8a**), the incorporation of Mg slightly modifies the transmittance behavior. The 3% Mg–ZnO film shows a higher transmittance compared to undoped ZnO, whereas further Mg doping (5–9%) tends to reduce the transparency, particularly in the visible region, suggesting an influence of Mg content on film densification and scattering. In contrast, the methanol-based samples (**Fig III.8b**) display more uniform transmittance profiles across all doping concentrations, with only minor differences observed.

This indicates that methanol as a solvent yields films with more consistent optical properties, less affected by the variation in Mg content.

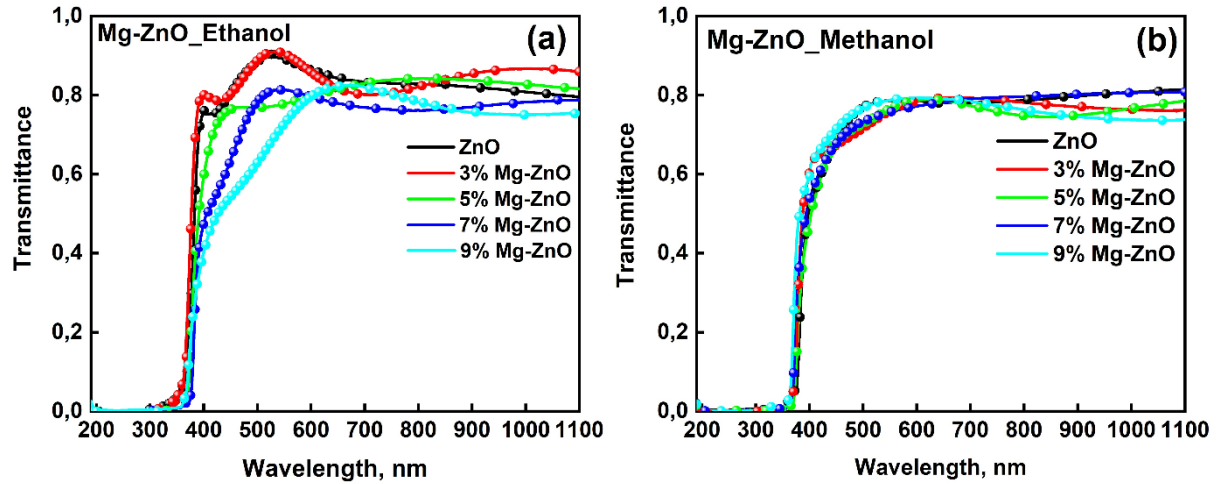


Fig III.8 Transmission spectra of ZnO, MZO thin films deposited on glass substrate at 500 °C. Measured (full circles) and calculated (solid lines) transmittance spectra of films using: (a) Ethanol and (b) Methanol solvents.

Fig III.9 shows the Tauc plots of $(\alpha h\nu)^2$ versus photon energy ($h\nu$) for undoped ZnO and Mg-doped ZnO (MZO) thin films synthesized using (a) ethanol and (b) methanol as solvents. The direct band gap values were estimated by extrapolating the linear portions of the curves to the energy axis.

For the ethanol-based films (**Fig. III.9a**), the band gap of pure ZnO is about ~3.27 eV. With Mg incorporation, the band gap exhibits a clear blue shift, increasing progressively with Mg concentration. For example, 3% Mg–ZnO shows a slight increase, while higher doping levels (5–9%) shift the band edge further toward higher photon energies (up to ~3.33–3.35 eV). This behavior is attributed to the substitution of Zn^{2+} ions by smaller Mg^{2+} ions in the ZnO lattice, which leads to an increase in the band gap energy due to the widening of the conduction band.

In the case of methanol-based films (**Fig. III.9b**), a similar trend of band gap widening with Mg doping is observed, though the shift is more gradual and uniform compared to the ethanol-based samples. The pure ZnO film prepared with methanol has a slightly higher initial band gap (~3.29 eV), and with Mg doping, the band gap steadily increases up to ~3.34 eV for 9% Mg–ZnO. The smoother variation in methanol-based samples suggests better incorporation of

Mg into the ZnO lattice and reduced defect-induced band tailing compared to ethanol-based films.

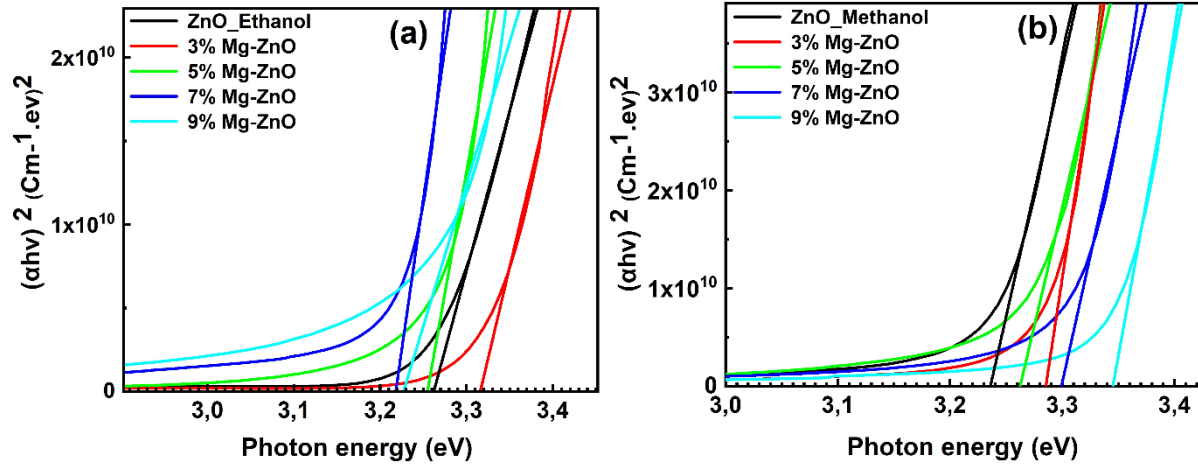


Fig III.9 the plots of $(\alpha h\nu)^2$ versus photon energy ($h\nu$) of undoped and Mg-doped ZnO thin films prepared by: (a) Ethanol and (b) Methanol solvents and their band gaps.

Table III.4 Dispersion parameters of the films prepared for ethanol and methanol solvents extracted by fitting the experimental data.

Samples	Ethanol				Methanol			
	Eg (eV)	Thickness (nm)	n at 598nm	n_{∞}	Eg (eV)	Thickness (nm)	n at 598 nm	n_{∞}
Pure	3.31	293	1.71	3.24	3.24	274	1.74	1.90
3% Mg	3.36	278	1.89	3.35	3.35	193	1.77	1.82
5% Mg	3.27	220	1.76	3.15	3.15	351	1.75	1.76
7% Mg	3.24	278	1.75	3.29	3.29	307	1.70	1.74
9% Mg	3.27	322	1.79	3.38	3.38	249	1.71	1.75

Table III.4 summarizes the optical dispersion parameters of pristine ZnO and Mg-doped ZnO thin films deposited using ethanol and methanol solvents. The parameters include optical band gap (E_g), film thickness, refractive index at 598 nm (n_{598}), and the infinite-wavelength refractive index (n_∞).

For ethanol-based films, the optical band gap values fluctuate slightly with Mg incorporation. The undoped ZnO exhibits a band gap of 3.31 eV, which increases to 3.36 eV at 3% Mg doping, consistent with the Burstein–Moss effect, where Mg incorporation widens the band gap by raising the conduction band minimum. However, a slight reduction to 3.27 eV and 3.24 eV is observed at 5% and 7% doping, respectively, possibly due to lattice strain and defect states. At 9% doping, the band gap recovers to 3.27 eV, indicating a partial balance between Mg substitution and structural disorder. The film thickness varies from 220 to 322 nm, with the lowest thickness at 5% Mg doping, suggesting denser packing at moderate concentrations. The refractive index at 598 nm increases from 1.71 (pure) to 1.89 (3% Mg), before stabilizing around 1.75–1.79 for higher doping, while n_∞ follows a similar trend, peaking at 3.38 for 9% Mg. This behavior indicates improved optical density at low-to-moderate doping levels.

In the case of methanol-based films, the band gap values are slightly higher overall, ranging from 3.15 to 3.38 eV. The undoped film shows a band gap of 3.24 eV, which increases progressively to 3.38 eV at 9% Mg doping. This continuous band gap widening reflects effective Mg substitution into the ZnO lattice, which increases the optical transition energy. Film thickness shows strong fluctuations: the lowest value appears at 3% Mg (193 nm), while the highest thickness is recorded at 5% Mg (351 nm), suggesting that Mg concentration strongly affects the growth rate and film compactness when methanol is used. The refractive index at 598 nm is nearly constant across doping levels (1.70–1.77), indicating relatively stable optical response regardless of Mg content. Similarly, n_∞ varies only slightly (1.74–1.90), showing weaker sensitivity to doping compared to ethanol-based films.

Comparative analysis reveals that ethanol-based samples exhibit more pronounced variations in refractive index with Mg doping, suggesting that ethanol enhances the sensitivity of ZnO optical properties to dopant incorporation. In contrast, methanol-based films display more stable refractive index values but stronger fluctuations in film thickness, reflecting differences in solvent–solute interactions during growth. Overall, ethanol tends to yield films with higher optical density at moderate doping (3–5%), while methanol promotes more consistent refractive behavior but less uniform thickness control.

III.6 Photoluminescence Spectra Analysis

Fig III.10 presents the room-temperature photoluminescence (PL) spectra of ZnO and Mg-doped ZnO (MZO) thin films synthesized using (a) ethanol and (b) methanol as solvents, along with the Gaussian deconvolution of the emission peaks.

For the ethanol-based films (**Fig. III.10a**), the PL spectra exhibit a strong near-band-edge (NBE) emission centered at ~388 nm, which corresponds to the recombination of free excitons, and two additional peaks at ~408 nm and ~445 nm associated with shallow-level defects and deep-level defect-related emissions, respectively. The intensity of the PL signal increases with Mg incorporation, especially at higher doping levels (7–9%), indicating improved excitonic recombination. This enhancement may be attributed to lattice modifications and a reduction in non-radiative recombination centers induced by Mg substitution.

In the methanol-based films (**Fig. III.10b**), the PL spectra also show a dominant NBE emission around ~391 nm, accompanied by defect-related peaks at ~408 nm and ~450 nm. Compared to ethanol-derived samples, the methanol-prepared films exhibit sharper and more intense NBE peaks with relatively reduced defect-band emissions. This suggests that methanol promotes higher crystalline quality and fewer defect states, thereby enhancing the optical purity of the films.

The Gaussian fitting of the spectra further confirms the presence of three main emission components: (i) UV excitonic emission (388–391 nm), (ii) violet-blue emission (~408 nm) related to zinc interstitials or oxygen vacancies, and (iii) blue emission (445–450 nm) attributed to deep-level defects. The relative intensities of these peaks vary with Mg concentration and solvent type. Ethanol-based films display stronger defect-related emissions, whereas methanol-based films maintain a more prominent NBE peak, signifying reduced defect density.

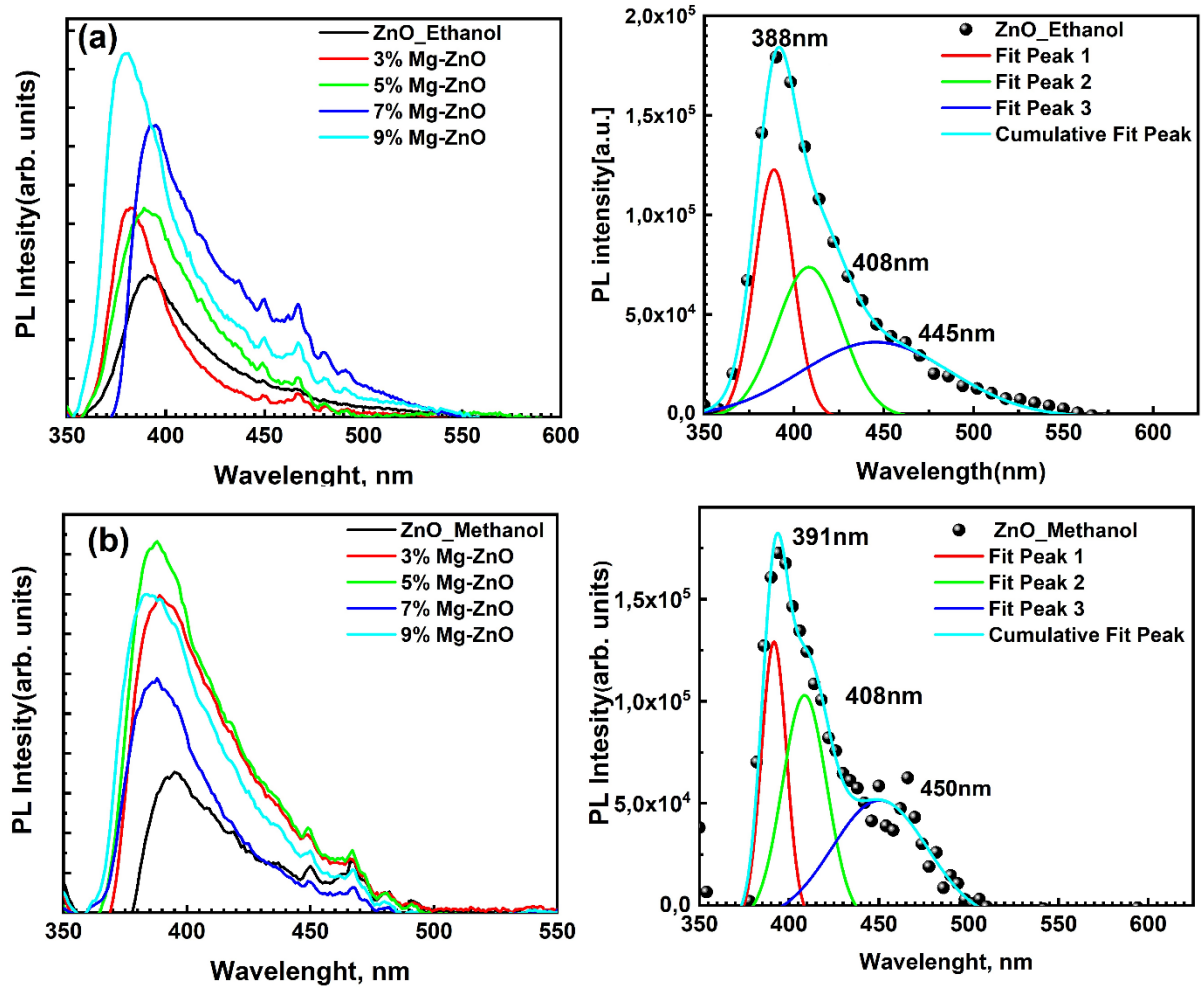


Fig III.10 Photoluminescence spectra of ZnO and MZO films and the Gaussian deconvolution of the PL intensity using :**(a)** Ethanol and **(b)** Methanol solvents.

The graphs in **Figure III.11** present the variation of the Seebeck coefficient (S) of ZnO and Mg-doped ZnO thin films prepared using two different solvents, methanol (left) and ethanol (right), as a function of the temperature difference (ΔT). In both cases, the output voltage (ΔV) shows a linear relationship with ΔT , indicating stable thermoelectric behavior of the films. The slope of each curve corresponds to the Seebeck coefficient, which decreases progressively with the increase in Mg concentration, regardless of the solvent used.

For methanol-based samples, pure ZnO exhibits the highest Seebeck coefficient of $-525.31 \mu\text{V/K}$, which decreases significantly with Mg doping: $-386.76 \mu\text{V/K}$ (3% Mg), $-280.66 \mu\text{V/K}$ (5% Mg), $-246.53 \mu\text{V/K}$ (7% Mg), and $-210.24 \mu\text{V/K}$ (9% Mg). This strong reduction highlights that Mg incorporation into the ZnO lattice effectively suppresses the thermopower,

possibly due to increased carrier concentration and reduced mobility caused by lattice distortion or defect generation.

In the case of ethanol-based samples, a similar decreasing trend is observed, although the Seebeck coefficients are generally less negative compared to methanol. Pure ZnO has $-400.12 \mu\text{V/K}$, while the values decrease with higher Mg content: $-381.68 \mu\text{V/K}$ (3% Mg), $-375.58 \mu\text{V/K}$ (5% Mg), $-309.95 \mu\text{V/K}$ (7% Mg), and $-226.98 \mu\text{V/K}$ (9% Mg). Interestingly, the reduction in S with Mg doping is less steep in ethanol than in methanol, particularly at lower Mg concentrations (3% and 5%). This suggests that the solvent plays an important role in the crystallinity, defect structure, or carrier density of the thin films, ultimately influencing their thermoelectric response.

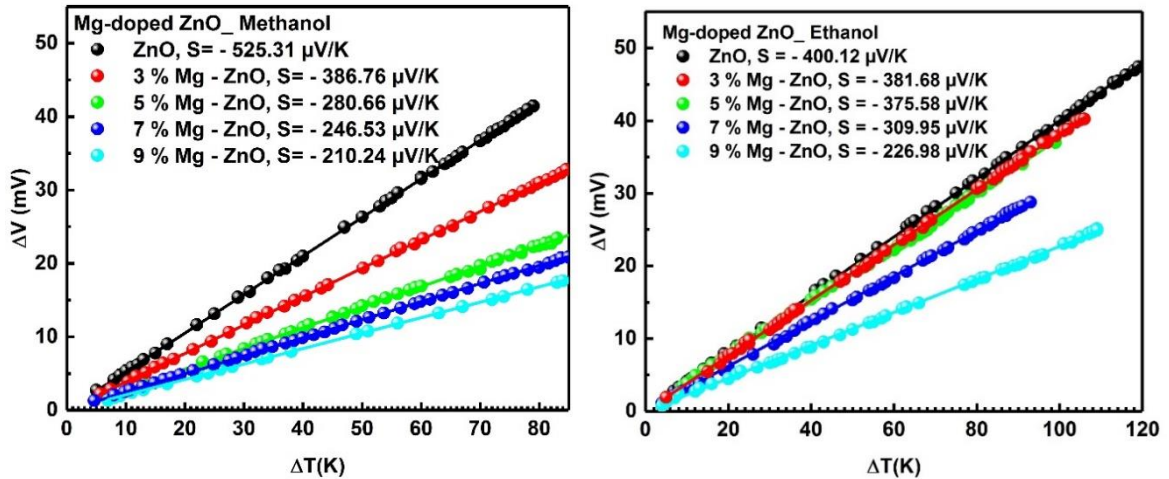


Fig III.11 Seebeck coefficients for ZnO and Mg-doped ZnO thin films with varying Mg concentrations for both solvents (Ethanol- Methanol).

Fig III.12 illustrates the dependence of the Seebeck coefficient $|S|$ on the carrier concentration n for ZnO and Mg-doped ZnO thin films synthesized using ethanol (left) and methanol (right) as solvents. In both cases, the experimental data are compared with a theoretical fitting curve, confirming the expected inverse relationship between $|S|$ and n : as the carrier concentration increases, the absolute value of the Seebeck coefficient decreases. This trend aligns with the fundamental thermoelectric principle that higher carrier densities enhance electrical conductivity but suppress the thermopower.

For ethanol-based samples, pure ZnO displays the highest Seebeck coefficient ($|S| \approx 400 \mu\text{V/K}$ at a relatively low carrier concentration. With increasing Mg doping (3–9%), $|S|$ gradually decreases while the carrier concentration shifts toward higher values. The

corresponding Fermi energy levels (EFE) extracted for ethanol-synthesized films range from 18.32 meV for pure ZnO up to 32.29 meV for 9% Mg-doped ZnO. This reflects a modest rise in carrier density induced by Mg substitution, which explains the reduction in Seebeck values.

In the case of methanol-based samples, a similar but more pronounced behavior is observed. Pure ZnO shows a very high Seebeck coefficient ($|S| \approx 525 \mu\text{V/K}$), which decreases sharply with Mg incorporation. As the Mg content increases, the carrier concentration grows significantly, pushing the Fermi energy from 13.95 meV (ZnO) to 34.86 meV (9% Mg). Compared to ethanol-derived samples, the methanol-based films exhibit higher initial $|S|$ but also a steeper reduction with doping, indicating stronger sensitivity of the thermoelectric properties to Mg incorporation.

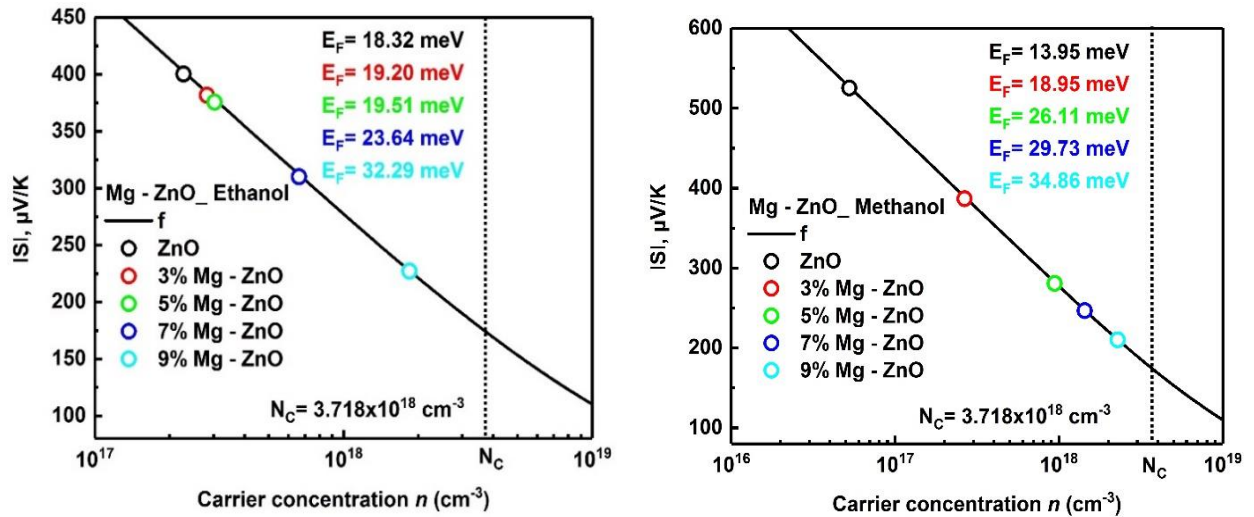


Fig III.12 Seebeck coefficients plotted against carrier concentrations for ZnO and Mg-doped ZnO thin films for both solvents (Ethanol- Methanol).

III.7 UV Photodetector

Fig III.13 presents the time-dependent photocurrent response ($I-t$) of ZnO and Mg-doped ZnO thin films synthesized with ethanol (a) and methanol (b) as solvents under periodic UV illumination at 30-second on/off intervals. The cyclic switching between “on” and “off” states clearly demonstrates the reproducibility and stability of the UV photodetector behavior in all samples.

For ethanol-based films (Fig. III.13a), pure ZnO shows the highest photocurrent response, reaching nearly 0.7 nA, with sharp increases upon UV illumination and rapid decay when the

light is switched off. However, with Mg doping, the photocurrent decreases progressively, with 3% and 5% Mg-ZnO showing moderate responses, while higher doping levels (7% and 9%) exhibit significantly reduced photocurrent intensities. This decrease suggests that Mg incorporation introduces defects or modifies the carrier concentration in a way that suppresses the generation or transport of photoexcited carriers, thereby weakening the UV response.

In contrast, methanol-based films (**Fig. III.13b**) exhibit an opposite trend. Here, pure ZnO has the lowest photocurrent intensity, whereas doping with Mg strongly enhances the UV response. With increasing Mg content, the photocurrent rises steadily, with 9% Mg-ZnO achieving the highest response, exceeding 0.7 nA. The switching characteristics also appear sharper and more stable, indicating improved charge separation and transport dynamics under UV exposure. This enhancement suggests that methanol synthesis may favor a defect structure or microstructural quality that enhances carrier lifetime and mobility upon Mg doping.

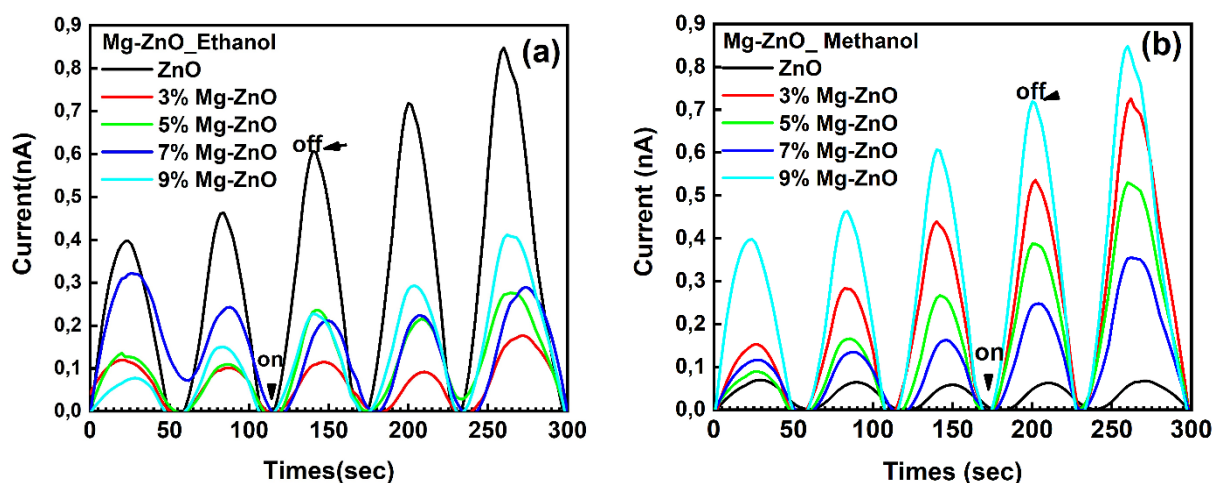


Fig III.13 depicts the photocurrent as a function of time (*I.t*) for: (a) Ethanol and (b) Methanol states during the activation and deactivation of UV light at 30-second intervals

Fig III.14(a) presents the current–voltage (*I–V*) characteristics of ZnO and Mg-doped ZnO (MZO) thin films prepared using ethanol as a solvent, measured both in the dark and under UV illumination. Pure ZnO shows a relatively low current response, with only a slight increase under UV light. When Mg is introduced, the electrical response changes noticeably depending on the doping level. Among all samples, the 5% Mg–ZnO thin film under UV illumination displays the highest photocurrent, reaching about 0.24 nA at 5 V. This suggests that ethanol

promotes efficient charge carrier mobility and enhances the photoconductive properties at this optimal doping concentration. However, further increasing the Mg content to 7% and 9% leads to a decrease in current, which can be attributed to the creation of excess defects or recombination centers that hinder carrier transport.

In **Fig III.14(b)**, the I–V curves of ZnO and MZO thin films prepared with methanol as a solvent are shown. Compared to ethanol-based films, the overall photocurrent values are lower, not exceeding 0.12 nA at 5 V. A similar trend is observed: pure ZnO maintains a weak photoresponse, while Mg incorporation improves the conductivity under UV light. Again, the 5% Mg–ZnO sample demonstrates the best performance among all doping levels, confirming the existence of an optimal Mg concentration. At higher doping ratios, the current response diminishes, reflecting the negative effect of excessive Mg substitution on the structural and electrical quality of the films.

A direct comparison between the two solvents highlights that ethanol produces higher photocurrent responses than methanol for all doping concentrations. The difference suggests that ethanol ensures better precursor solubility and film quality, which positively impacts charge transport and photoresponse. In both cases, however, the application of UV illumination consistently increases the current compared to the dark condition, confirming the intrinsic photoconductive behavior of ZnO and Mg–ZnO thin films. These results demonstrate that both the solvent type and the Mg concentration are key parameters in tuning the optoelectronic performance of MZO thin films.

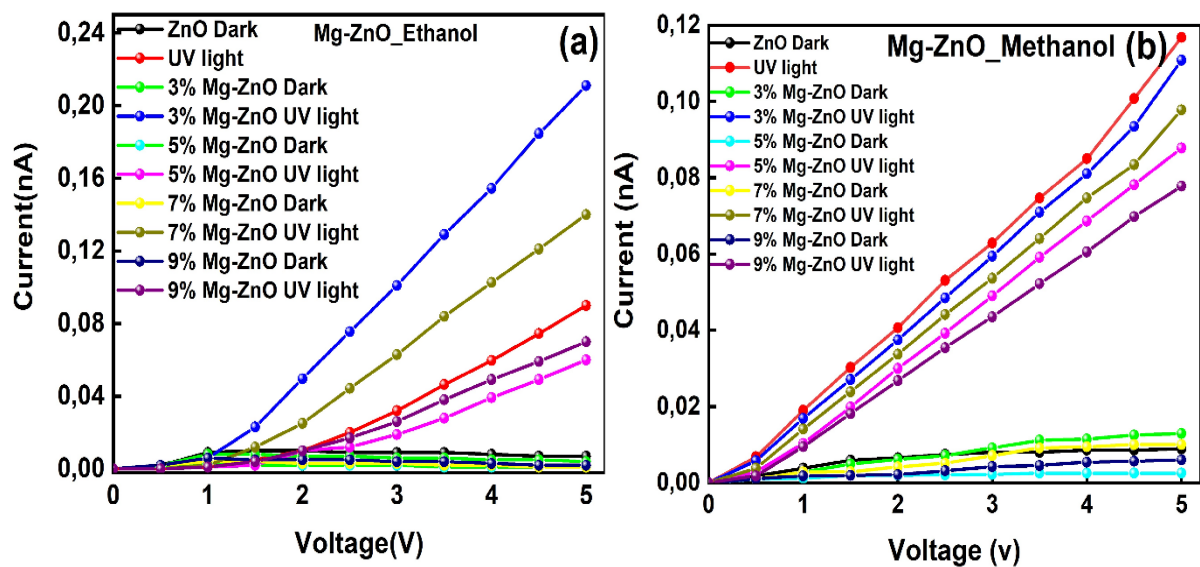


Fig III.14 The I–V curves of ZnO and MZO samples measured in the dark and under UV illumination utilizing : (a) Ethanol and (b) Methanol solvents.

Table III.5 summarizes the electrical parameters of ZnO and Mg-doped ZnO samples measured at 5 V, both in the dark and under UV illumination, using ethanol and methanol as solvents. For pure ZnO, the dark current (I_{dark}) remains low in both solvents (0.007 nA for ethanol and 0.008 nA for methanol), with photocurrent (I_{photo}) values of 0.09 nA and 0.116 nA, respectively. The calculated sensitivity is higher for methanol (13.5) compared to ethanol (11.85), indicating that the solvent slightly influences the initial performance of undoped ZnO.

Upon Mg incorporation, a significant variation in the optoelectronic response is observed. For ethanol-based samples, the 3% Mg–ZnO thin film shows a remarkable increase in photocurrent (0.21 nA), with a sensitivity of 51.75, much higher than that of pure ZnO. The maximum sensitivity is reached at 7% Mg doping, where a sensitivity value of 139 is obtained, reflecting the optimal balance between charge carrier generation and reduced recombination. At higher Mg content (9%), however, the sensitivity decreases to 34, confirming that excessive Mg incorporation degrades the photoresponse by introducing additional defects or scattering centers.

In the case of methanol-based samples, the trend is slightly different. While the photocurrent increases upon doping, the sensitivity values remain lower compared to ethanol-based samples, except for the 5% Mg–ZnO film, which shows a strong response with a sensitivity of 42.5. Other doping levels, such as 3% and 7%, present much weaker sensitivities (8.6 and 8.7, respectively), suggesting that methanol is less effective than ethanol in producing films with high optoelectronic quality. The highest performance for methanol is thus observed at 5% Mg doping, in contrast to ethanol where 7% doping is more favorable.

Table III.5 *The results exhibited the parameters of the prepared ZnO samples with and without Mg content at 5 V for both solvents.*

Samples	Ethanol			Methanol		
	I_{dark} (nA)	I_{photo} (nA)	Sensitivity	I_{dark} (nA)	I_{photo} (nA)	Sensitivity
Pure	0.007	0.09	11.85	0.008	0.116	13.5
3% Mg	0.004	0.21	51.75	0.012	0.110	8.6
5% Mg	0.001	0.06	59	0.002	0.087	42.5
7% Mg	0.001	0.14	139	0.010	0.097	8.7
9% Mg	0.002	0.07	34	0.006	0.077	11.83

III.8 The Photocatalytic Performance of the Mg-doped ZnO Thin Films

Fig III.15 illustrates the photocatalytic activity of ZnO and Mg-doped ZnO thin films prepared with ethanol as a solvent, tested for the degradation of methylene blue (MB) under UV irradiation. The absorbance spectra recorded at different irradiation times (30, 60, 90, and 120 min) show a gradual decrease in the main absorption peak of MB around 660 nm, indicating progressive dye degradation with increasing exposure time. The decrease is much more significant in the presence of Mg-doped ZnO compared to pure ZnO, confirming the beneficial effect of Mg incorporation on the photocatalytic efficiency.

For pure ZnO, the absorbance intensity decreases moderately with irradiation time, reflecting a decent but limited photocatalytic activity. When 3% Mg is introduced, the photocatalytic response improves, as shown by a faster decrease in absorbance, although the degradation remains less efficient than at higher Mg levels. The 5% Mg–ZnO sample shows a remarkable improvement in photocatalytic performance, with a sharp decline in MB absorbance within 120 minutes, suggesting enhanced generation and separation of photogenerated charge carriers.

At 7% Mg doping, the absorbance drops even more significantly, confirming superior photocatalytic activity compared to lower doping levels. Interestingly, the 9% Mg–ZnO thin film also exhibits a strong photocatalytic effect, with rapid degradation of MB. This indicates that at higher Mg concentrations, the catalytic performance does not deteriorate as sharply as it does for the electrical properties, which suggests that defect states introduced at higher doping levels may act as active sites for photocatalysis rather than recombination centers.

The bar chart on the lower right provides a comparative overview of MB degradation percentages at different reaction times for all samples. After 120 minutes, pure ZnO achieves around 70% degradation, while Mg-doped samples exhibit significantly higher efficiencies, with 5%, 7%, and 9% Mg reaching nearly complete degradation above 90%. This confirms that Mg incorporation greatly enhances photocatalytic efficiency, with the best performance observed for 7% and 9% Mg–ZnO thin films.

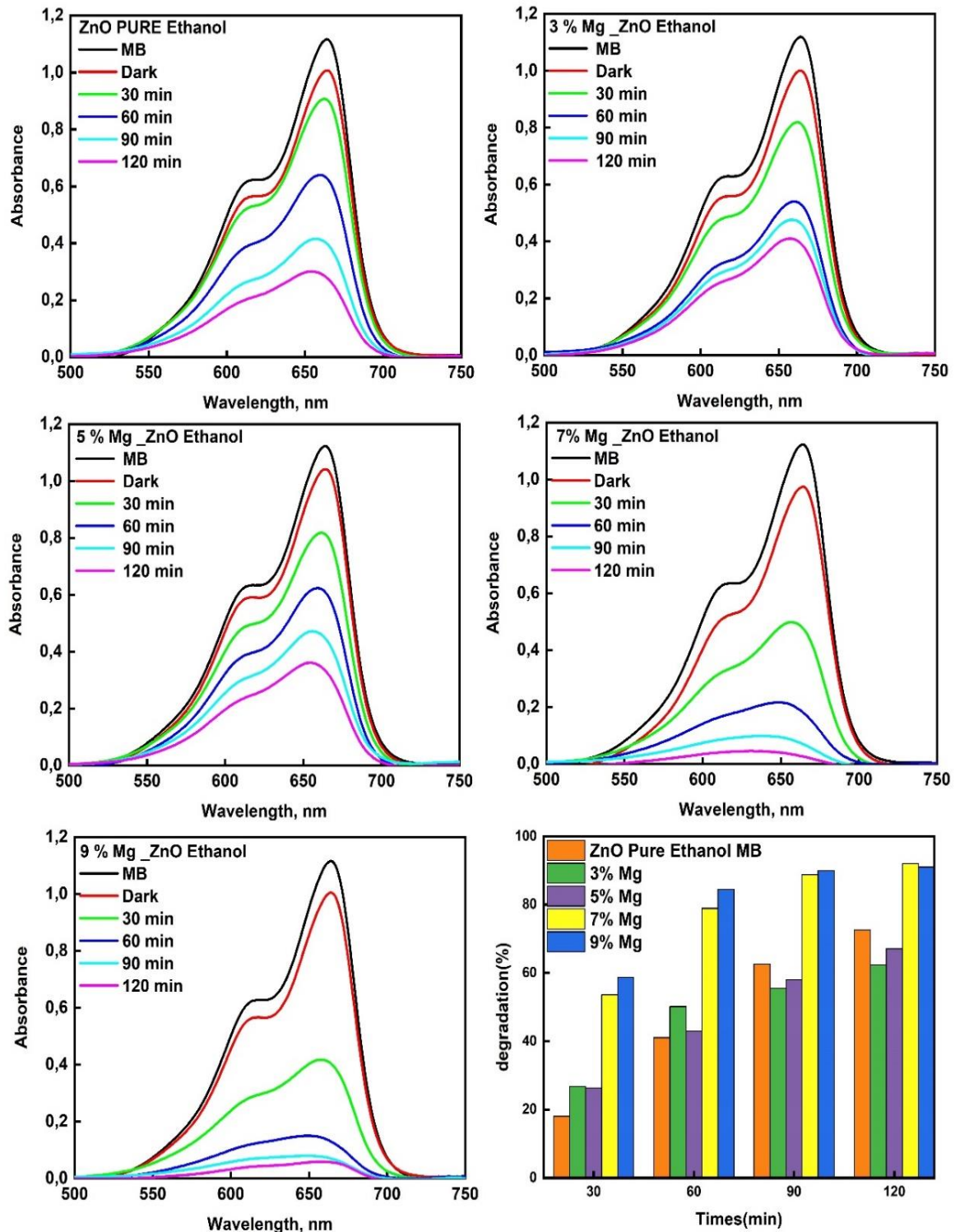


Fig III.15 Photocatalytic activity of ZnO and Mg doped ZnO thin films in MB solution under UV irradiation for different reaction time using Ethanol solvent.

Fig III.16 presents the photocatalytic activity of ZnO and Mg-doped ZnO thin films prepared with ethanol as a solvent, evaluated in methylene blue (MB) solution under natural sunlight irradiation. The absorbance spectra measured at different reaction times (30, 60, and 90 minutes) display a gradual decrease in the MB absorption peak centered at ~ 660 nm, confirming the degradation of the dye with increasing irradiation time. The degradation is noticeably stronger for Mg-doped ZnO films compared to pure ZnO, highlighting the role of Mg incorporation in enhancing photocatalytic efficiency under solar light conditions.

For pure ZnO, the absorbance intensity decreases progressively with irradiation time, but the degradation remains moderate compared to the doped samples. The 3% Mg–ZnO film shows a more pronounced reduction in absorbance, with faster MB degradation observed within 90 minutes. The performance improves further at 5% Mg doping, where a sharp decrease in absorbance is recorded, indicating efficient charge carrier generation and separation under sunlight.

The 7% Mg–ZnO thin film exhibits one of the highest photocatalytic activities, with almost complete MB degradation achieved within 90 minutes. Similarly, the 9% Mg–ZnO sample also shows excellent performance, with a significant drop in absorbance, confirming that higher Mg doping levels remain effective under solar irradiation. Unlike in the electrical measurements, where excessive doping led to reduced conductivity, here the additional Mg may introduce defect states that act as active catalytic sites, boosting dye degradation.

The bar chart in the lower right corner provides a comparative overview of degradation efficiency as a function of irradiation time. After 90 minutes, pure ZnO shows around 75% degradation, whereas Mg-doped samples, especially those with 7% and 9% Mg content, reach nearly 100% degradation. This demonstrates that Mg incorporation substantially improves the solar-driven photocatalytic activity of ZnO thin films, with higher doping concentrations showing particularly strong performance.

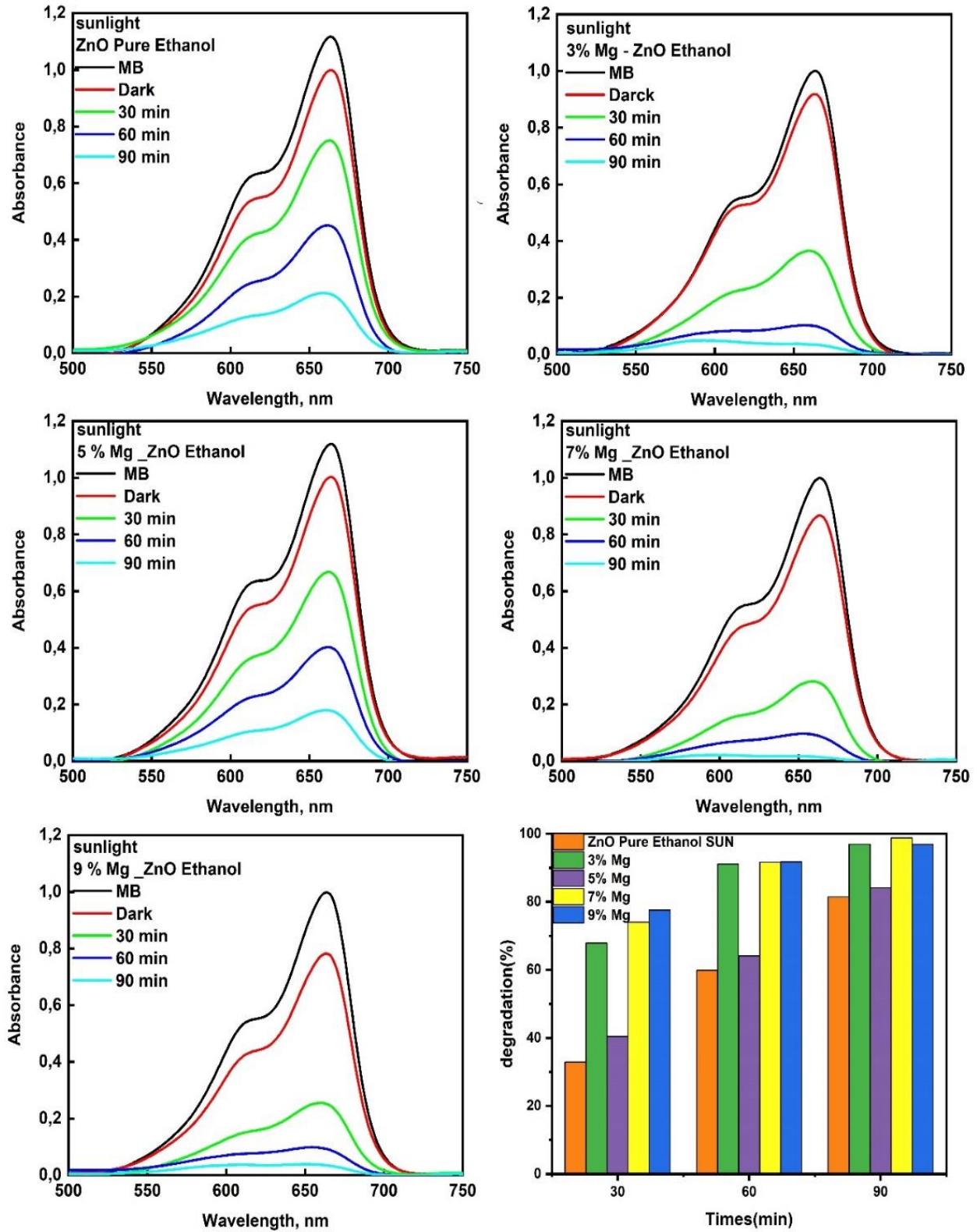


Fig III.16 Photocatalytic activity of ZnO and Mg doped ZnO thin films in MB solution under Sunlight irradiation for different reaction time using Ethanol solvent.

Fig III.17 illustrates the photocatalytic degradation behavior of methyl orange (MO) solution using pristine ZnO and Mg-doped ZnO thin films (3%, 5%, 7%, and 9%) under UV irradiation with ethanol as the solvent. The absorbance spectra were recorded at different irradiation times (0, 30, 60, 90, 120, 150, and 180 minutes), and the degradation efficiency was subsequently evaluated.

For pristine ZnO, a gradual decrease in the characteristic MO absorption peak at ~465 nm is observed with increasing irradiation time, indicating effective photocatalytic activity. However, the degradation rate is moderate, reflecting the inherent limitations of undoped ZnO, such as fast electron–hole recombination.

The incorporation of Mg significantly modifies the photocatalytic performance. At 3% Mg doping, the absorbance decreases more rapidly compared to undoped ZnO, suggesting enhanced photocatalytic efficiency due to improved charge separation and band gap widening, which favors reactive oxygen species (ROS) generation. Similarly, the 5% Mg-doped ZnO film shows further improvement, with faster degradation kinetics and higher overall photocatalytic activity, indicating that moderate Mg content optimizes the electronic structure and surface reactivity of ZnO.

At 7% Mg doping, the photocatalytic activity reaches its maximum. The absorption spectra show the most pronounced reduction in MO peak intensity over time, and the degradation efficiency bar chart confirms that 7% Mg–ZnO exhibits the highest photocatalytic performance, achieving nearly complete degradation (~90–95%) after 180 minutes. This superior behavior is attributed to the synergistic effects of optimal band gap tuning, improved surface morphology, and enhanced charge carrier dynamics at this doping level.

Conversely, at 9% Mg doping, the photocatalytic activity declines compared to the 7% sample. Although MO degradation still occurs, the efficiency is reduced, as shown in both the spectral decay and the bar chart. This reduction can be attributed to excessive Mg incorporation, which introduces structural defects and charge trapping centers, thereby increasing electron–hole recombination and decreasing photocatalytic performance.

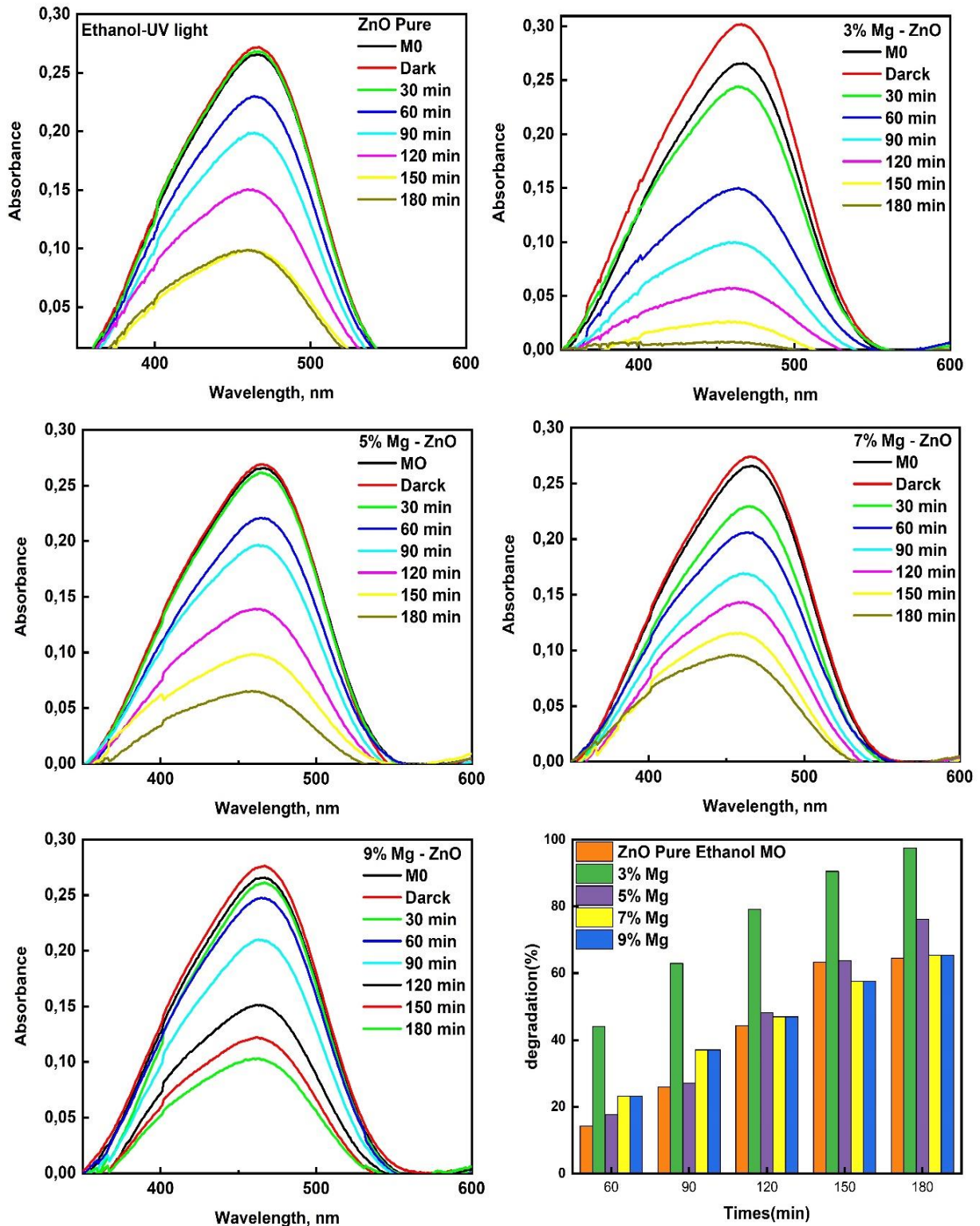


Fig III.17 Photocatalytic activity of ZnO and Mg doped ZnO thin films in MO solution under UV irradiation for different reaction time using Ethanol solvent.

Fig III.18 presents the UV–Vis absorbance spectra of methylene blue (MB) solution under UV irradiation in the presence of pure ZnO and Mg-doped ZnO thin films prepared with methanol as solvent. The measurements were taken at different reaction times (30, 60, 90, and 120 minutes), and the corresponding degradation efficiencies are summarized in the bar chart.

For pure ZnO, a steady decrease in the MB absorption peak (~664 nm) is observed with increasing irradiation time, indicating progressive dye degradation. However, the degradation efficiency remains moderate, suggesting that undoped ZnO suffers from limitations such as rapid electron–hole recombination and a relatively wide band gap.

The photocatalytic activity improves significantly upon Mg incorporation. At 3% Mg doping, the reduction in absorbance is more pronounced compared to pure ZnO, reflecting enhanced charge separation and increased generation of reactive radicals due to the slight band gap tuning introduced by Mg substitution. Similarly, the 5% Mg-doped ZnO films display strong photocatalytic performance, with a faster decrease in MB intensity and higher degradation efficiency, indicating that this doping concentration provides a favorable balance between crystallinity and defect density.

The 7% Mg-doped ZnO films exhibit the highest photocatalytic efficiency. Both the absorbance spectra and the degradation percentage confirm nearly complete MB removal after 120 minutes of irradiation. This superior activity can be attributed to optimal Mg concentration, which enhances light absorption, reduces recombination rates, and increases the number of surface-active sites that participate in photocatalysis.

Interestingly, the 9% Mg-doped ZnO films show reduced photocatalytic activity compared to the 7% sample. Although MB degradation still occurs, the efficiency decreases due to the excessive Mg incorporation, which likely introduces lattice distortions and deep-level defect states acting as recombination centers for photogenerated carriers.

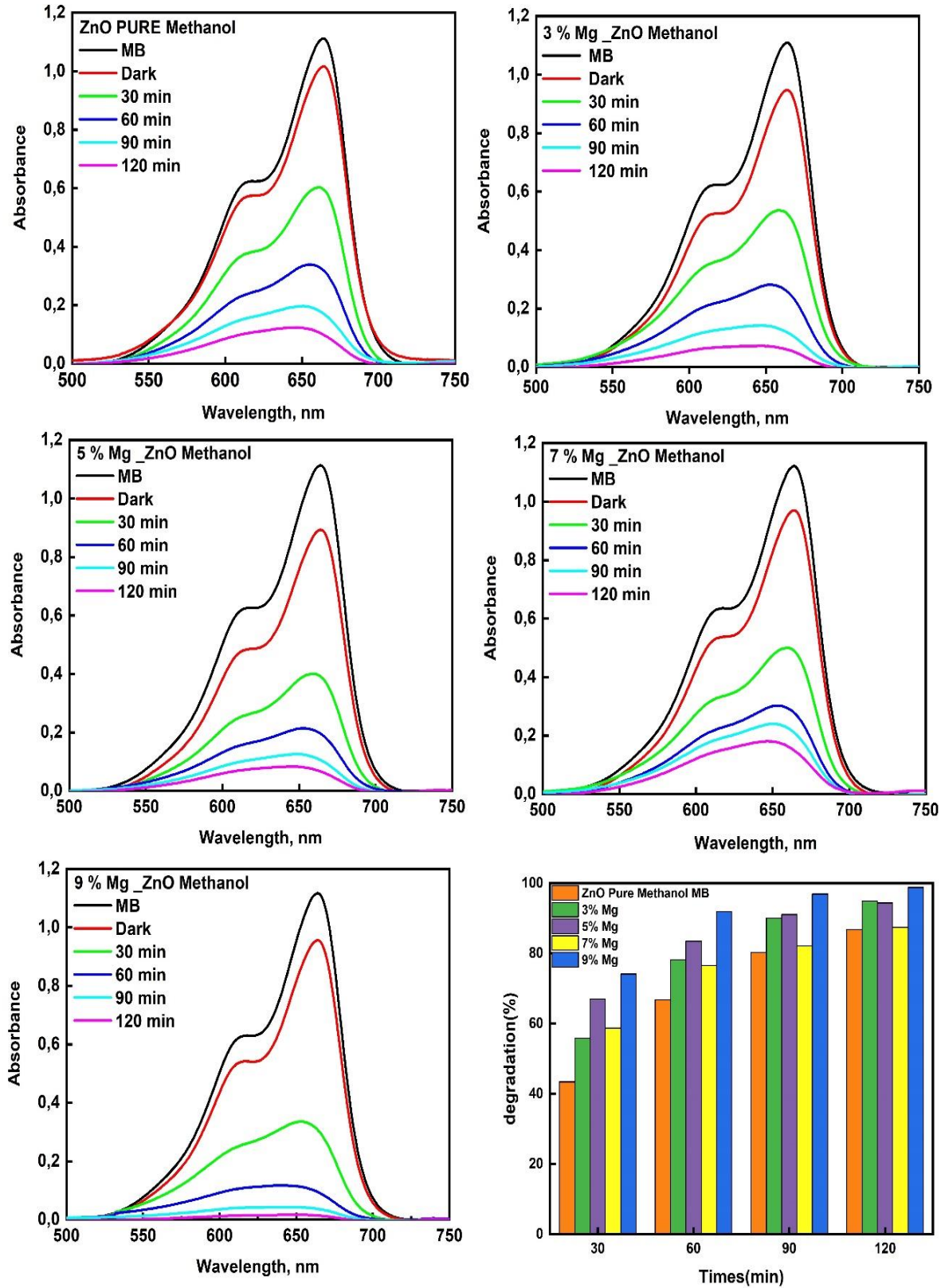


Fig III.18 Photocatalytic activity of ZnO and Mg doped ZnO thin films in MB solution under UV irradiation for different reaction time using Methanol solvent.

Fig III.19 shows the absorbance spectra of MB solution degraded by pure and Mg-doped ZnO thin films under natural sunlight irradiation for reaction times of 30 and 60 minutes. The results confirm that the films exhibit strong photocatalytic activity when exposed to solar radiation, with noticeable differences depending on the Mg concentration.

For pure ZnO, the characteristic MB absorption band at ~664 nm decreases steadily with irradiation time. After 60 minutes, the dye is significantly degraded, but the activity is still limited compared to the doped samples. This moderate efficiency can be attributed to the intrinsic wide band gap of ZnO, which restricts absorption mainly to the UV portion of sunlight, leaving much of the visible spectrum unused.

The introduction of Mg doping improves the degradation performance. At 3% Mg, a stronger reduction in absorbance is observed compared to pure ZnO, indicating enhanced charge separation and increased light absorption efficiency. Similarly, the 5% Mg-doped ZnO films display remarkable photocatalytic activity, with the MB peak intensity almost disappearing after 60 minutes, confirming faster degradation.

The 7% Mg-doped ZnO samples demonstrate the highest efficiency, with nearly complete degradation of MB achieved within 60 minutes of sunlight exposure. This superior activity can be attributed to the optimal doping level, which enhances solar spectrum utilization, improves electron-hole separation, and increases surface defect sites favorable for photocatalysis.

In contrast, 9% Mg-doped ZnO exhibits reduced photocatalytic activity compared to the 7% sample. Although MB degradation still occurs, the efficiency declines due to excessive Mg incorporation, which likely causes structural distortions and introduces recombination centers, reducing the availability of free carriers for the degradation reaction.

The bar chart further confirms these trends: the degradation efficiency under sunlight follows the order:

$$7\% \text{ Mg-ZnO} > 5\% \text{ Mg-ZnO} > 3\% \text{ Mg-ZnO} > \text{Pure ZnO} > 9\% \text{ Mg-ZnO}.$$

This behavior highlights that sunlight, with its broader spectral range compared to UV alone, significantly accelerates MB degradation, particularly when the films are optimally doped with Mg. These findings demonstrate that Mg doping around 7% provides the best compromise between structural quality and electronic properties, making it highly effective for solar-driven photocatalytic applications.

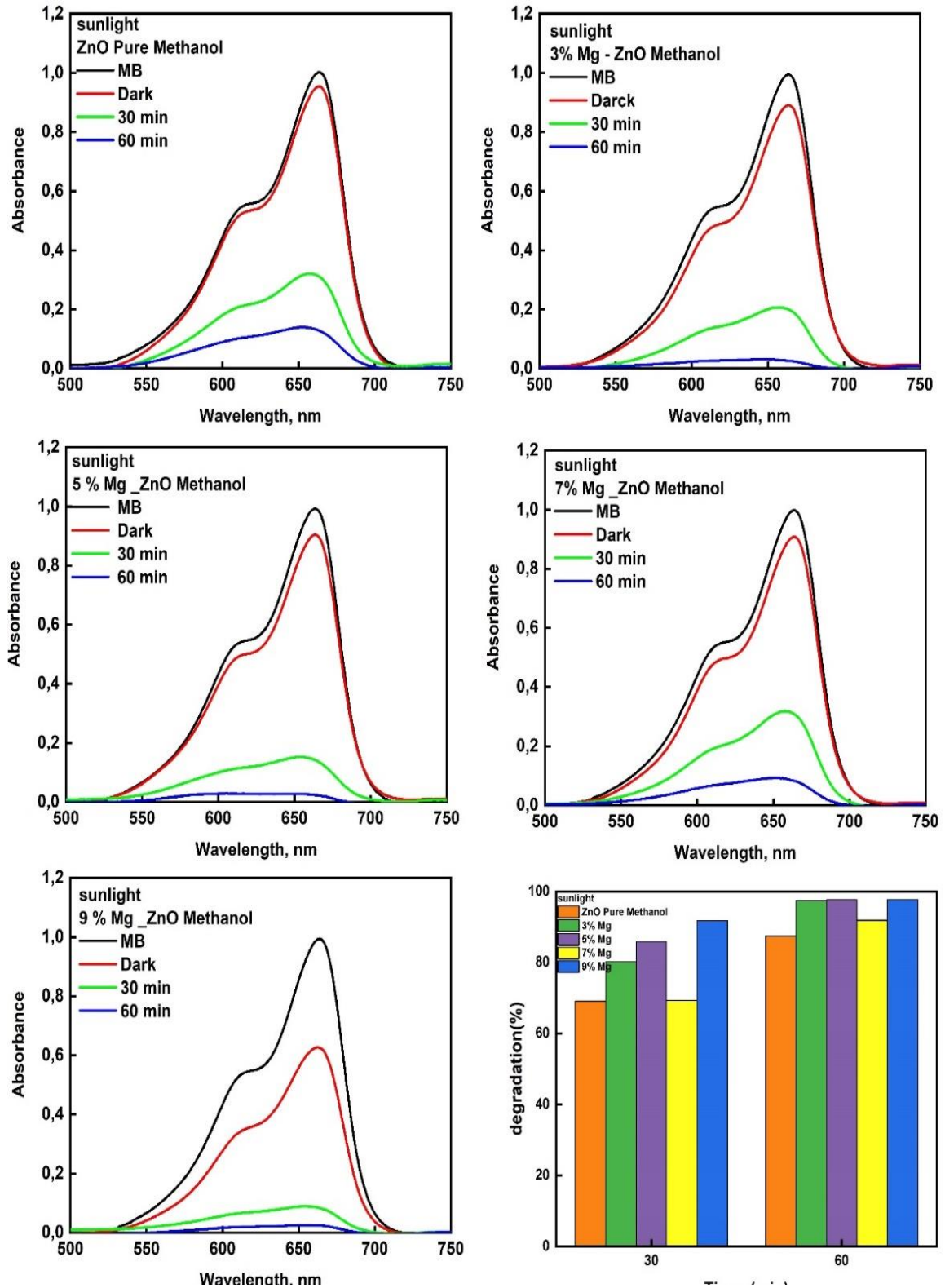


Fig III.19 Photocatalytic activity of ZnO and Mg doped ZnO thin films in MB solution under Sunlight irradiation for different reaction time using Methanol solvent.

Fig III.20 illustrates the photocatalytic activity of ZnO and Mg-doped ZnO thin films synthesized using methanol as a solvent, evaluated by the degradation of Methyl Orange (MO) solution under UV irradiation at different reaction times (30, 60, 90, and 120 minutes). The absorbance spectra in the range of 350–600 nm are shown for pure ZnO and for different Mg doping levels (3%, 5%, 7%, and 9%), while the bar chart summarizes the corresponding degradation efficiencies.

For pure ZnO, the absorbance of MO decreases gradually with irradiation time, reaching a moderate level of degradation after 120 minutes. The addition of Mg significantly enhances the photocatalytic performance. At 3% Mg, the degradation rate improves compared to pure ZnO, and a further increase to 5% and 7% Mg leads to even more efficient photocatalytic activity, as evidenced by the faster decline in absorbance peaks and higher removal percentages of MO. At 9% Mg, the films show the strongest photocatalytic activity, with nearly complete degradation of MO after 120 minutes of exposure.

The bar chart reinforces these findings, showing a clear trend of increased degradation efficiency with higher Mg doping. After 120 minutes, pure ZnO degrades approximately 65% of MO, while 9% Mg-doped ZnO achieves almost 100% degradation, confirming the beneficial role of Mg incorporation. This enhancement can be attributed to improved charge separation and reduced recombination of electron–hole pairs due to doping, which boosts the generation of reactive oxygen species responsible for the photodegradation process.

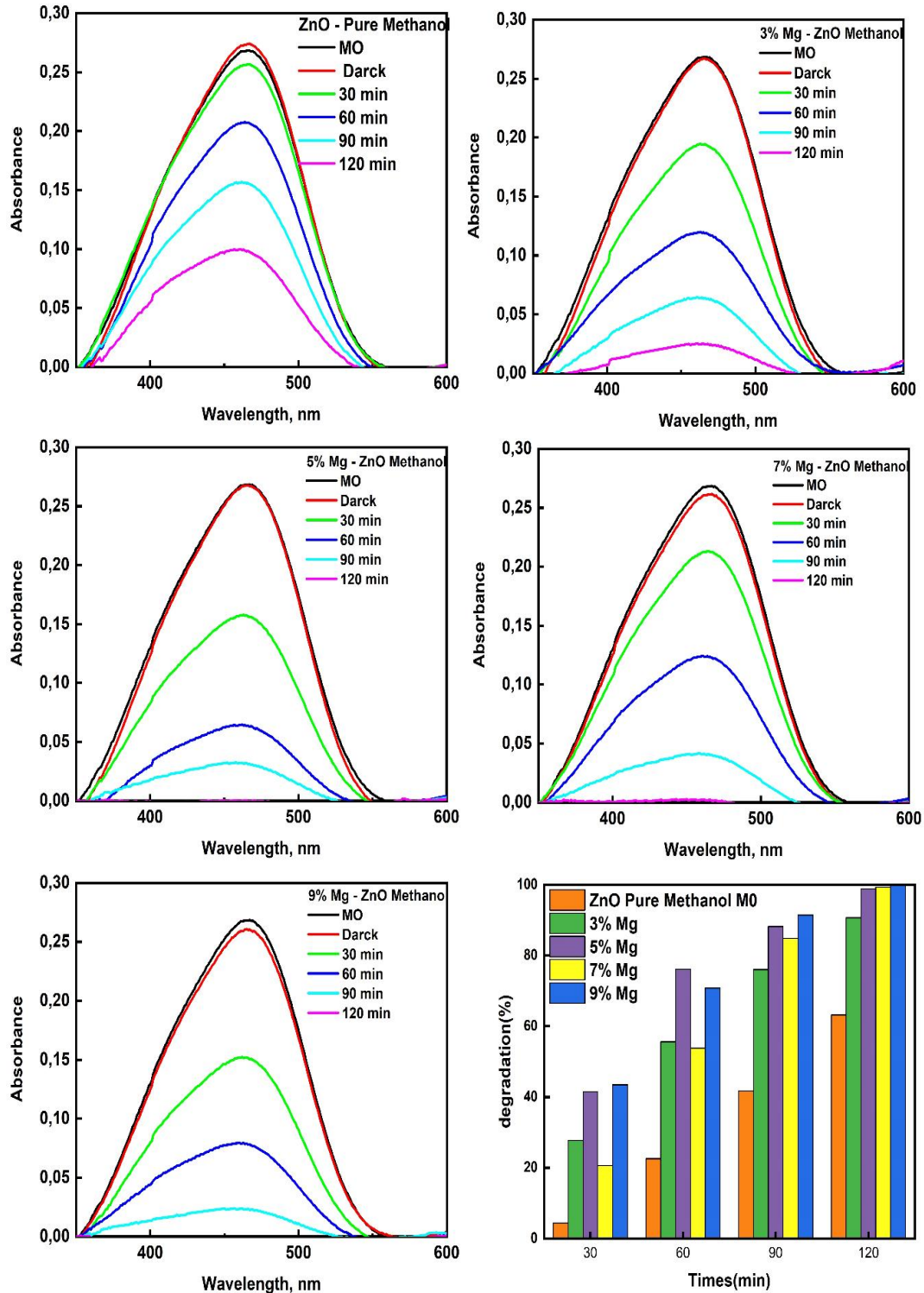


Fig III.20 Photocatalytic activity of ZnO and Mg doped ZnO thin films in MO solution under UV irradiation for different reaction time using Methanol solvent.

Fig III.21 illustrates the photocatalytic degradation kinetics of Methylene Blue (MB) and Methyl Orange (MO) dyes using ZnO and Mg-doped ZnO thin films synthesized with ethanol and methanol solvents, under both UV light and sunlight irradiation. The plots represent the variation of $\ln(C_0/C_t)$ as a function of reaction time, where higher slopes indicate faster degradation rates.

In **Fig. III.21a** (Ethanol–UV for MB), the degradation efficiency increases with Mg doping, with 9% Mg-ZnO showing the steepest slope, indicating the highest photocatalytic activity. Pure ZnO exhibits the lowest performance under these conditions. Similarly, in **Fig. III.21b** (Ethanol–Sunlight for MB), the degradation is significantly enhanced compared to UV light, with 7% and 9% Mg-doped samples outperforming the others. The strong activity under sunlight highlights the suitability of ethanol-synthesized Mg-ZnO films for solar-driven photocatalysis.

For methanol-based samples with MB (**Fig. III.21c–d**), a comparable trend is observed. Under UV light (**Fig. III.21c**), the photocatalytic activity improves with increasing Mg content, with 9% Mg-ZnO again exhibiting the best performance. Under sunlight irradiation (**Fig. III.21d**), the degradation rates are markedly higher, and Mg doping strongly enhances the photocatalytic efficiency compared to pure ZnO. The results confirm that sunlight is more effective than UV light for MB degradation in both ethanol- and methanol-derived films, with higher Mg doping providing the greatest benefit.

For MO degradation, the results are shown in **Fig. III.21e** (Methanol–UV) and **Fig. III.21f** (Ethanol–UV). In methanol-based films, photocatalytic efficiency improves steadily with Mg doping, with 9% Mg-ZnO reaching the highest degradation rate. Interestingly, for ethanol-based films (**Fig. III.21f**), the behavior is slightly different: 3% Mg-ZnO shows an exceptional photocatalytic activity compared to other doping levels, with much faster degradation kinetics than pure ZnO. However, higher Mg doping levels (5–9%) do not exhibit the same acceleration, suggesting that optimal doping depends on the dye type and solvent conditions.

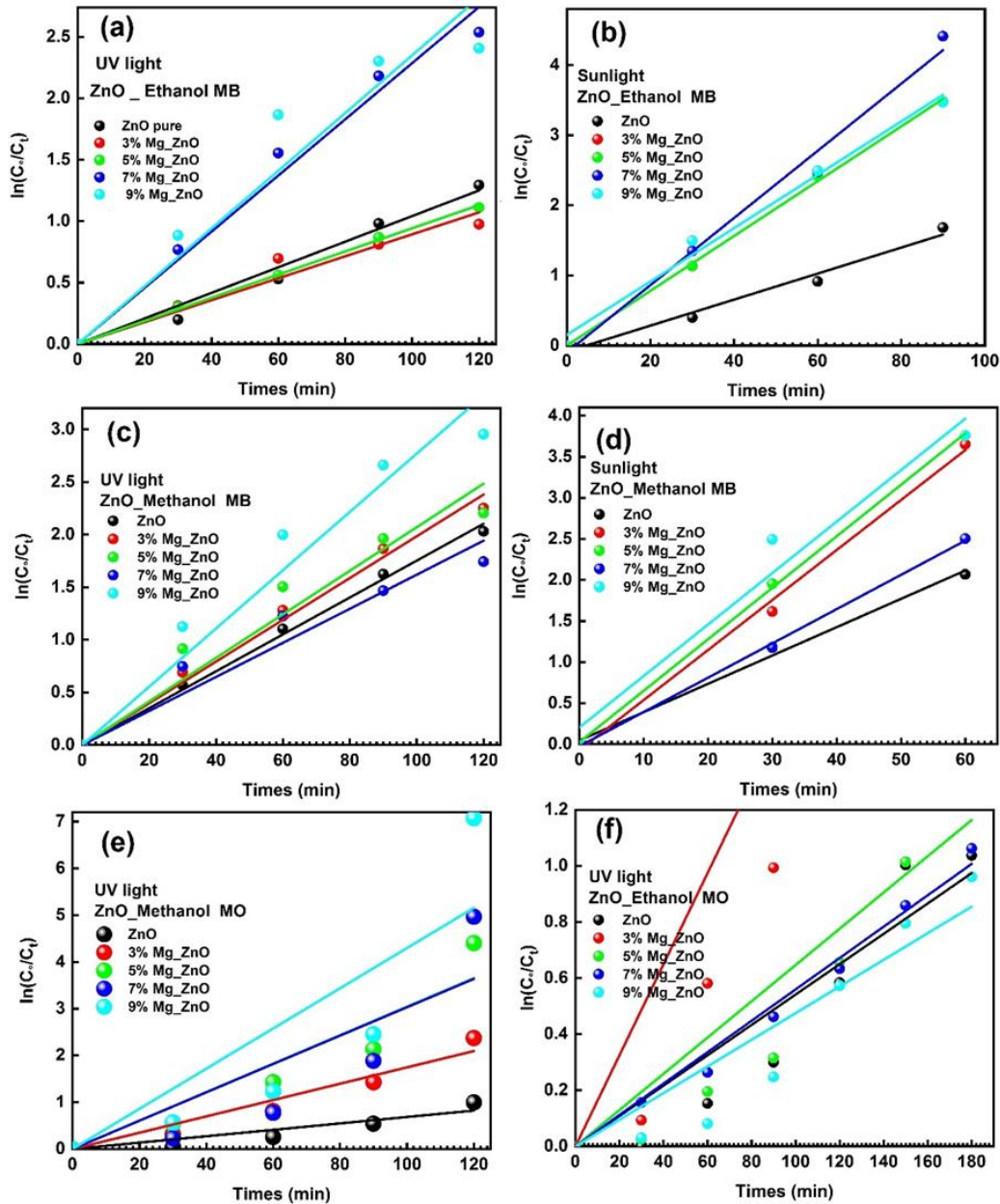


Fig III.21 (a) variation of $\ln (C_0/C_t)$ as functions of reaction time for MB degradation using Ethanol solvent under UV Light, (b) variation of $\ln (C_0/C_t)$ as functions of reaction time for MB degradation using Ethanol solvent under sunlight irradiation, (c) variation of $\ln (C_0/C_t)$ as functions of reaction time for MB degradation using Methanol solvent under UV Light, (d) variation of $\ln (C_0/C_t)$ as functions of reaction time for MB degradation using Methanol solvent under sunlight irradiation, (e) variation of $\ln (C_0/C_t)$ as functions of reaction time for MO degradation using Methanol solvent (f) variation of $\ln (C_0/C_t)$ as functions of reaction time for MO degradation using Ethanol solvent.

Table III.6 summarizes the calculated reaction rate constants (k) and degradation efficiencies (D) obtained from the first-order kinetic model for MB and MO dye degradation using ZnO and Mg-doped ZnO thin films synthesized with ethanol and methanol under UV light and sunlight irradiation.

For MB degradation under UV light, ethanol-based samples achieve a degradation efficiency of 92.08% within 120 minutes, with a rate constant of $k = 0.02349 \pm 0.00203 \text{ min}^{-1}$ (optimal at 7% Mg doping). In comparison, methanol-based samples reach a higher efficiency of 98.77% within the same time, with a slightly higher rate constant of $k = 0.02769 \pm 0.00184 \text{ min}^{-1}$ (optimal at 9% Mg doping). This indicates that methanol-derived films provide superior performance for MB degradation under UV light.

For MO degradation under UV light, ethanol-based films degrade 97.46% of MO after 180 minutes with $k = 0.01968 \pm 0.00254 \text{ min}^{-1}$ (best at 3% Mg), while methanol-derived films achieve almost complete degradation (99.91%) in just 120 minutes, with a much higher rate constant of $k = 0.040 \pm 0.008 \text{ min}^{-1}$ (best at 9% Mg). This clearly demonstrates the enhanced photocatalytic activity of methanol-based thin films for MO dye removal.

Under sunlight irradiation, the performance improves significantly for both solvents. For MB degradation, ethanol-based films achieve 98.78% efficiency in 90 minutes with $k = 0.04786 \pm 0.00393 \text{ min}^{-1}$ (7% Mg), while methanol-derived films reach 97.66% degradation in just 60 minutes with an even higher rate constant of $k = 0.06265 \pm 0.01182 \text{ min}^{-1}$ (9% Mg). These results underline the superior efficiency of methanol-derived films, particularly under solar irradiation.

Table III.6 lists the reaction rate constants (k) and degradation efficiency (D) values for the kinetic data fit by the first-order model for MB and MO dye solutions with ZnO and Mg-doped ZnO thin films under UV light and sunlight irradiation.

	Ethanol			Methanol		
	Times(min)	D (%)	$k \text{ (min}^{-1}\text{)}$	Times(min)	D (%)	$k \text{ (min}^{-1}\text{)}$
MB UV light	120	92.1	$k_7 = 0.023 \pm 0.002$	120	98.8	$k_9 = 0.028 \pm 0.002$
MO UVlight	180	97.5	$k_3 = 0.016 \pm 0.001$	120	99.9	$k_9 = 0.040 \pm 0.008$
MB Sunlight	90	98.8	$k_7 = 0.049 \pm 0.004$	60	97.7	$k_9 = 0.06 \pm 0.01$

III.9 Mechanism for the photocatalytic degradation of ZnO and MZO thin films

Fig III.22 schematically illustrates the photocatalytic degradation mechanism of Methylene Blue (MB) solution by ZnO thin films under sunlight irradiation. When the ZnO (or Mg-doped ZnO, MZO) thin film is exposed to sunlight, photons with sufficient energy excite electrons (e^-) from the valence band (VB) to the conduction band (CB), leaving behind corresponding holes (h^+) in the VB. This process generates electron–hole pairs, which play a crucial role in initiating redox reactions at the photocatalyst surface.

The photoexcited electrons in the CB can react with dissolved oxygen molecules (O_2) to form reactive oxygen species, such as superoxide radicals ($O_2^{\cdot-}$). Simultaneously, the photogenerated holes in the VB can oxidize water molecules (H_2O) or hydroxide ions (OH^-) adsorbed on the surface, leading to the formation of hydroxyl radicals ($OH^{\cdot}$). Both species ($O_2^{\cdot-}$ and $OH^{\cdot}$) are highly reactive oxidants that can attack the MB dye molecules, breaking down their complex aromatic structures into intermediate compounds and eventually into simple, non-toxic degradation products such as CO_2 and H_2O .

However, not all electron–hole pairs contribute to photocatalysis. A portion undergoes recombination, where the excited electrons fall back into the VB, neutralizing the holes and dissipating energy as heat or light. This recombination process reduces the overall photocatalytic efficiency. Incorporation of Mg into ZnO helps mitigate recombination by modifying the band structure and introducing defect states that act as trapping centers, thereby prolonging carrier lifetimes and enhancing the probability of redox reactions.



Fig III.22 Degradation mechanism of MB solution by ZnO thin film under sunlight irradiation.

III.10 Conclusion

In this chapter, ZnO thin films doped with different concentrations of Mg were successfully fabricated using the sol-gel immersion deposition technique, and their structural, optical, and electrical properties were systematically investigated. Structural analysis revealed that Mg incorporation influenced crystallinity, grain size, and lattice parameters, confirming the effective substitution of Zn^{2+} by Mg^{2+} ions within the ZnO lattice. Optical studies showed a widening of the band gap with increasing Mg content, accompanied by modifications in the absorption edge, demonstrating the tunability of optical properties through doping.

Electrical measurements under dark and UV illumination highlighted the significant role of Mg concentration and solvent type in enhancing photoconductivity and sensitivity. The optimum performance was observed at intermediate Mg doping levels, where charge separation was promoted and recombination minimized. Furthermore, photocatalytic experiments using methylene blue degradation confirmed the beneficial impact of Mg incorporation, with 7%–9% Mg-doped ZnO films exhibiting the highest degradation efficiency under both UV and sunlight.

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CHAPTER IV

*Structural, Optical, and
Electrical Properties of
ZnO:Na Thin Films
Fabricated by the Sol-Gel
Immersion Deposition
Technique*

IV.1 Introduction

Zinc oxide (ZnO) is a wide-bandgap semiconductor with excellent optical transparency, high exciton binding energy, and good chemical stability, making it suitable for applications in optoelectronics, sensors, and transparent conductive films [1-2]. Among the various deposition techniques, the sol-gel immersion method is particularly attractive due to its simplicity, low cost, and ability to produce uniform and doped thin films [3].

Sodium (Na) doping has recently attracted attention as a means to tailor the structural, optical, and electrical properties of ZnO, potentially overcoming the challenges of achieving stable p-type conductivity. Incorporation of Na can influence crystallinity, surface morphology, bandgap energy, and charge carrier transport, thereby enhancing device performance [4-6].

In this chapter, we present a detailed investigation of ZnO: Na thin films synthesized by the sol-gel immersion deposition technique, focusing on their structural, optical, and electrical characteristics to assess their potential for optoelectronic and photocatalytic applications.

IV.2 Experimental Procedures

IV.2.1 Chemicals and Substrates

For the synthesis of Na-doped ZnO thin films, analytical-grade reagents were employed without further purification. Zinc acetate dihydrate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$, 99.9%, Sigma-Aldrich) served as the zinc precursor, while sodium nitrate (NaNO_3 , 99.9%, Sigma-Aldrich) acted as the dopant source. Absolute ethanol ($\text{C}_2\text{H}_5\text{OH}$, 99.8%, Sigma-Aldrich) was used as the solvent, and monoethanolamine (MEA, 99%, Sigma-Aldrich) was added as a stabilizing agent to regulate the sol-gel process. Microscope glass slides were chosen as substrates. Prior to deposition, the substrates were sequentially cleaned in acetone, methanol, and distilled water using ultrasonic agitation to remove organic and particulate impurities.

IV.2.2 Photocatalytic Activity Tests

Photocatalytic degradation experiments were carried out using methylene blue (MB, $2 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$) under two illumination sources:

- UV irradiation: Provided by a 15 W Philips G15T8 germicidal lamp ($\lambda = 254 \text{ nm}$), with the film immersed in 5 mL of MB solution at a distance of 9 cm.

- Sunlight irradiation: Conducted outdoors in Khenchela, Algeria (~30 °C ambient temperature).

Prior to irradiation, film samples were immersed in MB solution and kept in the dark for 30 min to reach adsorption–desorption equilibrium. Dye degradation was monitored spectrophotometrically at 664 nm every 30 min.

Radical Trapping Studies: To identify active species, scavengers were introduced into the MB solution: ascorbic acid ($O_2^{\bullet-}$), EDTA (h^+), isopropanol ($\bullet OH$), and silver nitrate (e^-). MB degradation was monitored after 3 h UV or 2 h sunlight exposure.

IV.2.3 UV Photo response Measurements

For UV photodetection analysis, silver electrodes were deposited on ZnO: Na films to fabricate two-terminal devices. Current–voltage (I–V) characteristics were recorded under dark and illuminated conditions using a Keithley 2400 source meter. A 365 nm UV LED lamp (100 mW/cm²) served as the light source. The photocurrent response, sensitivity, and response/recovery times were evaluated to assess the films' suitability for UV sensing applications.

IV.3 Structural Analysis

The crystalline structure of the undoped and Na-doped ZnO thin films was investigated by X-ray diffraction (XRD). **Fig IV. 1** presents the diffraction patterns for pure ZnO and ZnO: Na thin films with different Na concentrations (3, 5, 7, and 9 at. %). All samples display the characteristic peaks of the hexagonal wurtzite ZnO phase (JCPDS card no. 36-1451), with the most prominent reflections located at $2\theta \approx 31.7^\circ$, 34.4° , and 36.2° , corresponding to the (100), (002), and (101) planes, respectively. The absence of impurity-related reflections confirms the single-phase nature of the deposited films and suggests that Na incorporation does not induce secondary phases within the detection limit of XRD.

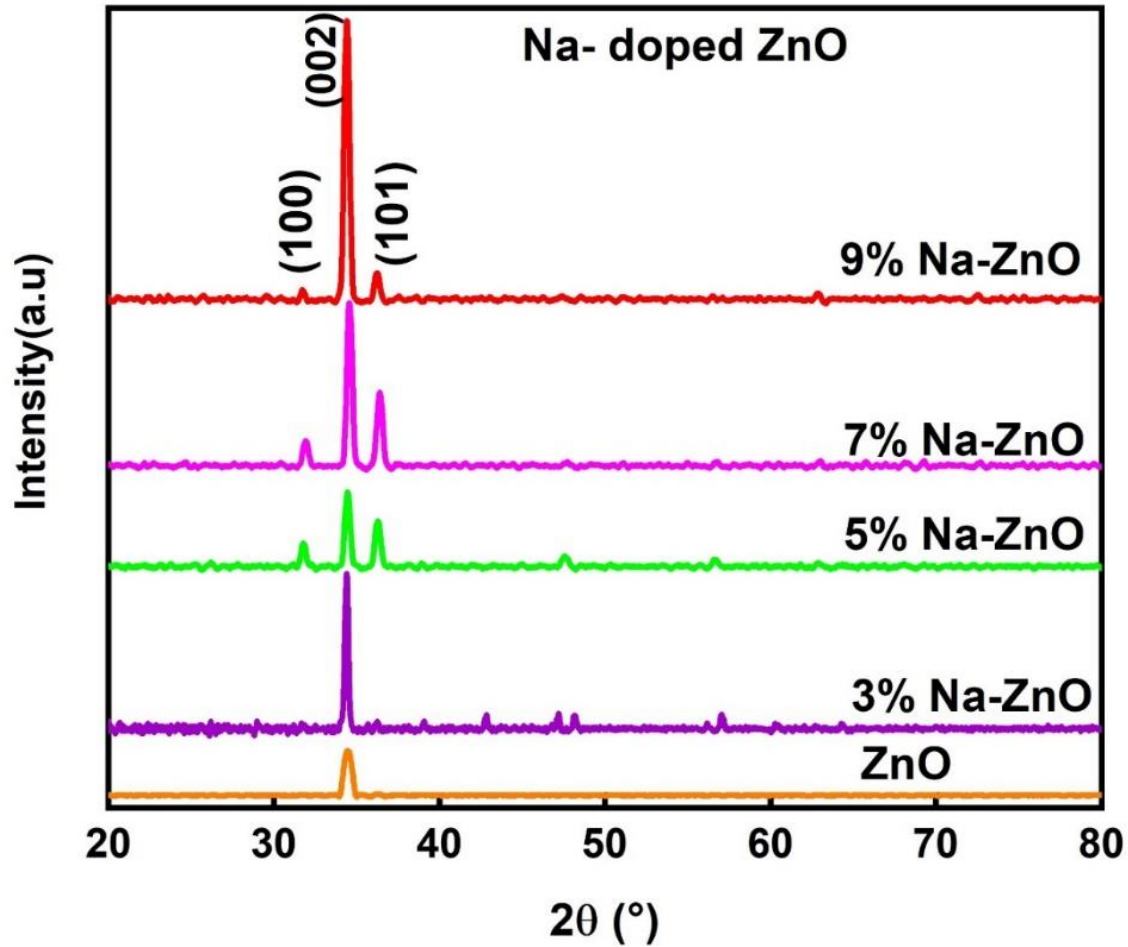


Fig IV. 1 X-ray Diffraction spectra of undoped and Na-doped ZnO thin films as a function of Na content (3, 5, 7, and 9%).

For all compositions, the (002) reflection dominates the diffractograms, indicating that the films exhibit a strong c-axis preferred orientation, which is highly favorable for optoelectronic applications. Subtle changes in peak position, width, and intensity are observed with Na doping:

- ✚ At low doping levels (3%), a slight broadening of the (002) peak is visible, likely arising from lattice strain due to the incorporation of Na^+ ions, whose ionic radius ($\sim 1.02 \text{ \AA}$) is larger than that of Zn^{2+} ($\sim 0.74 \text{ \AA}$).
- ✚ Increasing the Na concentration to 5–7% results in a gradual enhancement of the (002) peak intensity, implying improved crystallinity and better alignment of the crystallites.

- ✚ At 9% Na doping, the (002) reflection exhibits its maximum intensity, suggesting that crystalline quality continues to improve with higher Na incorporation. However, excessive substitution may also induce local lattice distortions.

These observations indicate that Na is effectively incorporated into the ZnO lattice, either by substituting Zn^{2+} cation sites or by occupying interstitial positions. The associated structural modifications influence lattice parameters and crystallite size. A quantitative estimation of these effects, for example through Debye–Scherrer analysis, can provide further insights into the crystallite size evolution as a function of Na content.

Table IV. 1 summarizes the microstructural parameters of undoped and Na-doped ZnO thin films, as extracted from XRD data. The evaluated parameters include the lattice constants a and c , crystallite size (D), microstrain (ϵ), dislocation density (δ), interplanar spacing $d(hkl)$, unit cell volume (V_{cell}), X-ray density (ρ_{x-ray}), and the specific surface area (S).

The lattice constants and interplanar spacing were calculated using Bragg’s law and standard hexagonal geometry relations [35,36]. The average crystallite size was estimated using the Debye–Scherrer formula, while the microstrain and dislocation density were derived from peak broadening analysis. The unit cell volume was determined from the hexagonal structural parameters (Eq. 1), whereas the X-ray density was obtained from the molecular weight and unit cell dimensions (Eq. 2) [37,38]. Finally, the specific surface area was estimated using the relation between crystallite size and surface-to-volume ratio (Eq. 3) [37,38].

This comprehensive microstructural evaluation provides valuable insights into the effects of Na incorporation on ZnO crystallinity, lattice distortion, and defect density, which in turn influence the films’ optical and electrical properties.

$$V_{cell} = \frac{\sqrt{3}}{2} a^2 c \quad (IV. 1)$$

$$\rho_{x-ray} = \frac{ZM}{V_{cell} Na} \quad (IV. 2)$$

$$S * = \frac{6000}{\rho_{x-ray} D} \quad (IV. 3)$$

Table IV. 1 presents the microstructural characteristics derived from the XRD data for all deposited thin films.

*CHAPTER IV: Structural, Optical, and Electrical Properties of ZnO:Na Thin Films
Fabricated by the Sol-Gel Immersion Deposition Technique*

Samples	(hkl)	2 θ (°)	FWHM	a= b(Å)	c(Å)	c/a	<i>D</i> (nm)	δ	d(hkl)	V _{cell}	$\rho_{x\text{-ray}}$	ε $\times 10^{-3}$	S* (m ² /g)
Pure	002	34.467	0.5077	3.0022	5.2000	1.7320	17.1099	0.0034	2.6000	46.24	5.84	2.1	60.04
3% Na	002	34.393	0.2407	3.0084	5.2107	1.7321	36.0775	0.0007	2.6053	40.84	6.51	1.00	25.54
5% Na	002	34.450	0.3574	3.0036	5.2025	1.7321	24.3053	0.0016	2.6012	40.64	6.48	1.48	38.09
7% Na	002	34.569	0.3624	2.9936	5.1850	1.7321	23.9758	0.0017	2.5925	40.24	6.47	1.51	38.67
9% Na	002	34.406	0.3686	3.0073	5.2088	1.7321	23.5647	0.0018	2.6044	40.79	6.32	1.53	40.28

The evaluation of these parameters provides valuable insight into the structural evolution induced by Na doping in ZnO thin films:

- ✚ Lattice parameters and unit cell volume (V_{cell}): The calculated lattice constants confirm the retention of the hexagonal wurtzite structure. Slight fluctuations in a and c with increasing Na content indicate substitutional incorporation of Na^+ into Zn^{2+} sites or interstitial positions. This substitution induces local lattice distortion due to the ionic radius mismatch. The unit cell volume decreases from 46.24 Å³ (undoped) to ~40.24–40.84 Å³ at low doping, reflecting lattice compaction before stabilizing at higher concentrations.
- ✚ Crystallite size (D): The crystallite size increases markedly from 17.1 nm (undoped) to 36.1 nm (3% Na), pointing to grain growth and improved crystallinity at low doping. Beyond 3% Na, however, the crystallite size decreases (down to ~23.5 nm at 9% Na), which can be attributed to enhanced strain and defect density introduced by excessive dopant incorporation.
- ✚ Microstrain (ε) and dislocation density (δ): A reduction in microstrain ($\varepsilon \times 10^{-3}$) with initial doping suggests partial relaxation of the crystal lattice. At higher doping levels, ε rises slightly, reflecting local lattice distortions. Similarly, dislocation density (δ) decreases from 0.0034 (pure ZnO) to 0.0007 (3% Na), consistent with enhanced crystallinity, but increases again at higher doping, highlighting the reintroduction of lattice imperfections.
- ✚ X-ray density ($\rho_{x\text{-ray}}$) and specific surface area (S): The X-ray density increases with Na doping due to the reduction in unit cell volume. Conversely, the specific

surface area decreases from 60.04 m²/g (undoped) to 25.54 m²/g (3% Na), then rises again to 40.28 m²/g (9% Na). This trend suggests that moderate doping promotes grain growth and crystallinity, while higher doping reduces crystallite size, thereby increasing surface activity.

IV.4 Morphological Analysis

Fig IV. 2 displays the field emission scanning electron microscopy (FE-SEM) images of undoped and Na-doped ZnO thin films at various doping concentrations (3%, 5%, 7%, and 9%). The micrographs highlight significant changes in surface morphology and grain distribution with increasing Na incorporation:

- Undoped ZnO (Fig IV. 2a): The surface exhibits a relatively dense structure composed of small, irregularly distributed grains. The morphology is less uniform, with visible voids and compact regions. Grain boundaries are indistinct, reflecting moderate crystallinity and some degree of agglomeration.
- 3% Na-ZnO (Fig IV. 2b): Doping with 3% Na results in a more homogeneous and densely packed surface. The grains become larger, spherical, and well-defined, with enhanced coverage compared to the undoped film. This improvement suggests that Na ions promote crystallization and facilitate grain growth during film formation.
- 5% Na-ZnO (Fig IV. 2c): At 5% Na, the film maintains a uniform granular structure similar to the 3% sample but with slightly smaller grain sizes. The grains remain compact and smooth, indicating balanced dopant incorporation and favorable film uniformity. This doping level appears optimal for controlling both grain size and packing density.
- 7% Na-ZnO (Fig IV. 2d): With 7% Na, the surface becomes more heterogeneous, featuring grains of varying sizes and the emergence of larger agglomerates. Although the film remains relatively compact, this distribution reflects the onset of structural disorder induced by excessive dopant concentration.

- 9% Na-ZnO (Fig IV. 2e): At the highest doping level, the morphology loses uniformity. Grain coalescence and surface roughness increase, and irregularly shaped particles appear. Such features suggest dopant segregation or phase inhomogeneity, which may disrupt uniform grain growth and negatively influence the film's optoelectronic performance.

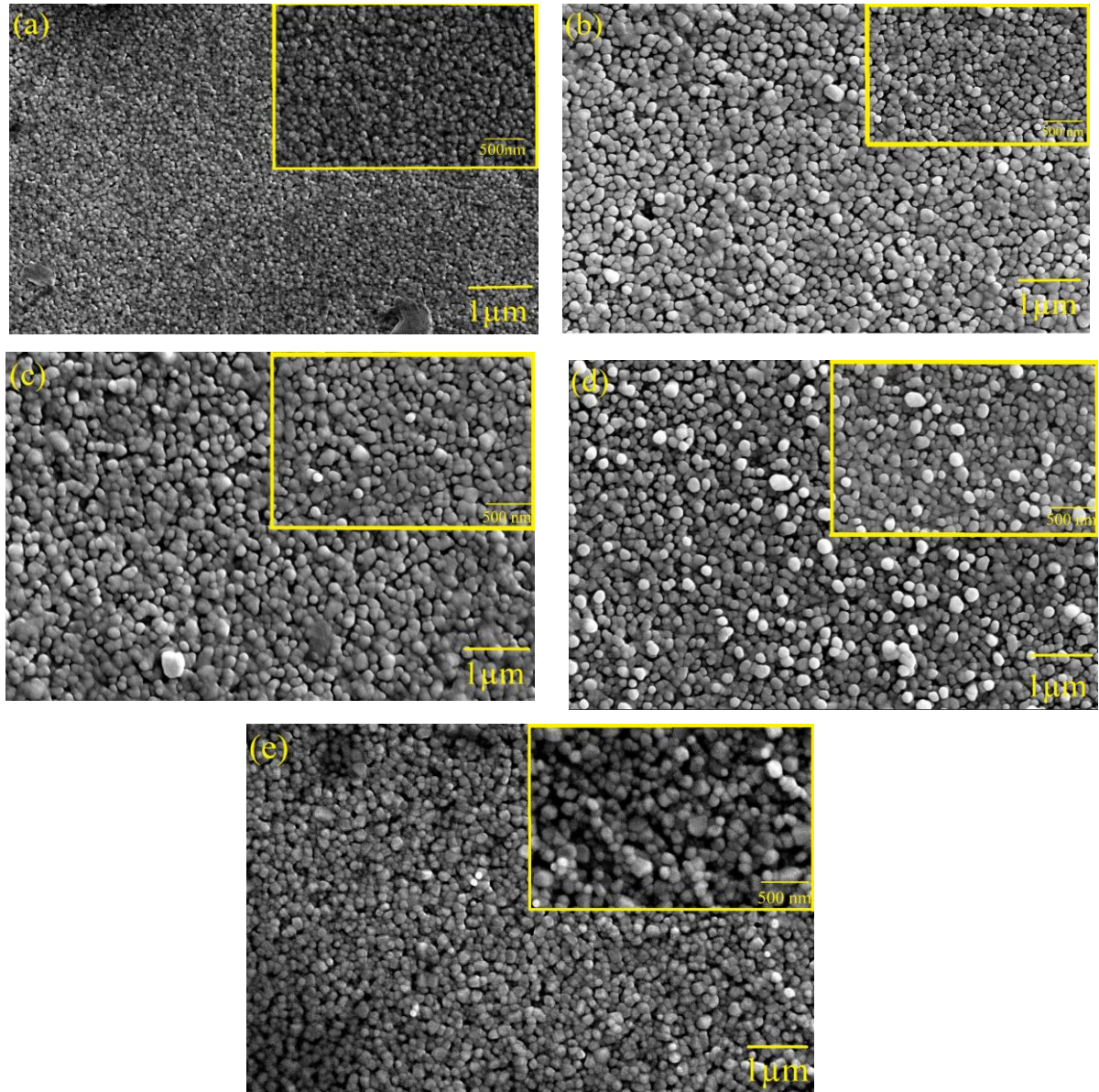


Fig IV. 2 FE-SEM images of (a) ZnO, (b) 3% Na -ZnO, (c) 5% Na – ZnO, (d) 7% Na - ZnO, and (e) 9% Na – ZnO.

IV.5 Compositional Analysis

The Energy Dispersive X-ray (EDX) spectrum of the 7% Na-doped ZnO thin film, presented in Figure IV. 3, confirms the elemental composition of the material. The spectrum

displays distinct peaks corresponding to oxygen (O), zinc (Zn), and sodium (Na), verifying the expected stoichiometry of the doped ZnO system.

The strong peaks observed at $\sim 0.5\text{--}0.6\text{ keV}$ correspond to the O K-edge, confirming the significant presence of oxygen consistent with the ZnO matrix.

The Zn K-lines, detected at $\sim 8.5\text{--}9.6\text{ keV}$, confirm zinc as the major constituent of the film.

The Na L peak, appearing around $1.0\text{--}1.2\text{ keV}$, validates the successful incorporation of sodium into the ZnO lattice. The relatively lower intensity of this peak compared to Zn and O is consistent with the 7% doping level.

No additional peaks corresponding to extraneous elements are detected, indicating that the films are free from detectable impurities. Overall, the EDX analysis confirms the effective incorporation of Na into the ZnO structure and validates the compositional purity of the synthesized thin films.

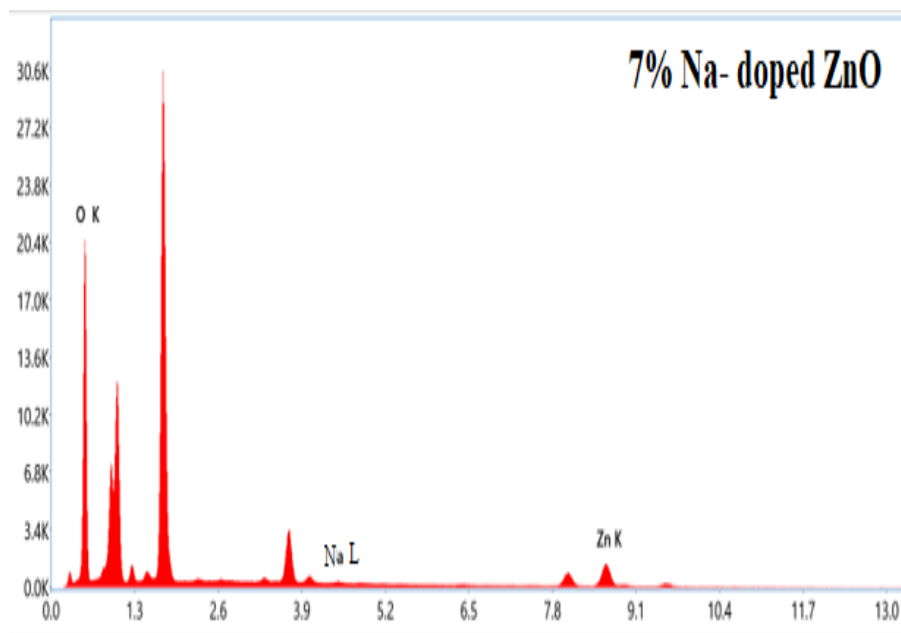


Fig IV. 3 EDX spectra of 7% Na- ZnO.

The Energy Dispersive X-ray (EDX) spectrum of the 7% Na-doped ZnO thin film (**FigIV. 3**) confirms the presence of zinc (Zn), oxygen (O), and sodium (Na) within the synthesized material. Strong peaks corresponding to Zn and O dominate the spectrum, consistent with the ZnO lattice, while the appearance of a distinct Na peak validates the successful incorporation of sodium dopants.

These qualitative results are supported by the quantitative data summarized in **Table IV.2**, which reports the elemental composition of undoped and Na-doped ZnO samples. For the pure ZnO film, only Zn (39.59%) and O (30.38%) are detected, as expected. Upon doping, sodium becomes detectable, reaching a maximum of 2.3% in the 5% Na-doped sample, before slightly decreasing to 1.6% in the 7% Na-doped sample. A notable trend is the increase in oxygen content with doping, rising to 66.6% for the 7% Na-doped film, suggesting enhanced oxygen incorporation or possible surface adsorption. Conversely, Zn content shows fluctuations, which may be attributed to lattice distortion or variations in atomic substitution efficiency caused by Na incorporation.

Overall, the EDX analysis confirms the effective doping of ZnO with sodium and highlights the compositional changes induced by varying Na concentrations. These results demonstrate that Na incorporation not only modifies the Zn and O distribution but also potentially alters the defect chemistry and stoichiometry of the ZnO thin films.

Table IV. 2 The ratio of ZnO undoped and Na-doped ZnO chemical components.

Weight. %			
Phases	Zn	O	Na
Pure	39.59	30.38	0
3% Na	36.5	62.5	1
5% Na	49.1	48.6	2.3
7% Na	31.8	66.6	1.6
9% Na	43.79	33.25	1.69

Fig IV. 4 shows the particle size distribution histograms for undoped and Na-doped ZnO thin films at different doping levels (3%, 5%, 7%, and 9%). Pure ZnO exhibits a narrow size distribution with an average particle diameter of ~66.6 nm. With 3% Na doping, the mean size increases to ~112.2 nm, indicating that low-level doping enhances particle growth, likely due to improved grain boundary mobility or modified nucleation kinetics.

At 5% Na, the average particle size reaches a maximum of ~161.5 nm, suggesting optimal dopant incorporation that promotes grain coalescence and growth. However, beyond this

concentration, the average size decreases progressively: ~131.1 nm at 7% Na with a broader distribution, and ~85.5 nm at 9% Na. This reduction implies that higher Na content introduces strain, defects, or dopant segregation, which suppress grain growth and promote structural disorder.

Overall, the particle size evolution indicates a non-linear dependence on Na concentration, with 5% Na representing a critical level for maximum particle growth before crystallinity is progressively inhibited at higher doping levels.

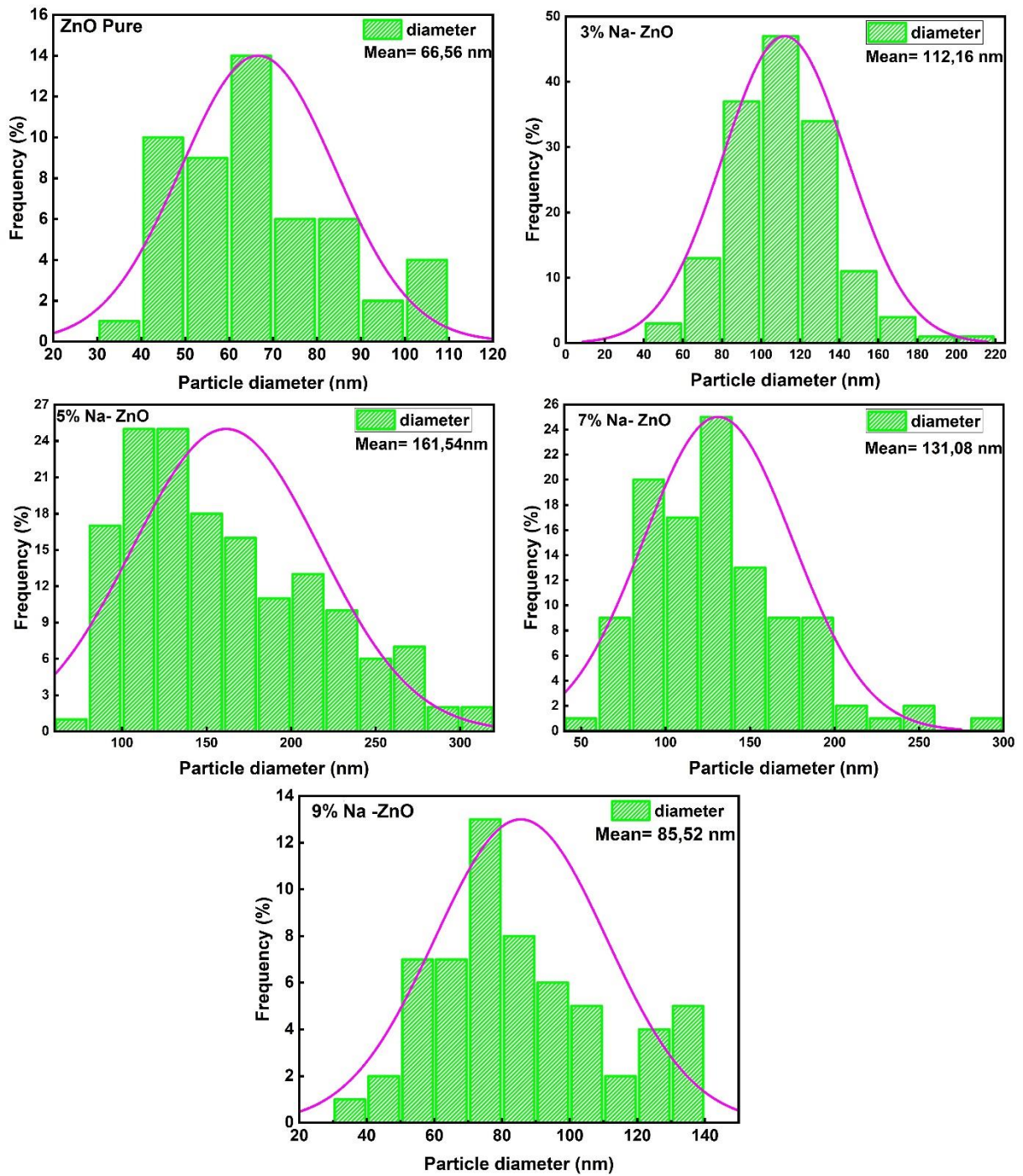


Fig IV.4: Evolution of particle size of zinc oxide-sodium as a function of particle number.

IV.6 Fourier Transform Infrared (FTIR) Analysis

Fig IV. 5 illustrates the FTIR spectra of pure and Na-doped ZnO thin films with different Na concentrations (3%, 5%, 7%, and 9%). The spectra display several characteristic absorption features linked to ZnO vibrations and surface functional groups.

A broad band centered around $\sim 3400\text{ cm}^{-1}$ corresponds to the O–H stretching vibration, indicating the presence of surface hydroxyl groups or adsorbed water molecules. The progressive decrease in its intensity with increasing Na content suggests reduced hydroxylation and lower water adsorption on the doped films. Similarly, the absorption band near 1630 cm^{-1} , assigned to the H–O–H bending mode of molecular water, diminishes with higher Na concentrations, further supporting this observation.

The most prominent feature is the strong absorption peak below 600 cm^{-1} (around $\sim 500\text{ cm}^{-1}$), which is attributed to the Zn–O stretching vibration, confirming the wurtzite ZnO structure. Slight variations in the intensity and sharpness of this band across the doped samples reflect modifications in the local bonding environment and possible lattice distortion induced by Na incorporation.

In summary, FTIR analysis verifies the formation of ZnO and highlights that Na doping modifies the surface chemistry by reducing moisture-related groups, while preserving the Zn–O bonding framework of the lattice.

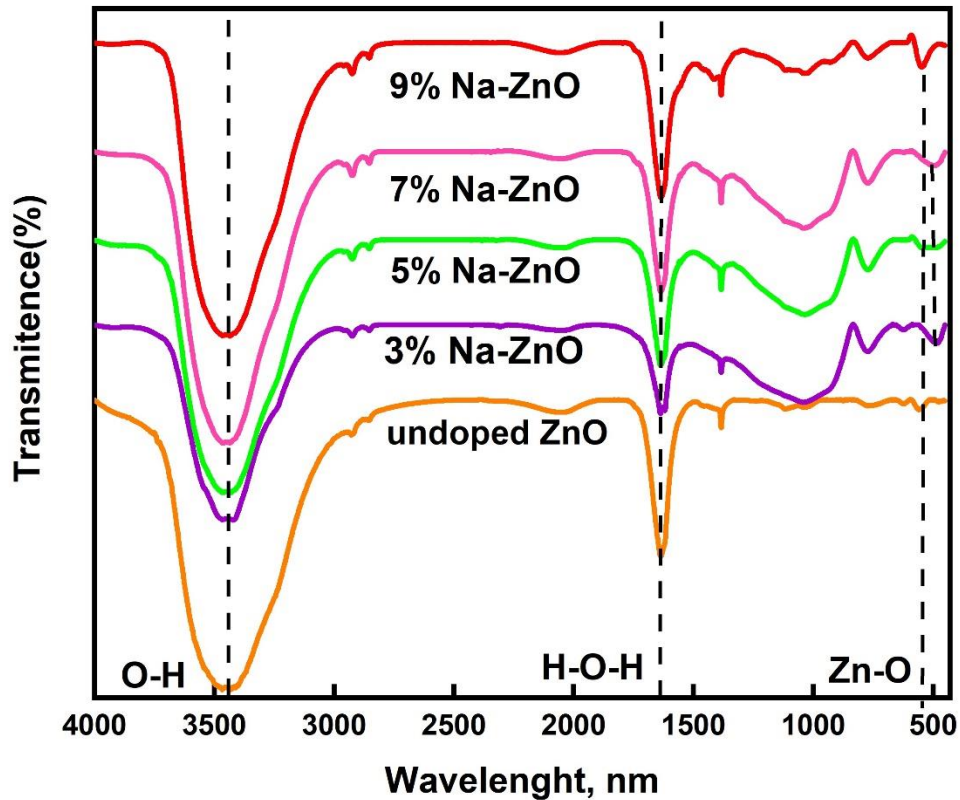


Fig IV.5 FTIR spectra of undoped ZnO and Na-doped ZnO thin films.

IV.7 Optical analysis

The optical properties of undoped and sodium (Na)-doped ZnO (NZO) thin films deposited at 500 °C were investigated through their transmittance and refractive index spectra, as shown in **Fig IV. 6**. The transmittance spectra, recorded in the wavelength range of 200 to 1100 nm, reveal that pure ZnO films exhibit the highest optical transparency, with transmittance values exceeding 90% in the visible region. This high transparency is characteristic of good-quality ZnO films and is favorable for optoelectronic applications. Upon doping with Na, a noticeable decrease in transmittance is observed with increasing dopant concentration. Specifically, films doped with 3%, 5%, 7%, and 9% Na show progressively lower transmittance, likely due to increased light absorption or scattering effects caused by defect states or structural inhomogeneities introduced by the dopant.

All films exhibit a sharp absorption edge located around 380–400 nm, which is consistent with the near-band-edge absorption of ZnO. The position of the absorption edge slightly shifts toward longer wavelengths (redshift) as the Na content increases. This behavior may be associated with a reduction in the optical band gap, possibly due to band tailing or defect-related localized states in the band structure. Despite the decrease in transmittance with higher

Na concentrations, the films maintain relatively high transparency (around 80%) in the visible range, indicating that the optical quality of the thin films is preserved to a good extent even with increased doping levels.

The variation of the refractive index with wavelength further supports the influence of Na doping on the optical characteristics of the films. For all compositions, the refractive index shows a typical dispersion trend, decreasing as the wavelength increases. Pure ZnO films possess the highest refractive index values, starting near 1.9 at 400 nm and gradually decreasing to about 1.8 at 1100 nm. In contrast, Na-doped samples exhibit significantly lower refractive indices, with the 9% Na-ZnO film showing values as low as 1.65 at longer wavelengths. This reduction in refractive index with increased Na content can be attributed to factors such as increased porosity, reduced film density, or enhanced structural disorder, which affect the film's polarizability and optical density.

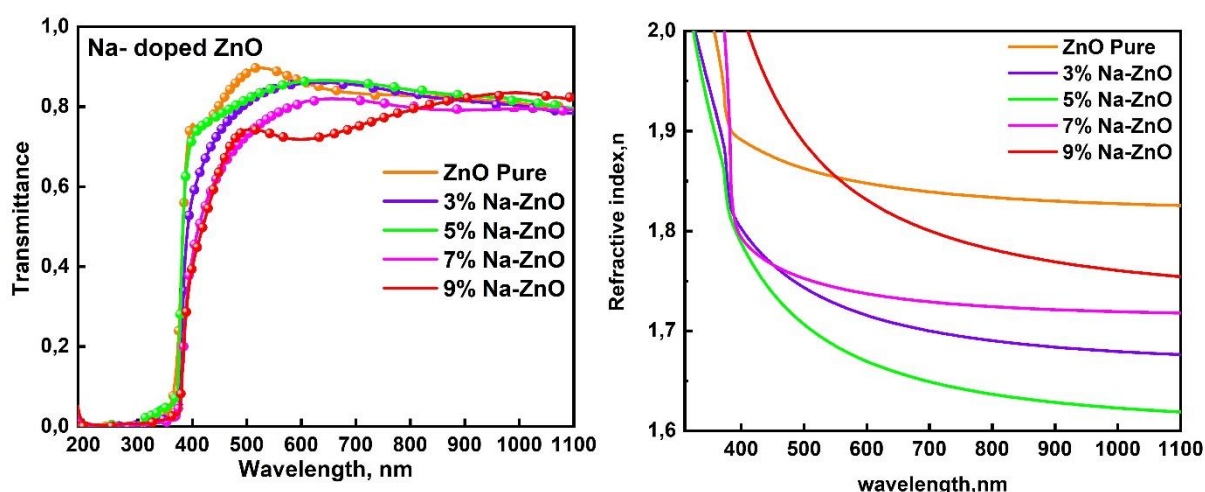


Fig IV.6 Transmittance spectra of ZnO undoped and Na-doped ZnO thin films and Spectra values of refractive index change with wavelength of ZnO and NZO thin films deposited onto glass substrate at 500°C.

To further assess the optical properties of pure and Na-doped ZnO (NZO) thin films, Tauc plots of $(\alpha h\nu)^2$ versus photon energy ($h\nu$) were constructed, as shown in Figure 7. The optical band gap energy (E_g) was determined by extrapolating the linear portion of the plots to the energy axis at which $(\alpha h\nu)^2 = 0$, assuming a direct allowed transition.

For the undoped ZnO film, the estimated band gap is approximately 3.33 eV, which is consistent with the reported values for intrinsic ZnO (3.3–3.4 eV). With the introduction of Na,

a progressive reduction in band gap energy is observed. Specifically, the band gap decreases to about 3.21 eV for the 9% Na-doped ZnO film, indicating a systematic redshift with increasing dopant concentration.

This narrowing of the band gap can be attributed to the incorporation of Na, which introduces localized states within the band structure, leading to band tailing and enhanced defect density. Furthermore, structural distortions and variations in crystallinity associated with Na doping may also contribute to the observed reduction.

Overall, the results confirm that Na doping provides an effective means of tailoring the optical band gap of ZnO thin films. Such tunability is highly valuable for optoelectronic applications, particularly in devices requiring engineered absorption edges, such as UV photodetectors and photovoltaic cells.

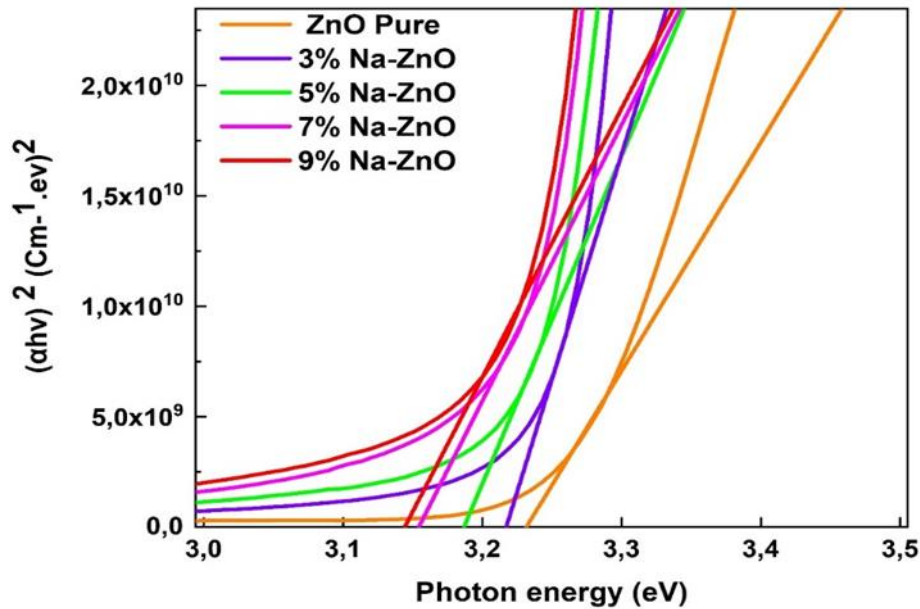


Fig IV. 7 the plots of $(\alpha h\nu)^2$ versus photon energy ($h\nu$) of undoped and Na-doped ZnO thin films and their band gaps

The dispersion parameters of undoped and Na-doped ZnO (NZO) thin films were extracted by fitting the experimental optical data, with the results summarized in Table 3. A gradual reduction in the optical band gap (E_g) is observed with increasing Na content, decreasing from 3.31 eV for pure ZnO to 3.22 eV for the 9% Na-doped sample. This downward shift is consistent with the redshift trends identified in the Tauc plot analysis (**Fig IV. 7**), reinforcing the influence of Na incorporation on the electronic band structure of ZnO.

Film thickness also varies with doping concentration, ranging from 293 nm in pure ZnO to as low as 100 nm for the 7% Na-doped sample. Such variations can be attributed to modifications in film growth dynamics and precursor chemistry during deposition. Notably, thinner films may exhibit higher defect densities or increased surface roughness, which can, in turn, affect their optical response.

The refractive index at 598 nm (n_{598}) provides further insight into the optical density and microstructural compactness of the films. While fluctuations are observed, the refractive index increases overall from 1.71 (pure ZnO) to 1.92 (9% Na-doped ZnO). This trend suggests that higher Na concentrations enhance the packing density of the films, likely reducing porosity and improving material compactness.

Intermediate doping levels, such as 5% Na, exhibit a reduced refractive index (1.77), suggesting that structural variations and defects induced by Na incorporation do not follow a strictly linear trend. Furthermore, the high-frequency refractive index (n_{∞}) decreases from 1.84 (pure ZnO) to 1.60–1.72 in the doped films, indicating that Na doping diminishes the dielectric response at high photon energies. This reduction can be attributed to modifications in electronic polarizability and microstructural changes within the films.

Table IV. 3 Dispersion parameters of the films obtained by fitting the experimental data of ZnO and Na-doped ZnO thin films.

Samples	E _g (eV)	Thickness (nm)	n at 598nm	n _∞
Pure	3.31	293	1.71	1.84
3% Na	3.30	187	1.89	1.65
5% Na	3.29	198	1.77	1.60
7% Na	3.23	100	1.87	1.70
9% Na	3.22	249	1.92	1.72

IV.8 Photoluminescence Properties of Na-Doped ZnO Thin Films

The PL spectra of undoped and Na-doped ZnO thin films (350–500 nm) highlight the role of sodium incorporation in modifying optical recombination pathways. Pure ZnO shows a moderate near-band-edge (NBE) emission at ~388 nm, while Na doping enhances both intensity and spectral broadening, with the 9% Na-doped sample exhibiting the strongest response due to increased crystallinity and donor-related states.

Gaussian deconvolution further reveals three emission peaks for pure ZnO (388, 408, 445 nm), attributed to excitonic recombination and intrinsic defects, whereas the 9% Na-doped film displays five peaks (390–466 nm). These additional blue and long-wavelength emissions confirm the creation of new defect states, indicating that Na incorporation reshapes the defect structure and amplifies both NBE and deep-level recombination mechanisms.

The PL spectra of undoped and Na-doped ZnO thin films (**FigIV. 8**) reveal near-band-edge (NBE) and visible emissions strongly influenced by Na concentration. Pure ZnO shows moderate emission at ~388 nm, attributed to excitonic recombination, while doping enhances the PL intensity, with the 9% Na-ZnO film exhibiting the strongest and broadest profile due to increased crystallinity and Na-related shallow donor levels.

Gaussian deconvolution confirms these trends: pure ZnO presents three peaks (388, 408, 445 nm) linked to NBE and deep-level emissions from Zn interstitials and oxygen vacancies, while 9% Na-doped ZnO exhibits five peaks (390–466 nm). The additional blue and long-wavelength emissions indicate new defect states introduced by Na, highlighting that doping modifies the defect landscape and enhances both radiative and deep-level recombination processes.

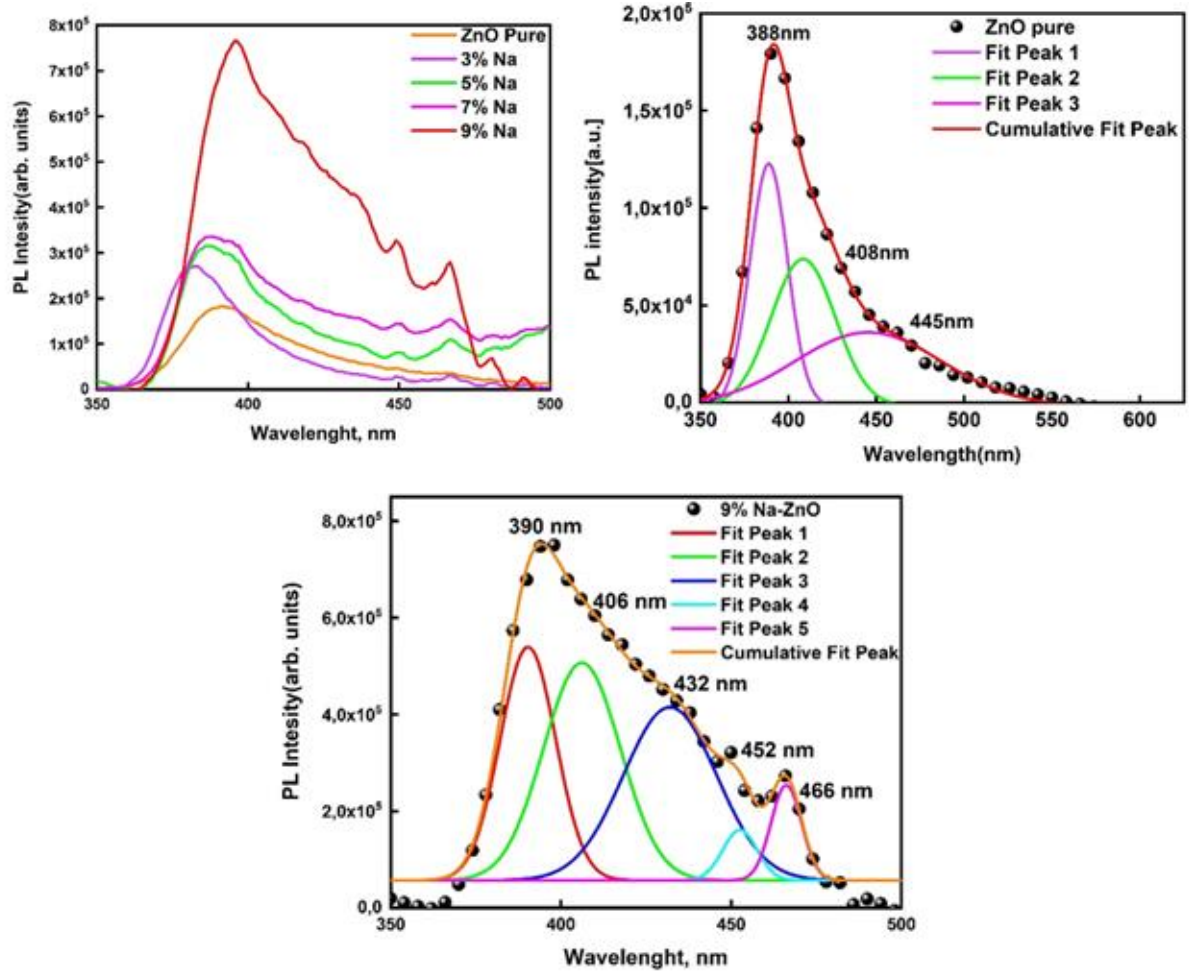


Fig IV.8 illustrates the photoluminescence spectra of ZnO and NZO films, together with the Gaussian deconvolution of the photoluminescence intensity.

IV.9 Thermoelectric Behavior: Seebeck Coefficient

The Seebeck coefficient of undoped and Na-doped ZnO thin films was measured to assess their thermoelectric response (**Fig IV. 9**). All samples exhibit a positive slope in $\Delta V - \Delta T$ plots, confirming n-type conduction with electrons as the dominant carriers. Pure ZnO shows the highest Seebeck coefficient, consistent with its lower carrier concentration and stronger thermopower.

With increasing Na incorporation, the Seebeck coefficient decreases progressively from 3% to 9% doping, reflecting the higher carrier density introduced by sodium substitution. This reduction highlights the typical trade-off between electrical conductivity and thermopower in thermoelectric materials. Overall, the results confirm successful Na incorporation into the ZnO

lattice and demonstrate the tunability of electronic transport properties for thermoelectric and optoelectronic applications.

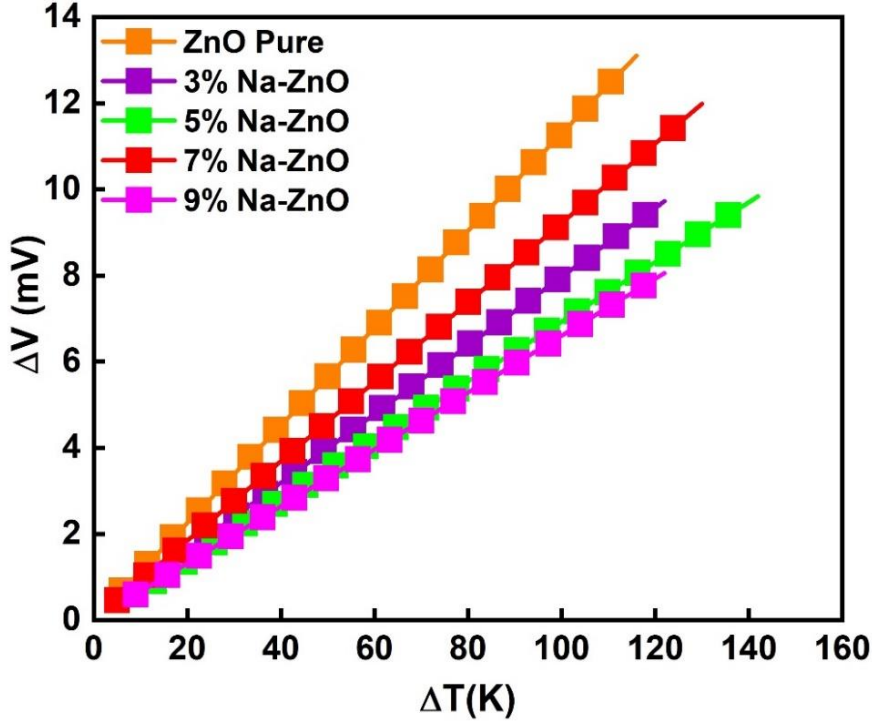


Fig IV.9 displays the Seebeck coefficients for ZnO and sodium-doped ZnO thin films with different sodium concentrations.

IV.10 Seebeck Coefficient and Electronic Transport Parameters

The Seebeck coefficient and associated electronic transport parameters of pure and Na-doped ZnO thin films were evaluated to assess the influence of sodium incorporation on thermoelectric performance (**Fig IV. 9**). All samples exhibited negative Seebeck coefficients, confirming their n-type semiconducting character with electrons as the majority carriers. Pure ZnO showed the highest absolute Seebeck value ($-112.93 \mu\text{V/K}$), consistent with its relatively low carrier concentration.

With progressive Na incorporation, the Seebeck coefficient decreased to $-66.02 \mu\text{V/K}$ for 9% Na-ZnO, reflecting enhanced carrier density induced by Na^+ substitution. The extracted transport parameters (**Table IV. 4**) further support this trend: pure ZnO exhibited a Fermi energy of 18.32 meV and a carrier concentration of $2.27 \times 10^{17} \text{ cm}^{-3}$, while heavily doped films (5% and 9% Na-ZnO) showed substantially higher carrier concentrations ($\sim 1.7 \times 10^{18} \text{ cm}^{-3}$) and

elevated Fermi levels. Intermediate doping levels (3% and 7%) yielded lower carrier densities, likely due to compensation effects or defect-related scattering.

These findings demonstrate that Na incorporation systematically modifies carrier concentration and Fermi energy, enabling controlled tuning of ZnO's electronic transport properties—an essential aspect for advancing thermoelectric and photocatalytic applications.

Table IV. 4: Seebeck Coefficient, Fermi Energy, and Carrier Concentration of Pure and Na-Doped ZnO Thin Films.

Samples	The Seebeck coefficient ($\mu\text{V/K}$)	The Fermi energy (EF) (mev)	the carrier concentration
Pure	-112.93	18.32	2.27×10^{17}
3% Na	-79.7	8.99	1.84×10^{15}
5% Na	-69.26	31.73	1.74×10^{18}
7% Na	-92.16	6.67	6.90×10^{13}
9% Na	-66.02	31.62	1.73×10^{18}

IV.11 Ultraviolet Photodetection Properties

The ultraviolet (UV) photodetection behavior of pure and Na-doped ZnO thin films was examined using the photoconductivity setup shown in **Fig IV. 10**. In this configuration, ZnO-based films deposited on glass substrates were contacted with copper electrodes to enable electrical measurements under UV illumination. Exposure to UV light excites electrons from the valence band into the conduction band, creating electron–hole pairs that contribute to the photocurrent.

Na incorporation was found to enhance the photoconductive response by improving carrier separation and transport while suppressing recombination processes. As a result, Na-doped films exhibited higher photocurrent values compared to pure ZnO, confirming the beneficial role of sodium in modulating charge dynamics and conductivity.

These results highlight the improved UV-sensing performance of Na-doped ZnO thin films, demonstrating their potential as efficient and cost-effective materials for UV photodetector applications.

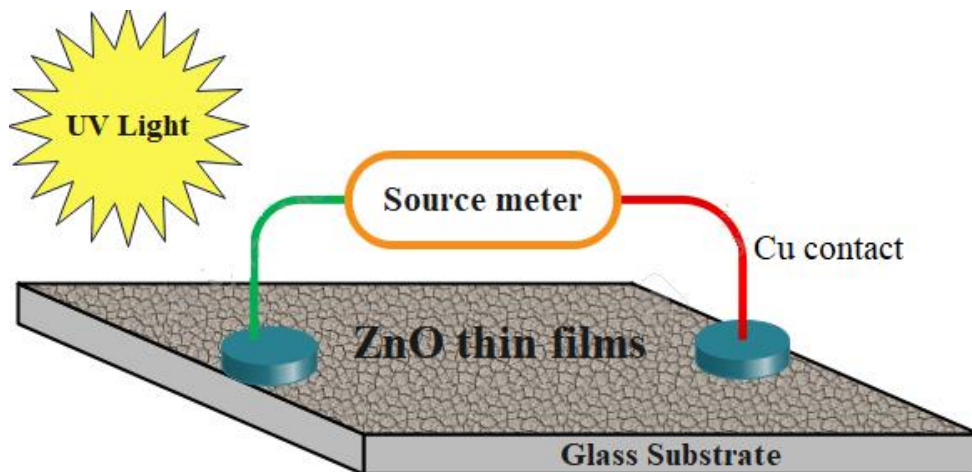


Fig IV. 10 Schematic Illustration of the Photoconductivity Measurement Setup for ZnO Thin Films Under UV Light Irradiation.

IV.12 Dynamic Photoresponse Behavior

The dynamic photoresponse of pure and Na-doped ZnO thin films was examined under periodic UV light irradiation, as illustrated in **Fig IV. 11**. The photocurrent was monitored during repeated on–off switching cycles of the UV source to evaluate stability, reproducibility, and response speed.

All samples exhibited sharp increases in photocurrent upon UV illumination, followed by a rapid return to baseline when the light was switched off, demonstrating fast response and recovery times. Notably, the 9% Na-doped ZnO film showed the highest photocurrent across all cycles, confirming its superior photoconductive performance. This enhancement is attributed to improved charge carrier separation and the higher density of photo-generated carriers introduced by sodium incorporation.

The stable and consistent photocurrent observed over multiple cycles highlights the excellent repeatability and durability of Na-doped ZnO thin films under UV exposure, underscoring their potential for reliable UV photodetector applications.

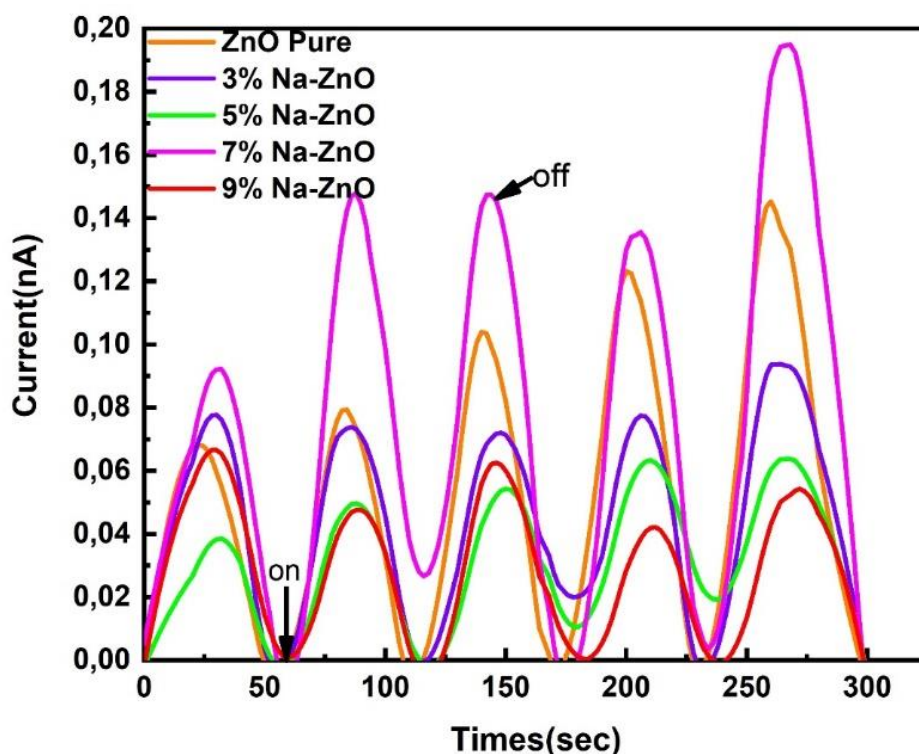


Fig IV. 11 Time-Resolved Photocurrent Response of ZnO and Na-Doped ZnO Thin Films Under Periodic UV Illumination.

The UV photodetection performance of ZnO and Na-doped ZnO thin films was assessed at a bias voltage of 5 V, with the results summarized in **Table IV. 5**.

For the dark current (I_{dark}), pure ZnO exhibited a value of 0.12 nA. Remarkably, Na incorporation at 3% and 5% reduced I_{dark} to 0.01 nA, indicating suppressed carrier recombination and enhanced charge separation. However, at higher doping levels (7% and 9%), the dark current slightly increased to 0.02 nA, suggesting the possible introduction of defect states acting as recombination centers.

The photocurrent (I_{photo}) reached a maximum of 0.65 nA for undoped ZnO. With 3% Na doping, the value decreased slightly to 0.49 nA but remained relatively strong, indicating effective photocarrier extraction. At higher doping levels, photocurrent progressively declined to 0.40 nA, 0.29 nA, and 0.03 nA for 5%, 7%, and 9% Na-ZnO, respectively. This reduction is likely linked to increased defect density and trap-mediated recombination.

Device sensitivity showed a substantial enhancement at moderate doping levels, increasing from 4.41 (pure ZnO) to 48 for 3% Na-ZnO. Beyond this point, sensitivity decreased to 39, 13.5, and 0.5 for 5%, 7%, and 9% doping, respectively, reflecting the detrimental effect of excessive Na incorporation. A similar trend was observed for responsivity, which decreased steadily from $5.89 \text{ mA/W} \times 10^{-6}$ (pure ZnO) to $0.111 \text{ mA/W} \times 10^{-6}$ (9% Na-ZnO).

In contrast, photoconductive gain exhibited a different behavior. While pure ZnO showed a gain of 200×10^{-4} , doping initially reduced it slightly (181×10^{-4} at 3% Na). Interestingly, the 9% Na-ZnO film exhibited an anomalously high gain of 5000×10^{-4} , possibly due to charge trapping effects. However, this was accompanied by poor responsivity and sensitivity, limiting its practical utility.

Detectivity, a key figure of merit for weak-signal detection, increased significantly with moderate Na incorporation. The 3% Na-ZnO sample achieved the highest detectivity of 9.42×10^6 Jones, far exceeding that of pure ZnO (3×10^6 Jones). Detectivity declined with further doping, reaching 0.139×10^6 Jones at 9% Na.

Overall, these results highlight that moderate Na doping, particularly at 3%, optimizes the UV photodetection performance of ZnO thin films by enhancing sensitivity, detectivity, and stability. Excessive doping, however, leads to defect-mediated degradation, underscoring the importance of controlled dopant concentration for device optimization.

Table IV. 5 Photodetection Performance Parameters of ZnO and Na-Doped ZnO Thin Films
Measured at 5 V

Samples	I_{dark} (nA)	I_{photo} (nA)	Sensitivity	Responsivity (mA/W) 10^{-6}	Gain 10^{-4}	Detectivity 10^6 (Jones)
Pure ZnO	0.12	0.65	4.41	5.89	200	3
3%Na	0.01	0.49	48	5.33	181	9.42
5%Na	0.01	0.40	39	4.33	147	7.65
7%Na	0.02	0.29	13.5	3	102	3.75
9%Na	0.02	0.03	0.5	0.111	5000	0.139

IV.13 Photocatalytic Activity Study

The photocatalytic performance of ZnO and Na-doped ZnO (NZO) thin films was evaluated through the degradation of methylene blue (MB) aqueous solution under UV light. **Fig IV.12** presents the absorbance spectra of MB at different exposure times. For all samples, the characteristic absorption peak of MB at ~664 nm progressively decreased with irradiation, confirming the photocatalytic degradation of the dye.

Pure ZnO thin films exhibited significant activity, with the MB peak nearly disappearing after 180 minutes of UV exposure. Sodium incorporation further enhanced this performance. The 3% Na-ZnO film showed a faster reduction in MB absorbance than pure ZnO, indicating improved photocatalytic efficiency due to enhanced charge carrier separation and an increased number of active sites. The (7% and 9% Na), samples achieved the highest activity, with rapid MB degradation within the first 180 minutes, suggesting this doping level offers the optimal balance for photocatalysis.

At (5% Na), the activity slightly declined, although it remained better than pure ZnO. This decrease can be attributed to excessive defect formation and the introduction of recombination centers, which hinder charge separation.

The photocatalytic efficiency versus irradiation time (**Fig IV. 12**, lower right panel) further supports these observations. All samples displayed a rapid efficiency increase during the initial stage, followed by saturation. The superior performance of the 7% and 9% Na-ZnO films highlights the critical role of moderate doping in enhancing ZnO's photocatalytic activity, while excessive Na incorporation can be detrimental.

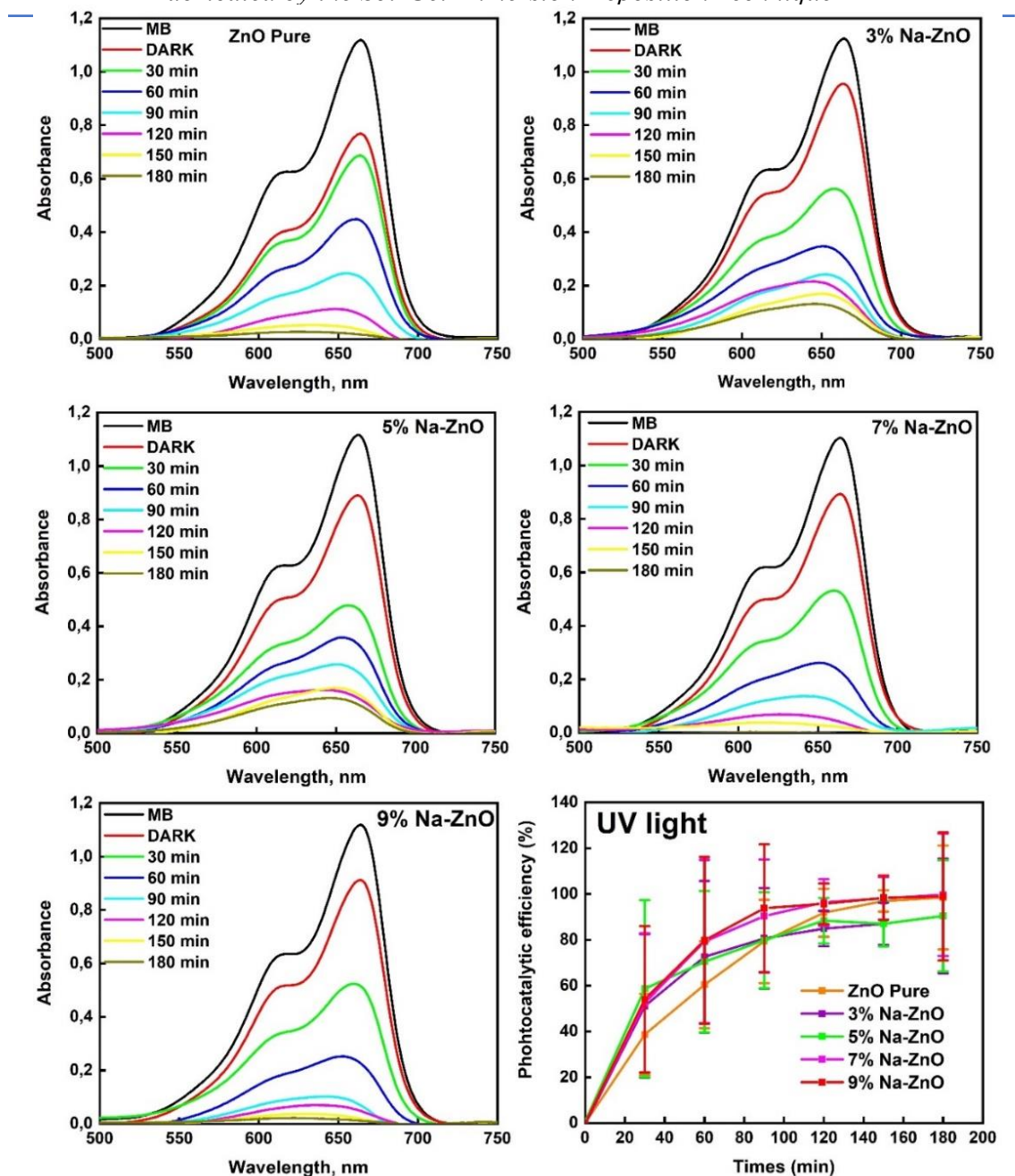


Fig IV.12. illustrate the absorption spectra of methylene blue (MB) aqueous solution and Photocatalytic efficiency of MB versus UV light exposure time for ZnO and NZO thin films synthesized.

The photocatalytic activity of ZnO and Na-doped ZnO (NZO) thin films was further examined under natural sunlight using methylene blue (MB) as a model dye. Fig IV. 13 shows the absorbance spectra at different irradiation times. For all samples, the characteristic MB peak at ~664 nm progressively decreased with exposure, confirming effective degradation by the photocatalysts.

Pure ZnO films exhibited relatively weak activity, with only moderate peak reduction after 60 minutes, reflecting limited sunlight-driven efficiency due to their wide bandgap and fast electron-hole recombination. By contrast, Na doping significantly enhanced performance. The 3% Na-ZnO sample showed rapid degradation, with the MB peak nearly disappearing within 60 minutes, indicating improved visible light absorption and charge separation. Similarly, the 5% Na-ZnO film demonstrated excellent activity, closely matching that of the 3% sample.

At higher doping levels (7% and 9%), photocatalytic efficiency slightly decreased, although still outperforming pure ZnO. This reduction is attributed to defect formation and recombination centers introduced at excessive Na concentrations.

Efficiency versus time curves (Fig IV. 13, lower right panel) support these results: 3% and 5% Na-ZnO reached nearly 100% degradation within 60 minutes, while pure ZnO remained below 30%. The intermediate performance of 7% and 9% Na-ZnO highlights the importance of optimizing sodium doping levels to maximize photocatalytic activity under sunlight.

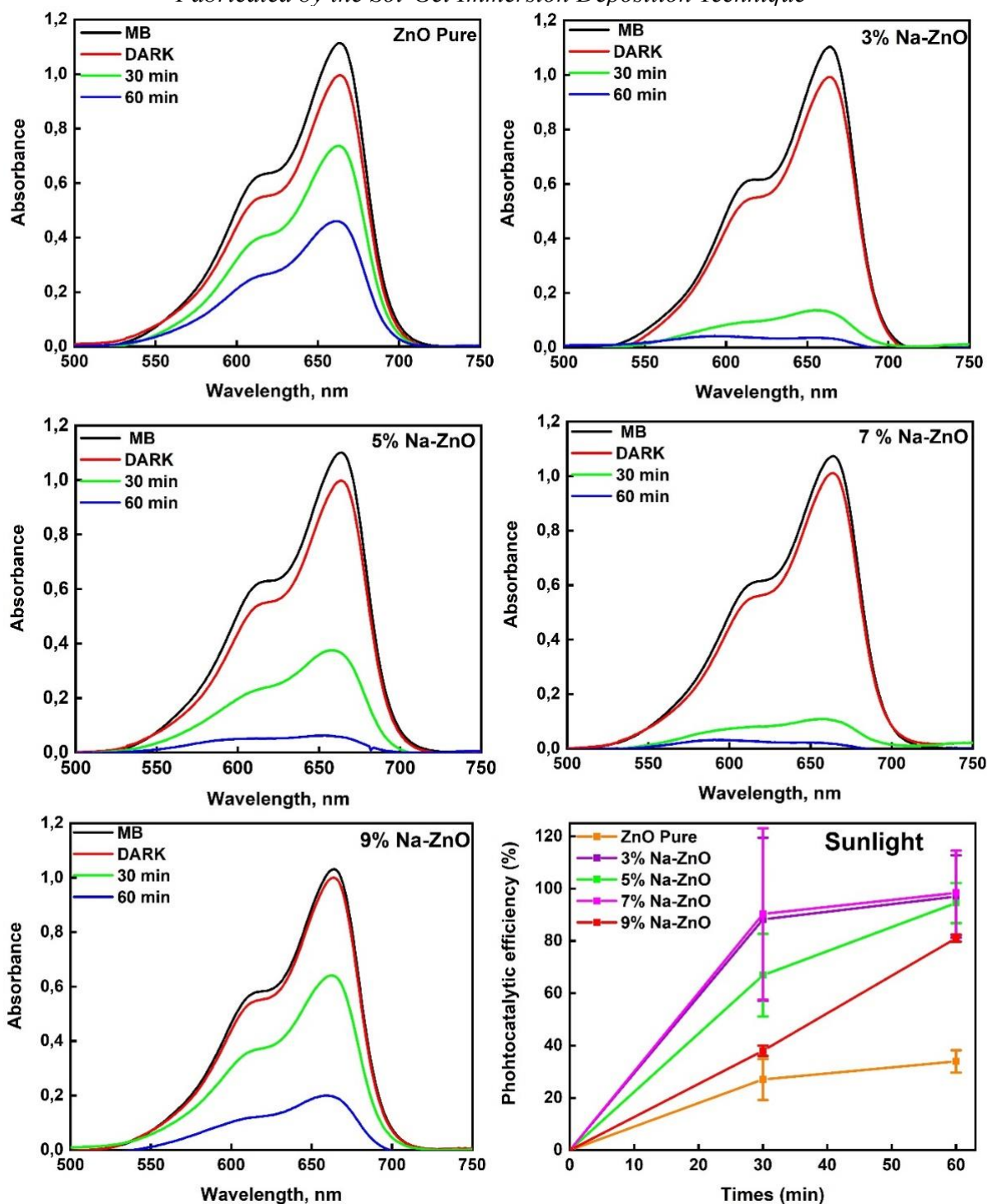


Fig IV.13. Depict the absorption spectra of methylene blue (MB) in aqueous solution and the photocatalytic effectiveness of MB in relation to sunlight exposure duration for ZnO and NZO thin films produced.

The photocatalytic degradation kinetics of methylene blue (MB) using ZnO and Na-doped ZnO (NZO) thin films were evaluated under both UV and sunlight irradiation, based on the Langmuir–Hinshelwood (L–H) model. The concentration ratio (C/C_0) and its logarithmic form ($\ln(C_0/C_t)$) were plotted as functions of irradiation time (Fig IV. 14).

Under UV light, all samples showed a progressive decrease in C/C_0 , with 3% and 5% Na-ZnO films exhibiting the fastest degradation. The linearity of $\ln(C_0/C_t)$ versus time confirmed that the reaction followed pseudo-first-order kinetics, with the highest apparent rate constants (k) obtained for the 3% and 5% Na-doped films. This demonstrates that moderate Na doping effectively accelerates the degradation rate by improving charge separation and surface reactivity.

Under sunlight, the photocatalytic performance was further enhanced. The 3% and 5% Na-ZnO films achieved near-complete MB degradation within 60 minutes, while pure ZnO showed slower activity. The $\ln(C_0/C_t)$ plots again confirmed pseudo-first-order kinetics, and the rate constants under sunlight were notably higher than those under UV light. This suggests that Na doping not only enhances UV-driven photocatalysis but also extends activity into the visible range, improving efficiency under natural solar irradiation.

Overall, the results highlight that moderate Na incorporation (3–5%) optimizes the kinetics of photocatalytic degradation by enhancing light absorption and charge carrier dynamics, whereas higher doping levels (7–9%) introduce defects and recombination centers that diminish activity.

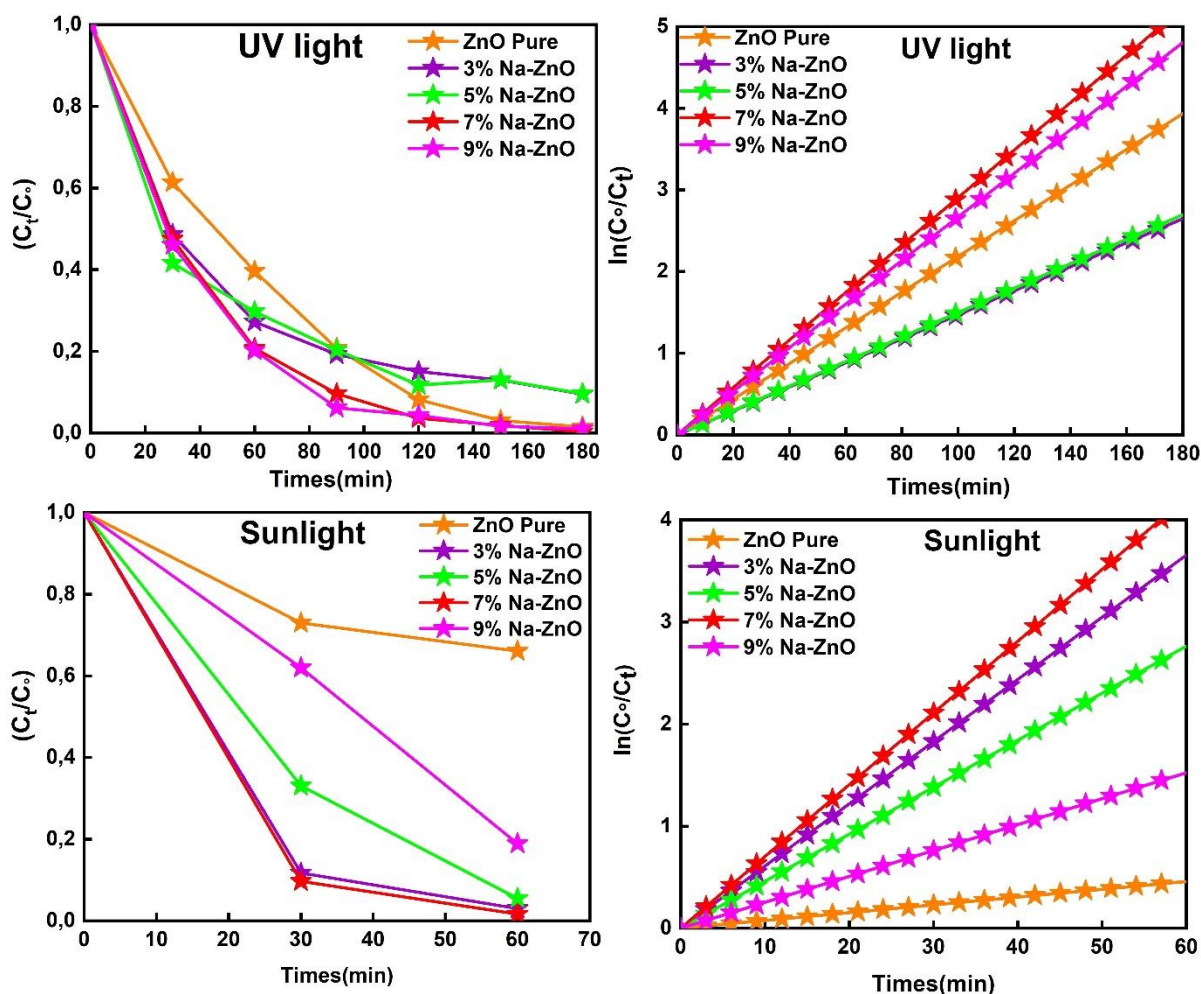


Fig IV.14 indicates the graphs of $\ln (C_0/C_t)$ and (C_t/C_0) as functions of reaction time for the degradation of MB dye under UV and sunlight exposure. The kinetics of photocatalytic degradation of ZnO and NZO thin films were analyzed using the Langmuir-Hinshelwood (L-H) model.

The reaction rate constants (k) and degradation efficiencies (D) for methylene blue (MB) degradation using ZnO and Na-doped ZnO thin films were determined by fitting the data to a pseudo-first-order kinetic model (**Table IV. 6**).

Under UV irradiation (180 minutes), the films achieved a high degradation efficiency of 99.72% with a rate constant of $k_{UV} = 0.02906 \pm 0.00121 \text{ min}^{-1}$ and an excellent correlation coefficient ($R^2 = 0.98967$). Similarly, under sunlight irradiation (60 minutes), the degradation efficiency reached 98.34% with a higher rate constant of $k_{Sunlight} = 0.07029 \pm 0.00268 \text{ min}^{-1}$ and $R^2 = 0.99711$.

The higher rate constant and efficiency under sunlight confirm that Na-doped ZnO thin films are not only highly effective under UV light but also well-suited for natural sunlight applications. This enhancement is attributed to extended light absorption and improved charge separation introduced by sodium doping.

Table IV. 6 presents the reaction rate constants (k) and degradation efficiency (D) values derived from the first-order model for MB dye solutions utilizing ZnO and Na-doped ZnO thin films under UV and sunlight irradiation.

	UV light	Sunlight
Times (min)	180	60
D (%)	99.72	98.34
k (min^{-1})	$K_7 = 0.02906 \pm 0.00121$	$K_7 = 0.07029 \pm 0.00268$
R^2	0.98967	0.99711

IV.14 Mechanism for the photocatalytic degradation of ZnO and NZO thin films

Fig IV.15 illustrates the photocatalytic degradation mechanism of methylene blue (MB) solution under solar irradiation using ZnO and Na-doped ZnO (NZO) thin films. Upon illumination, photons with energy greater than or equal to the bandgap of ZnO excite electrons from the valence band (VB) to the conduction band (CB), generating electron–hole pairs. The photogenerated electrons in the CB react with adsorbed oxygen molecules (O_2) to produce superoxide radicals ($\text{O}_2^{\bullet-}$), while the holes in the VB oxidize water (H_2O) or hydroxyl groups (OH^-) to form hydroxyl radicals ($\bullet\text{OH}$). Both reactive oxygen plays a critical role in the oxidative degradation of MB molecules.

Na doping enhances the separation efficiency of charge carriers by reducing electron–hole recombination, thereby improving photocatalytic activity. Consequently, NZO thin films demonstrate higher photocatalytic efficiency compared to undoped ZnO thin films.

Fig IV. 15 Proposed mechanism of photocatalytic degradation of methylene blue by ZnO and NZO thin films under solar irradiation.

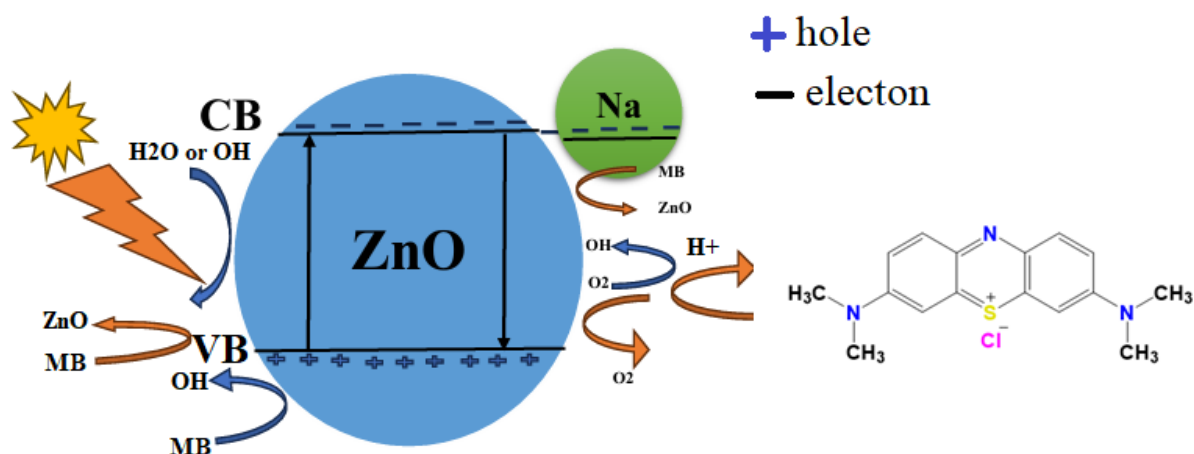


Fig IV. 15 illustrates the degradation mechanism of methylene blue solution by zinc oxide thin film under solar irradiation.

III.15 Scavenger Test

To elucidate the photocatalytic mechanism and identify the main reactive species involved in methylene blue (MB) degradation, scavenger experiments were carried out under optimized conditions (Fig IV. 16).

In the absence of scavengers, the Na-doped ZnO catalyst achieved a high degradation efficiency of 99.72%, confirming its strong photocatalytic activity. When silver nitrate (AgNO_3 , an electron scavenger) was added, the efficiency decreased to 77.53%, indicating that photogenerated electrons contribute to the process. The introduction of ammonium oxalate (ASCA, a hole scavenger) caused a sharp drop to 23.34%, highlighting the dominant role of photoinduced holes (h^+) in MB oxidation. Similarly, ethylenediaminetetraacetic acid (EDTA), another hole scavenger, reduced efficiency to 58.96%, reinforcing the crucial role of holes.

The addition of isopropanol (IPA, a hydroxyl radical scavenger) lowered the efficiency to 32.05%, confirming that hydroxyl radicals ($\cdot\text{OH}$) are also key reactive species.

Overall, the scavenger experiments demonstrate that the photocatalytic degradation of MB by Na-doped ZnO thin films is primarily driven by holes and hydroxyl radicals, with electrons also playing a secondary role. The results highlight the synergistic effect of sodium doping in enhancing charge separation and reactive oxygen species generation, thereby boosting photocatalytic performance.

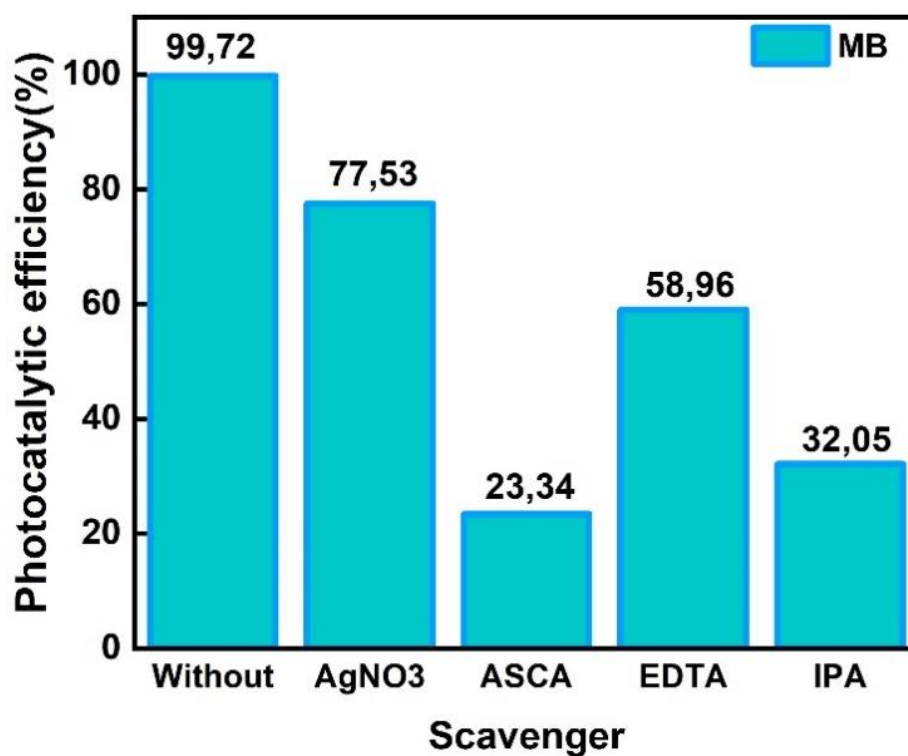


Fig IV.16 photodegradation efficiency of MB over the Na-doped ZnO catalyst in the absence and presence of various scavengers (AgNO₃, ASCA, EDTA, IPA).

IV.16 Conclusion

Na-doped ZnO thin films were successfully synthesized and systematically studied to evaluate their structural, optical, electrical, photocatalytic, and UV photodetection properties. The incorporation of sodium was found to strongly influence crystallinity, morphology, band gap, refractive index, and carrier concentration. Moderate Na doping levels (3% and 5%) proved optimal, yielding significant improvements in both photocatalytic and photodetection performance.

Under UV and sunlight irradiation, the 3% and 5% Na-ZnO films achieved degradation efficiencies exceeding 99%, with the process well described by the Langmuir–Hinshelwood kinetic model. Scavenger tests confirmed that photoinduced holes and hydroxyl radicals are the primary reactive species driving the photocatalytic process. In addition, Na doping enhanced UV photodetection characteristics, with the 3% Na-ZnO film exhibiting superior sensitivity, responsivity, gain, and detectivity.

Overall, these results demonstrate that controlled sodium incorporation is an effective strategy to engineer the multifunctional properties of ZnO thin films, making them highly promising candidates for future applications in photocatalysis, UV sensing, and optoelectronic devices.

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General Conclusion

General conclusion

This thesis used the sol-gel dip coating method to produce thin layers of zinc oxide (ZnO) on glass substrates using optimal zinc acetate dihydrate solutions. The molarity of the solution is 0.4 M. We examined the effects of magnesium (Mg) and sodium (Na) doping, as well as the impact of various solvents (ethanol and methanol), on the properties of ZnO thin films employed in photocatalytic applications for the degradation of methyl blue and orange II dyes under UV and sunlight exposure, respectively. The synthesis of thin ZnO layers, both undoped and doped with Mg and Na at various concentrations ($x = 3\%$, 5% , 7% , and 9%), using the sol-gel dip coating method on glass substrates, enables the investigation of the effects of doping elements with varying ionic radii on ZnO in photocatalytic and photodetection applications. We analyzed the structural, morphological, optical, and electrical characteristics of these layers. The degradation of orange II and methyl blue dyes was examined using XRD, FT-IR, FE-SEM, photoluminescence, and UV-Visible spectrophotometry.

The principal findings are as follow:

Mg-doped ZnO thin films

This study compared the solvents ethanol and methanol while varying the concentration of magnesium dopant, demonstrating that the optical, structural, morphological, and electrical properties of zinc oxide can be tailored for diverse applications, including photocatalysis and photodetection.

- XRD data indicate that all peaks affirm the polycrystalline nature with a hexagonal structure for both solvents, as well as a preferred orientation along the (002) plane for ethanol solvent.

7% Mg-doped ZnO thin films prepared with methanol as a solvent exhibited the greatest crystal size of 22.82 nm.

- EDS and FT-IR spectra confirm that ZnO is present and that magnesium has been successfully added, supporting the XRD results.

- In FE-SEM investigation, the methanol-based layer exhibited bigger grain than those fabricated with ethanol, with grain being uniformly distributed for both solvents.

- Ethanol-based films outperformed methanol-based films, attaining the highest level of transparency at 90%. Regarding the band gap, we noted a rise of up to 3.34 eV for methanol-based films.

- The findings indicate a rise in the intensity of UV emission correlating with elevated magnesium concentration across both solvents.

- Owing to elevated conductivity at higher magnesium concentrations, methanol-based films possess a clear advantage over ethanol-based films in terms of photocatalytic activity, illustrating their superiority. 9% Mg-doped ZnO thin films synthesized with methanol solvent with methylene blue as a pollutant exhibited enhanced photocatalytic efficacy under sunlight in comparison to ethanol-based films.

- The photocurrent response was enhanced to 139 for ethanol-based films, demonstrating their superiority over methanol-based films regarding electrical attributes.

- These findings allow us to choose solvents and assess the influence of magnesium on the development of high-efficiency ZnO thin films, enhancing their properties for diverse applications in photocatalysis and optoelectronic devices.

Na-doped ZnO thin films

- XRD measurements indicated that all peaks verified the polycrystalline nature with a hexagonal wurtzite crystalline structure.

- 3% Na-doped ZnO thin films exhibited the greatest crystal size of 36.07 nm.

- EDS and FT-IR spectra confirm that ZnO is present and that sodium has been successfully added, supporting the XRD results.

- For FE-SEM, there was a modification in the surface morphology and an uneven distribution of grains.

- The gap energy fluctuated between 3.31 eV and 3.22 eV, diminishing with increased salt content. With a transparency of 90%, ZnO thin films achieved the best performance.

- We determined that 7% Na-doped ZnO thin films represent the best stimulation for photocatalytic activity under UV and sunlight irradiation, with a degradation efficiency over 98%. Regarding the scavenger test, we determined that hydroxyl radicals are the primary agents

responsible for the breakdown process of methylene blue in 7% Na-doped ZnO, attributable to the influence of sodium on ZnO thin films.

- It reached 3% Na-doped ZnO thin film sensitivity and a high response of 48, which suggests the influence of sodium on ZnO thin films.

Upon completion of this comprehensive investigation, which examined solvents and their impact on the characteristics of Zinc oxide as well as n-type and p-type doping, we determined that Zinc oxide is the optimal selection for many applications, particularly in photocatalysis and photodetection.