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By:

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Development of Nanostructured Metal Oxides for Their Applications in the Environment

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يَرْفَعُ اللَّهُ الَّذِينَ ءَامَنُوا مِنْكُمْ وَالَّذِينَ أُوتُوا الْعِلْمَ دَرَجَاتٍ

To My Dad

**I will keep your dream in my heart, and cross the days
and years with it...**

لعلني اني تلك الالة حقا، و ان كان لا يعني بكيد و لا وزن..
فأعظم مجدي انك لي ابا و اكبر خري

قولك "هذه ابنتي"

Selwa

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Abstract

This thesis focuses on the development and optimization of nanostructured metal oxide thin films for multifunctional environmental applications. ZnO- and CuO-based thin films were synthesized using controlled deposition techniques, combined with dopant engineering and multilayer heterostructure design in order to tailor their structural, optical, and surface properties.

In the first stage, pure and doped ZnO thin films were systematically investigated by varying precursor concentration, deposition parameters, and annealing conditions. The photocatalytic activity of the optimized films was evaluated through the degradation of organic pollutants under UV irradiation. Experiments showed that pure ZnO has a limited capacity to degrade methylene blue. Performance was enhanced using non-metallic dopants such as urea, which outperformed thiourea, and metallic dopants like silver. The optimal silver concentration was 5%, and the addition of 20% urea to this compound achieved nearly complete dye degradation within 90 minutes.

Subsequently, Ag-doped ZnO thin films were deposited on silicon substrates for ultraviolet photodetector applications. Structural analyses confirmed the preservation of the wurtzite phase with progressive lattice modification induced by silver incorporation. Electrical measurements, including current-voltage ($I-V$) characteristics and time-dependent photoresponse, demonstrated that a 1% silver doping level yielded instead provided the highest electrical response under UV illumination.

Finally, Mg-doped ZnO thin films and ZnO/CuO multilayer heterostructures were investigated for CO₂ gas sensing applications. For CO₂ gas sensing, the study was divided into two parts: In the first part, 7% Mg-doped ZnO demonstrated exceptionally high sensitivity, reaching 461.76%. In the second part, multilayer ZnO/CuO structures were investigated, showing that pure ZnO delivered superior sensing performance compared to multilayer configurations.

Overall, these findings highlight that controlling the type and concentration of dopants in ZnO can significantly enhance its performance in photocatalytic and gas sensing applications, paving the way for the development of more efficient and reliable devices.

Keywords:

ZnO thin films; CuO thin films; Sol–gel method; photocatalytic; UV photodetector; CO₂ Gas sensing.

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الملخص

تركز هذه الأطروحة على تطوير وتحسين افلام رقيقة من أكاسيد المعادن النانوية لتطبيقات بيئية متعددة الوظائف. تم تصنيع افلام من أكسيد الزنك (ZnO) وأكسيد النحاس (CuO) باستخدام تقنيات ترسيب مضبوطة، بالإضافة إلى هندسة الشوائب وتصميم هياكل غير متجانسة متعددة الطبقات، وذلك لتحديد خصائصها البنيوية والبصرية والسطحية.

في المرحلة الأولى، تم دراسة افلام اكسيد الزنك النقية والمطعمة بشكل منهجي من خلال تغيير تركيز المواد الأولية ومعايير الترسيب وظروف التلدين. تم تقييم النشاط التحفيزي الضوئي للافلام المُحسَّنة من خلال تحليل الملوثات العضوية تحت الأشعة فوق البنفسجية. أظهرت التجارب أن اكسيد الزنك النقي لديه قدرة محدودة على تحليل أزرق الميثيلين. تم تحسين الأداء باستخدام شوائب غير معدنية مثل اليوريا، التي تفوقت على الثيوريا، وشوائب معدنية مثل الفضة. كان التركيز الأمثل للفضة 5%، وأدت إضافة 20% من اليوريا إلى هذا المركب إلى تحليل شبه كامل للصبغة في غضون 90 دقيقة.

لاحقاً، طُوِّرت افلام من أكسيد الزنك المُطعم بالفضة والمُرسبة على ركائز السيليكون لتطبيقات كاشفات الأشعة فوق البنفسجية. أكدت التحليلات البنيوية الحفاظ على طور الورتزيت مع تعديل تدريجي للشبكة البلورية ناتج عن دمج الفضة. أظهرت القياسات الكهربائية، بما في ذلك خصائص التيار-الجهد والاستجابة الضوئية المعتمدة على الزمن، أن مستوى تطعيم الفضة بنسبة 1% يوفر أعلى استجابة كهربائية تحت إضاءة الأشعة فوق البنفسجية.

أخيراً، دُرست افلام من أكسيد الزنك المُطعم بالمغنيسيوم وهياكل غير متجانسة متعددة الطبقات من أكسيد الزنك/أكسيد النحاس لتطبيقات استشعار غاز ثاني أكسيد الكربون. بالنسبة لاستشعار غاز ثاني أكسيد الكربون، قُسمت الدراسة إلى جزئين: في الجزء الأول، أظهر أكسيد الزنك المُطعم بالمغنيسيوم بنسبة 7% حساسية عالية استثنائية، تصل إلى 461.76%. في الجزء الثاني، دُرست هياكل متعددة الطبقات من أكسيد الزنك/أكسيد النحاس، مما أظهر أن أكسيد الزنك النقي يُقدم أداء استشعار فائقاً مقارنةً بالتكوينات متعددة الطبقات.

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List of abbreviation

List of abbreviations

A: Constant

A: Absorbance

AFM: Atomic Force Microscopy

Ag: Silver

Ag₂O: Silver Oxide

AgNO₃: Silver nitrate

CB: Conduction band

CO₂: Carbon Dioxide

CO₃²⁻: Carbonate Species

Cos: Cosinus

C₂H₆O: Ethanol

C₀: The initial concentration of MB

C_t: The concentration of MB after time t of irradiation

CuO: Copper Oxide

D: Crystallite Size

d: Thickness of layer

dhkl: The distance of lattice planes

δ: Dislocation density

EDS: Energy Dispersive Spectroscopy

EDX: Energy dispersive X-ray spectroscopy

E_g: Band gap energy / Energy Band Gap

FTIR: Fourier Transform Infrared

FESEM: Field Emission Scanning Electron Microscopy

FWHM: Full Width at Half Maximum

GPa: Gega Pascal

h: hours / Planck's constant

List of abbreviation

h^+/e^- : electron-hole pair

$h\nu$: Photon energy

hkl : Miller indices

I : Intensity of light

I_0 : Incident light

$I-t$: Current–time

$I-V$: Current–Voltage

I_{photo} : Photocurrent

I_{dark} : Dark current

IPA : Isopropanol

K : Kelvin

K : Pseudo rate constant

k : constant rate

M : Molaire (mol/l)

Mg : Magnesium

$Mg (CH_3COO)_2 \cdot 4H_2O$: Magnesium acetate tetrahydrate

MB : Methylene blue

MZO : Mg-doped ZnO

min : minutes

μ : Electron mobility

μm : micrometer

μA : micro-Amper

N : Nitrogen

n : Density of electron

$n-type$: Negative-type semiconductor

O_2^- : Adsorbed Oxygen Ion

$\bullet OH$: Hydroxyl radical

List of abbreviation

pH: Potential of hydrogen

p–n: Junction type

ppm: Parts Per Million

R: Reflectance

Ra: Average Roughness

RMS: Root Mean Square Roughness

RT: Room Temperature

ROS: Reactive oxygen species

S: Sulfur

S: Sensitivity

s: second

Sin: Sinus

Sol-gel: Solution-gelation

Si: Silicon

SiO₂: Silicium dioxyde

T: Transmittance

τ_{rec} : Recovery Time

τ_{rep} : Response Time

TiO₂: Titanium dioxide

UV: Ultraviolet

UV–Vis: Ultraviolet–Visible Spectroscopy

UV-Vis: Ultraviolet–Visible

V: volt / unit cell volume

XRD: X-ray Diffraction

ZnO: Zinc Oxide

Zn (C₂H₃O₂)₂·2H₂O: Zinc acetate dihydrate

°C: Degree Celsius

List of abbreviation

λ : The wavelength of the X-ray beam

θ : The diffraction angle

α : The absorption coefficient

ε : Lattice strain

β : The width at half height

General Introduction

General Introduction

Environmental pollution and the increasing demand for sustainable technologies have become major global concerns in recent decades. Rapid industrialization, population growth, and the intensive use of fossil fuels have significantly contributed to the deterioration of environmental quality. Water contamination by persistent organic pollutants such as dyes, pharmaceuticals, and pesticides represents a serious environmental problem because many of these compounds are chemically stable and resistant to conventional treatment processes. At the same time, atmospheric pollution caused by greenhouse and toxic gases, including carbon dioxide (CO₂), carbon monoxide (CO), nitrogen oxides (NO_x), and volatile organic compounds (VOCs), has intensified global concerns related to climate change and environmental safety (Fujishima et al., 2008; Hoffmann et al., 1995). Consequently, the development of advanced materials capable of addressing environmental remediation and monitoring challenges has become an important research topic.

Among the different classes of materials investigated for environmental and energy-related applications, semiconductor metal oxides have attracted considerable attention due to their remarkable physicochemical properties. These materials exhibit high chemical and thermal stability, tunable electronic structures, and strong surface reactivity. Such characteristics make them suitable for a wide range of technological applications, including photocatalysis, gas sensing, and optoelectronic devices (Korotcenkov, 2007; Wang, 2004). In addition, metal oxides are generally abundant, relatively inexpensive, and environmentally friendly, which makes them attractive candidates for large-scale practical applications.

Zinc oxide (ZnO) is one of the most extensively studied metal oxide semiconductors. It is a wide band gap semiconductor ($E_g \approx 3.37$ eV) with a high exciton binding energy of about 60 meV. ZnO typically exhibits n-type conductivity that originates mainly from intrinsic defects such as oxygen vacancies and zinc interstitials. These properties provide ZnO with high optical transparency in the visible region, strong absorption in the ultraviolet range, and relatively high electron mobility. As a result, ZnO has been widely investigated for applications in photocatalysis, UV photodetectors, gas sensors, and other optoelectronic devices (Özgür et al., 2005), (Klingshirn, 2007; Pearton et al., 2003). Despite these advantages, the practical efficiency of pure ZnO is often limited by the rapid recombination of photogenerated electron–hole pairs and its relatively weak response under visible light irradiation. Therefore, several strategies have been developed to enhance its performance, including elemental doping, defect engineering, surface modification, and the formation of heterostructures with other semiconductors (Chen & Mao, 2007; Janotti & Van De Walle, 2009).

General Introduction

Copper oxide (CuO) is another semiconductor that has attracted increasing interest in recent years. CuO is a p-type semiconductor with a relatively narrow band gap ranging between 1.2 and 1.7 eV, which enables strong absorption in the visible region. Moreover, CuO exhibits interesting catalytic properties and good adsorption capability for various gas molecules, making it suitable for applications such as gas sensing and photocatalysis (Balamurugan & Mehta, 2001). However, CuO-based materials may suffer from relatively low carrier mobility and limited stability when used alone. For this reason, combining CuO with other semiconductors has been widely explored as an effective approach to improve its functional performance.

The combination of ZnO and CuO in the form of heterostructures or multilayer systems represents a promising strategy for improving charge transport and surface reactivity. When these two semiconductors are brought into contact, an n-p heterojunction is formed at the interface between n-type ZnO and p-type CuO. This heterojunction generates an internal electric field that promotes the separation of photogenerated electron-hole pairs and reduces their recombination rate. Consequently, the photocatalytic efficiency and sensing performance of the material can be significantly enhanced (Baruah & Dutta, 2009; Yamazoe & Shimanoe, 2008). Such heterostructured systems have therefore attracted increasing attention for applications in environmental remediation and gas detection.

In many practical applications, semiconductor materials are often prepared in the form of thin films rather than powders or bulk materials. Thin films offer several advantages, including a high surface-to-volume ratio, improved mechanical stability, and easier integration into electronic devices. Moreover, thin-film deposition techniques allow precise control of parameters such as film thickness, microstructure, and surface morphology, which strongly influence the optical, electrical, and sensing properties of the materials (Klingshirn et al., 2010).

Various deposition techniques have been developed to fabricate metal oxide thin films, including physical vapor deposition, chemical vapor deposition, and solution-based techniques. Among these methods, solution-based approaches such as the sol-gel dip-coating technique have attracted particular interest because of their simplicity, low cost, and flexibility. Dip-coating enables the deposition of uniform thin films over large areas and allows easy incorporation of dopants as well as the fabrication of multilayer structures. In addition, the structural and morphological properties of the films can be tuned by adjusting parameters such as precursor concentration, withdrawal speed, and annealing conditions (Brinker & Scherer, 1990).

Within this context, the present doctoral work focuses on the preparation, characterization, and application of ZnO- and CuO-based thin films for environmental and optoelectronic applications. Particular attention is devoted to understanding how doping and heterostructure design influence the

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structural, optical, and functional properties of the prepared materials. The performance of the developed thin films is investigated in three main application fields: photocatalytic degradation of pollutants, ultraviolet photodetection, and CO₂ gas sensing at room temperature.

This manuscript is organized into five chapters.

- Chapter 1 presents a literature review, emphasizing the state-of-the-art of ZnO and CuO for photocatalysis, UV photodetectors, and CO₂ gas sensing, highlighting recent developments, challenges, and strategies reported in the field.
- Chapter 2 describes the experimental procedures used for the preparation of the thin films as well as the characterization techniques employed to investigate their structural, morphological, optical, and electrical properties.
- Chapter 3 is devoted to the study of the photocatalytic performance of pure and doped ZnO thin films, with particular emphasis on the influence of non-metallic and metallic doping and co-doping on the degradation efficiency of organic pollutants.
- Chapter 4 investigates the use of Ag-doped ZnO thin films deposited on silicon substrates for ultraviolet photodetector applications.
- Finally, Chapter 5 explores the gas sensing performance of ZnO-based thin films, including Mg-doped ZnO and ZnO/CuO multilayer structures, for carbon dioxide detection at room temperature.

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Chapter I

Literature Review and State of the Art

I.1 Introduction

This chapter offers an insight into the current line of research in ZnO and CuO thin films dealing with environmental and optoelectronic applications, i.e., photocatalysis, UV photodetection, and CO₂ gas sensing. The cases of pure and doped ZnO are studied as well as multilayered structures of ZnO/CuO. Recent advances in experimental work are critically reviewed to discuss synthesis approaches, material modifications, performance results, and challenges. A summary of the results is shown in table format for each application to give clearer insights into the background literature as a basis for the research objectives applied in this thesis.

I.2 Fundamental Properties of Materials

I.2.1 Fundamental Properties of ZnO

Zinc oxide (ZnO) is a typical II-VI type semiconductor, which has been considered one of the most promising materials for environmental and optoelectronic applications owing to its superior optical, electronic, and chemical properties. Structurally, ZnO tends to facilitate the wurtzite hexagonal phase, which is non-centrosymmetric, featuring each Zn²⁺ ion coordinated by four O²⁻ ions in a tetrahedral fashion (Capper & Mauk, 2007a). This geometry lends the ZnO its piezoelectric and pyroelectric properties, which are useful in applications such as sensing and electromechanical devices. ZnO is optically a direct band gap semiconductor (e.g., 3.37 eV at room temperature); therefore, it shows strong absorption in ultraviolet (UV) but transparency in the visible region (Capper & Mauk, 2007b; Janotti & Van De Walle, 2009). This wide band gap contributes to its outstanding properties in UV photodetectors and some photocatalytic applications under UV irradiation. In addition, ZnO exhibits a high exciton energy (60 meV) that is much larger than the room-temperature thermal energy, thus favoring efficient exciton transitions and rendering it of interest in the field of devices emitting/absorbing photons in UV light (Capper & Mauk, 2007b; Özgür et al., 2005a). From the electrical point of view, ZnO is usually an n-type semiconductor even without intentional doping, as a consequence of the presence of intrinsic defects such as oxygen vacancies (V-O) and zinc interstitials (Zn_i), which serve as those charge donors (Capper & Mauk, 2007b; Janotti & Van De Walle, 2009). Such native defects may alter carrier density and recombination dynamics with regard to the performance in photocatalysis and photodetection. The existence of deep-lying defect levels in the band gap is also responsible for secondary emissions present in photoluminescence spectra (Crapanzano et al., 2020). Nevertheless, such pure ZnO has a serious drawback due to the fast carrier recombination that reduces its utility in various applications requiring photoactivation upon sunlight or visible light owing to the lack of absorption in this range. Therefore, material engineering techniques, including metal or non-metal doping, nanostructure forming, and heterojunction

construction (junction between two dissimilar semiconductors), have been attracting increasing attention in their optical, electrical, and catalytic fields of application (Cauda et al., 2014; Norton et al., 2004).

I.2.2 Fundamental properties of CuO

Copper oxide (CuO) is a member of the transition metal oxides, and it has intrinsic p-type conduction, mainly due to copper vacancies (V-Cu), which introduce acceptor levels near the valence band (Nolan & Elliott, 2006a). Structurally, CuO crystallises in a uniaxial (tenorite) structure, which is thermally stable at room temperature, as confirmed by numerous structural studies (Ekuma et al., 2014a). This crystalline configuration strongly influences its electronic and optical properties. Unlike ZnO, CuO has a relatively narrow band gap, generally between ~ 1.2 and 1.9 eV, depending on the synthesis conditions and morphology (Ekuma et al., 2014b; Nolan & Elliott, 2006b). Such a small band gap leads to strong absorption of visible light and renders it promising for photovoltaic devices, photocatalysis using visible light illumination, as well as low-temperature gas sensors (Klinbumrung et al., 2014; Nolan & Elliott, 2006b). The p-type conduction occurs due to the presence of intrinsic defects and the electronic structure of CuO. Cu vacancies behave as acceptor centers and introduce holes in the valence band, which become the majority carriers (Klinbumrung et al., 2014; Nolan & Elliott, 2006b). Such behavior promotes the generation of p-n heterojunctions with negative n-type semiconductors, such as ZnO, which are utilized in numerous device geometries to increase charge carrier separation and minimize their recombination, both for optoelectronic and environmental applications. Optical and electrical characteristics of CuO are also very much correlated with the morphology, crystal defects, and processing method. For instance, defect density, controlled grain size, and crystal orientation have been reported to be directly related to carrier mobility, electrical resistance, and surface reactivity, which are the most essential enablers for performance in sensor or photocatalysis-based devices (Ekuma et al., 2014b; Klinbumrung et al., 2014). Because of its visible light absorption, p-type majority carrier generation, and strong interaction with adsorbed molecules, CuO has frequently been employed in composite or multilayer structures, especially together with ZnO, to take advantage of synergetic effects on optical absorption, charge separation, and gas detection.

I.2.3 Comparative Analysis of ZnO and CuO Properties

The comparison in Table I.1 presents the complementary structural, electronic, and surface characteristics of ZnO against CuO. ZnO is an n-type semiconductor with a wide band gap, high electron mobility, and excellent chemical stability; it can be applied to UV-excited photocatalysis and sensitive gas-sensing behaviors. On the other hand, CuO is a p-type semiconductor with a narrow

band gap and possesses superior visible-light absorption, hole-conducting nature for solar-driven catalytic reactions and selective gas sensing. At the surface and defect level, ZnO is conventionally known to be O vacancy-rich (donor-like source), which causes it to conduct electrons, whereas CuO is dominantly p-type due to copper vacancies. These native defects control not only the electronic structure of materials, but also surface adsorption and reaction pathways. This contrast evidences the fact that, while all oxides present different advantages and drawbacks, they rather exhibit complementary features than being in competition. This complementary nature implies that the combination of ZnO and CuO in a heterostructure is an effective way to overcome the shortcomings of each material. Especially, the wide band gap and fast electron transferring ability of ZnO could have a synergic effect with the visible light responding activity and hole carrier separation capability of CuO, which would enable novel opportunities for excellent usages in the environment.

Table I.1 physical, chemical, and structural properties (Look, 2006; Özgür et al., 2005b; Welegergs et al., 2021).

Parameters	Cupric Oxide (CuO)	Zinc Oxide (ZnO)
Chemical name	Copper (II) oxide, Cupric oxide, Copper monoxide, Copper oxide, Oxo coppe	Zinc white, Calamine, Philosopher's wool, Chinese white, Flowers of zinc
Molecular formula	CuO	ZnO
Crystal structure	Monoclinic	Wurtzite
Stable phase for 300 K	Polycrystalline	Wurtzite
Lattice parameters for 300 K	$a = 4.6837 \text{ \AA}$, $b = 3.4226 \text{ \AA}$, $c = 5.1288 \text{ \AA}$, $\beta = 99.548^\circ$, $\alpha = \gamma = 90^\circ$	$a = 3.25 \text{ \AA}$, $c = 5.2 \text{ \AA}$ (JCPDS-36-1451)
Molar mass	79.55 g/mol	81.408 g/mol
Appearance	Black powder	White solid
Density, ρ	6.32 g/cm ³	5.606 g/cm ³
Melting point	1134 °C	1975 °C
Boiling point	2000 °C	2360 °C
Band gap	1.2–2.1 eV	3.37 eV (direct)
Refractive index	2.63	2.0041
Electron affinity (eV)	4.38	≈ 4.2

L. energy (kcal/mole)	981	965
Odor	Odorless	Odorless
Solubility in water	Insoluble	0.16 mg/100 mL (30 °C)

I.3 Environmental Applications of Metal Oxides-Comparative Literature Review

I.3.1 Photocatalysis – Comparative Literature Review

It is thus clear, based on the foregoing discussions, that ZnO thin film-based photocatalysis depends largely on structural modulation, dopant addition, and heterojunction formation (Table I.2). For pure ZnO thin films, the photodegradation efficiency is usually moderate under UV radiation, coming from fast recombination of photo-induced electron–hole pairs (Atta et al., 2024). A low k_{app} was monitored in pristine ZnO, indicating that the inherent defect states are not capable of prolonging charge separation.

As the case is for transition-metal doping, i.e., Co-doped $n\text{-Zn}_{1-x}\text{Mg}_x\text{O}$ (Latif et al., 2023), The degradation capability and kinetics are significantly improved. This enhancement is ascribed to the defect-level engineering in which dopant ions introduce intermediate energy states that provide efficient trapping sites for the charge carriers and hence decrease in recombination probability. Comparable enhancing effects are also found in Ni–Eu co-doped ones (Blažeka et al., 2022), where the simultaneous action of rare-earth and transition-metal cations pushes up k_{app} values, which means higher surface redox activity enhancements.

The TBP heterostructure-based architectures also show better photocatalytic activity. For example, a ZnO/Ag₃PO₄ composite (V et al., 2023) has higher activity under visible light irradiation as a result of the efficient interfacial charge transfer in the heterojunction. The band matching from ZnO and Ag₃PO₄ contributes to the directional electron transferring, which can enhance the lifetime of charge carriers and, accordingly, accelerate pollutant degradation. Similarly, CuO/ZnO multilayered films (Mrabet et al., 2023)[use p–n junctions to create an internal electric field, leading to charge recombination inhibition and improved photocatalytic kinetics under solar light illumination.

In addition, processing parameters, i.e., annealing temperature, are the key factor governing photocatalytic performance. As was shown in (Castañeda De La Hoya et al., 2025), optimized thermal treatment increases the crystallinity and diminishes the structural defects, which serve as recombination centers, and therefore the degradation rates were improved. Excessive grain growth, however, can decrease active surface area, and an optimum structure balance must then be present.

Last, but not least, spray pyrolyzed nanostructured thin films (Cherif et al., 2022) show the crucial role of surface morphology and porosity in controlling adsorption–desorption behavior. Larger roughness and higher effective surface area of a material can contribute to more adsorption of pollutants, which also affects the pseudo-first-order constant.

In general, the literature reports that photocatalytic activity in ZnO thin films is controlled by a multitude of factors, including crystallinity and defect chemistry as well as interfacial band alignment and light absorption. Of the reported methods, dopant engineering and heterojunction formation were found to be the two most practical routes for improving degradation efficiency and reaction kinetics (Latif et al., 2023), (V et al., 2023), (Mrabet et al., 2023), (Blažeka et al., 2022). Such comparison provides a state-of-the-art benchmark for the later structural optimization of ZnO thin films towards improved environmental photocatalysis.

Table I.2 Literature comparison of ZnO-based Thin Films in Photocatalysis Application.

photocatalyst	pollutant	Light source	Synthesis method	time	Degradation (%)	Reference
ZnO thin films	MB	UV irradiation	Sol-gel	3h	26%	(Atta et al., 2024)
Co-doped ZnO films	MB	Sunlight	Spray pyrolysis	3h	~93%	(Latif et al., 2023)
ZnO/Ag₃Po₄ heterostructure	MB	Visible& sunlight	Hydrothermal + SILAR	~2h	~86%	(V et al., 2023)
ZnO thin films	2,4-D herbicide	Germicide lamp/sunlight	Sol-gel sintering	+ 3h	significant degradation best at 450°C	(Castañeda De La Hoya et al., 2025)
CuO-ZnO composite thin films	MB	Sunlight	Spray pyrolysis	Not specified	Enhanced pure	(Mrabet et al., 2023)
Nanostructured ZnO	RB13 & DR227 dyes	UV light	Spray pyrolysis	~390 min	~82-92%	(Cherif et al., 2022)
ZnO thin films	B(RhB) DR-23	UVA light	Hydrothermal	180 min	~97%	(Look, 2006)

Ag-doped ZnO films	MB	UV & Visible	PLD synthesized doped ZnO	60 min	~73%	(Blažeka et al., 2022)
C-doped g-C₃N₄	BPA	Simulated solar	Bio-template hydrothermal	180	92.5	(Meena et al., 2025a)
C-ZnO	RhB	Visible	MOF pyrolysis	210	>90	(Zhang et al., 2019)
ZnO	RhB	UV	Hydrothermal	240	99	(Yu & Yu, 2008)
Ag-doped ZnO	BM	visible	Doctor Blade method	140	45	(B.D. Cullity, S.R. Stock - Elements of X-Ray Diffraction-Pearson Education Limited (2014), s. d.)
C-N-co-doped ZnO	MB	visible	Sol-gel & physical grinding	60	91	(Meena et al., 2025b)
Cu doped ZnO	Monocrotophos pesticide	Visible	hydrothermal	180	80	(Hanh et al., 2019)

I.3.2 UV Photodetector – Comparative Literature Review

ZnO thin film has been intensely studied for UV photodetection due to its wide bandgap and high exciton binding energy. ZnO thin film has shown modest UV responsivity with high dark current and slow response/recovery times (Laudari et al., 2020; Z. Shang et al., 2023). In order to improve the device performance, doping of Ag, Al, or Ga was applied. Ag-doped ZnO films also showed enhanced photocurrent and faster response due to an enhanced charge separation and reduced trap

state, while overdoping caused the recombination to increase with poor device stability (Lu et al., 2021),(De Andrade et al., 2022). Al-doped ZnO films exhibited an increase in carrier mobility and a decrease in dark current, leading to higher detectivity, but production repeatability was difficult (Sajjad et al., 2021). To enhance the photoresponse further, heterostructures of ZnO with CuO or TiO₂ were studied. For instance, ZnO/CuO bilayers displayed improved UV responsiveness as a result of the n–p junction formation that assists in effective electron-hole separation and noise minimization (Calderón-Olvera et al., 2023; Liu et al., 2015). Device performance was sensitive to film thickness, deposition method, and interface quality, thus causing variation in the responsivity and response/recovery time rates reported. The experimental setting and analysis results of these studies are presented in Table I. 3.

Table I.3 Comparison of the ZnO pure and doped UV photoconductors' performance.

Sample/ Device	Photodete ctor	Fabrication method	Key (Responsivity/ Sensitivity/ Detectivity/ Response Time)	Performance	Measurement Conditions	Refer -ences
Flexible ZnO- based UV PD	ZnO film paper	thin on ZnO film, graphite electrodes	R= 6.75 A/W; detectivity~ 4.6×10^{12} jones; sensitivity ~ 7.2×10^3 ; $\tau_{\text{resp}} \sim 13\text{ms}$		UV@ 253 nm: 30 V bias	(Khan zode et al., 2025)
Annealed ZnO thin film	ZnO film SiO ₂ /Si	thin on Thermal evaporation + annealing	Highest photocurrent & fastest response (optimized at 600°C)		UV photoconducti vity test	(C & Arulra j, 2025)
ZnO NRs with Al NPS	ZnO decorated with nanoparticl es	NRs Hydrotherma l + e-beam evaporation	Responsivity ≈ 0.267 A/W; photocurrent $\tau_{\text{resp}} < 0.4\text{s}$	high ratio;	UV illumination	(S. Shang et al., 2022)
Ag-doped ZnO TF UV PD	Ag-doped ZnO films	Laser- assisted chemical bath	$R \approx 10.78\text{A/W}$; Sensitivity $\approx 14661.9\%$; Detectivity $\approx 2.25 \times 10^7$ jones		-3 V bias, UV	(Zyou d & Omar, 2024)

	MSM contacts	growth (LACBG)				
Ni-doped nanoparticle PD	Ni-doped ZnO nanoparticl es	Polyol process	R=121 Rise~5.5s; Fall~12s	A/W; 375 nm laser, 1 V bias	(Ben Elkam el et al., 2018)	
V-doped ZnO nano-flowers PD	V-ZnO nanostructu res	Co-precipitation	R~5.1*10 ³ mA/W; Enhanced self-poered response	UV illumination	(Palla volu et al., 2023)	
GZO/AZO MSM PD	Ga- and Al-doped ZnO thin films	Sol-gel spin coating	Best R=46.2A/W uned UVA; I _{UVA} /I _{dark} ≈ 73.3	5V bias, UVA~0.825 Mw/cm ²	(Tsay & Hsu, 2017)	
Al-doped ZnO UV PD	AZO nanostructu red film	Sol-gel/scalable process	On/off ratio >10 ⁴ ; Detectivity≈1.85*10 ¹² Jones; fast response	Self-powered UVA	(Tran et al., 2023)	

1.3.3 CO₂ Gas Sensing – Comparative Literature Review

The CO₂-detecting features of monolayer ZnO and CuO thin films and bilayers with the structure ZnO/CuO and CuO/ZnO have been discussed widely in the literature. When a DC magnetron-sputtered ZnO thin film was used as a sensing layer, we got moderate sensitivity of this type at high temperature (10% at 300°C for 2000 ppm CO₂) with a fast response/recovery time of 10–20 s/20–50 s (Lavanya et al., 2015). Low-temperature precipitated-synthesized ZnO nanoflakes were more sensitive (22.5%) with a fast response/recovery time of 9/17 s (Hjiri et al., 2020). Co-Doped ZnO thin films exhibited 53% sensitivity at 350°C for the presence of 50,000 ppm CO₂, but with delayed response/recovery times (135/180 s) (S. Ghosh & Rajan, 2021). Conversely, 1D hybrid Au–ZnO nanostructures showed 80% sensitivity at 250°C for 200 ppm CO₂, along with moderate response and recovery times of about 70/60 s (Naganaboina et al., 2022).

CuO-governed sensors demonstrated diverse responses according to the deposition technique, film thicknesses, and detecting conditions. For example, the sol-gel deposited CuO thin films showed no response at 250 °C, but a 21% response was obtained at 300 °C with high CO₂ concentration (8354

ppm), and also, there has been a rapid sensor response of (5/5 s) (26459823, s. d.). Bi-layered ZnO/CuO and CuO/ZnO thin films exhibited sensitivity that is significantly higher due to the formation of n–p heterojunction with increasing modulation of the depletion layer (Bhowmick et al., 2018),(Musa et al., 2021).

A comprehensive summary of the CO₂ sensing reports is compiled in Table I.4, including the material category, synthesis process, morphology shape, working conditions, sensitivity/response/recovery times, etc.

Table I.4 CO₂ Gas Sensing Performance of Pure ZnO, and ZnO/CuO Multilayer Thin Films.

Sensor Materials	Synthesis Method	Morphology	Temperature (°C)	Response (%)	(τ_{rep}) (τ_{rec}) (s)	Concentration (ppm)	Reference
ZnO	DC Magnetron Sputtering	Thin Film	300	10	10-20/20-50	2000	(Kannan et al., 2014)
ZnO	Precipitation	NFs	250	22.5	9-17	200-1025	(Kanaparthi & Singh, 2019)
ZnO	Sol/Gel	Thin Film	300	11	20/20	1000	(Bhattacharyya, 2014)
Ca-ZnO	Chemical Synthesis	Thin Film	350	53	135/180	50000	(A. Ghosh et al., 2019)
Au-ZnO	VLS Technique	1-D Nanostructure	250	80	70/60	200	(González-Garnica et al., 2021)
CuO	Sol/Gel	Thin Film	300/250	21/10	5 /5	8354	(Non confirmé 63952, s. d.)

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CuO	Thermal Evaporation	Thin Film	Room T°	14	320/230	500 mbar	(Maki & Mahmoud, 2017)
CuO	Spray Pyrolysis	Thick Film	Room T°	3.5	10/6	100	(Abdelmounaïm et al., 2016)
CuO	Thermal Evaporation	Nanowires	400	101	15/35	1.05	(Kasian & Pukird, 2010)
CuO/ZnO	Chemical Deposition	Bi-layer Thin Film	375	47	44/217	2500	(Bhowmick et al., 2022)
CuO/ZnO	Dip Coating	Thin Film	Room T°	48	180/660	10000	(Musa et al., 2023)
CuO/ZnO	Mechanical	Pellets	300	30	-	1000	(Nakamura et al., 1998)
ZnO	Sol-gel coating	dip- Thin films	Room T°	44.7	14.0/12.6	31	(Kebaili et al., 2026)
CuO				14.6	21.6/14.4		
ZnO/CuO				3.9	8.1/5.4		
CuO/ZnO				21.1	7.2/1.8		

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Chapter II

Experimental Methodology.

II.1 Introduction

This chapter introduces the experimental procedure, which serves as the groundwork for all that was investigated through this work, with reference to the critical points as well as limitations that have been taken into consideration in Chapter 1. Pure, doped ZnO and ZnO/CuO multilayer thin films were prepared using a well-designed sol–gel dip-coating technique. Precursor, substrate, doping element, and processing parameters were not randomly selected but were guided by the intended functional applications, as well as by systematic studies of the influence of key variables such as molarity, dopant concentration, number of coating cycles, and thermal treatment conditions. Besides discussing synthesis routes, the characterization techniques used to determine film structural, morphological, optical, and electrical properties are presented. Experimental setups for photocatalytic evaluation, UV photodetection testing, and gas-sensing measurements were demonstrated. As a whole, these methodological aspects determine the experimental template to be used and serve as the basis for the explanation, analysis, and interpretation of the results presented in the following chapters.

II.2 Experimental Strategy and Research Approach

The experiments in this study were developed based on an advanced and application-oriented approach. Instead of treating material synthesis and device performance as separate steps, we took a more systematic approach to understand how processing conditions link with thin film properties and with functional behavior. The work commenced by developing pure ZnO thin films to serve as a reference baseline. With the baseline performances set, targeted deviations could now be achieved via doping and structural manipulation. Urea and silver doping for tuning charge transport, defect states, and surface reactivity was studied, and multilayer ZnO/CuO systems were synthesized to investigate heterojunction behavior and interfacial charge transfer processes.

Significant experimental parameters (i.e., molarity of precursors, concentration of dopants, cycles for the dip-coating process, and type of substrate) were changed systematically in order to satisfy the aimed application. Glass substrates were chosen for photocatalytic and gas sensitivity measurements, which require optical transparency and surface accessibility, while silicon substrates were used in the fabrication of UV photodetectors to enable effective electrical access and device operation.

This graduated development from films to doped systems and multilayered constructs enabled us to gain insight into the relation between controlled alterations at the material level and function. The chosen method guarantees comparability between sample sets and the same experimental platform for application-oriented studies described in Chapters 3, 4, and 5.

II.3 Materials and Chemicals

The materials used in this study were carefully selected to ensure high purity, reproducibility, and suitability for the targeted applications. Zinc oxide thin films were prepared from zinc precursors, including zinc acetate dihydrate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$), Sigma–Aldrich, 99.9%, which served as a reliable source of ZnO. Isopropanol ($\text{C}_3\text{H}_8\text{O}$), Sigma–Aldrich, 99.8%, was used as a solvent to dissolve the zinc precursors, while diethanolamine (DEA), Sigma – Aldrich, 99.8%, was used as a stabilizer to control hydrolysis and condensation during sol-gel processing. Ethylene glycol (EG), Sigma–Aldrich, 99.8%, was used as a viscosity modifier and film-forming agent.

Silver nitrate (AgNO_3) and magnesium acetate tetrahydrate ($\text{Mg}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$), Sigma–Aldrich, 99.9%, were used as precursors for silver and magnesium, respectively, for contamination purposes. Urea ($\text{CO}(\text{NH}_2)_2$) Sigma–Aldrich, 99.9%, was introduced as a nitrogen source, while thorium ($\text{CH}_4\text{N}_2\text{S}$) Sigma – Aldrich, 99.9% was used to incorporate sulfur additives into the films. For the synthesis of copper oxide, copper acetate monohydrate [$\text{Cu}(\text{CH}_3\text{COO})\text{H}_2\text{O}$], Sigma–Aldrich, 99.9%, was chosen as a precursor for producing high-quality CuO thin films.

II.4 Preparation of Substrate

II.4.1 Choice of Substrate

The choice of substrate is crucial for thin film deposition, as it affects adhesion, morphology, and functional performance. In this study, two types of substrates were used:

Glass slides: used for photocatalytic applications and gas sensing. Glass provides a smooth, transparent surface ideal for optical characterization and degradation studies of dyes.

Silicon wafers (Si): used for UV photodetector studies and also for gas sensing. Silicon offers high thermal stability and electrical conductivity necessary for electronic applications.

II.4.2 Cleaning Procedure: This step is very important for obtaining thin films of good quality because the slightest impurity can cause contamination and detachment of the deposited layers.

For Glass Substrates:

The glass substrates (SAIL BRAND, CAT. NO. 7101, China), were cleaned with a steel ultrasonic cleaner at different stages, as follows:

- Rinse for 10 min in an ultrasonically activated acetone bath.
- Rinse with distilled water.
- Immersion in an ultrasonically activated methanol bath for 5 minutes.

- Rinse with distilled water.
- Immersion in an ultrasonically activated, ethanol bath for 5 minutes.

For Si Substrates:

The silicon substrates were cleaned by immersion in a diluted HF solution for 1-2 minutes to remove the negative oxide layer, followed by thorough rinsing with deionized water.

Finally, substrates were rinsed with deionized water and dried using a hot air blower (hair dryer)

This cleaning procedure ensures a contaminant-free surface, which is essential for reproducible film deposition and reliable performance in photocatalysis, UV detection, and gas sensing applications.

II.5 Preparation of Precursor Solution

II.5.1 Pure ZnO Solution

The pure ZnO solution was synthesized by the sol–gel method. Zinc acetate was dissolved in 28 mL of isopropanol per 30 mL total solution volume. Subsequently, 1 mL each of DEA and EG were pipetted into the solution for further stabilization. The solution was magnetically stirred at 60 °C for 2 h to dissolve the precursors completely and to obtain a homogeneous solution. The solution was stirred and kept at room temperature for 24 h to obtain the stable sol required for dip-coating deposition. In order to explore the concentration effect on the film's quality, three concentrations (0.4 M, 0.7 M, and 0.9 M) were synthesized; this molarities were chosen to investigate their influence on photocatalytic performance.

II.5.2 Doped ZnO Solutions

The doped solutions were fabricated by directly adding the dopant to the pure ZnO solution. The amounts were calculated to achieve specific atomic percentages: Ag: (1, 3, 5%), Mg: (2, 5, 7%), Urea: 20%, Thuria: 20%. The mixture was magnetically stirred at 60°C for 2 h after adding to ensure complete dissolution and homogeneous distribution of the dopant ions in the sol. As for the pure ZnO solutions, the doped sols were aged for 24 h before deposition.

II.5.3 Pure CuO Solutions

Copper citrate was dissolved in isopropanol under magnetic stirring at 60°C for 2 hours. DEA and EG were added to stabilize the sol and promote uniform film formation. The solution was then aged at room temperature for 24 hours before deposition.

II.6 Thin Films Deposition (Dip Coating Technique)

II.6.1 Definition and Principle

Dip coating is a process for thin film deposition from solutions, which has been extensively used in the fabrication of metal oxide coatings owing to its simplicity, low cost, and versatility. The method is to immerse a solid substrate into a precursor solution and subsequently withdraw at a constant speed, from which the surface of the substrate forms a thin liquid layer. It yields a solid film after the solvent removal and the temperature crystallization (*B.D. Cullity, S.R. Stock - Elements of X-Ray Diffraction-Pearson Education Limited (2014)*, s. d.; Zayat et al., 2011). Besides those, solution concentration, aging time, substrate surface energy, ambient humidity, and temperature are important factors to determine the final morphology and microstructure of the deposited film (*s0022-30932980078-3*, s. d.). In the case of metal oxide thin films, dip coating is also frequently accompanied by the sol–gel method in which precursors of metal alkoxide/salts produce hydrolysis and condensation reactions leading to a three-dimensional inorganic network. Further drying and annealing steps are necessary to eliminate organic remnants, improve densification, and crystallize the oxide phase (Musa et al., 2021). This method is highly compatible with the synthesis of ZnO-based thin films due to its stoichiometry control and incorporation of dopants (Ag, Mg or organic additives) capabilities.

II.6.2 Advantages of Dip Coating

The simplicity and low cost of the experiment are a primary advantage of dip coating. Unlike PVD or CVD methods, dip coating does not involve the use of vacuum systems and special devices that need to be used in conjunction with them. This fact makes it applicable to laboratory studies as well as large surface area applications (Musa et al., 2021). Such a property in particular proves beneficial for studies aimed at environmental and energy applications, necessitating low-cost fabrication techniques. Another important advantage is the capability to control the composition of films. As the deposition is performed using a liquid precursor, doping elements can be conveniently incorporated into the solution and homogeneously distributed in the metal oxide matrix. This property has been widely used to regulate the optical, electrical, and catalytic properties of ZnO thin films via doping and co-doping methods (*1446184410066683*, s. d.; Musa et al., 2021). In addition, when dip coating, coating on substrates of complex shapes can be made, and the thickness is controllable by changing the withdrawal speed or the number of coating cycles. The dip-coated films are frequently porous nanostructured, which is favourable for applications related to photocatalysis or gas sensing. The expanded specific surface area contributes to surface reactions, absorption of gas molecules, and light

interaction, which is beneficial for functional performance improvement (*Elaboration and characterization of nanostructuring NiO thin films for gas sensing applications*, s. d.).

II.6.3 Limitations of Dip Coating

Dip coating has the advantage; however, it also has a limitation that needs to be taken into account. Among these, the generation of defects (cracks, pinholes, and thickness non-uniformity) is one of the key problems that are caused by the stress during solvent evaporation and volume shrinkage in the drying process (*L-G-0000585014-0023610108*, s. d.). These defects may negatively affect the electrical conductance of the films and their optical transparency. Furthermore, a weakness of the process is its high sensitivity to environmental factors. Changes in humidity, temperature, and air current greatly affect the rates of solvent evaporation and can be a source of poor repeatability unless made rigorous (*Materials_science_of_thin_films_ohring*, s. d.). Moreover, dip-coated films could suffer from lower density and poorer adhesion with respect to those based on vacuum because of the thin film in a single cycle or thick deposited coating. Finally, dip coating has poor nanometer-scale thickness control relative to more advanced deposition methods, such as atomic layer and chemical vapor deposition. However, for applications that emphasize chemical flexibility, scalability, and surface property characteristics, dip coating remains a powerful and one of the commonly used techniques for metal oxide thin film preparation (Thornton, 1974).

II.6.4 Film Deposition Parameters

Films in this study were deposited by the sol-gel dip coating technique. Substrates were vertically immersed in the precursor solution. Withdrawal speed was controlled at a 0.4 mm/s rate to ensure uniform thickness. Sequential deposition was performed with intermediate drying for 10 min at 400 °C with different numbers of cycles (1, 3, 5, 8, 11, 14).

II.6.5 Thermal Treatment (Annealing)

The thin films underwent annealing to improve their structural and morphological properties, as well as their photocatalytic activity. The annealing process was carried out in an electric furnace at 400 °C for two hours, then at 500 °C for one hour, and finally at 500 °C for an additional hour (depending on the composition and application of the prepared films). The process was performed in an atmospheric environment to completely remove any remaining solvents and to promote crystallization. Annealing is important not only for activating the additives but also for promoting granule growth and increasing film density, which significantly impacts their photocatalytic activity, UV detector response, and CO₂ sensing.

II.7 Summary of Fabricated Samples

For a clear perspective on the experimental setup and several parameters studied in the present work, all such thin films were fabricated using a predefined and logical method. All ZnO-based thin films were deposited using the sol–gel dip-coating method under the same baseline conditions, while some of the parameters were intentionally modified to investigate their effects on structural, optical, and photocatalytic behavior. These parameters involve the annealing temperature and time, dip-coating cycles, precursor solution molarity, and the addition of metallic and non-metallic dopants. The detailed preparation conditions of all the samples studied in this work are summarized in Table II. 1.

Table II.1. Summary of the preparation conditions of the fabricated ZnO-based thin film samples.

Sample	Film composition	Number of dip-coating cycles	Solution molarity (M)	Doping/co-doping agent	Annealing temperature (°C)	Annealing time (h)
ZnO-400-8C-0.4M	Pure ZnO	8	0.4	None	400	2
ZnO-500-8C-0.4M	Pure ZnO	8	0.4	None	500	1
ZnO-500-8C-0.4M-2h	Pure ZnO	8	0.4	None	500	2
ZnO-400-1C-0.4M	Pure ZnO	1	0.4	None	400	2
ZnO-400-3C-0.4M	Pure ZnO	3	0.4	None	400	2
ZnO-400-5C-0.4M	Pure ZnO	5	0.4	None	400	2
ZnO-400-11C-0.4M	Pure ZnO	11	0.4	None	400	2
ZnO-400-14C-0.4M	Pure ZnO	14	0.4	None	400	2
ZnO-400-1C-0.7M	Pure ZnO	1	0.7	None	400	2
ZnO-400-1C-0.9M	Pure ZnO	1	0.9	None	400	2

ZnO-Urea	Urea-doped ZnO	1	0.4	20% Urea (N/C doping)	400	2
ZnO-Thiourea	Thiourea-doped ZnO	1	0.4	20% Thiourea (S doping)	400	2
ZnO-Ag 0.5%	Ag-doped ZnO	1	0.4	0.5% Ag	400	2
ZnO-Ag 1%	Ag-doped ZnO	1	0.4	1% Ag	400	2
ZnO-Ag 3%	Ag-doped ZnO	1	0.4	3% Ag	400	2
ZnO-Ag 5%	Ag-doped ZnO	1	0.4	5% Ag	400	2
ZnO-Ag 5%-U 20%	Ag/Urea co-doped ZnO	1	0.4	5% Ag + 20% Urea	400	2

II.8 Characterization Techniques

To improve the performance of the components of the prepared films, additional characterization techniques are also used. The techniques in these classes are the appropriate ones: structural, morphological, optical, and chemical.

II.8.1. Structural Characterization

These techniques allow for determining the crystalline structure, the purity of the phase, the presence of deficiencies, and the natural chemistry of the liaisons in the films.

X-ray Diffraction (XRD): Used to analyze the crystalline structure, the surface parameters, and the pure phase of the ZnO and CuO films. X-ray diffraction (XRD) patterns were recorded in the range of 20°–80° and a scan rate of 3°/min using a Philips X'Pert diffractometer equipped with a Cu-K α radiation source ($\lambda = 1.5418 \text{ \AA}$).

The interplanar spacing $d(hkl)$ was calculated using (Kebaili, Iaiche, Bensouici, Djelloul, et al., 2026a):

$$d = \frac{\lambda}{2 \sin \theta} \quad (\text{II.1})$$

For the hexagonal wurtzite structure, the lattice parameters a and c were determined using (Kebaili, Iaiche, Bensouici, Djelloul, et al., 2026a):

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

The full-width at half maximum (FWHM) values show a progressive variation with Ag doping. The crystallite size (D) was estimated using the Debye–Scherrer equation(Chouk et al., 2020):

$$D = \frac{K\lambda}{\beta \cos\theta} \quad (\text{II.3})$$

where K = 0.9, λ is the X-ray wavelength, and β is the FWHM in radians.

A reduction in FWHM from 0.67° (pure ZnO) to 0.40° (3% Ag) indicates an increase in crystallite size, suggesting grain growth induced by Ag incorporation.

The microstrain (ε) was calculated using(Velayi & Norouzbeigi, 2019):

$$\varepsilon = \frac{\beta}{4 \tan\theta} \quad (\text{II.4})$$

while the dislocation density (σ), representing crystal defects, was estimated as(Velayi & Norouzbeigi, 2019):

$$\sigma = \frac{1}{D^2} \quad (\text{II.5})$$

Fourier Transform Infrared Spectroscopy (FTIR): Enables the identification of functional groups and chemical bonds present in the films. Chemical bonds and functional groups were identified by recording Fourier-transform infrared (FTIR) spectra in the range of 400–4000 cm^{-1} at a resolution of 8 cm^{-1} using a Thermo Nicolet (Nexus) instrument.

Raman Spectroscopy: Analyzes crystalline vibration modes and detects the presence of defects and the incorporation of defects. Molecular composition and structure were analyzed at a 532 nm wavelength (green laser) using a RENISHAW inVia Raman Microscope.

II.8.2. Morphological Characterization

These techniques help value the surface morphology, the tail of the grains, and the rugosity, essential for the performance of the films in all applications.

Scanning Electron Microscopy (SEM): Provides images with higher surface resolution and grains. Morphological observations were performed by scanning electron microscopy (SEM) using a Thermo Fisher Apero 2C model operating at 20 kV.

Atomic Force Microscopy (AFM): Allows you to monitor the topography and use the nanometer films. The surface topography and roughness were characterized by atomic force microscopy (AFM) using MFP3D Asylum Research Oxford Instruments.

Profile: Allows you to monitor the film and use the macroscopic film.

II.8.3. Optical Characterization

These techniques allow you to study the appropriate options, absorption, and intermediary bands of films.

UV-Visible Spectroscopy (UV-Vis): Measure the transmission and absorption of films to determine the interdigit band. The optical transmittance was measured in the range 190–1800 nm using a PerkinElmer UV–Vis–NIR Lambda 19 spectrophotometer.

II.8.4. Chemical Characterization

These techniques allow the determination of the elemental composition and distribution of dopants in the films.

Energy Dispersive X-ray Spectroscopy (EDS): Coupled with SEM, this technique provides elemental analysis of the films and confirms the presence and distribution of dopants.

II.8.5. Thickness Measurement (Stylus Profilometry)

The thickness of the deposited thin films was measured using a stylus profilometer. This technique is based on scanning a sharp diamond stylus across a step formed between the coated and uncoated regions of the substrate. The vertical displacement of the stylus is recorded to determine the step height, which corresponds to the film thickness. Profilometry provides a simple, accurate, and non-destructive method for evaluating thin-film thickness and surface profile.

II.9 Application-Specific Experimental Procedures

II.9.1 Photocatalysis Measurements

The photocatalytic activity of the produced ZnO-based thin films was thoroughly investigated using methylene blue as a model organic pollutant. All thin films utilized in this investigation were produced using the dip-coating process described in Chapter 2, with modifications in deposition cycles, precursor molarity, and annealing conditions to optimize their structural and optical characteristics. For the photocatalytic studies, an aqueous solution of methylene blue was produced at a concentration of $2 \cdot 10^{-5}$ mol/l, achieving full dissolution by magnetic stirring for 30 minutes at room temperature. Each thin film sample (1*2 cm) was submerged in 4 mL of the dye solution under

continuous ultraviolet (UV) irradiation, keeping a constant distance of 10 cm from the UV (G15 T8 lamp germicidal Philips 254nm) source to assure uniform lighting. The photodegradation process was monitored at regular intervals by measuring the absorbance of the solution using a UV–Visible spectrophotometer at the characteristic wavelength of 664 nm. The degradation efficiency D , was determined using the following expression(Ameur et al., 2021):

$$D(\%) = \frac{C_0 - C_t}{C_0} \times 100 \quad (\text{II.6})$$

where C_0 is the initial concentration of methylene blue and C_t is the concentration at a given irradiation time. Before exposure, all samples were allowed to equilibrate in the dark for 20 minutes to account for any adsorption of the dye on the film surface. This methodology provided a consistent and reproducible assessment of the photocatalytic performance, enabling a direct comparison between pure and doped ZnO thin films under various deposition and post-treatment conditions.

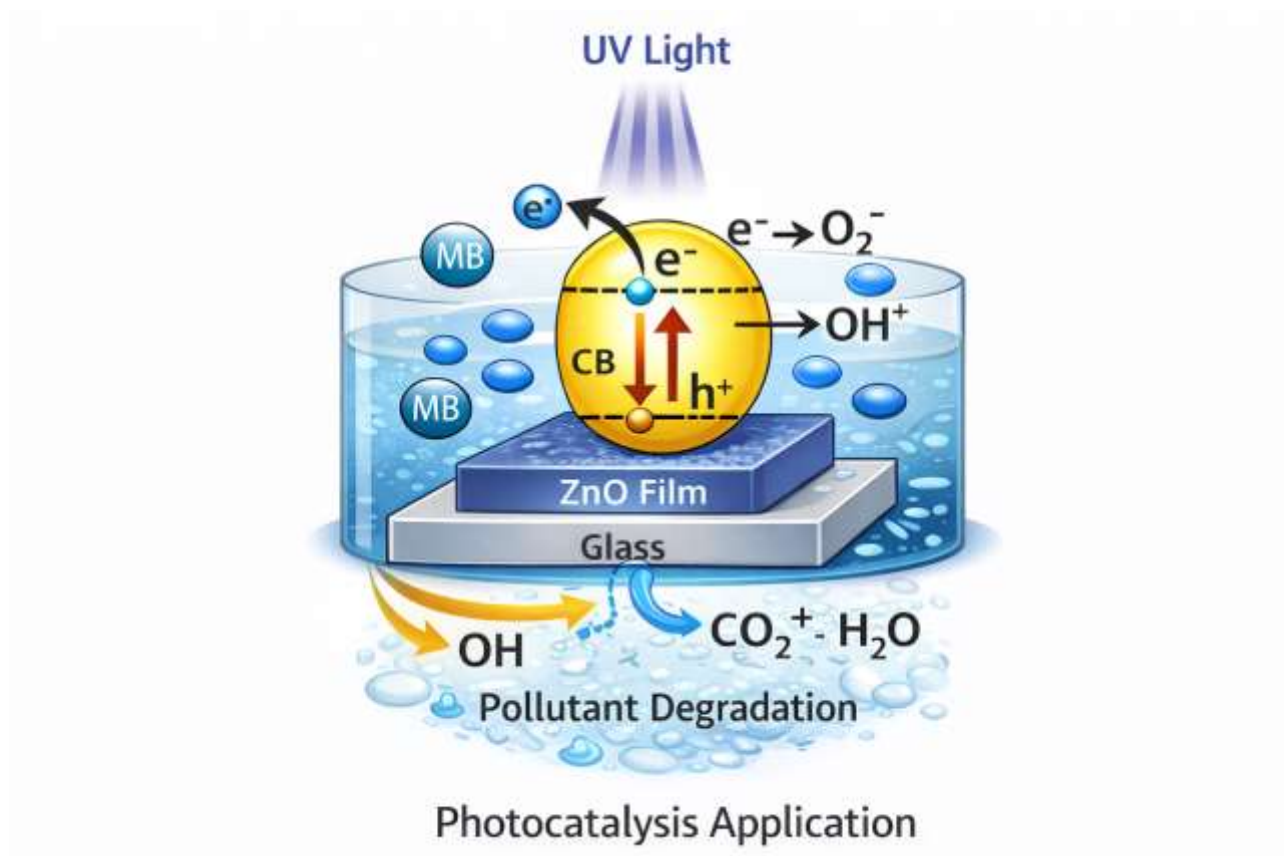


Figure II.1 Schematic Illustration of the Photocatalytic Degradation Mechanism under UV Irradiation.

II.9.2 UV Photodetector Measurements

The UV photodetection performance of the pure and Ag-doped ZnO-based thin films was evaluated through systematic optoelectronic characterization. Copper (Cu) contacts were used as contacts to

enable electrical probing. Current-voltage (I-V) characteristics were measured in both dark and under UV intensity of 1500 mW/cm².

by sweeping the bias voltage from 0 V to +5 V. The temporal photoresponse was investigated by recording current-time (I-t) transients at a fixed bias of 5 V over multiple on-off illumination cycles, allowing the extraction of key performance parameters, including photosensitivity, calculated as (Kumar & Dhar, 2024)

$$S (\%) = \frac{(I_{photo} - I_{dark})}{I_{dark}} \times 100 \quad (II.7)$$

Response and recovery times (τ_{rep} and τ_{rec} from 90% to 10% of the maximum photocurrent) (Kebaili, Iaiche, Bensouici, Djelloul, et al., 2026b).

These measurements enabled a comprehensive assessment of the influence of doping concentration on the UV detection capabilities of the elaborated Ag-doped ZnO thin films.

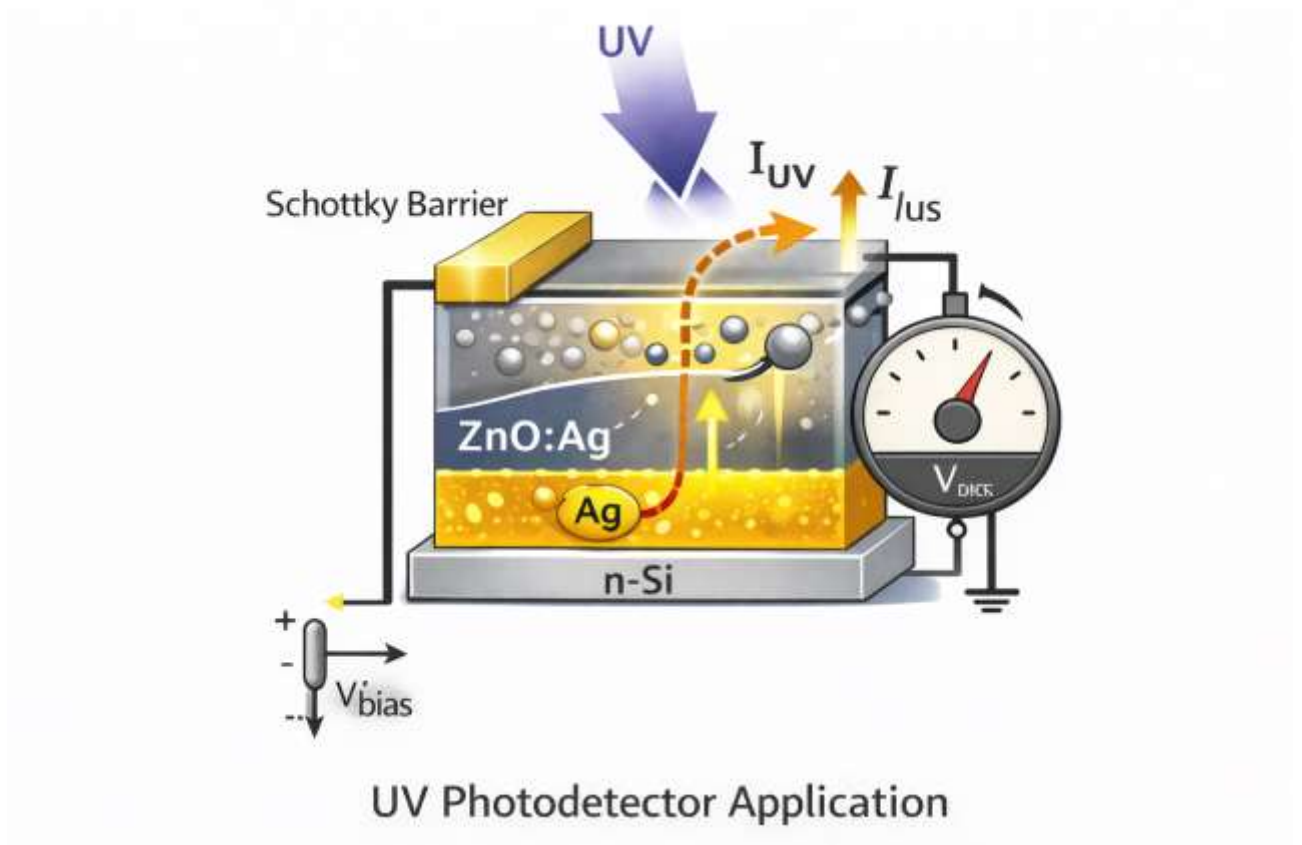


Figure II.2: Schematic Illustration of the UV Photodetection Mechanism.

II.9.3 CO₂ Gas Sensing Measurements

The CO₂ gas sensing characteristics were performed at room temperature by monitoring the change of the electrical current while modulating the gas concentration. This system measures the current

using (Al) ohmic metallic contact electrodes attained by the deposition of 99.99% pure Al from computer-controlled (programmable scanning). A potentiostat/galvanostat is used as a source of power supply (Princeton Applied Research EG&G 362 Model) placed on top of the samples (coplanar contact for the multilayer films and sandwich contact for Mg-doped ZnO films). The experimental setup involves positioning the samples within a gas chamber outfitted with a detector device to measure the gas pressure, and gas valves were used to inject gas into the chamber, as illustrated in Fig. 1b. Prior to CO₂ gas introduction, the chamber was evacuated using a rotary pump. The gas sensitivity (*S* in %) was quantitatively determined as follows (Kebaili, Iaiche, Bensouici, Saeed, et al., 2026),

$$S (\%) = \frac{(I - I_0)}{I_0} \times 100 \quad (\text{II.8})$$

where *I*₀ and *I* represent the currents of the films measured in vacuum and at various gas concentrations, respectively.

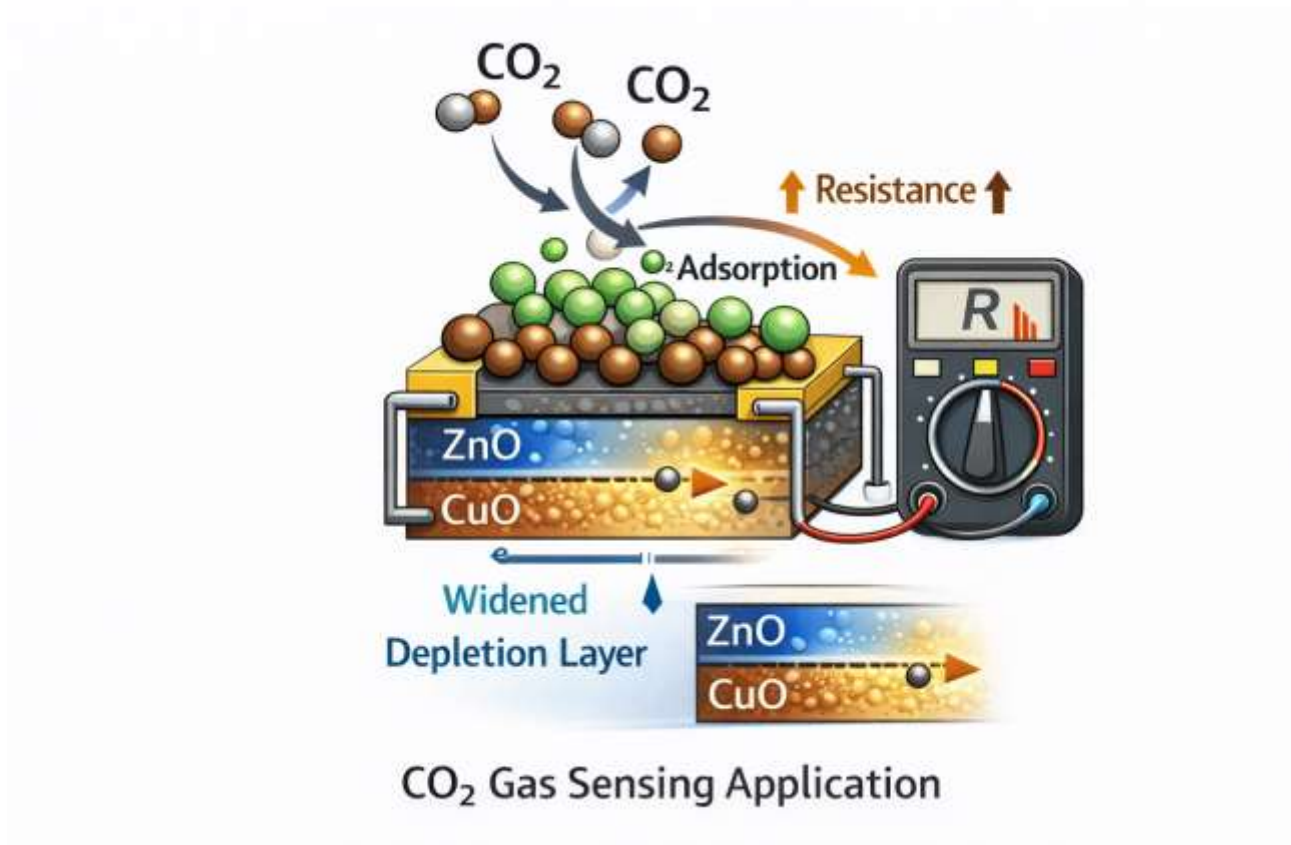


Figure II.3: Schematic Illustration of the CO₂ Gas Sensing Mechanism.

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Chapter III

Photocatalytic Performance of Pure and Doped ZnO Thin Films

Chapter III: Photocatalytic Performance of Pure and Doped ZnO Thin Films

III. 1 Introduction

This chapter presents a comprehensive investigation of the photocatalytic degradation of organic pollutants using zinc oxide ZnO thin films. The study is structured into two main parts: (i) the optimization of the synthesis parameters of pure ZnO thin films and (ii) the modification of ZnO through doping with different elements. Photocatalytic efficiency is evaluated by measuring the degradation of organic pollutants under UV-visible light irradiation. The main objective is to determine the optimal fabrication conditions that maximize the photocatalytic activity of ZnO thin films and to establish correlations between the structural properties of the films and their photocatalytic performance.

III. 2 Part i: Optimization of Pure ZnO Thin Films

This section focuses on the optimization of the synthesis parameters influencing the photocatalytic activity of undoped ZnO thin films prepared by the sol–gel dip-coating method

III.2.1 Series 1: The effect of annealing

In this series, the influence of annealing temperature and duration on the photocatalytic activity of ZnO thin films was investigated. Three annealing conditions were considered: 500°C for 1 h, 500°C for 2 h, and 400°C for 2 h. The experimental preparation parameters used for this series are summarized in Table II.1 (Chapter II).

III. 2.1.1 Photocatalysis Application

The photocatalytic activity of the prepared ZnO thin films was evaluated through the degradation of methylene blue (MB) under UV–visible irradiation. The photocatalytic performance was assessed by calculating the degradation efficiency (D%) after 180 min of irradiation as well as the apparent pseudo-first-order kinetic constant (k), obtained from the linear fit of $\ln(C_0/C_t)$ versus irradiation time.

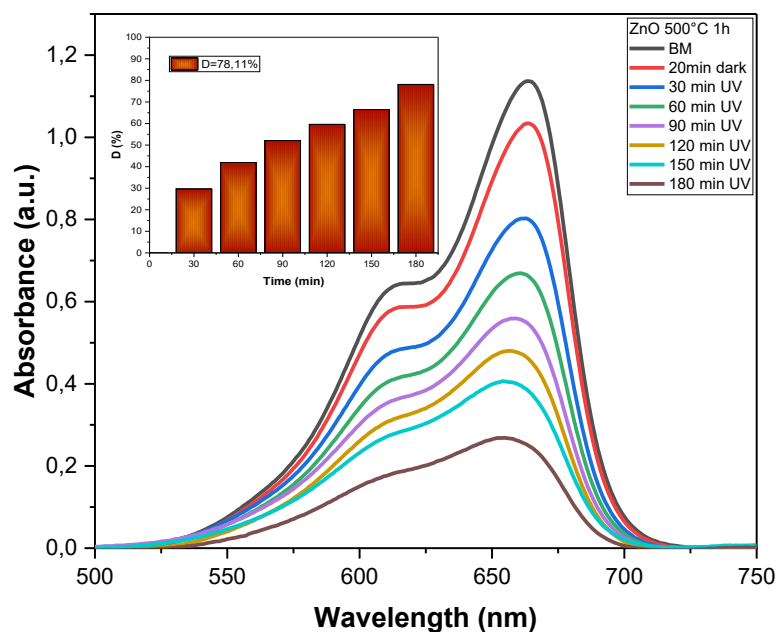
The obtained results indicate that the annealing temperature and duration strongly influence the photocatalytic activity of ZnO thin films. Among the investigated samples, the film annealed at 400°C for 2 h exhibited the highest photocatalytic performance, with a degradation efficiency of 94.51% and a kinetic constant of $k = 0.01589 \text{ min}^{-1}$.

Interestingly, this activity is higher than that obtained for films annealed at 500°C, which suggests that photocatalytic activity is not determined solely by crystallinity. Instead, it results from a balance between structural order and the presence of catalytically active surface defects. Intrinsic defects, particularly oxygen vacancies, play a crucial role in enhancing the photocatalytic performance of ZnO materials. These defects can act as electron traps, reducing the recombination probability of

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photogenerated electron–hole pairs and thus increasing the lifetime of charge carriers involved in surface redox reactions (Fujishima et al., 2008) (Özgür et al., 2005a), (C. Wang et al., 2010). Therefore, the superior activity of the ZnO film annealed at 400°C for 2 h may be attributed to an optimal concentration of such defects, which improves charge separation and facilitates the oxidative degradation of methylene blue molecules. At higher annealing temperatures (500°C), partial annihilation or redistribution of oxygen vacancies may occur. Although higher temperatures generally improve crystallinity, they can simultaneously reduce defect density and modify surface chemistry, which may decrease the number of active catalytic sites (Lv et al., 2011a) (Baruah & Dutta, 2009a).

Moreover, higher annealing temperatures are commonly associated with grain growth and surface densification, which can reduce the effective surface area available for dye adsorption. Since photocatalytic reactions mainly occur at the catalyst surface, this reduction in surface active sites can negatively affect the overall photocatalytic performance (Lv et al., 2011b). Overall, these results demonstrate that moderate annealing conditions (400°C for 2 h) are more favorable for enhancing the photocatalytic activity of ZnO thin films prepared via the sol–gel dip-coating method. The optimal photocatalytic performance is therefore achieved when an appropriate balance between crystallinity, defect density, and surface properties is established (Hoffmann et al., 1995a).



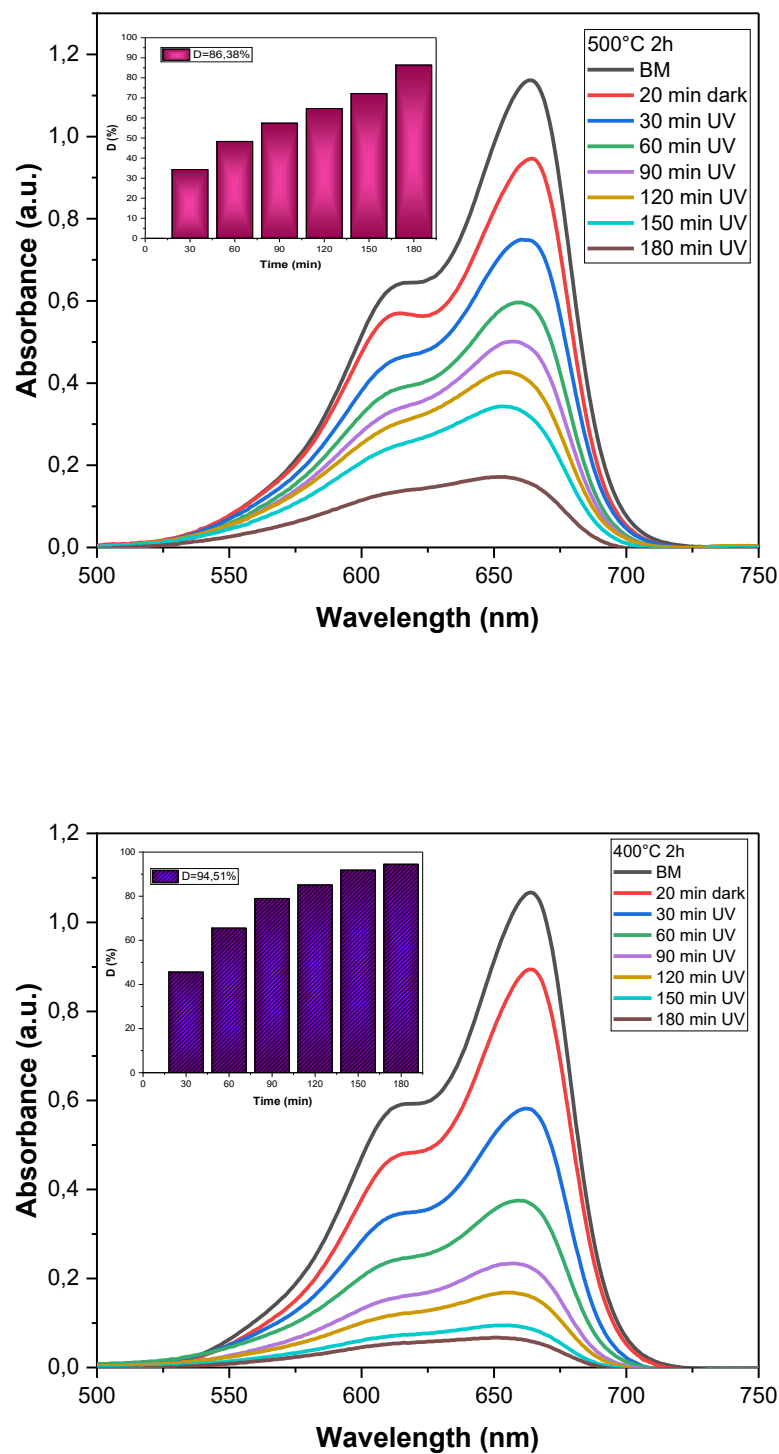


Figure III.1.1. (a) UV–visible absorbance spectra of methylene blue aqueous solution recorded during photocatalytic degradation under UV irradiation using pure ZnO thin films annealed at 400°C for 2 h, 500°C for 1 h, and 500°C for 2 h; (b) corresponding photocatalytic degradation of methylene blue as a function of irradiation time (inset).

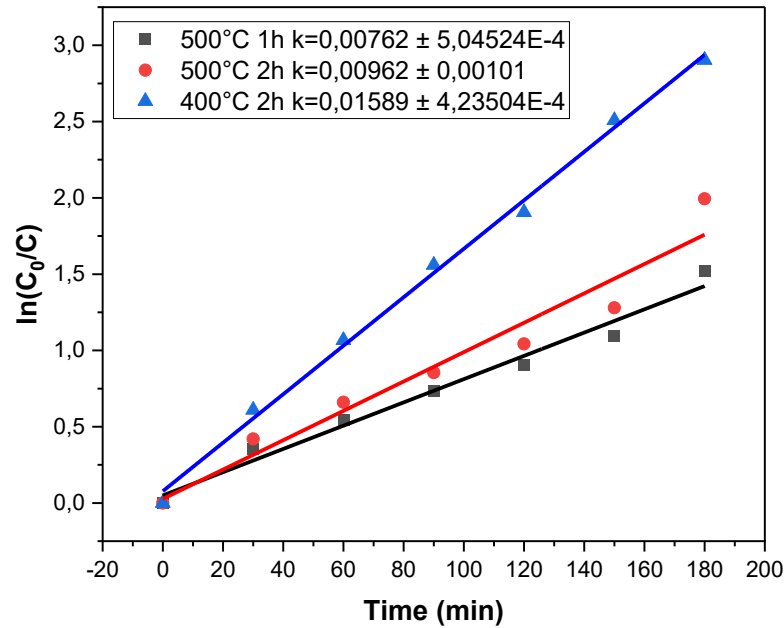


Figure III.1.2. Pseudo-first-order kinetic plots of methylene blue photocatalytic degradation, expressed as $\ln(C_0/C_t)$ versus irradiation time, for pure ZnO thin films annealed at 400°C for 2 h, 500°C for 1 h, and 500°C for 2 h.

III. 2.2 Series 2: Effect of the Number of Dip-Coating Cycles

Following the investigation of the annealing temperature and duration, a second series of ZnO thin films was prepared in order to examine the influence of the number of dip-coating cycles on the photocatalytic performance. In this series, all samples were fabricated under the same experimental conditions described in Chapter II, except for the variation in the number of deposition cycles.

Based on the results obtained in the previous series, the annealing condition of 400°C for 2 h was selected as the optimal thermal treatment. It was therefore applied to all samples in this series. This approach ensured that any variation in photocatalytic activity could be attributed mainly to the change in the number of coating cycles rather than to differences in thermal treatment.

The prepared films were subsequently evaluated for the photocatalytic degradation of methylene blue under UV–visible light irradiation. This allowed us to investigate how variations in film thickness and surface coverage, induced by different numbers of dip-coating cycles, influence the generation, separation, and transport of photogenerated charge carriers.

III. 2.2.1 Photocatalysis Application

To investigate the influence of film thickness on photocatalytic performance, ZnO thin films were synthesized employing various numbers of dip-coating cycles (1, 3, 5, 8, 11, and 14 cycles) while preserving the optimal annealing condition of 400°C for 2 hours.

The photocatalytic activity was evaluated through the degradation of methylene blue under UV–visible irradiation for 180 minutes. The degradation efficiency (D%) and the pseudo-first-order kinetic rate constant (k) were used as quantitative indicators of photocatalytic performance.

The obtained results reveal that the photocatalytic activity does not vary linearly with the number of coating cycles. The ZnO thin film prepared with one coating cycle exhibited a high degradation efficiency ($D = 94.56\%$, $k = 0.01572 \text{ min}^{-1}$). This behavior can be attributed to the formation of a thin and uniform film, which allows efficient light penetration and promotes the effective generation and separation of photogenerated electron–hole pairs (Fujishima et al., s. d.; Hoffmann et al., 1995b).

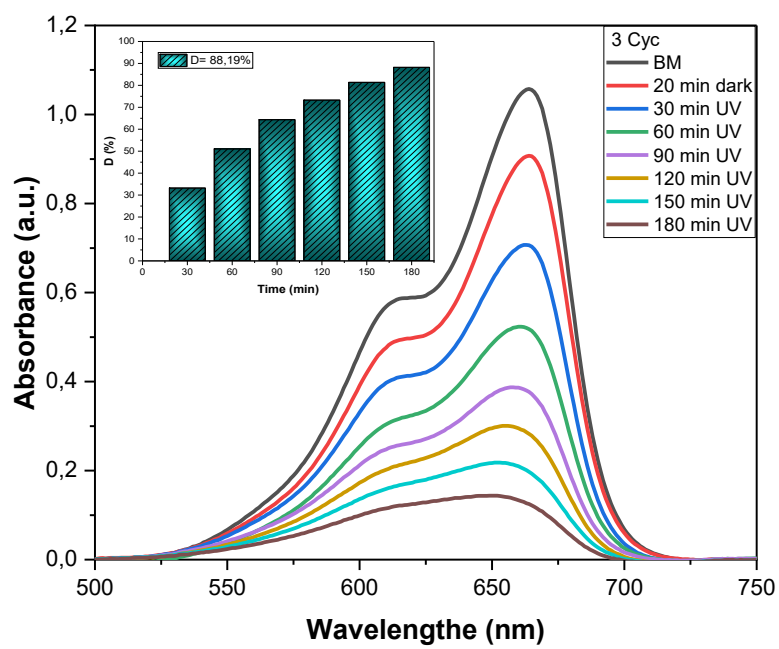
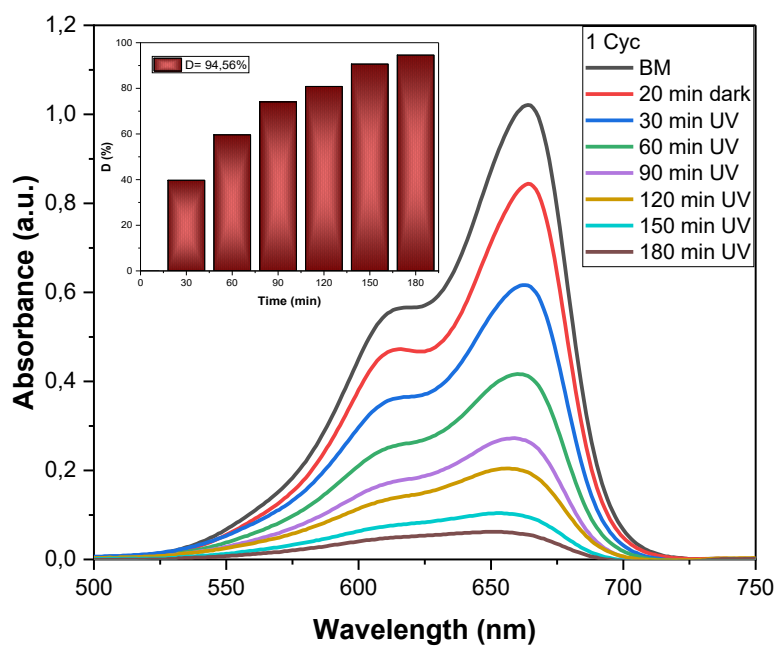
When the number of cycles increased to 3 and 5, a noticeable decrease in photocatalytic activity was observed ($D = 88.19\%$ and 71.75% , respectively). This decrease can be explained by the increase in film thickness, which may limit light penetration and promote recombination of charge carriers within the bulk of the film before reaching the surface.(Kaneva et al., s. d.; Ye et al., 2006).

Interestingly, the photocatalytic performance improved again for the film prepared with 8 cycles ($D = 94.51\%$, $k = 0.01589 \text{ min}^{-1}$). This behavior suggests the existence of an optimal thickness where the film contains a sufficient amount of active material to absorb light while still maintaining efficient charge transport toward the surface(Lv et al., 2011c),(Chong et al., 2010).

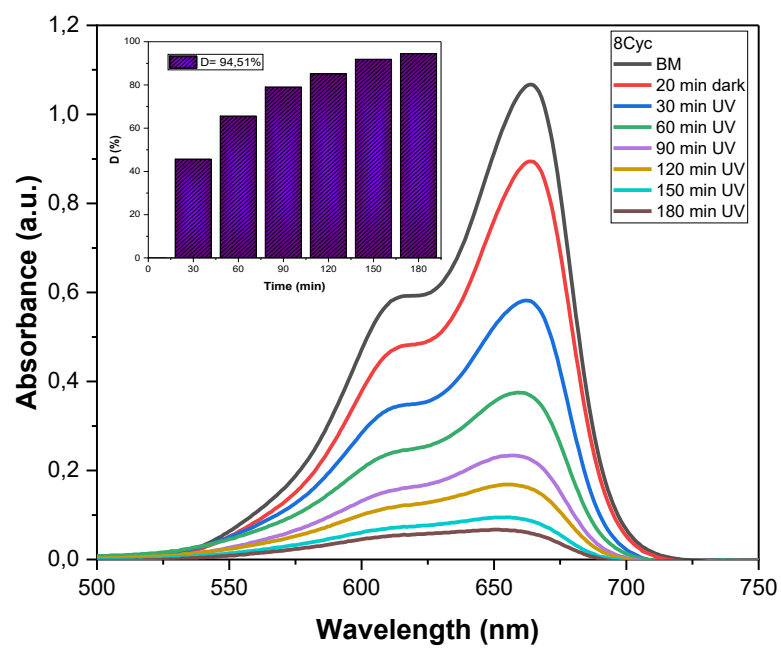
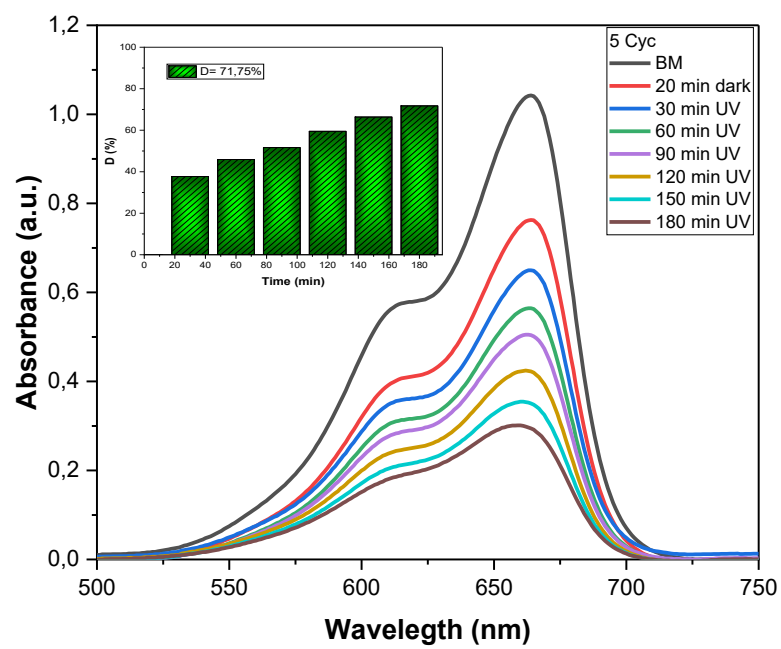
For films prepared with 11 and 14 cycles, the photocatalytic activity slightly decreased ($D = 90.20\%$ and 91.77% , respectively). In thicker films, diffusion limitations for both light and reactant molecules, as well as increased recombination of charge carriers within the bulk, may reduce the overall photocatalytic efficiency.

Overall, these results demonstrate that the photocatalytic activity of ZnO thin films is strongly influenced by film thickness, which is controlled by the number of dip-coating cycles. The highest activity is not necessarily obtained with the largest number of layers but rather with an optimal balance between light absorption, surface area, and charge carrier transport.(Lv et al., 2011c), (Meng et al., 2025).

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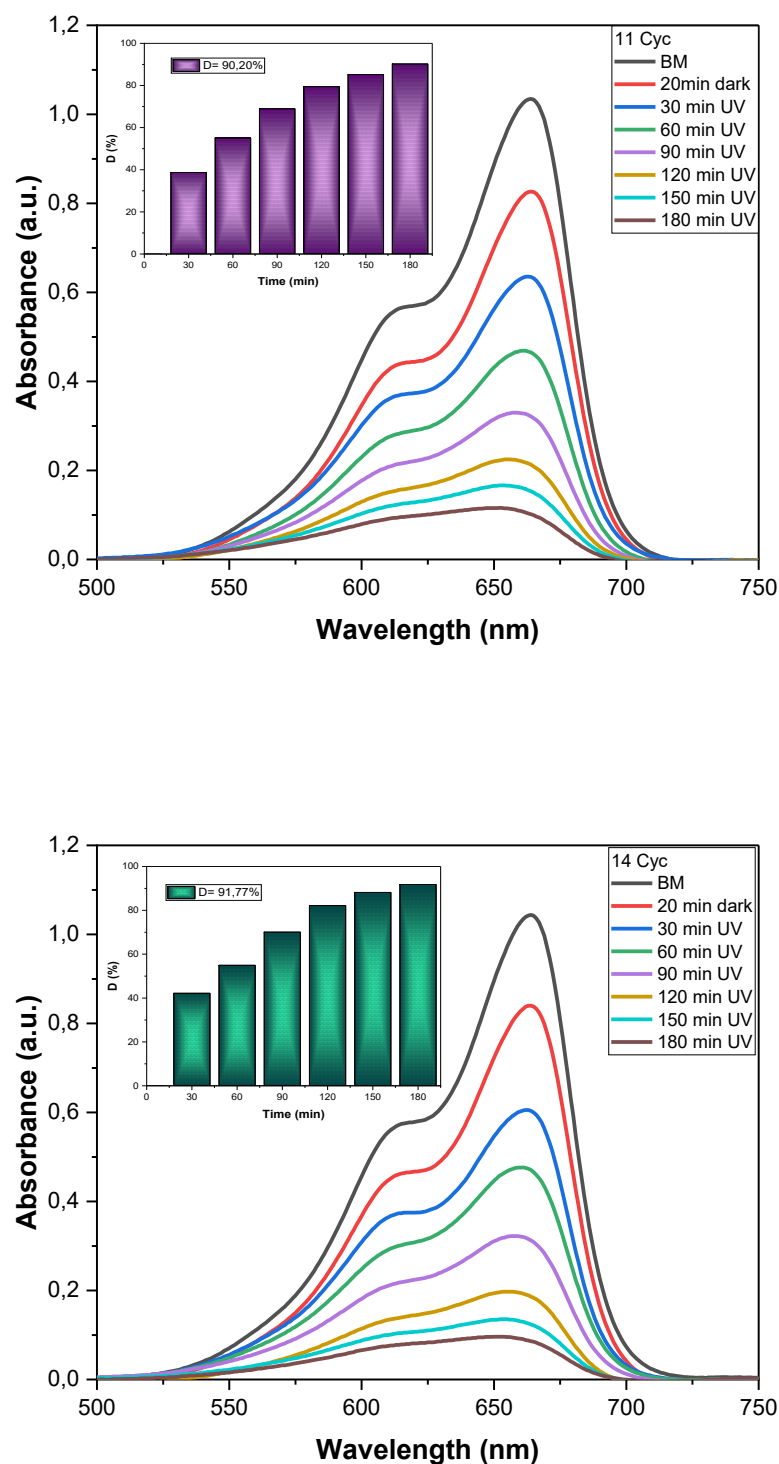


Figure III.2.1. (a) UV–visible absorbance spectra of methylene blue aqueous solution during photocatalytic degradation under UV irradiation using pure ZnO thin films prepared with different dip-coating cycles (1, 3, 5, 8, 11, and 14 cycles) and annealed at 400°C for 2 h; (b) corresponding photocatalytic degradation efficiency as a function of irradiation time (inset).

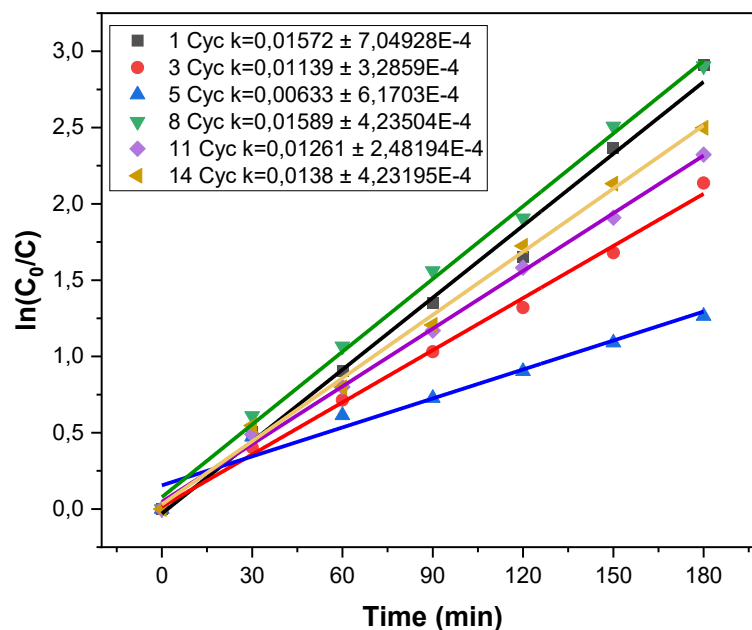


Figure III.2.2. Pseudo-first-order kinetic plots ($\ln(C_0/C_t)$ versus irradiation time) for methylene blue degradation using pure ZnO thin films prepared with different dip-coating cycles and annealed at 400°C for 2 h.

III. 2.3 Series 3: Effect of Precursor Molarity

In order to further optimize the preparation conditions of ZnO thin films, the effect of precursor molarity on photocatalytic performance was investigated. The films were prepared using the same sol-gel dip-coating procedure described in Chapter II.

Based on the previous optimization results, the annealing condition of 400°C for 2 h was maintained for all samples. Additionally, a single dip-coating cycle was selected in order to simplify the deposition process while maintaining high photocatalytic performance.

In this series, the concentration of the zinc precursor solution was varied between 0.4 M, 0.7 M, and 0.9 M in order to evaluate the influence of precursor concentration on the structural characteristics and photocatalytic efficiency of ZnO thin films.

III. 2.3.1 Photocatalysis Application

The photocatalytic activity of ZnO thin films prepared with different precursor molarities was evaluated through the degradation of methylene blue under UV-visible irradiation for 180 minutes.

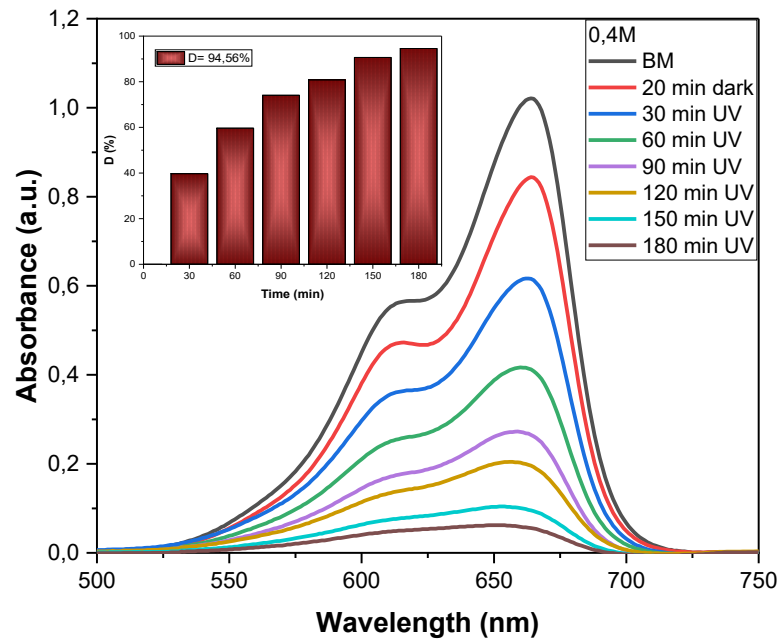
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The obtained results indicate that precursor molarity has a noticeable influence on the photocatalytic performance of ZnO thin films. The film prepared with a precursor concentration of 0.4 M exhibited a degradation efficiency of 94.56% with a kinetic rate constant of $k = 0.01572 \text{ min}^{-1}$.

When the molarity increased to 0.7 M, a slight decrease in photocatalytic activity was observed ($D = 91.01\%$, $k = 0.01171 \text{ min}^{-1}$). This reduction may be attributed to the formation of thicker or less uniform films, which can limit light penetration and reduce the effective surface area available for photocatalytic reactions.(X. Chen & Mao, 2007a; Khatibi et al., 2019; Onfroy et al., 2005).

Interestingly, when the precursor molarity was further increased to 0.9 M, a slight improvement in photocatalytic performance was observed ($D = 95.08\%$, $k = 0.01671 \text{ min}^{-1}$). This enhancement may be associated with the formation of a higher density of structural defects, such as oxygen vacancies, which can act as active sites for photocatalytic reactions and facilitate charge carrier separation.(Yaemsunthorn et al., 2024).

These results demonstrate that precursor molarity plays a crucial role in controlling the microstructure and photocatalytic activity of ZnO thin films. Both low and high molarity values can produce comparable photocatalytic performances when the deposition and annealing conditions are optimized, whereas intermediate molarity may lead to less favorable structural characteristics



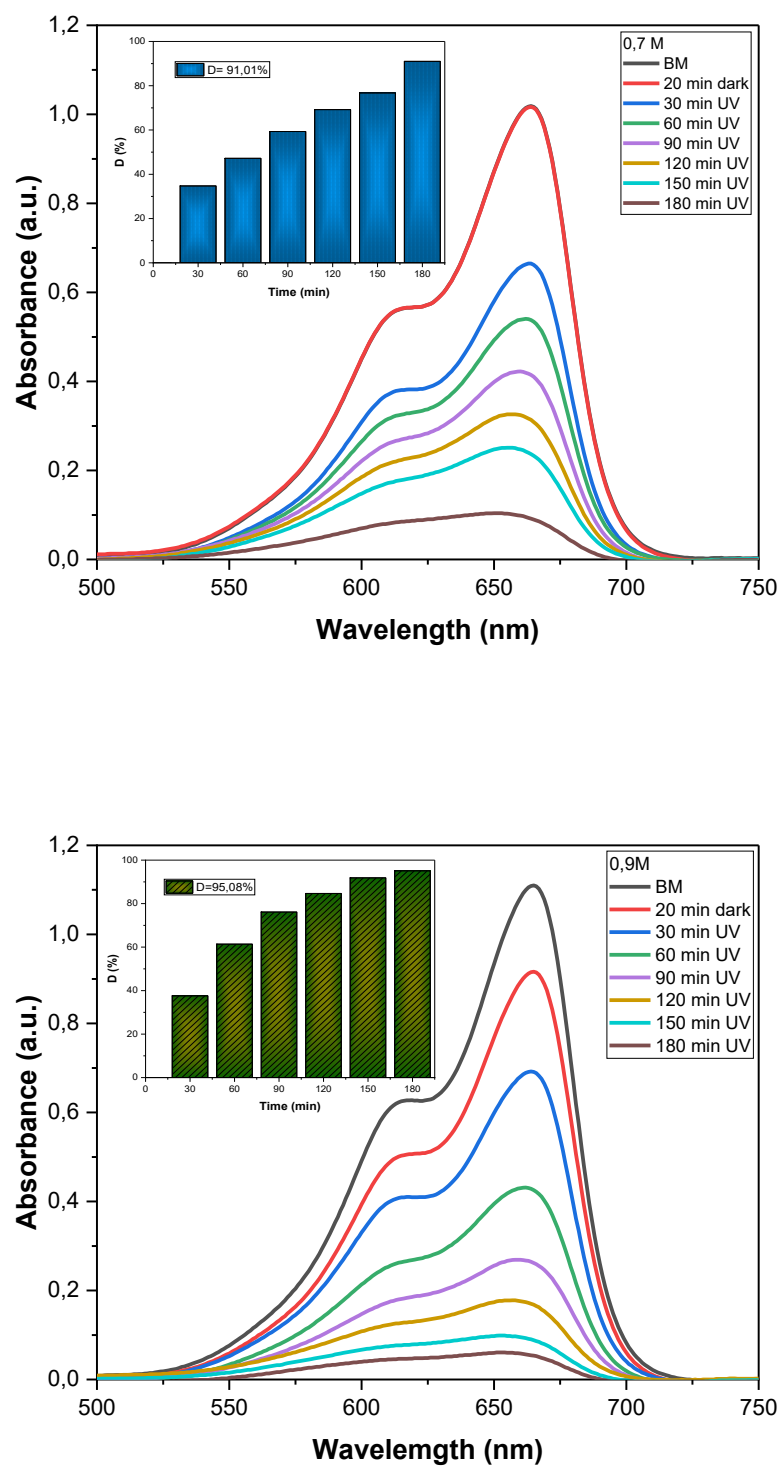


Figure III.3.1. (a) UV–visible absorbance spectra of methylene blue aqueous solution during photocatalytic degradation under UV irradiation using pure ZnO thin films prepared with different precursor molarities (0.4 M, 0.7 M, and 0.9 M), annealed at 400°C for 2 h; (b) corresponding photocatalytic degradation behavior as a function of irradiation time (inset).

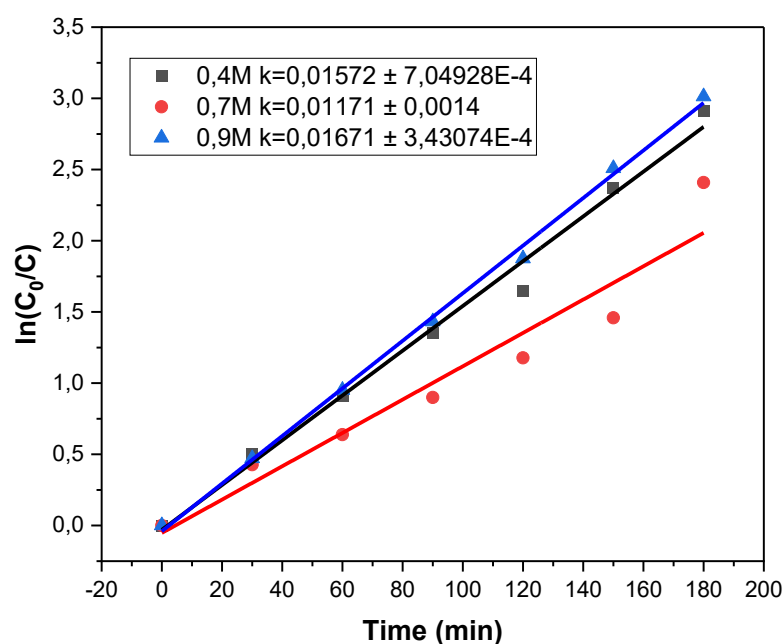


Figure III.3.2. Pseudo-first-order kinetic analysis of methylene blue photocatalytic degradation for pure ZnO thin films prepared with different precursor molarities (0.4 M, 0.7 M, and 0.9 M), expressed as $\ln(C_0/C_t)$ versus irradiation time.

The optimized values for the pure ZnO thin film deposition have been unambiguously determined from full optimization studies and are presented in Table III.1 below. These conditions produce the most optimal balance of photocatalytic activity for use as a non-doped control in all subsequent doping trials in this thesis.

Table III.1: Summary of Optimized Elaboration Parameters for Pure ZnO Thin Films

Sempales	Molarities (mol/l)	Number of cycles	Annealing	Degradation rate (%)	K (min ⁻¹)
Pure ZnO	0.4	8	500°C 1h	78.11%	0.0076
			500°C 2h	86.38%	0.0096
			400°C 2h	94.51%	0.016
Pure ZnO	0.4	1	400°C pour 2h	94.56%	0.016
		3		88.19%	0.011
		5		71.75%	0.006
		8		94.51%	0.016
		11		90.20%	0.03

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		14		91.77%	0.01
Pure ZnO	0.4	3	400°C pour 2h	94.56%	0.016
	0.7			91.01%	0.012
	0.9			95.08%	0.017

III. 3 Part ii: Enhancement via Doping of ZnO Thin Film

This section examines how dopant addition affects the photocatalytic performance of ZnO thin films. After determining the best preparation conditions for pure ZnO in Part I, different dopants are added to modify the material's structural and morphological properties, aiming to improve its photocatalytic efficiency. The approach involves adding non-metal elements that can alter the defect chemistry of ZnO and influence the generation, separation, and lifespan of photogenerated charge carriers.

Therefore, for the next doping studies, we fixed the parameters: 400°C for 2hours, 1 dip-coating cycle, and we selected 0.4M as the optimal precursor concentration of 0.4 M, although 0.9M gave slightly higher performance, the results are very close. Therefore, for practical reasons-material economy, ease of dissolution, and to avoid any precipitation or aging issues of the solution over time.

III. 3.1 Non-Metallic Doping

Based on the results obtained for pure ZnO thin films, the sample annealed at 400 °C for 2 h, prepared with one dip-coating cycle, and using a precursor concentration of 0.4 M, exhibited the most favorable photocatalytic performance. Therefore, these optimized parameters were selected as the reference synthesis conditions for the non-metal doping study in order to ensure a reliable comparison between doped and undoped samples.

All doped ZnO thin films were synthesized following the same sol–gel dip-coating method described in Chapter II, while maintaining identical deposition and annealing conditions (400 °C for 2 h and one coating cycle). The modification of the ZnO films was achieved by introducing two different non-metal dopant precursors into the sol solution, namely thiourea and urea.

Thiourea $\text{CH}_4\text{N}_2\text{S}$, was used as a sulfur, carbon, and nitrogen-containing precursor capable of introducing sulfur-related defect states within the ZnO lattice or at the surface. In contrast, urea $\text{CH}_4\text{N}_2\text{O}$ mainly acts as a nitrogen and carbon precursor and may also contribute to the formation of carbon-related surface species. The incorporation of these non-metal elements can modify the defect structure of ZnO and influence the efficiency of photogenerated charge carrier separation. The objective of this study is therefore to compare the influence of these two dopants on the photocatalytic activity of ZnO thin films under identical synthesis and irradiation conditions.

III. 3.1.1 Photocatalysis Application

The photocatalytic activity of the prepared thin films was evaluated through the degradation of methylene blue (MB) under UV–visible irradiation for 150 min. The degradation efficiency (D%) and the apparent pseudo-first-order kinetic constant (k) were used as indicators to assess the photocatalytic performance of the different samples.

For comparison purposes, the reference sample corresponds to pure ZnO prepared under the optimized conditions described previously. This sample exhibited a degradation efficiency of 90.94 % at 150 min of irradiation.

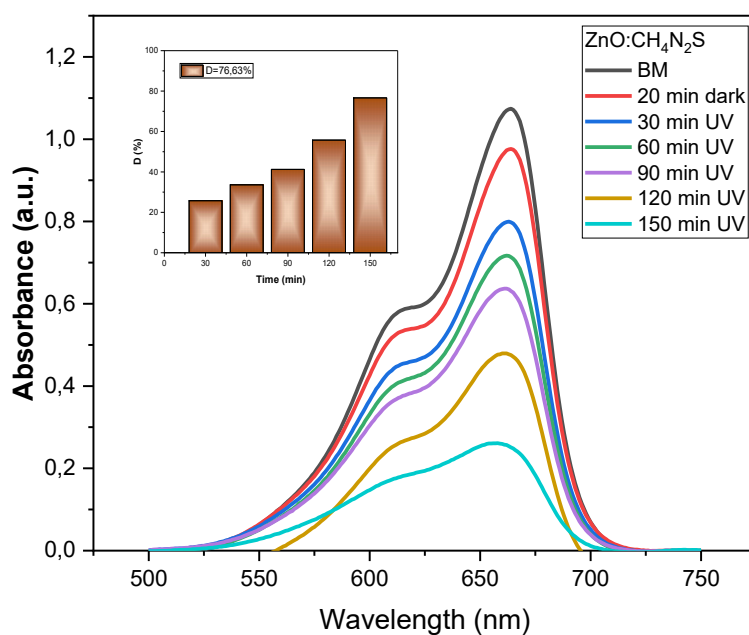
The photocatalytic results reveal that the two dopants affect the ZnO activity in significantly different ways. The thiourea-doped ZnO sample showed a noticeable decrease in photocatalytic performance, with a degradation efficiency of 76.63 % after 150 min of irradiation and a lower kinetic constant ($k = 0.00852 \text{ min}^{-1}$). This reduction in activity may be attributed to the excessive incorporation of sulfur-related species, which can act as recombination centers for photogenerated electron–hole pairs. Although sulfur doping has been reported to enhance light absorption in certain oxide semiconductors, uncontrolled incorporation may disturb the ZnO lattice and promote non-radiative recombination processes of the photogenerated charge carriers (Boasiako et al., 2023; X. Chen & Mao, 2007b; Xu & Schoonen, 2000). In addition, sulfur-containing residues may partially cover the surface-active sites of ZnO, thereby reducing dye adsorption and limiting the efficiency of surface redox reactions involved in the photocatalytic degradation process.

In contrast, the urea-doped ZnO thin film exhibited a significant improvement in photocatalytic activity, reaching a degradation efficiency of 98.90 % after 150 min of irradiation, accompanied by a higher kinetic constant of $k = 0.02633 \text{ min}^{-1}$. This enhancement suggests that urea incorporation leads to beneficial modifications in the defect structure and surface chemistry of ZnO. Urea is commonly associated with nitrogen doping, which may introduce shallow acceptor states or promote the formation of oxygen vacancies, both of which facilitate charge carrier separation and extend the lifetime of photogenerated electrons and holes (Asahi et al., 2001; Di Valentin et al., 2004; Wedemeyer et al., 2002). These defect states can act as electron trapping centers, suppressing electron–hole recombination and promoting the formation of reactive oxygen species such as $\bullet\text{OH}$ and $\bullet\text{O}_2^-$ radicals, which play a key role in the oxidative degradation of methylene blue molecules.

Overall, these results demonstrate that non-metal doping does not necessarily lead to a systematic improvement in photocatalytic performance. Instead, the photocatalytic behavior strongly depends on the nature of the dopant and its interaction with the ZnO host lattice. Under the present

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experimental conditions, thiourea doping proved detrimental to the photocatalytic activity, whereas urea doping significantly enhanced the degradation efficiency of ZnO thin films. These findings highlight the importance of carefully selecting dopant precursors and optimizing their incorporation in order to achieve an effective balance between defect generation and suppression of charge carrier recombination in ZnO-based photocatalysts.



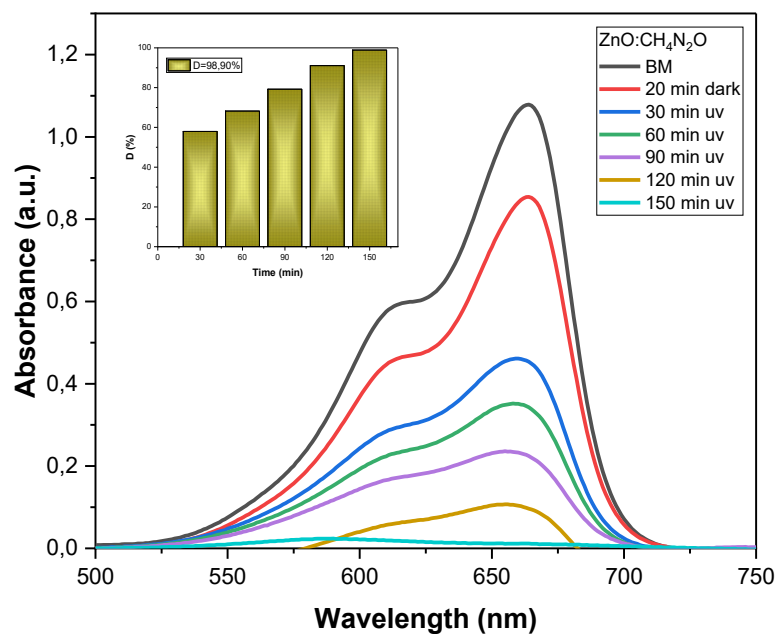


Figure III.4.1. (a) UV–visible absorbance spectra of methylene blue aqueous solution recorded during photocatalytic degradation under UV irradiation using pure ZnO, urea-doped ZnO, and thiourea-doped ZnO thin films (annealed at 400°C for 2 h); (b) corresponding photocatalytic degradation as a function of irradiation time (inset).

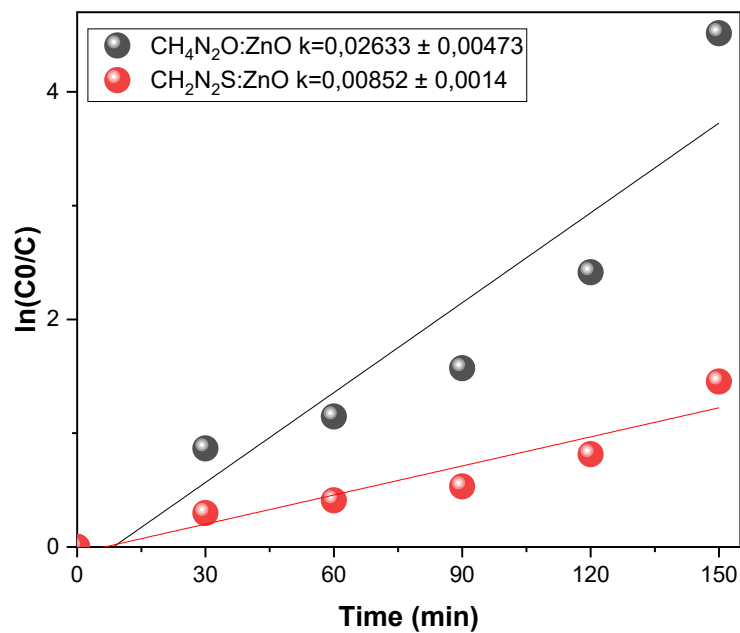


Figure III.4.2. Pseudo-first-order kinetic plots ($\ln(C_0/C_t)$ versus irradiation time) for methylene blue photocatalytic degradation using pure ZnO, urea-doped ZnO, and thiourea-doped ZnO thin films.

III.3.2 The effect of Ag-doped and Ag-Urea co-doping ZnO

Based on the results obtained in Part I, the optimized preparation conditions were selected for the synthesis of Ag-doped and Ag-urea co-doped ZnO thin films. These conditions correspond to an annealing temperature of 400 °C for 2 h, a precursor molarity of 0.4 M, and one dip-coating cycle, which previously showed the best photocatalytic performance. Furthermore, as discussed in the previous section of this chapter, urea was selected as a non-metal dopant (an organic compound because it contains carbon covalently bonded to other elements) because it significantly improved the photocatalytic activity of ZnO thin films. Therefore, these optimized parameters were adopted in this part in order to investigate the structural, morphological, optical, and photocatalytic properties of Ag-doped and Ag-urea co-doped ZnO thin films. The detailed experimental conditions used for the preparation of these samples are summarized in Table II. 1 in Chapter II.

III. 3.2.1 Structural analysis by X-ray diffraction

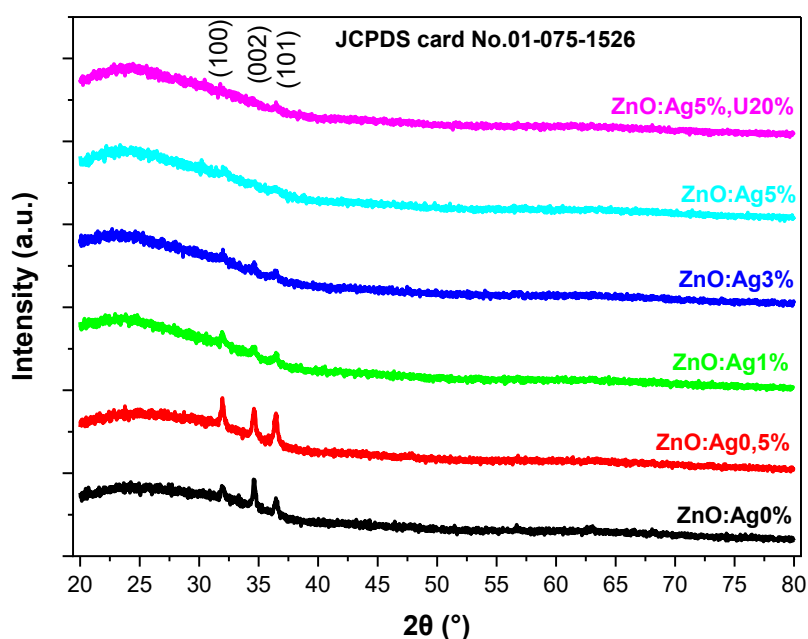


Figure III.5.1 X-ray diffraction (XRD) patterns of pure ZnO and Ag-doped ZnO thin films with different Ag concentrations (0%, 0.5%, 1%, 3%, and 5%), together with Ag/urea co-doped ZnO thin film.

The crystalline properties of dip-coated ZnO thin films on a glass substrate were investigated after the addition of different percentages of Ag (0%, 0.5%, 1%, 3%, and 5%) and a sample co-doped with 5% Ag + 20% U. These films were then heat-treated at 400°C for 2 hours to evaluate the effect of doping on crystallinity and lattice structure.

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The undoped (0%) and low-doping (1% and 3%) samples exhibited three main peaks at the Angular 2 θ planes, corresponding to the (100), (002), and (101) planes, based on JCPDS card number 01-055-1526. The 5% Ag sample also exhibited the three peaks, but with very low intensity, indicating decreased crystallinity and increased defects with increasing doping percentage. For the co-doped sample (5% Ag + 20% U), only one peak was observed at (101), which is why this peak was chosen for measuring crystallographic parameters such as crystal size and the distance between crystal planes.

The position of peak (101) was observed to be almost constant across all samples, indicating that the doping did not significantly alter the lattice dimensions. However, the peak width and intensity varied markedly with increasing doping, reflecting changes in crystallinity and the presence of new defects such as vacancies and lattice errors.

Figure III.5.1 shows the XRD curves for all samples, illustrating the evolution of peak intensity with increasing doping concentration. Table III.2 summarizes the baseline values for each sample, such as peak angular position, FWHM, and estimated crystal size, allowing for direct comparison between the different samples.

Table III.2 Structural parameters of pure and doped Ag thin films.

Sample	2 θ (°)	FWHM (°)	d(Å)	D (nm)	ϵ	$\delta \cdot 10^{-3}$
0%Ag:ZnO	36.58	0,37	2,45	23.62	0,27	1.79
0.5%Ag:ZnO	36.58	0,31	2,45	28.19	0,23	1.25
1%Ag:ZnO	36.58	0,25	2,45	34.96	0,19	0.81
3%Ag:ZnO	36.58	0.30	2,45	29.13	0.22	1.18
5%Ag:ZnO	36.58	0.70	2,45	12.48	0.53	6.42
5%Ag,20%U:ZnO	36.58	0.48	2,45	18.21	0.36	3.02

The full peak width at half height (FWHM) and crystal size (D) were calculated for all samples using peak (101), and the results are shown in Table III.2 and the XRD curves in Figure III.5.1. The XRD result for various samples distinctly demonstrates the crystallinity and lattice changes due to doping. The (101) peak observed at $2\theta = 36.58^\circ$ with interplanar spacing of $d = 2.45 \text{ \AA}$ exhibited a similar angular position for all samples, confirming that the doping did not affect the basic lattice dimensions significantly. In contrast, gradual decreases in the full width at half maximum (FWHM) of a XRD peak were observed for low-doped samples from 0.37° for a 0% sample to 0.25° for an extreme

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dopant concentration of just 1%, with increases in crystallite size and reductions in both microstrain (ϵ) and dislocation density (σ), clearly indicating increased crystallinity where lattice order is improved through moderate doping. At 3% Ag, crystallinity began to decrease slightly, with FWHM increasing to 0.30° and crystallite size decreasing to 29.13 nm, coupled with a minor increase in strain and defect density reflecting the initiation of the formation of crystallographic defects. Upon further increase to 5% Ag, another considerable structural deterioration is observed—FWHM of 0.70° and crystallite size of 12.48 nm were shown, while the strain and dislocation density were calculated as 0.53 and 6.42×10^{-2} , respectively, indicating these defects arise from significant crystallinity loss. Specifically, 0.48° and 18.21 nm of FWHM and crystallite size were found for a sample co-doped with Ag (5%) + U(20%), respectively, while strain and dislocation density were obtained as 0.36 and 3.02×10^{-2} , meaning that the synergistic effect of doping led to low crystallinity relative to moderate single doping but greater than high Ag doping only. Examination of the various structural characteristics presented here shows that moderate levels of doping lead to improved crystallinity and increased crystallite size, whereas high level or co-doping encourages defect generation and reduce lattice order, which in turn can profoundly affect both photocatalytic and photodetector performance within the ZnO thin films.

III. 3.2.2 FESEM-EDS elemental analysis

The surface morphology of the prepared films was investigated using scanning electron microscopy SEM, and the corresponding micrographs are presented in Figure III.5.2. The FESEM images show that the surface of the samples is mainly composed of quasi-spherical grains distributed over the substrate, forming a relatively continuous layer with some degree of particle agglomeration. Such spherical or nearly spherical morphologies are commonly observed in ZnO nanostructures prepared by chemical methods, where the nucleation and growth processes lead to the formation of nanostructured grains with different shapes depending on the synthesis conditions (Baruah & Dutta, 2009b). The presence of grain agglomeration may be attributed to the tendency of oxide nanoparticles to minimize their surface energy during the growth process (Klingshirn, 2007). In addition, the SEM micrographs of the Ag-doped samples reveal the appearance of brighter regions compared to the surrounding ZnO matrix. These bright spots may be associated with Ag-rich regions or small Ag clusters distributed on the surface of the ZnO grains. This contrast can be explained by the difference in the atomic number between silver ($Z = 47$) and the elements forming ZnO, namely zinc ($Z = 30$) and oxygen ($Z = 8$), which leads to stronger electron scattering and consequently higher brightness in SEM images. Similar observations have been reported in Ag-doped ZnO nanostructures, where silver particles appear as brighter regions in SEM micrographs due to their higher atomic number (Hosseini et al., 2015). For a quantitative evaluation of the microstructure, the average grain size was

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estimated from the SEM images using ImageJ software, and the obtained values are summarized in Table III.3. The undoped ZnO sample exhibits an average grain size of about 78.54 nm. After introducing a small amount of silver (0.5% Ag), the grain size decreases significantly to 48.29 nm, indicating that Ag incorporation affects the nucleation process and promotes the formation of smaller grains. A similar value of 50.90 nm is obtained for the 1% Ag-doped sample, confirming that low concentrations of Ag tend to inhibit grain growth. This behavior may be related to lattice distortions induced by the incorporation of Ag ions in the ZnO structure, which can increase the number of nucleation sites and limit the growth of crystallites (Saravanan et al., 2014). However, when the Ag concentration increases further, the grain size increases again to 71.55 nm and 77.49 nm for the 3% Ag and 5% Ag samples, respectively. This increase may be attributed to the agglomeration of grains and possible clustering of silver atoms, which favors the coalescence of adjacent crystallites and leads to larger particle formation. Interestingly, the sample containing 5% Ag with urea addition exhibits a reduced grain size of about 57.59 nm, suggesting that urea can act as a complexing or growth-controlling agent during the synthesis process, limiting excessive grain growth and promoting a more homogeneous microstructure. Overall, these observations indicate that both the Ag doping level and the presence of additives such as urea strongly influence the surface morphology and grain size distribution of ZnO thin films, which may subsequently affect their optical and photocatalytic properties.

Table III.3 The average grain size for 0% Ag, 0.5% Ag, 1% Ag, 3% Ag, 5% Ag doped ZnO and 5% Ag- 20% U co-doped

Samples	The average grain (nm)
0% Ag: ZnO	78.54
0.5% Ag: ZnO	48.29
1% Ag: ZnO	50.90
3% Ag: ZnO	71.55
5% Ag: ZnO	77.50
5% Ag +20%U: ZnO	57.60

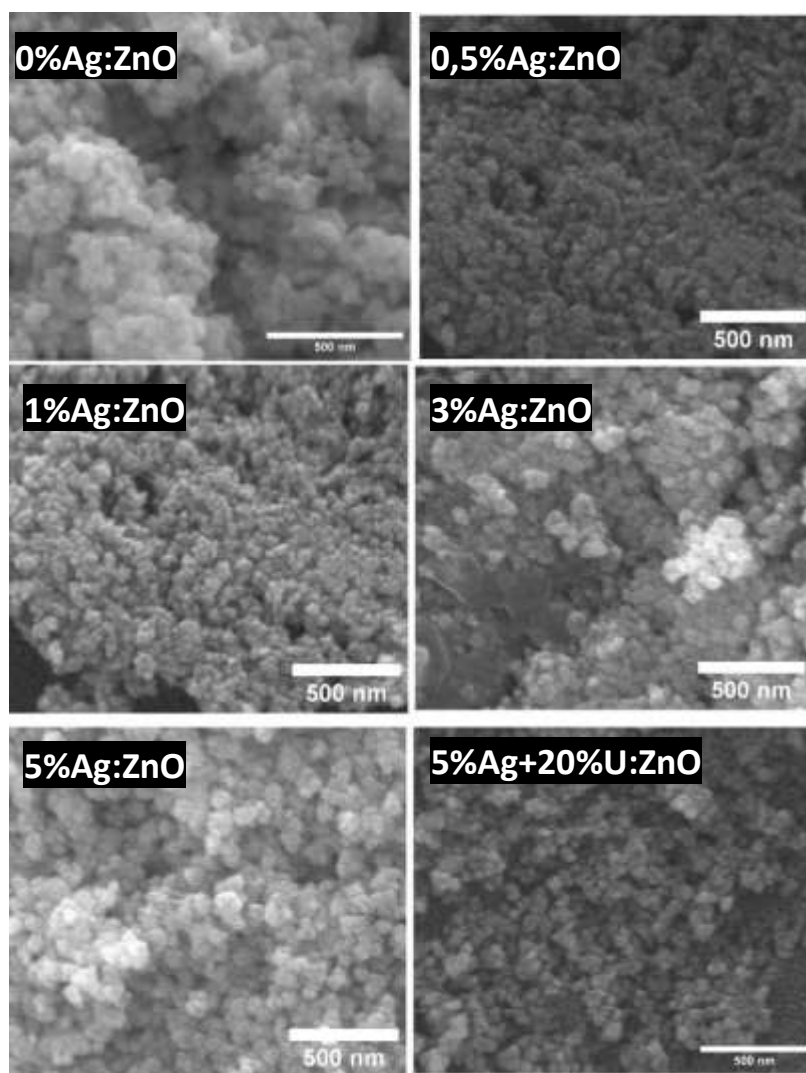


Figure III.5.2. SEM micrographs of 0%, 0.5%, 1%, 3%, 5%, 5%Ag+20%U doped ZnO thin film.

The elemental composition of the prepared samples was investigated using energy-dispersive X-ray spectroscopy (EDS), and the obtained spectra are presented in Figure III.4. The EDS results confirm the presence of Zn and O in all samples, indicating the successful formation of ZnO. For the undoped sample, only Zn and O peaks are observed, which is consistent with the expected stoichiometry of ZnO. For the sample containing 0.5% Ag, the EDS spectrum mainly shows the presence of Zn and O, while the Ag peak is not clearly detected. This can be attributed to the very low Ag concentration, which may fall below the detection limit of EDS or be homogeneously distributed within the ZnO matrix. However, when the Ag concentration increases to 1%, 3%, and 5%, the EDS spectra clearly reveal the presence of Ag peaks, confirming the successful incorporation of silver into the ZnO structure. In the case of the sample containing 5% Ag and 20% urea, the EDS spectrum shows the presence of Zn, O, Ag, and C elements. The appearance of carbon is attributed to the decomposition

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residues of urea used during the synthesis process, which may leave carbon-containing species on the surface of the material. On the other hand, the nitrogen signal is not detected in the EDS spectrum, which can be explained by the low atomic number of nitrogen and the limited sensitivity of EDS for light elements.

Overall, the EDS analysis confirms the successful incorporation of Ag into the ZnO matrix and supports the morphological observations obtained from the FESEM images.

Table III.4 Elemental composition (EDS analyses) of pure ZnO, Ag-doped ZnO, and A-urea co-doped ZnO thin films.

Samples	Element	Weight (%)	Atomic (%)
0% Ag:ZnO	O	70.13	90.56
	Zn	29.87	9.44
0.5% Ag:ZnO	O	81.55	94.75
	Zn	18.45	5.25
	Ag	00	00
1% Ag:ZnO	O	85.64	96.74
	Zn	10.06	2.78
	Ag	1.65	0.28
3% Ag:ZnO	O	39.64	73.20
	Zn	57.69	26.07
	Ag	2.67	0.73
5% Ag:ZnO	O	51.36	82.55
	Zn	40.75	16.03
	Ag	3.58	0.85
	Au	4.32	0.56
5% Ag+20%U:ZnO	O	77.86	80.65
	Zn	6.55	1.66
	Ag	0.96	0.15
	C	12.61	17.40
	N	00	00

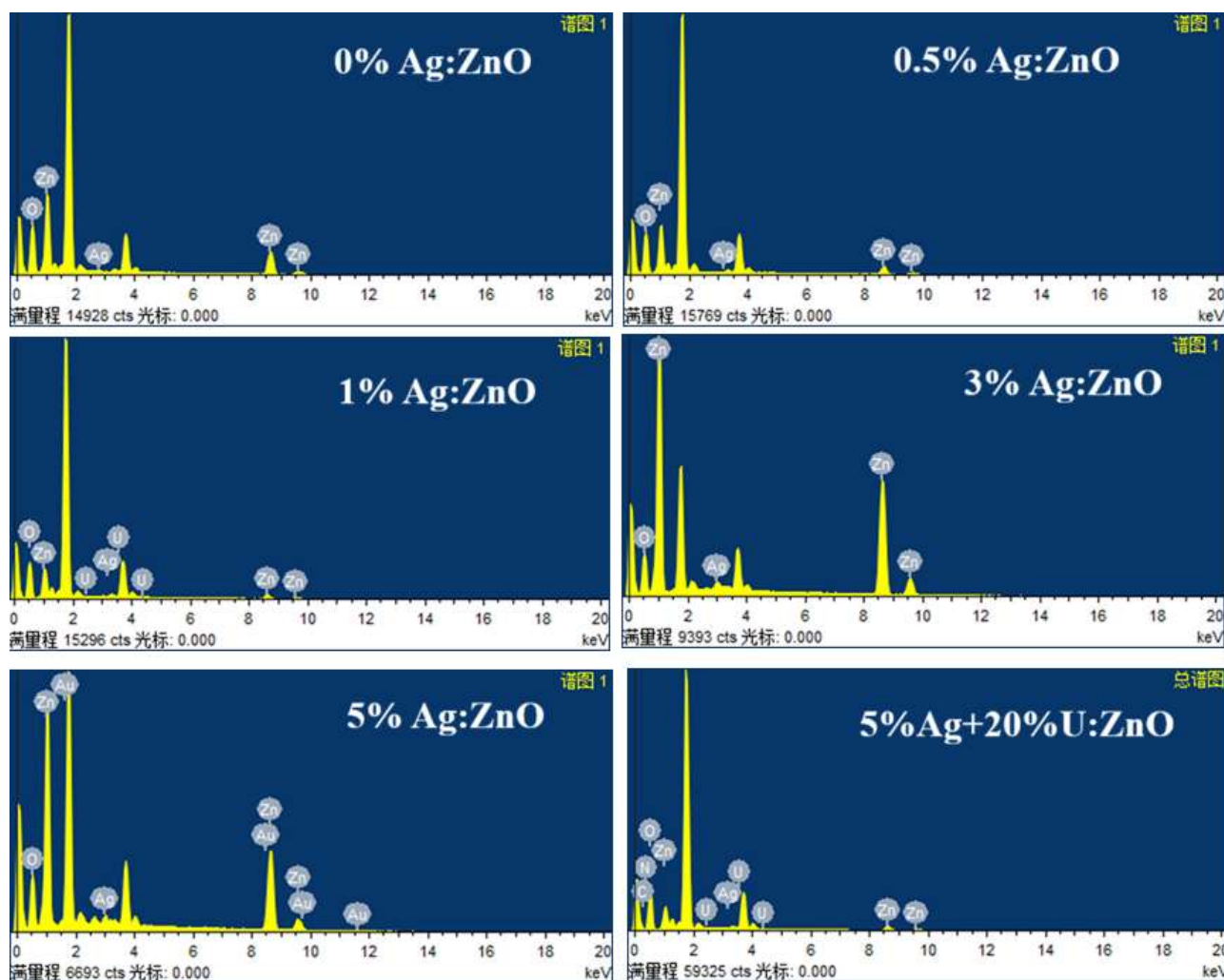


Figure III.5.3 EDS spectra of pure ZnO, Ag-doped ZnO thin films with different Ag concentrations (0.5 – 5%), and Ag-urea co-doped ZnO (5% Ag + 20% urea).

III. 3.2.3 Optical Transmittance and Band Gap Analysis

Figure III.5.4 (a) shows the optical transmittance spectra of ZnO thin films doped with different silver (Ag) concentrations and the Ag–urea co-doped sample. All samples exhibit a sharp absorption edge located in the near-UV region, around 370–400 nm, which is characteristic of ZnO and confirms its wide band gap semiconducting nature. The undoped ZnO thin film Ag 0%:ZnO presents the highest transmittance in the visible region, reaching values close to 90%, indicating good optical transparency. Upon Ag doping, a gradual decrease in transmittance is observed, with the Ag 5%:ZnO sample showing the lowest transparency among the mono-doped films. This behavior can be attributed to increased light scattering and absorption caused by the incorporation of Ag species, which may introduce additional localized states and increase structural disorder within the films. The Ag 5%-20%:ZnO co-doped sample exhibits the lowest transmittance across the entire spectral range. This pronounced reduction in transparency suggests a combined effect of metallic doping and organic

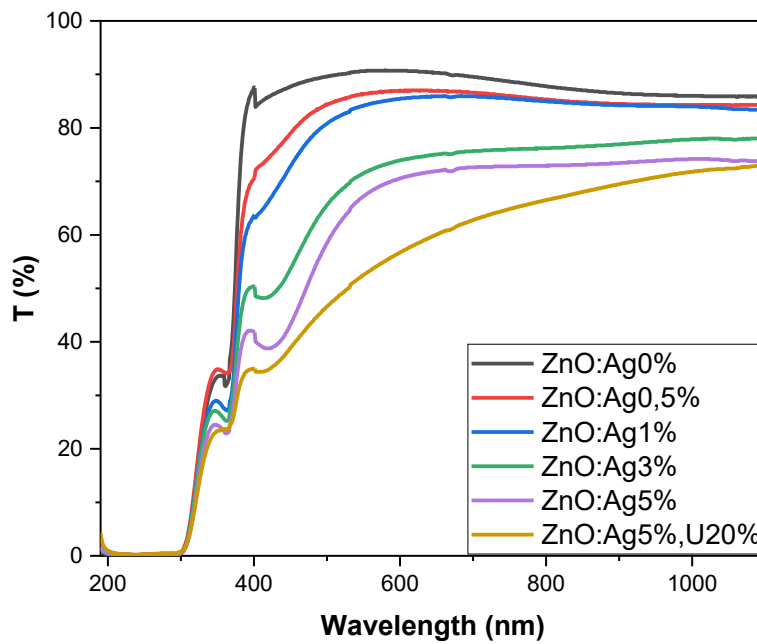
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modification, leading to enhanced optical absorption. Such behavior is generally favorable for photocatalytic applications, as it promotes improved light harvesting and increased generation of photogenerated charge carriers.

The optical band gap energy (E_{gap}) of the films was determined using the first derivative method by plotting $\frac{dT}{d(h\nu)}$ as a function of photon energy $h\nu$, as illustrated in Figure III.5.4 (b). The position of the maximum in the derivative curve corresponds to the optical band gap energy.

The extracted band gap values are found to be approximately 3.3 eV for all samples, regardless of the Ag or urea content. This result indicates that neither Ag doping nor Ag–urea co-doping significantly alters the intrinsic electronic band structure of ZnO. The invariance of E_{gap} suggests that the fundamental ZnO lattice remains preserved, and that the observed changes in optical transmittance are mainly related to defect states, disorder effects, and enhanced optical scattering rather than a true band gap narrowing.

Overall, the optical analysis confirms that doping primarily affects the light absorption behavior and optical density of ZnO thin films while maintaining their wide band gap, which is advantageous for UV-driven photocatalytic applications.



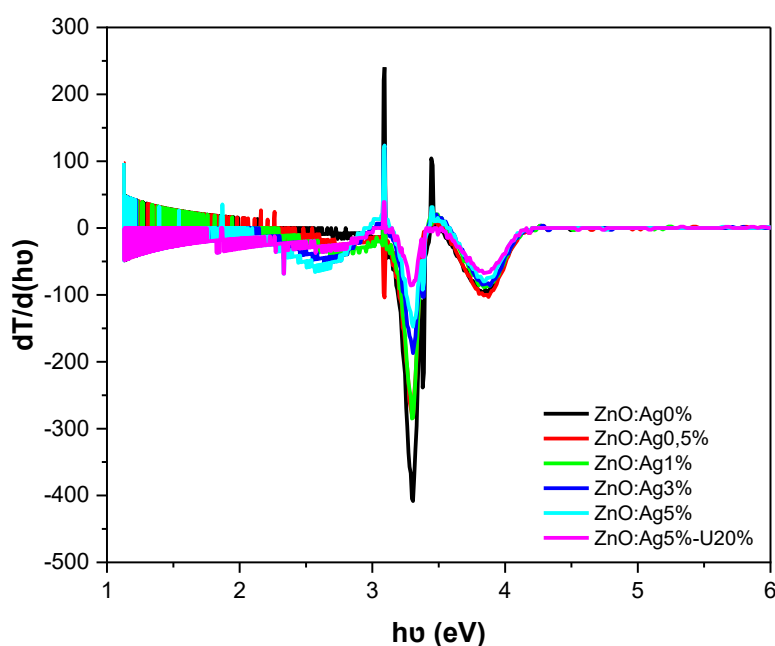


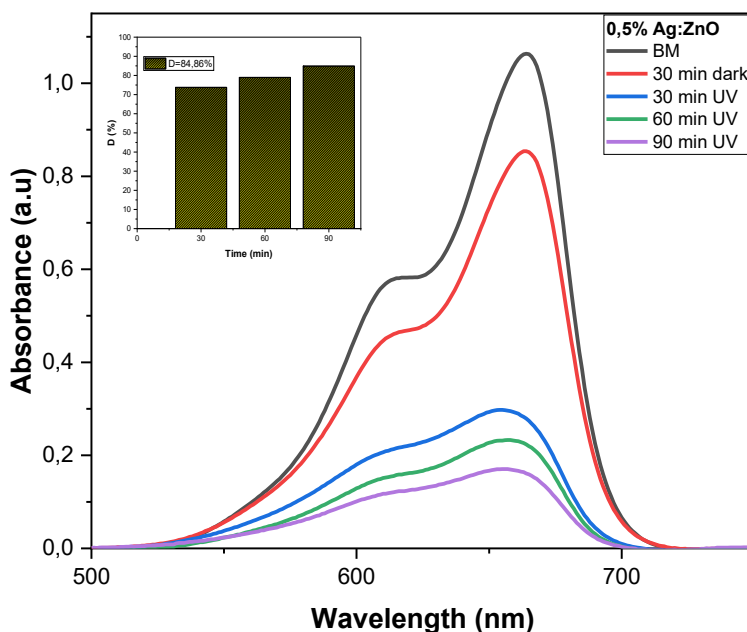
Figure III.5.4 (a) Optical transmittance spectra of pure ZnO, Ag-doped ZnO thin films with different Ag concentrations (0.5%, 1%, 3%, and 5%), and Ag/urea co-doped ZnO thin film (5% Ag, 20% urea); (b) corresponding first-derivative plots $dT/d(h\nu)$ used for the determination of the optical band gap energy.

III. 3.2.4 Photocatalytic Application

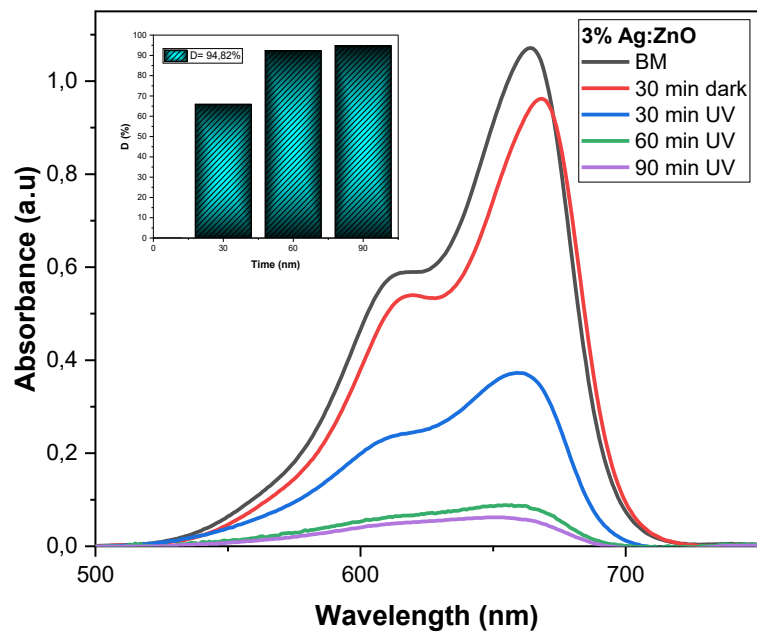
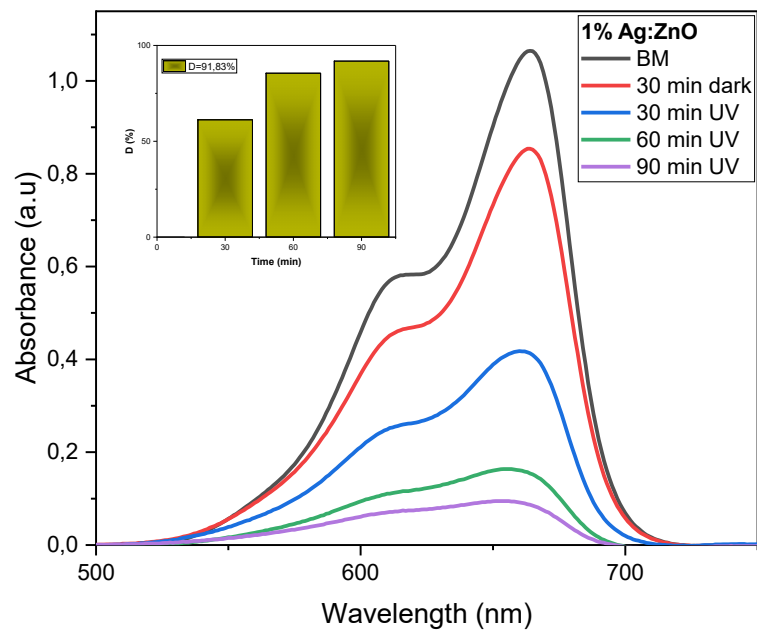
The photocatalytic performance of the prepared ZnO thin films was evaluated through the degradation of methylene blue (MB) solution under UV–visible irradiation. The degradation efficiency (D%) and the apparent reaction rate constant (k) were calculated in order to compare the activity of pure ZnO, Ag-doped ZnO, and Ag/urea co-doped ZnO thin films. The obtained results show in Figure 3 that the photocatalytic activity strongly depends on the doping level. The pure ZnO thin film exhibited a degradation efficiency of 74.9% after 90 min of irradiation with a rate constant $k = 0.01483 \text{ min}^{-1}$. After introducing a small amount of Ag, the photocatalytic activity increased noticeably. The degradation efficiency reached 84.86% for 0.5% Ag-doped ZnO with a rate constant of 0.01962 min^{-1} , indicating that the presence of Ag species promotes the photocatalytic reaction. A further increase in Ag concentration to 1% and 3% resulted in a significant enhancement of the degradation efficiency, reaching 91.83% and 94.82%, respectively. The corresponding rate constants also increased, reaching 0.02834 min^{-1} and 0.0346 min^{-1} . This improvement can be attributed to the role of Ag nanoparticles acting as electron traps that facilitate the separation of photogenerated electron–hole pairs, thereby reducing their recombination probability. Such behavior has been widely reported

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in Ag-doped ZnO photocatalysts, where metallic Ag acts as an electron sink and enhances interfacial charge transfer processes (Zhu et al., 2021). When the Ag content increased to 5%, the degradation efficiency slightly improved to 95.52%, while the rate constant decreased slightly to 0.02925 min^{-1} compared to the 3% sample. This slight reduction in the reaction rate may be related to excessive Ag loading, which can partially cover the active surface of ZnO and reduce the available photocatalytic sites (Pelaez et al., 2012). The best photocatalytic performance was obtained for the Ag (5%) + Urea (20%) co-doped ZnO thin film. In this case, the degradation efficiency reached 99.84% within 90 min, with a significantly higher rate constant $k = 0.06935 \text{ min}^{-1}$. The remarkable improvement observed in the co-doped sample can be attributed to the synergistic effect between metallic Ag and urea-derived nitrogen-related defects. While Ag facilitates electron trapping and transfer, the incorporation of nitrogen-related species may create additional defect states or oxygen vacancies that enhance charge separation and increase the lifetime of photogenerated carriers [30, 31, 32]. Overall, these results demonstrate that both the nature and the concentration of dopants play a crucial role in determining the photocatalytic efficiency of ZnO thin films. The combination of Ag and urea provides a favorable balance between improved light absorption, efficient charge separation, and increased surface reactivity, which ultimately leads to superior photocatalytic performance.



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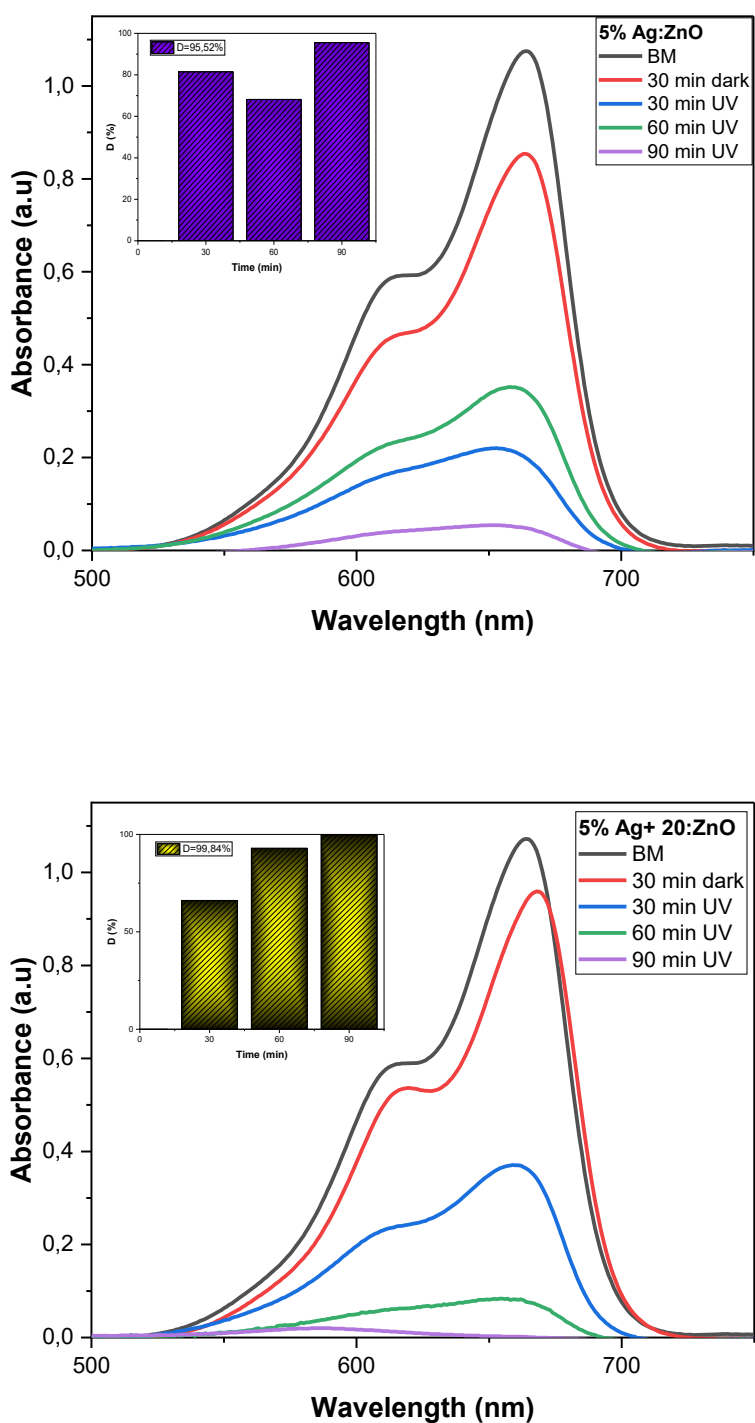


Figure III.5.5 (a) UV–visible absorbance spectra of methylene blue aqueous solution recorded during photocatalytic degradation under UV irradiation using 0.5%, 1%, 3%, and 5% Ag doped ZnO and 5% Ag-20% urea co- doped ZnO thin films; (b) corresponding photocatalytic degradation of methylene blue as a function of irradiation time (inset).

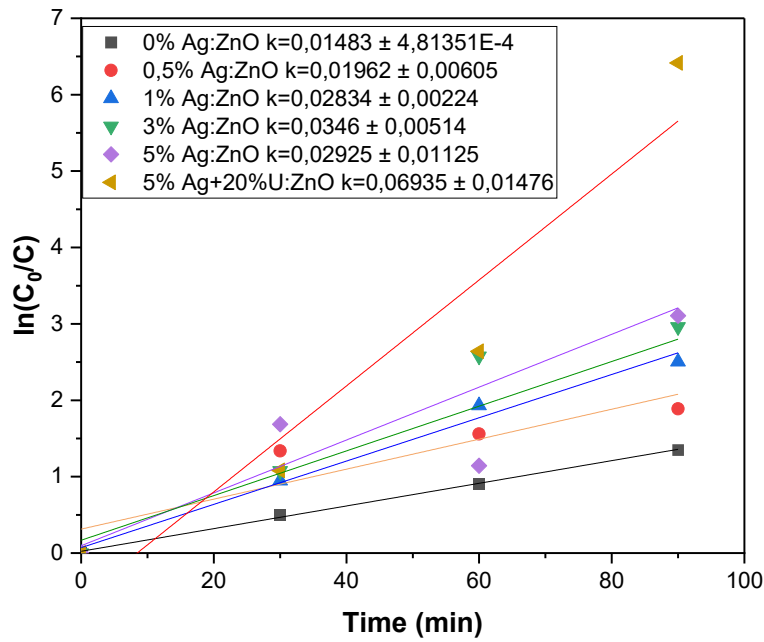
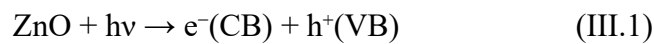


Figure III.5.6 Pseudo-first-order kinetic plots of methylene blue photocatalytic degradation, expressed as $\ln(C_0/C_t)$ versus irradiation time, 0.5%, 1%, 3%, and 5% Ag-doped ZnO and 5% Ag-20% urea co-doped ZnO thin films.

III .3.2.5 Photocatalytic Mechanism

The photocatalytic degradation of methylene blue using ZnO-based thin films occurs through a series of photo-induced redox reactions that take place at the semiconductor surface. ZnO is a wide band gap semiconductor (≈ 3.3 eV) that can be activated under UV irradiation to generate electron-hole pairs (Özgür et al., 2005b). When the ZnO photocatalyst is exposed to UV-visible light with energy equal to or greater than its band gap, electrons in the valence band (VB) are excited to the conduction band (CB), leaving positive holes in the valence band:

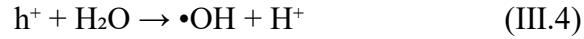


The photogenerated electrons and holes then migrate to the surface of the photocatalyst, where they participate in redox reactions with adsorbed species. The photogenerated electrons react with dissolved oxygen molecules to form superoxide radicals ($\bullet\text{O}_2^-$):



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Meanwhile, the photogenerated holes oxidize water molecules or hydroxide ions to produce hydroxyl radicals ($\bullet\text{OH}$):



Both hydroxyl radicals and superoxide radicals are highly reactive oxidizing species capable of decomposing organic pollutants such as methylene blue into smaller and less harmful molecules, eventually leading to mineralization into CO_2 and H_2O (D. Chen & Ray, 1998; Özgür et al., 2005b).

In Ag-doped ZnO systems, metallic Ag nanoparticles deposited on the ZnO surface play an important role in improving photocatalytic efficiency. Due to the difference in work function between Ag and ZnO, a Schottky junction is formed at the interface, allowing photogenerated electrons to transfer from ZnO to Ag. This process effectively suppresses electron–hole recombination and prolongs the lifetime of charge carriers, thereby enhancing photocatalytic activity (Ameta et al., 2012).

In the case of Ag/urea co-doped ZnO, the improvement is even more pronounced due to the combined effects of metallic and non-metallic modification. Nitrogen and carbon-related species originating from urea decomposition can introduce defect levels within the ZnO lattice or promote the formation of oxygen vacancies. These defects can act as trapping centers for charge carriers and facilitate their separation, further increasing the generation of reactive oxygen species (Istiroyah et al., 2023).

Consequently, the synergistic interaction between Ag nanoparticles and urea-derived defects enhances the overall photocatalytic performance by improving light utilization, suppressing charge recombination, and increasing the density of reactive radicals responsible for pollutant degradation.

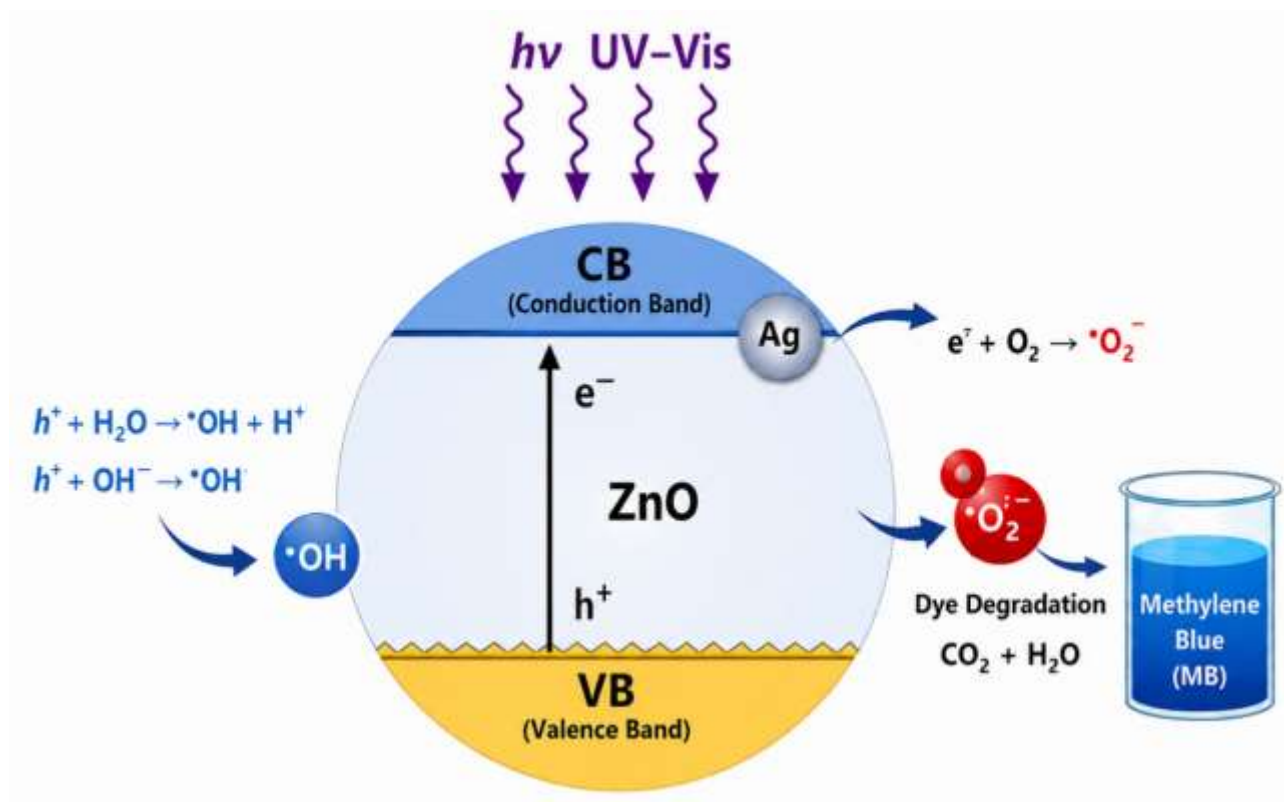


Figure III.5.7 Photocatalytic mechanism for methylene blue degradation using Ag/urea co-doped ZnO thin films under UV-visible irradiation.

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Chapter IV

UV Photodetector Based on Ag-Doped ZnO Thin Films

IV.1 Introduction

The fourth chapter of this thesis discusses the results and detailed analysis of the UV photodetector fabricated using the Ag-doped ZnO thin films deposited on silicon substrates. This work investigates the structural effect of Ag doping on photoresponse characteristics under UV exposure. Their electrical performance was studied in the dark and under UV light illumination to analyze the ability of the devices to generate photocurrent, sensitivities, responsivities, and response–recovery dynamics. Special emphasis is placed on the effects of doping, including changes in charge-carrier transport, defect density, and interfacial effects at metal–semiconductor interfaces. A full analysis is carried out to relate the structural, morphological, and optical properties of these structures presented in the previous chapters with the reported performance on photodetection. The photoresponse mechanism is also analyzed to explain the role of carrier generation/trapping and surface states in the efficiency of the devices. The experimental methods used for film deposition and device processing are described in Chapter 2.

IV.2 Structural Characterization

IV.2.1 XRD Analysis

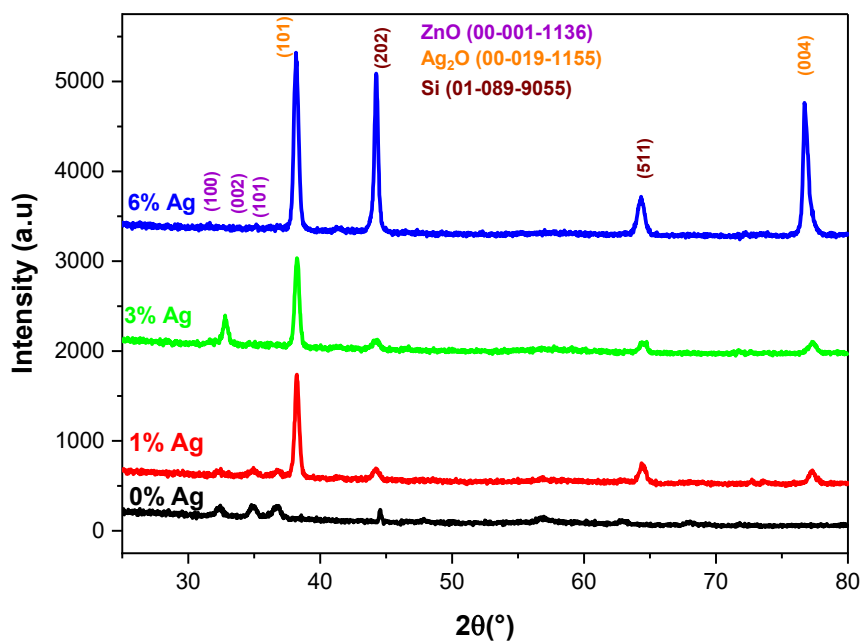


Figure IV.1. X-ray diffraction (XRD) patterns of pure and Ag-doped ZnO thin films with Ag concentrations of 0%, 1%, 3%, and 6%.

Chapter IV: UV Photodetector Based on Ag-Doped ZnO Thin Films

The measurements of dip-coating ZnO thin films on Si with different doping concentrations of 0, 1, 3, and 6% Ag, to study the effects of Ag incorporation on crystallinity and phase composition (Figure IV.1). displays the diffraction patterns of four samples prepared as well as the corresponding peak positions for each phase, which were assigned based on reference cards from JCPDS: ZnO (00-001-1136), Ag₂O (00-019-1155), and Si substrate (01-089-9055).

Undoped ZnO exhibits clear diffraction peaks at the (100), (002), and (101) planes of a hexagonal wurtzite structure, demonstrating that the films are polycrystalline with no preferential single-axis orientation. The comparable intensities of the (100) and (002) reflections indicate competitive growth along multiple crystallographic directions rather than a strong c-axis texture. As expected, peaks (202) and (511) associated with the Si substrate are also observed.

After doping with 1% Ag, new peaks corresponding to Ag₂O appeared at (101) and (004), higher in intensity than the ZnO peaks, signifying secondary phase formation. As there is a minor shift of the peak position observed, wherein the (100) reflection shifts from $2\theta = 32.34^\circ$ (0% Ag) to 32.27° (1%Ag). According to Bragg's law: $2d\sin\theta = n\lambda$, decreasing the diffraction angle increases the interplanar distance. In fact, the calculated d-spacing is still around 2.77 Å but indicates a slight expansion of the lattice, coupled with a minor variation of the lattice parameter *a* from 3.19 Å to 3.20 Å; this behavior is 1% Ag. Behavior can be explained by partial replacement of Zn²⁺ ions by Ag⁺ ones, whose greater ionic radius causes local dilation of the lattice. The value of full width at half maximum (FWHM) increases from 0.59° to 0.67° at this concentration, resulting in a corresponding decrease in the crystallite size calculated with the Debye–Scherrer equation from 14.64 nm to 12.89 nm. At the same time, a certain increase in microstrain (ϵ) from 0.34 to 0.57 and dislocation density is shown here, which shows that with low doping levels, there are more defects and lattice distortion emergence.

In contrast, a different structural behavior is seen with 3% Ag. The (100) peak is markedly shifted towards higher diffraction angles ($2\theta = 32.75^\circ$), which correlates to the reduction of d-spacing down to 2.73 Å and lattice parameter *a* down to 3.15 Å, offering evidence for increased compressive strain inside the ZnO matrix, where lattice contraction occurs as well, as evidenced by a shift towards higher angles. This contraction indicates that, at small doping levels and beyond simple substitutional incorporation, strain effects and structural reorganization play a larger role. Befittingly, the FWHM drops drastically to 0.40° with a consequent increase in crystallite size to 21.62 nm. At the same time, the microstrain decreases to a value of 0.34, and the dislocation density drops down even proportionally (by 2.21×10^{-3} GPa), which indicates that the structural relaxation has already occurred, thus leading to much more crystalline material at this intermediate doping level. These

Chapter IV: UV Photodetector Based on Ag-Doped ZnO Thin Films

results suggest a non-linear structural evolution, which begins with the defect-dominant regime (1% Ag) and progresses to lattice reorganization and grain coarsening (3% Ag).

For the film with 6 % Ag doping, it can be noted that no ZnO diffraction peaks are observed. Instead, we observe reflections solely corresponding to Ag₂O and the Si substrate. As the peaks associated with ZnO peaks become weak due to thickness and secondary phase dominance, we conclude that the Ag solubility limit in ZnO is achieved, and beyond this point, segregation occurs where ZnO phase crystallinity is suppressed. Thus, no distinctive reflections from ZnO were observed in this sample, and the lattice parameters, crystallite size, and strain could not be obtained.

Table IV.1 represents the variation of structural parameters, like 2θ and FWHM interplanar spacing d , lattice parameter a , crystallite size D , microstrain ϵ , and dislocation density σ , respectively, with respect to Ag concentration. In summary, this structural analysis discloses that Ag doping leads to a two-stage structure evolution in ZnO thin films: At low doping concentration levels, lattice expansion and defect formation occur; high doping content beyond the critical value introduces the shift from lattice contraction to strain relaxation, grain growth, and, finally, the phenomenon of phase transformation. The strong impact of Ag incorporation on lattice distortion, defect density, crystallinity, and phase stability of ZnO thin films is evidenced by this progression of structural evolution.

Table IV.1 Structural parameters of pure and doped Ag thin films.

Sample	phase	Peak (hkl)	2θ (°)	FWHM (°)	$d(\text{\AA})$	$a(\text{\AA})$	D (nm)	ϵ	$\delta \cdot 10^{-3}$ (nm ⁻¹)
0%Ag:ZnO	ZnO	100	32.34	0,59	2,77	3.19	14.64	0,34	4.66
1%Ag:ZnO	ZnO	100	32.27	0,67	2,77	3.2	12.89	0,57	6.01
3%Ag:ZnO	ZnO	100	32,75	0,40	2,73	3.15	21,62	0,34	2,21
6%Ag:ZnO	Ag ₂ O	-	-	-	-	-	-	-	-

IV.2.2 ATR-FTIR Analysis

Figure IV.2 shows a series of ATR-FTIR spectra. The positions and intensities of the absorption peaks for Ag-doped ZnO samples with different silver contents 0%, 1%, 3%, and 6%, reveal important details of molecular interactions, bond vibrations, etc., as well as structural changes when introducing silver into the ZnO lattice. Spectra were recorded from 4000 to 400 cm⁻¹ with the Y-axis denoting normalized absorbance. There are clear differences in the vibrational modes related to the ZnO lattice and potential forms of silver oxide (Ag₂O) phases.

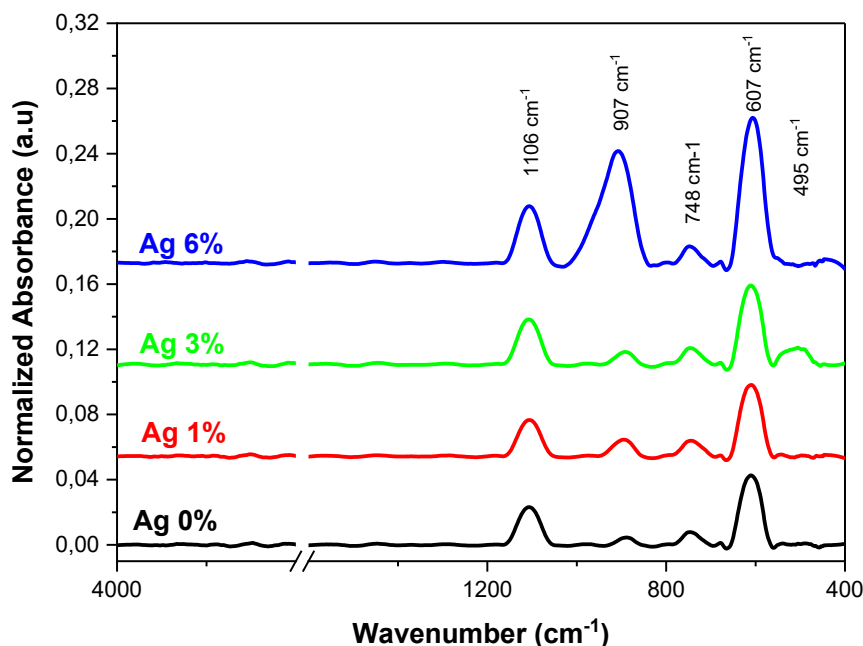


Figure IV.2 ATR-FTIR spectra of pure and Ag-doped ZnO thin films with different Ag contents (0%, 1%, 3%, and 6%).

A vibrational band located at approximately 495 cm^{-1} is observed exclusively in the 3% and 6% Ag-doped samples, while it is absent in pure and 1% Ag films. This band may be due to either the altered Zn–O stretching vibrations or Ag–O-related modes from lattice distortion upon doping. The emergence of this peak at intermediate doping concentration further attests to the feature that Ag incorporation modifies the local bonding environment in the ZnO matrix. The low 6% peak relative to the 3% one indicates a partial structural reorganization or dopant saturation at high concentration.

A strong band at $\sim 607\text{ cm}^{-1}$ is seen in all the samples and corresponds to Zn–O stretching vibrations of the wurtzite ZnO structure. In fact, its greater intensity at 6% Ag suggests more vibrational activity or local structural rearrangement due to higher dopant concentration.

The band at $\sim 748\text{ cm}^{-1}$ persists for all the samples with little deviation, indicating that the underlying fundamental ZnO lattice structure is retained as Ag is incorporated.

A band at $\sim 907\text{ cm}^{-1}$ increases in intensity with increasing Ag content, becoming most prominent at 6% doping. This phenomenon might be associated with a defect-mediated vibrational modes or the distribution of Zn–O stretching from an asymmetric lattice distortion. This evolving intensity with

Chapter IV: UV Photodetector Based on Ag-Doped ZnO Thin Films

systematic increase indicates that Ag doping aids the formation of further defects and localized structural disturbances.

Lastly, the band found at $\sim 1106\text{ cm}^{-1}$, which was detected with moderate intensity in all films, can be attributed to residual surface species or a hydroxyl-related vibration. This relative stability across samples suggests that it is not directly regulated by Ag incorporation.

Hence, FTIR analysis is well-supported by the measurement of XRD and provides a detailed insight into phase transitions and lattice distortion as well as molecular interactions upon doping silver in the ZnO matrix. The results are important for the design of the Ag-ZnO nanostructures with tailored properties since they are applied for optoelectronic application, sensors, and optoelectronic devices.

IV.3 Surface Morphology and Thickness Evaluation

This study systematically characterized the surface morphology and thickness of pure and silver-doped zinc oxide thin films to investigate the nanoscale and physical properties of these films subjected to silver addition. Surface topography and roughness were analyzed in detail by atomic force microscopy (AFM), and film thickness determination was done based on the surface topography measurements. The combined approach gives a better insight into the correlation between doping concentration, surface morphology, and film growth mechanisms in zinc oxide thin films.

IV.3.1 Surface Morphology Analysis (AFM)

The AFM images in Figure IV.3 show that pure ZnO films have a relatively smooth surface, with nanostructures observed uniformly, indicating uniform nucleation and controlled growth throughout the deposition process. Ag doping induces drastic changes in surface morphology that are strongly dependent on dopant concentration.

With a lower Ag content 1%, the surface appears significantly more textured, with more surface features, which could increase the surface area and active sites, thus exerting an influence on the following optical and electronic properties.

At intermediate doping levels 3% Ag, partial reorganization of the nanostructures is observed. The surface becomes less rough than at 1% Ag, suggesting coalescence of some nucleated grains and redistribution of Ag atoms within the ZnO lattice. At the most highly doped sample 6% Ag, the surface becomes more stable and reflected, suggesting that an excessive incorporation of dopant into a lattice increases the homogeneity of its structure by favoring the mobility of adatoms and accommodation in lattices. As listed in Table IV.2, the surface roughness parameters Ra and RMS

Chapter IV: UV Photodetector Based on Ag-Doped ZnO Thin Films

were estimated from AFM images using the Gwyddion software, show a non-monotonic dependence on the amount of Ag introduced. The values of Ra change rapidly from 1.994 nm for pure ZnO to 8.142 nm at 1% Ag, indicating early growth of surface texture owing to extra nucleation sites. Following this trend, Ra drops to 6.142 nm and 4.419 nm for the 3% and 6% Ag materials, respectively, suggesting surface reorganization and a partial smoothing effect at the higher dopant levels. The pattern of the RMS values is similar and externalizes surface roughness modulation by Ag doping, revealing that dopant concentration/nanostructural evolution are interlinked.

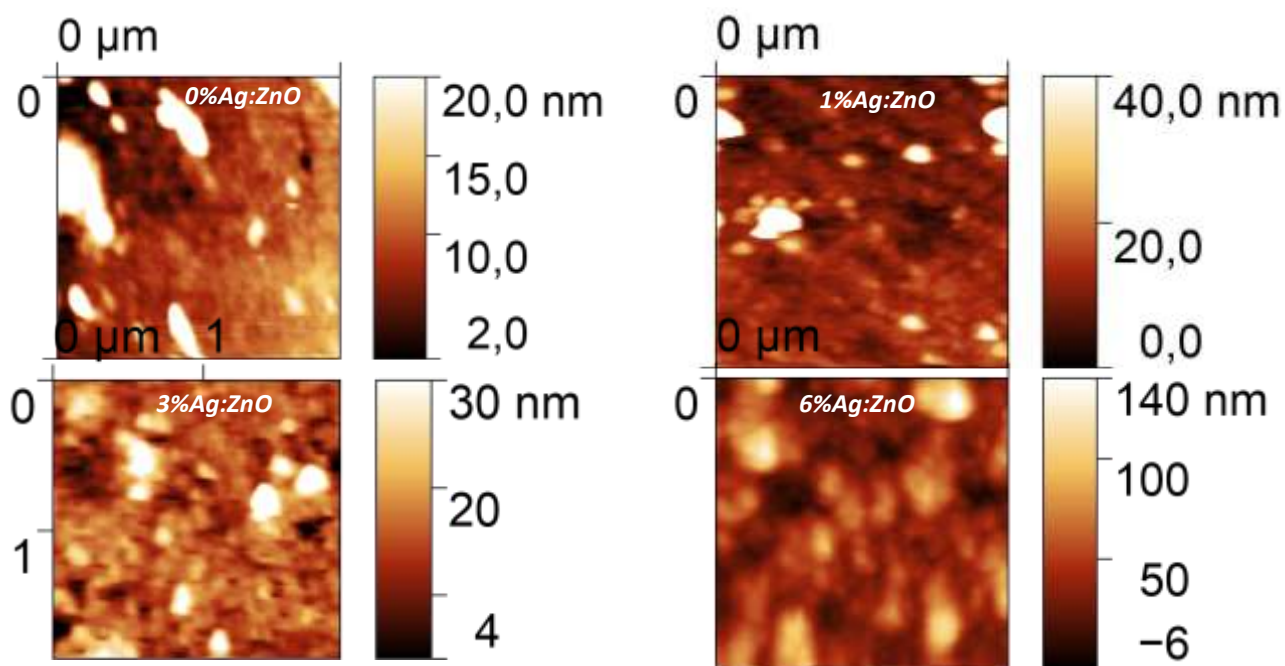


Figure IV.3 AFM surface topography images of pure and (0%, 1%, 3%, and 6% Ag).-doped ZnO thin films.

The AFM analysis demonstrates that the surface morphology is strongly influenced by Ag doping. Initial doping increases surface roughness by creating additional nucleation sites, whereas higher doping levels induce reorganization and smoothing, suggesting that dopant incorporation governs adatom mobility and lattice accommodation during film growth.

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Table IV.2: Surface roughness (Ra, RMS) and thickness values of pure and Ag-doped ZnO thin films.

Sample	Ra (nm)	RM _s (nm)	Thickness (nm)
0% Ag:ZnO	1.94	2.49	45
1% Ag:ZnO	8.14	10.30	81
3% Ag:ZnO	6.31	7.30	125
6% Ag:ZnO	4.42	5.65	152.5

IV.3.2 Thickness Measurement (Profilometer)

Profile measurements show that the film thickness increased gradually with higher levels of Ag, suggesting a growth from 45 nm for pure ZnO to 81 nm for 1%, 125 nm for 3%, and finally right up to 122.5 nm for a 6% Ag-doped film as presented in Table IV.2. This gradual increase indicates that the incorporation of Ag increases the nucleation density and facilitates vertical growth in the deposition process. Dopant incorporation affects adatom mobility and surface energy, which may be related to the increase in thickness. The films are still relatively thin (≤ 160 nm), which confirms the nanometrical nature of deposited layers and thus also suggests that the growth process is well controlled. These thickness values are relevant for optoelectronic applications, in particular UV photodetector devices, where thickness control is critical for carrier transport and light harvesting.

IV.3.3 Raman Analysis

Raman spectroscopy was used to study the vibrational properties and lattice dynamics of undoped and Ag-doped ZnO thin films. All sample spectra are shown in Figure IV.4. All samples show a prominent and sharp Raman peak at around 520 cm^{-1} that relates to the first-order optical phonon mode of the crystalline Si substrate. This peak is relatively strong in intensity due to the small thickness of the deposited films (≤ 160 nm), which allows for excitation laser penetration through the ZnO layer and lower Si wafer interaction. This finding supports the nanometric thickness of the films obtained from profilometry measurements. Besides the substrate-related contribution, very weak and broad spectral features appear in the high wavenumber range.

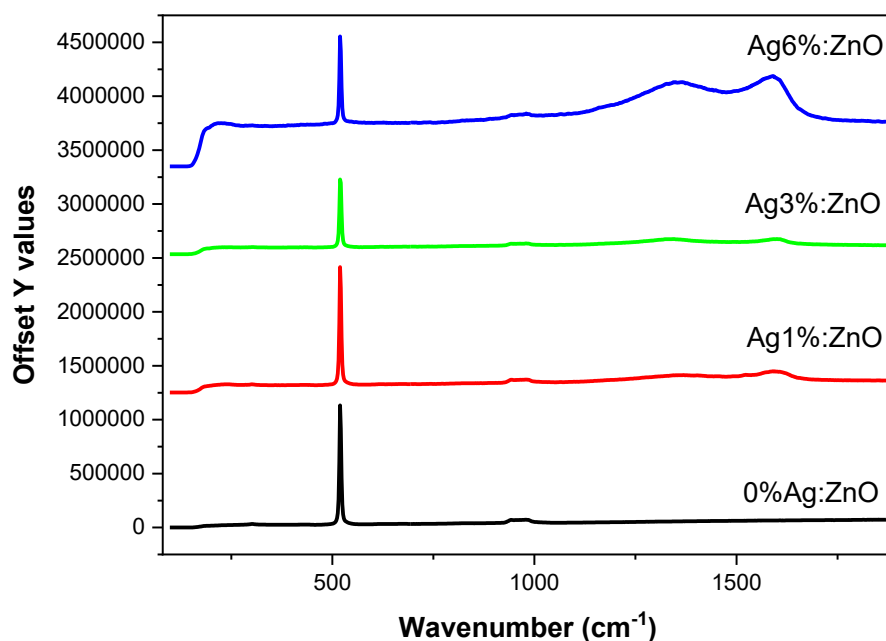


Figure IV.4 Raman spectra of Ag-doped ZnO thin films (0%, 1%, 3%, and 6% Ag), illustrating the vibrational modes and the effect of Ag incorporation.

A comparison of band intensities (peak to peak) shows bands (b, d, f) are much smaller than the Si peak, implying that, due to substrate signal growth, we likely do not get all responses from the ZnO layer. Furthermore, the lack of any additional sharp peaks attributable to secondary phases further indicates that Ag incorporation does not lead to detectable crystalline impurities in the Raman system (below detection limits). As a final note, the addition of Ag leads to minor changes in background and peak intensities in the spectra, suggesting small perturbations (in terms of concentration) from their local lattice surroundings. There are reasons for these changes: dopant-induced lattice distortion, local strain effects, and defect formation, which may affect phonon confinement and vibrational dynamics inside the ZnO matrix. Overall, the Raman results confirm that, after Ag doping, the films are structurally stable. No obvious secondary crystalline phases are observed. Thin films significantly influence the spectral response. Ag incorporation induces little lattice strain, while it should not break the structural framework. These results correlate with XRD and AFM studies, confirming the structural stability of Ag-doped ZnO thin films.

IV.4 Optical Characterization

IV.4.1 UV–Vis Reflectance Analysis

The optical behavior of the pure and Ag-doped ZnO thin films was systematically analyzed by UV–Vis reflectance spectroscopy, with Tauc plot analysis used to extract the values of the optical band

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gap E_g . Figure IV.5 shows the reflectance spectra of 0%, 1%, 3%, and 6% Ag samples. while Tauc plots are displayed in Figure IV.6.

For the undoped ZnO film, its characteristic reflectance edge at around 400 nm is associated with the intrinsic near-band-edge transition that confirms the large direct band gap of approximately 3.30 eV.

Upon the addition of Ag, the reflectance response changes in a concentration-dependent manner. Importantly, the 3% Ag-doped film renders an obvious and intense peak at ~550 nm in reflectance, which is not observed for the films doped with 0%, 1%, and 6% efficiently. This finding suggests the presence of a threshold doping effect, wherein localized electronic states and defect-mediated transitions begin to appear in the lattice structure of ZnO at this optimal ultrasonic concentration. This phenomenon indicates that Ag incorporation at intermediate amounts tailors the local electronic structure while preserving specific optical transitions without damaging the major wurtzite skeleton based on supporting XRD, Raman, and FTIR characterizations. The UV reflectance edge is redshifted, and the overall reflectivity decreases at higher doping (6% Ag), these findings are consistent with defect state formation, lattice distortion, and dopant clustering that modify light–matter interactions.

The optical band gap values were obtained through the Tauc formalism, assuming a direct allowed transition(Coulter & Birnie, 2018):

$$(\alpha h\nu)^2 = A(h\nu - E_g) \quad (\text{IV.1})$$

where α is the absorption coefficient, $h\nu$ the photon energy, and A a proportionality constant. All sample band gaps are compiled in Table IV.3. The undoped ZnO displays $E_g \approx 3.30$ eV and a slight increment up to 1% Ag concentration (3.31 eV), indicating a marginal Burstein–Moss effect resulted from the carrier redistribution of the samples. Importantly, at 3% Ag, the band gap changes slightly to a value of 3.29 eV, corresponding to dopant-induced localized states and lattice perturbation due to the incorporation of Ag into the ZnO lattice. At 6% Ag, there is a marked sharp transition at which E_g decreases down to 2.76 eV, with a clear deviation of the electronic structure compared to UCNCs resulting from defect-mediated band tailing and dopant-mediated states.

Tableau IV.3: Band gap energy of pure and Ag-doped ZnO thin films.

Sample	Band Gap (eV)
0% Ag:ZnO	3.30
1% Ag:ZnO	3.31
3% Ag:ZnO	3.29

6% Ag:ZnO	2.76
-----------	------

Both the reflectance spectra and Tauc-derived band gaps show that Ag doping effectively modulates the optical properties of these OMCs in a concentration-dependent manner. The appearance of the 550 nm peak exclusively at 3% Ag emphasizes that dopant incorporation affects the electronic structure in a non-linear way. These observations are consistent with AFM results that show a change in surface morphology and roughness, as well as FTIR and Raman analyses that demonstrate lattice distortion and trap states induced by dopant incorporation. These analyses using the reflectance and Tauc plot together create a strong correlation between Ag concentration, structural changes, and optical response, providing an approach for tailored tuning of ZnO thin films in view of practical optoelectronic applications.

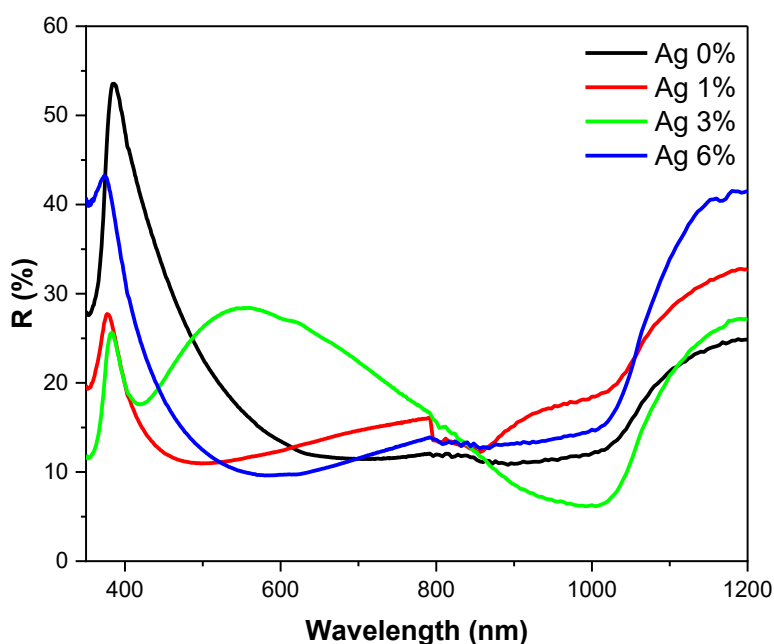


Figure IV.5: UV–Vis reflectance spectra of 0%, 1%, 3%, and 6% Ag thin films.

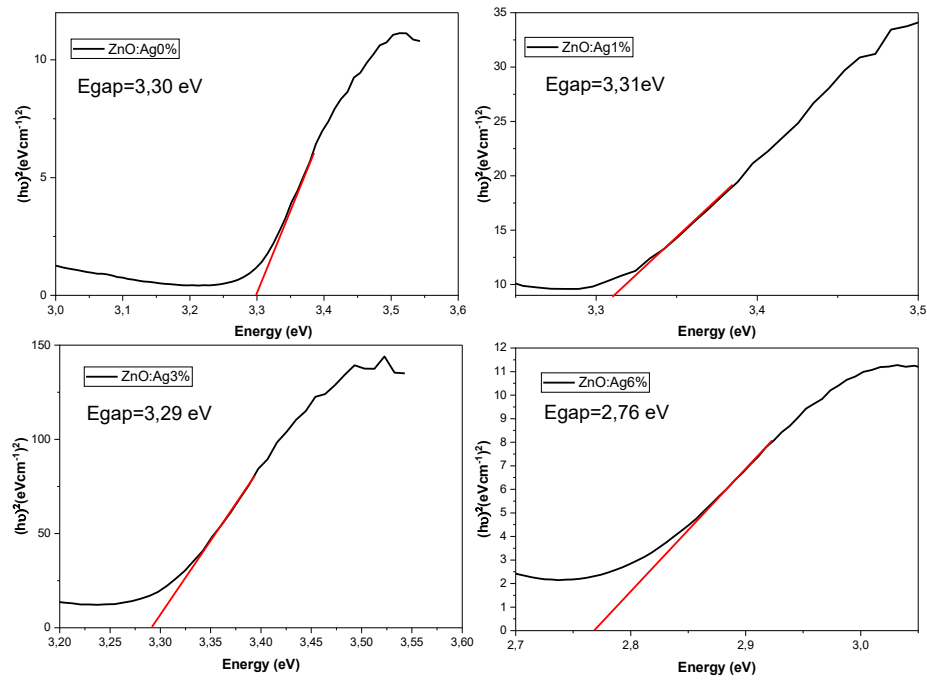


Figure IV.6: Tauc plots $((\alpha h\nu)^2 \text{ vs } h\nu)$ for all samples, showing the extrapolation to the energy axis to extract band gap values.

IV.5 UV Photodetector Performance

IV.5.1 I-V Characteristics

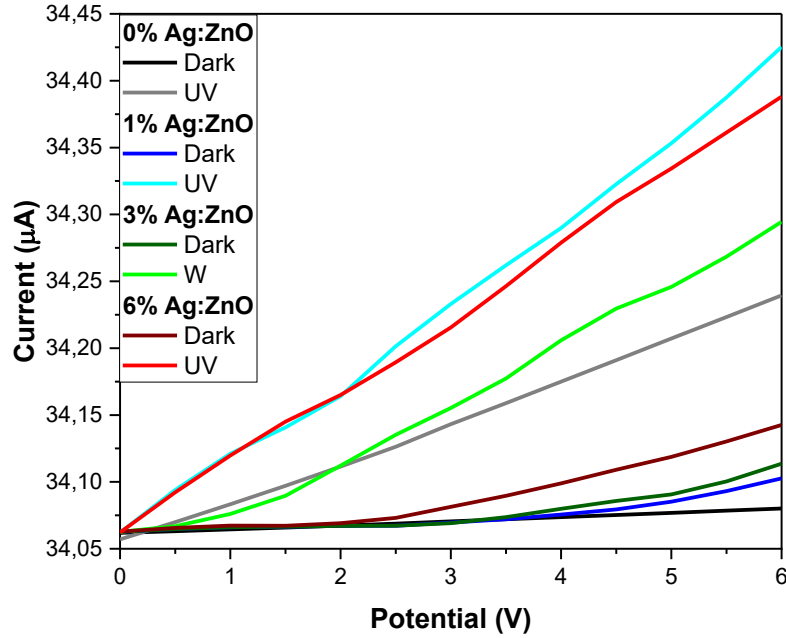


Figure IV.7. Current–voltage (I–V) characteristics of pure and Ag-doped ZnO thin films (0%, 1%, 3%, and 6% Ag), measured under dark and UV illumination.

The current–voltage (I–V) behavior of Ag-doped ZnO thin films on Si substrates was investigated under dark and UV illumination ($\lambda \approx 365$ nm, $P = 0.08$ W·cm⁻²). The measurements reveal that the photocurrent response strongly depends on the Ag doping concentration. All I–V curves are presented in Figure 6, while the derived electrical parameters are summarized in Table IV.4. The photocurrent (I_{ph}) was obtained from the difference between the UV-illuminated current (I_{UV}) and the dark current (I_{dark}) using the classical relation (Özgür et al., 2005a):

$$I_{ph} = I_{UV} - I_{dark} \quad (IV.2)$$

This method isolates the contribution of photo-induced carriers from intrinsic conduction.

The responsivity (R), defined as the ratio of photocurrent generated to incident optical power, was given by (Dang et al., 2015):

$$R = \frac{I_{ph}}{P} \quad (IV.3)$$

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where P is the power of the incident light. The specific detectivity D^* , which expresses the sensitivity of the photodetector to weak signals, was calculated based on (Dang et al., 2015):

$$D^* = \frac{R\sqrt{A}}{\sqrt{2qI_{dark}}} \quad (\text{IV.4})$$

with A as the active area and q the elementary charge.

The external quantum efficiency (EQE), which is the ratio of photons incident on the device to collected carriers, was calculated from (Wu & Chang, 2014):

$$EQE = \frac{Rhc}{q\lambda} \times 100\% \quad (\text{IV.5})$$

where h is Planck's constant, c the speed of light, and λ the illumination wavelength.

Analysis of the results Table IV.4 shows a maximum responsivity $R = 4.03 \times 10^{-6} \text{ A.W}^{-1}$ for the 1% Ag sample. The external quantum efficiency was obtained from EQE, confirming the same trend with a highest value of $1.37 \times 10^{-5} \%$ at 1% Ag. The specific detectivity was evaluated assuming shot-noise-limited performance, giving a maximum value of 3.86×10^5 Jones for the 1% Ag sample.

The variation of R , EQE , and D^* as a function of Ag concentration, illustrated in Figure (IV.Y), clearly demonstrates a non-linear dependence on dopant content, with all performance parameters reaching their optimum at 1% Ag. This behavior can be attributed to improved charge-carrier separation at moderate doping levels, where Ag acts as an electron-trapping center that suppresses recombination and enhances carrier lifetime. However, increasing Ag concentration beyond 1% introduces additional defect states and structural disorder, which promote carrier scattering and recombination, leading to reduced responsivity and detectivity for the 3% sample. A partial recovery at 6% Ag may be associated with thickness variation and modified defect distribution, yet it does not exceed the optimal 1% device. Despite the observed enhancement at moderate doping, the overall detectivity remains on the order of 10^5 Jones, limited by the relatively high dark current.

Therefore, the results confirm that controlled Ag incorporation significantly improves UV photoresponse, while interface engineering remains essential for achieving higher-performance ZnO/Si UV photodetectors.

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Table IV.4 Electrical Parameters of Ag-Doped ZnO Photodetectors

Samples	I_{ph} (μA)	R (A/W) $\cdot 10^{-6}$	D^* (Jones) $\cdot 10^5$	EQE (%) $\cdot 10^{-6}$
0%Ag: ZnO	0.156	1.99	1.91	6.7
1%Ag: ZnO	0.323	4.03	3.86	13.7
3%Ag: ZnO	0.181	2.26	2.17	7.7
6%Ag: ZnO	0.245	3.07	2.94	10.4

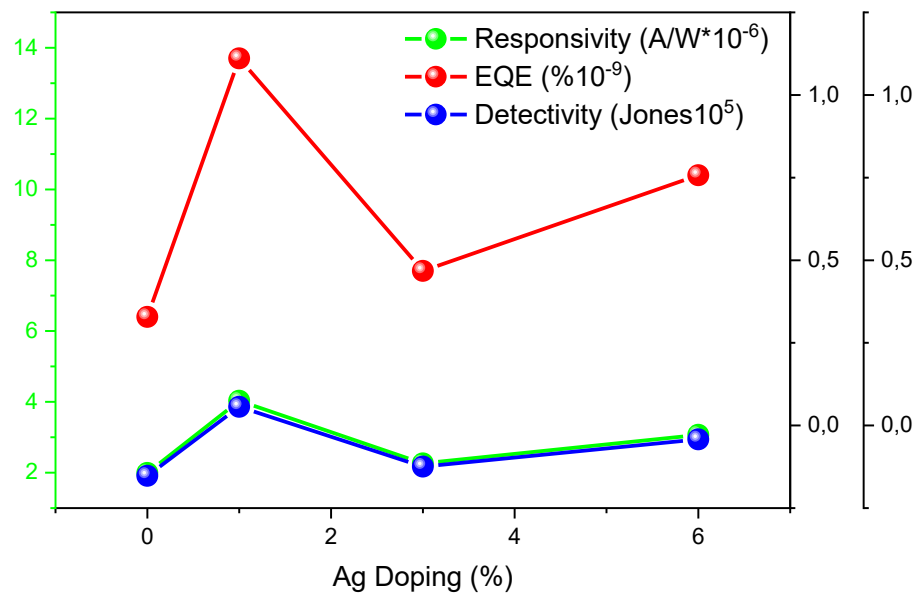


Figure IV.8 Evolution of the photodetector performance parameters (R , D^* , and EQE) with Ag doping concentration in ZnO UV photodetectors.

IV.5.2 Dynamic Photoresponse

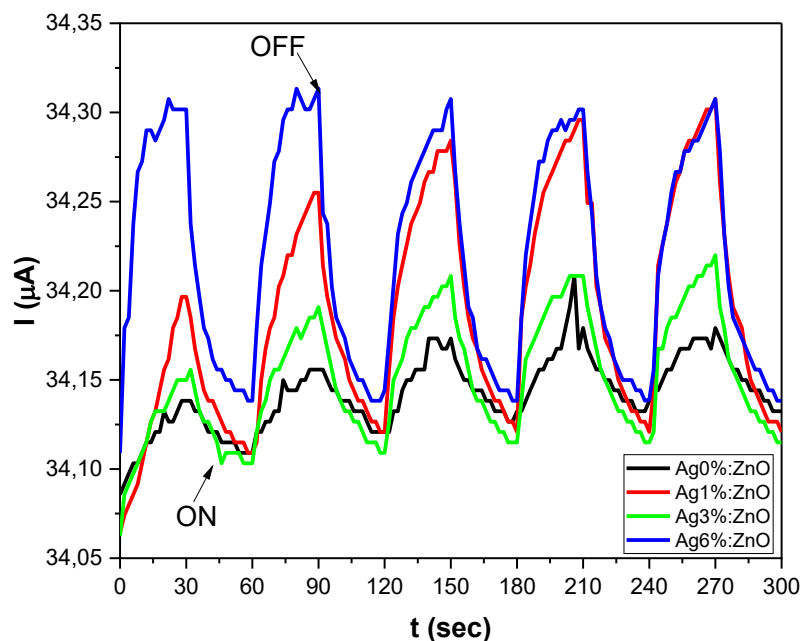


Figure IV.9 Current–time (I–t) response of pure and Ag-doped ZnO thin films (0%, 1%, 3%, and 6% Ag) under periodic UV light on/off cycles.

The photoresponse feature of the fabricated ZnO:Ag thin films were studied by a current–time (I–T) test under periodic UV light stimulus. Figure IV.9. The dynamic photocurrent curves obtained during six successive on/off cycles, indicating the reproducibility and stability of the devices. When exposed to UV light, a fast photocurrent increase is noted owing to the generation of electron–hole pairs, while switching off the light results in a slow current decay toward its initial dark value due to surface recombination and re-adsorption processes.

Response time (τ_{resp}) and recovery time (τ_{rec}) were determined from the I–T curves according to standard definitions described in literature. The response time is the time for the photocurrent to increase to 90% of its maximum steady-state value with illumination turned on, and the recovery time is defined as the time required for photocurrent decay to 10% above dark current after illuminating light off. These parameters give strong insight into the charge transport dynamics and recombination processes taking place in the films.

Table IV.5 presented the results than pure ZnO sample has a response time of 18.76 s and a recovery time of 21 s, which changed with Ag doping, as evident from the dynamic behavior. The 1% Ag-doped sample also has the fastest response (16.5 s) and a relatively short recovery time (16.83 s), indicating improved generation efficiency of separated charge carriers and a lower probability of

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recombination. The improved electron lifetime is due to the effect of Ag nanoparticles, where they behave as electron trapping centers and facilitate interfacial charge transfer.

Response times, therefore, decrease with doping up to an optimum of 1% Ag, beyond which, at higher levels such as 3%, the response time is found to increase again (23 s), implying slower carrier transport, which in part may be attributed to increased defect density and subsequent structural disorder. To our surprise, the 6% Ag sample shows an intermediate response time (17.67 s) and minimum recovery time (14.83 s), which may be ascribed to the supplanting of reaction kinetics of oxygen species on the surface. The differences in response and recovery time are related to the balance between improved charge separation and doping-induced recombination centers at increasing dopant concentrations.

Table IV.5 Response and recovery times extracted from I-t measurement of Ag-doped ZnO thin films.

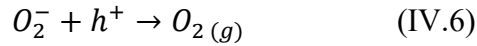
Samples	Cycle 1	Cycle 2	Cycle 3	Cycle 4	Cycle 5	Cycle 6	Average
0%Ag:ZnO	$\tau_{\text{Rep}}=20\text{s}$	$\tau_{\text{Rep}}=22\text{s}$	$\tau_{\text{Rep}}=14\text{s}$	$\tau_{\text{Rep}}=22\text{s}$	$\tau_{\text{Rep}}=16\text{s}$	$\tau_{\text{Rep}}=18\text{s}$	$\tau_{\text{Rep}}=18.67\text{s}$
	$\tau_{\text{Rec}}=18\text{s}$	$\tau_{\text{Rec}}=23\text{s}$	$\tau_{\text{Rec}}=20\text{s}$	$\tau_{\text{Rec}}=24\text{s}$	$\tau_{\text{Rec}}=20\text{s}$	$\tau_{\text{Rec}}=21\text{s}$	$\tau_{\text{Rec}}=21\text{s}$
1Ag:ZnO	$\tau_{\text{Rep}}=7\text{s}$	$\tau_{\text{Rep}}=20\text{s}$	$\tau_{\text{Rep}}=19\text{s}$	$\tau_{\text{Rep}}=20\text{s}$	$\tau_{\text{Rep}}=22\text{s}$	$\tau_{\text{Rep}}=11\text{s}$	$\tau_{\text{Rep}}=16.5\text{s}$
	$\tau_{\text{Rec}}=20\text{s}$	$\tau_{\text{Rec}}=25\text{s}$	$\tau_{\text{Rec}}=6\text{s}$	$\tau_{\text{Rec}}=19\text{s}$	$\tau_{\text{Rec}}=10\text{s}$	$\tau_{\text{Rec}}=21\text{s}$	$\tau_{\text{Rec}}=16.83\text{s}$
3Ag:ZnO	$\tau_{\text{Rep}}=23\text{s}$	$\tau_{\text{Rep}}=25\text{s}$	$\tau_{\text{Rep}}=24\text{s}$	$\tau_{\text{Rep}}=24\text{s}$	$\tau_{\text{Rep}}=20\text{s}$	$\tau_{\text{Rep}}=22\text{s}$	$\tau_{\text{Rep}}=23\text{s}$
	$\tau_{\text{Rec}}=21\text{s}$	$\tau_{\text{Rec}}=26\text{s}$	$\tau_{\text{Rec}}=17\text{s}$	$\tau_{\text{Rec}}=20\text{s}$	$\tau_{\text{Rec}}=11\text{s}$	$\tau_{\text{Rec}}=24\text{s}$	$\tau_{\text{Rec}}=19.67\text{s}$
6Ag:ZnO	$\tau_{\text{Rep}}=12\text{s}$	$\tau_{\text{Rep}}=13\text{s}$	$\tau_{\text{Rep}}=25\text{s}$	$\tau_{\text{Rep}}=13\text{s}$	$\tau_{\text{Rep}}=23\text{s}$	$\tau_{\text{Rep}}=17\text{s}$	$\tau_{\text{Rep}}=17.67\text{s}$
	$\tau_{\text{Rec}}=15\text{s}$	$\tau_{\text{Rec}}=15\text{s}$	$\tau_{\text{Rec}}=18\text{s}$	$\tau_{\text{Rec}}=15\text{s}$	$\tau_{\text{Rec}}=19\text{s}$	$\tau_{\text{Rec}}=7\text{s}$	$\tau_{\text{Rec}}=14.83\text{s}$

IV.6 Mechanism of Ag-Doped ZnO UV Photodetector

The ultraviolet (UV) photodetection mechanism of Ag-doped ZnO thin films deposited on a silicon substrate can be explained based on the adsorption–desorption process of oxygen molecules at the ZnO surface combined with the carrier transport across the ZnO/Si interface. In the dark, oxygen molecules from the ambient atmosphere are adsorbed onto the surface of ZnO and capture free electrons from the conduction band, forming negatively charged oxygen ions (O_2^-). This process leads to the formation of a depletion region near the surface and consequently reduces the free carrier concentration, resulting in a low dark current in the device (Özgür et al., 2005b), (Shao et al., 2014). When the photodetector is exposed to ultraviolet illumination with photon energy greater than the band gap of ZnO (~ 3.3 eV), electron–hole pairs are generated within the ZnO layer. The

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photogenerated holes migrate toward the surface and neutralize the adsorbed oxygen ions according to the reaction,



which releases the trapped electrons back into the conduction band. As a result, the electron concentration increases significantly, leading to a strong increase in the photocurrent (Shao et al., 2014; Syed, s. d.). In the ZnO/Si heterostructure, the formation of a Schottky or heterojunction barrier at the interface produces an internal electric field that facilitates the separation and transport of photogenerated carriers, thereby enhancing the photoresponse of the device (Wang, 2004). The incorporation of silver into the ZnO lattice further influences the photodetection performance by introducing localized electronic states and acting as electron trapping centers, which can improve charge separation and suppress recombination processes at moderate doping concentrations (Diguna et al., 2020). However, at higher Ag contents, the formation of secondary phases such as Ag₂O or excessive defect states may act as recombination centers, which can deteriorate the photodetector performance. Therefore, an optimal Ag concentration can significantly enhance the photodetection characteristics by balancing carrier generation, separation, and transport processes. The overall mechanism of charge generation, separation, and transport under UV illumination is schematically illustrated in the energy band diagram presented in Figure IV.10.

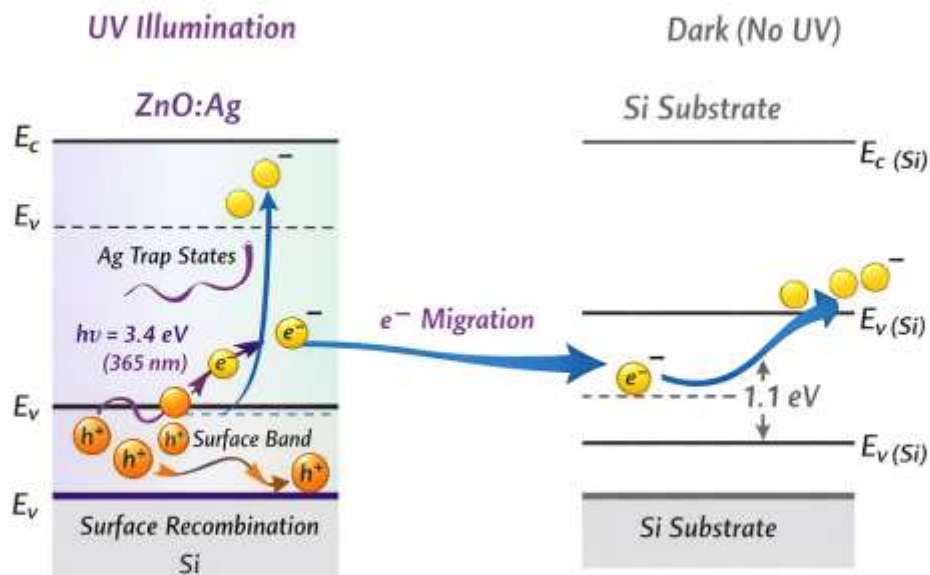


Figure IV.10 Schematic diagram of the UV photodetection mechanism in Ag-doped-ZnO/Si.

IV.7 Conclusion

In conclusion, the investigation of Ag-doped ZnO thin films deposited on Si substrates shows that controlled silver incorporation significantly impacts both the structural and UV photodetection properties of the devices. X-ray diffraction analysis revealed that undoped ZnO films maintain a well-defined polycrystalline wurtzite structure, while low-level Ag doping (1%) introduces Ag₂O secondary phases without affecting crystallinity. This leads to improved carrier separation and optimal photodetector performance. At higher Ag concentrations (3–6%), the intensity of Ag₂O peaks increases, and some ZnO reflections diminish, indicating increased structural disorder and the formation of additional defect states. These changes negatively influence responsivity, external quantum efficiency, and specific detectivity, as seen in the I–V characteristics and in the R–EQE–D* analysis. The highest performance is achieved at 1% Ag, where shallow trap states introduced by Ag effectively extend carrier lifetime and suppress recombination, resulting in maximum photocurrent, responsivity, and detectivity. Excessive doping raises recombination and scattering rates, reducing device efficiency. The UV photodetection mechanism involves photon-induced electron–hole generation in ZnO, oxygen-mediated surface modulation, Ag-assisted charge separation, and carrier transport across the ZnO/Si heterojunction, as depicted in the energy band diagram. This provides a clear explanation for how photodetector performance depends on Ag concentration. Overall, the study confirms that low-level Ag doping optimizes UV photoresponse by balancing structural integrity, defect engineering, and carrier dynamics, while emphasizing the crucial role of interface quality in achieving high-performance ZnO/Si photodetectors.

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Chapter V

CO₂ Gas Sensing Performance of Mg-Doped ZnO-Based and ZnO/CuO Thin Film

V.1 Introduction

This chapter presents a detailed investigation of the CO₂ gas sensing performance of the prepared thin-film sensors. Two different material systems are examined in this study: Mg-doped ZnO thin films and multilayer ZnO/CuO heterostructures. The objective is to evaluate the sensing characteristics of these materials in terms of sensitivity, selectivity, response–recovery behavior, and overall sensing efficiency at room temperature.

The sensing properties of Mg-doped ZnO (MZO) films are analyzed by correlating the gas response with their structural, morphological, and optical characteristics. Particular attention is given to the role of Mg doping in modifying defect states and charge transport processes within the ZnO lattice. In addition, the sensing behavior of ZnO/CuO multilayer structures is investigated.

V.2 Section One: Gas Sensing Performance of Mg-Doped ZnO Thin Films

The experimental procedures used for the preparation of the thin films and the fabrication of the sensing devices are described in detail in Chapter II. In order to avoid repetition, only the main results related to the sensing performance are discussed in this chapter. The synthesis parameters, including precursor composition, deposition conditions, and thermal treatment, are summarized in Table II.1 of Chapter II. All Mg-doped ZnO samples analyzed in this section were prepared following those experimental conditions. Consequently, the discussion presented here focuses mainly on the correlation between the structural, morphological, optical, and gas-sensing properties of the films.

V.2.1 Structural Analysis

The X-ray diffraction (XRD) patterns of Mg-doped ZnO thin films with Mg concentrations of 0%, 2%, 5%, and 7% are shown in Figure V.1.1. All samples exhibit diffraction peaks corresponding to the planes (100), (002), (101), (102), (110), (103), (112), (201), (004), and (202), which are characteristic of the hexagonal wurtzite structure of ZnO according to the standard JCPDS card (No. 01-075-1526). The absence of additional peaks related to metallic zinc, magnesium, or magnesium oxide indicates that Mg ions were successfully incorporated into the ZnO lattice without forming secondary phases.

In the diffraction pattern of the undoped sample, two additional peaks appear at approximately 44.3° and 64.4°, corresponding to the (202) and (511) planes of the silicon substrate (JCPDS No. 01-089-9055). These peaks originate from the substrate used for thin-film deposition.

To further evaluate the structural properties of the films, several crystallographic parameters were calculated, including the crystallite size (D), microstrain (ϵ), dislocation density (δ), and lattice

parameters. The average crystallite size was estimated using the Scherrer equation, and the results are shown in Table V.1.1.

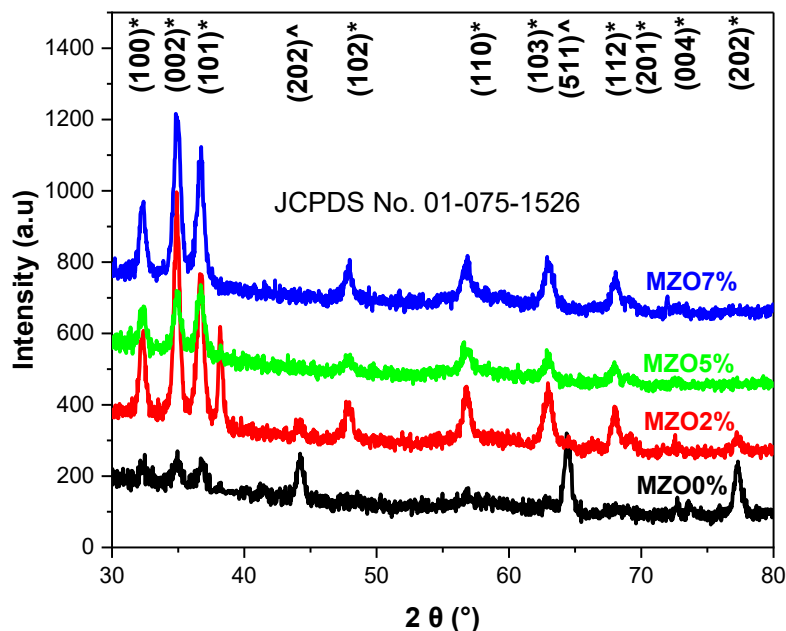


Figure V.1.1 XRD patterns of MZO 0%, MZO 2%, MZO 5%, and MZO 7% films.

The diffraction peak near $2\theta \approx 34.9^\circ$, associated with the (002) plane, remains visible for all samples, indicating that the basic wurtzite structure of ZnO is preserved after Mg doping. A noticeable reduction in the FWHM value is observed when the Mg concentration increases from 0% to 2%, decreasing from 0.739° to 0.449° . This reduction suggests an improvement in crystallinity and a decrease in structural defects at low Mg concentration. The relatively poor crystallinity observed for the undoped film may be related to its smaller thickness, which is later confirmed by profilometer measurements.

However, when the Mg concentration increases to 5% and 7%, the FWHM value increases again, indicating the introduction of lattice distortions and additional structural defects. This behavior may result from the excessive incorporation of Mg ions into the ZnO lattice, which can create strain and disrupt the crystal order.

The crystallite size increases from about 11.27 nm for undoped ZnO to approximately 18.55 nm at 2% Mg doping, confirming the improvement in crystalline quality. Similar behavior was observed by Abed et al. (Abed et al., 2015), who attributed the increase in crystallite size at 2% Mg doping to the filling of zinc vacancies, which directly indicates a reduction in structural defects and an improvement

Chapter V: CO₂ Gas Sensing Performance of Mg-Doped ZnO-Based and ZnO/CuO Thin Film

in crystalline quality. At higher Mg concentrations, the crystallite size decreases again, which is consistent with the increase in microstrain and defect density.

Overall, these results indicate that a moderate Mg concentration (around 2%) improves the crystalline quality of ZnO thin films, while higher doping levels introduce structural disorder and lattice strain.

Table V.1.1 Structural parameters of MZO thin films.

Films	2 θ (°)	FWHM β (°)	d(hkl)	D (nm)	Microstrai n ϵ (%) $\times$ 10^{-2}	dislocation density δ (nm ⁻²) $\times$ 10^{-2}	Lattice constant c
0%	34.91	0.739	2.56796	11.27	1.03	0.79	0.51
MZO	1		6				
2%	34.90	0.449	2.56860	18.55	0.62	0.29	0.51
MZO	2		8				
5%	34.91	0.605	2.56753	13.77	0.84	0.53	0.51
MZO	7		9				
7%	34.93	0.589	2.56647	14.14	0.82	0.50	0.51
MZO	2		1				

ATR-FTIR analysis elucidates the functional groups contained in the compounds, the molecular conformation, and the intra- and intermolecular interactions. The absorption peaks and band locations may change depending on the thin film's form, chemical composition, and structural properties (Goktas et al., 2019). This work conducted ATR investigations on MZO films with varied Mg doping levels (0%, 2%, 5%, and 7%) in the absorption mode extending from 400 to 4000 cm⁻¹. The spectra in Figure V.1.2 display distinct absorption bands that correlate to the vibrational modes of the ZnO lattice and the impact of Mg doping on the structural features of the films. The detected absorption peaks at about 1460, 1106, 886, 746, 609, and 509 cm⁻¹ are indicative of Zn-O bond vibrations and lattice dynamics. With increasing Mg content, large 1450 cm⁻¹ and broad peaks at 530 cm⁻¹, 748 cm⁻¹ are presumably attributable to the Mg-O stretching and Mg-O binding, respectively (Goktas et al., 2019) (Rahman et al., 2025), which are absent in the case of ZnO.

While a peak arises at 609 cm⁻¹ in all cases, which is due to the oscillations of the Zn-O stretching vibration (Saleem, Jameel, et al., 2022). At 886 cm⁻¹ and 1106 cm⁻¹, another faint absorption peak

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was identified, which may be associated with the C=O groups' vibration mode (Goktas et al., 2019), (Meena et al., 2025).

Overall, the FTIR data indicate the effective doping of Mg into the ZnO structure and are compatible with the structural conclusions obtained from XRD analysis.

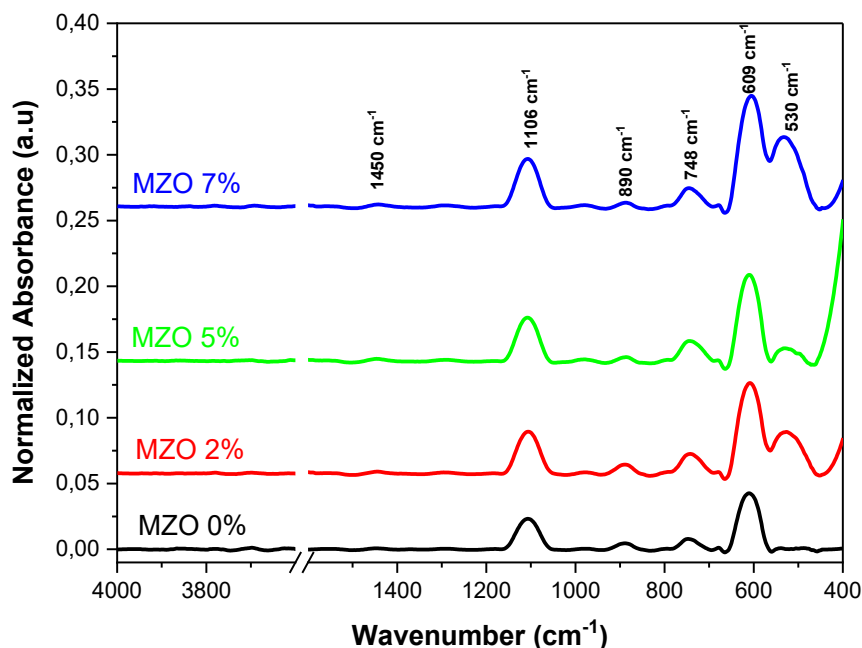


Figure V.1.2 FTIR spectra of the MZO 0%, MZO 2%, MZO 5%, and MZO 7% films.

The EDS spectra in Figure V.1.3 validate the elemental nature of the ZnO thin films. The undoped sample (MZO 0%) included just Zn, O, and a small quantity of Si (from the substrate holder). Upon doping with Mg (MZO 2%, 5%, 7%), the development of Mg peaks alongside Zn and O reveals the successful incorporation of magnesium into the ZnO lattice. This elemental presence is congruent with the XRD findings, where no secondary phases of MgO were discovered, suggesting that Mg²⁺ ions substitute Zn²⁺ ions in the ZnO wurtzite structure without forming different phases. Furthermore, the incorporation of Mg is further verified by ATR-FTIR spectra, where tiny alterations in Zn–O vibrational modes were found, suggesting local structural deformation produced by Mg substitution. This coherent interpretation across EDS, XRD, and ATR suggests the successful and gradual doping of Mg in the ZnO thin films. Adding Mg to the surface makes it rougher and grainier. The increase in surface roughness and grain boundaries presumably enhances gas adsorption and diffusion, which probably helps gas cling to it and move about, hence boosting sensitivity and reaction.

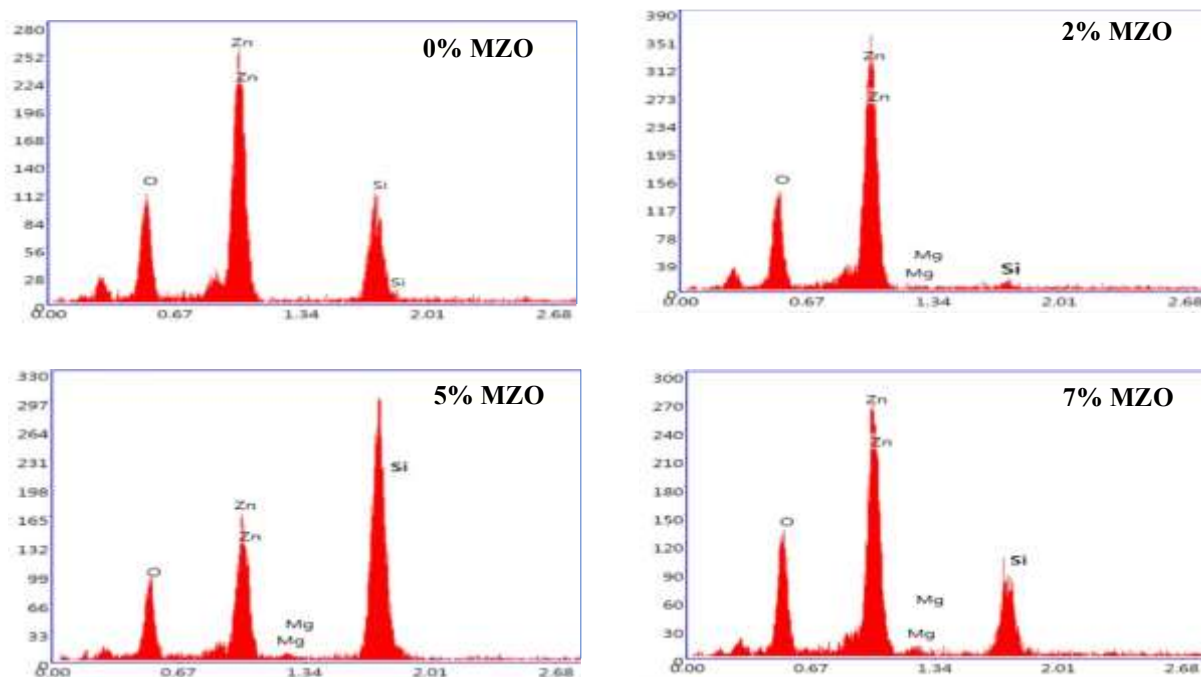


Figure V.1.3 EDS spectra of the MZO 0%, MZO 2%, MZO 5%, and MZO 7% films.

V.2.2 Morphological Analysis

Field Emission Scanning Electron Microscopy (FESEM) is used to explore how the concentration of Mg doping affects the surface shape and development of ZnO thin films. The FESEM pictures and related grain size histograms are given in Figure V.1.4 (a, b, c, d). For 0% MZO, the particles are generally tiny and close together, which makes the surface texture smooth and homogeneous. At 2% MZO, the particle size expands a lot, with grains growing larger and more clustered. makes the surface rougher due of agglomeration. With 5% MZO, the grain size stays quite huge, but the clusters are more compact, which makes the surface even rougher.

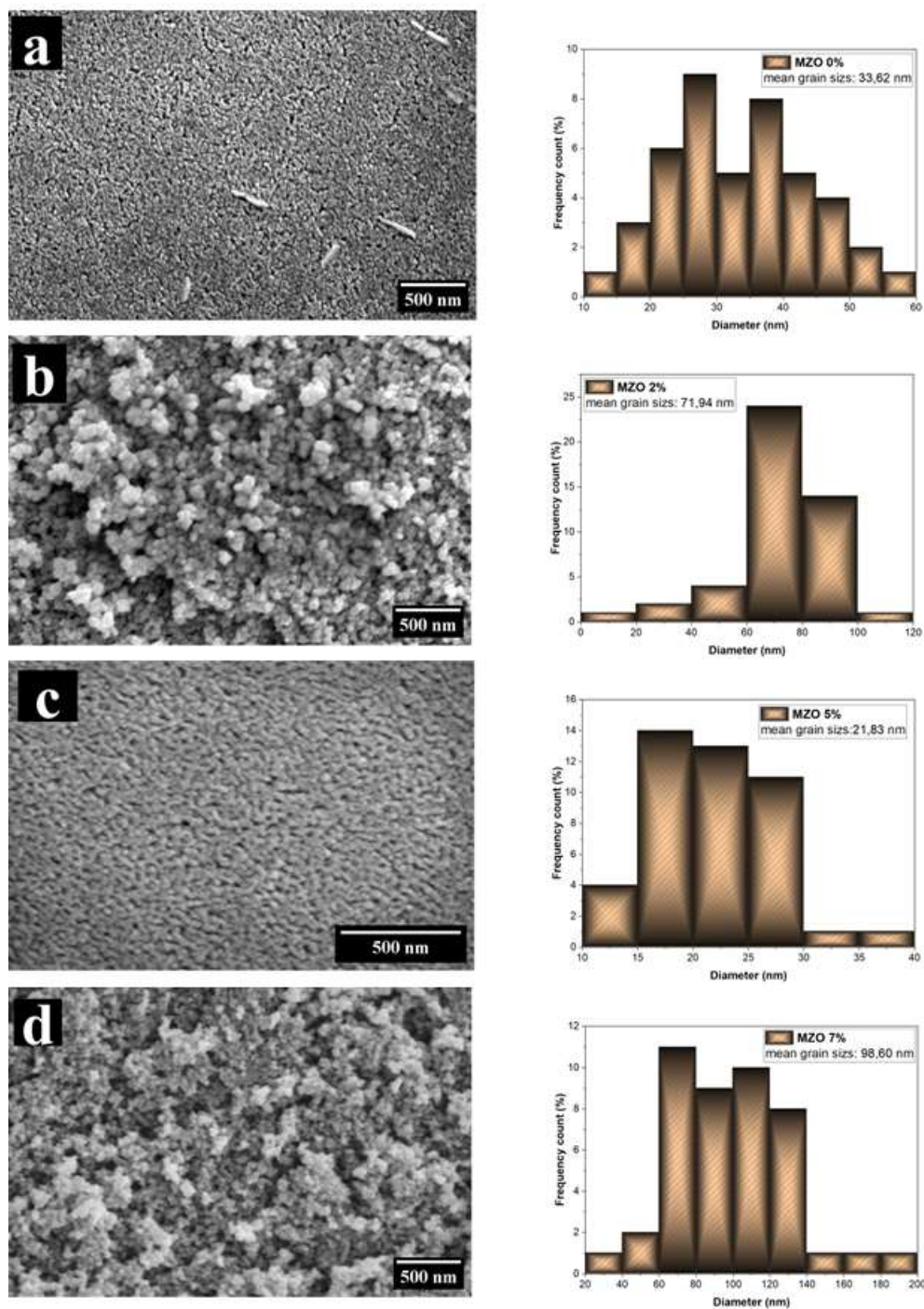


Figure V.1.4 FESEM images and grain size distribution histogram of (a) MZO 0%, (b) MZO 2%, (c) MZO 5%, and (d) MZO 7% films.

Interestingly, at 7% MZO, the particle size declines again, and the surface appears finer and more homogenous, suggesting grain refinement and enhanced dispersion of particles. This pattern indicates that Mg doping initially increases grain development and aggregation, increasing surface roughness, but growing Mg concentration refines the grain size and leads to a smoother, more uniform surface. Such morphological changes impact the physical and functional characteristics of the films, such as

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optical behavior and gas-sensing effectiveness. The average grain size of films is determined using the ImageJ 1.5.4 program, 2020 edition, which is displayed in Table V.1.2. The film thickness was determined using a profilometer; the findings reported in Table V.1.2 demonstrate a clear pattern of increasing thickness with increased Mg doping. This increase shows that Mg absorption increases film development during the dip-coating process.

Table V.1.2 Mean grain size, film thickness, and optical band gap E_g of MZO thin films.

Films	mean grain size (nm)	Film Thickness (nm)	E gap (eV)
0% MZO	33.62	45.28	3.30
2% MZO	71.94	247.95	3.23
5% MZO	21.83	300.38	3.35
7% MZO	98.60	418.91	3.26

V.2.3 Optical Analysis

Figure V.1.5(a) displays the reflectance spectra of Mg-doped ZnO thin films, which were measured in the range of 350–1200 nm, to assess the optical characteristics of MZO thin films, which exhibit considerable changes with increasing Mg concentration. A substantially greater reflectance of roughly 55% was recorded for 0% MZO in the visible area, indicating a smoother surface with fewer scattering centers. As Mg doping increases to 2% and 5%, the reflectance lowers, likely due to increasing surface roughness and increased grain boundary scattering, as supported by the FESEM results. At 7% Mg, a minor rise in reflectance is noticed again, likely due to higher homogeneity and finer particle dispersion. The optical gap (E_g) values were obtained using Tauc plots based on UV–Vis reflectance data. As seen in Table V.1.2, the band gap changes with magnesium concentration. The slight growth in E_g at a 5% impregnation ratio may be related to the Burstein–Moss effect, resulting from increasing carrier concentration. In contrast, the narrowing of the bandgap at 2% and 7% may be attributed to higher structural disorder or defect states originating after impregnation.

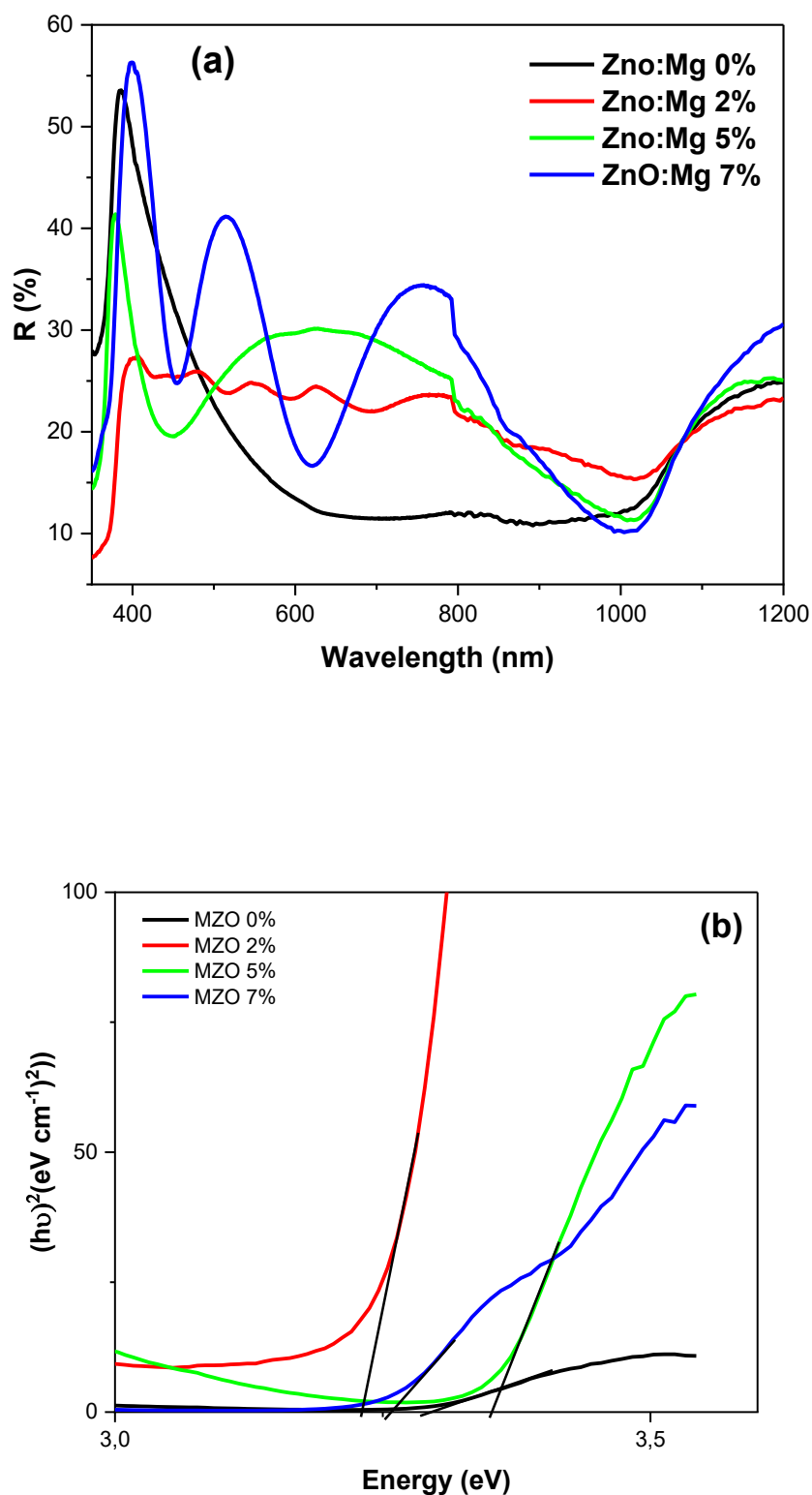


Figure V.1.5 (a) reflectance spectrum, (b) tauc plot spectrum of the MZO 0%, MZO 2%, MZO 5%, and MZO 7% films.

V.2.4 Gas Sensing Performance

In order to investigate the behavior of the MZO sensor, I-V characteristics were recorded at varying concentrations of CO₂ gas at room temperature, as shown in Figure V.1.6. It was revealed that the current increases greatly when CO₂ gas is introduced and increases even more in the case of 7% MZO, showing that the films have high sensitivity and effective CO₂ gas detection abilities at room temperature. The behavior of the Mg-doped ZnO is connected to enhanced electrical conductivity when exposed to CO₂ gas, which may be attributed to the interaction of CO₂ molecules with oxygen absorbed on the sensor surface. Thin films of MZO display remarkable sensitivity as CO₂ gas sensors, as reported in Table V.1.3 and depicted in Figure V.1.7. The 0% MZO film showed a good response of 35.68% to 15.5 ppm of CO₂ at ambient temperature. This result improved 1.55 times at 2% MZO to 55.47% and reduced 1.33 times at 5% MZO to 25.60% at the same gas concentration. However, at 5% MZO, the film displayed a response of 41.56% to 124 ppm of CO₂, demonstrating greater sensitivity at relatively high concentrations, whereas the lowest response values approached 0.05% at 31 ppm. The data may imply that excessive addition of magnesium below the ideal range (between 5-7%) may produce flaws or disturb charge transfer, resulting in poor sensor performance. The 7% MZO film displays the most substantial gain in sensitivity, reaching a high of 461.76% at 46.5 ppm, which is about 16 times the sensitivity of 0% MZO.

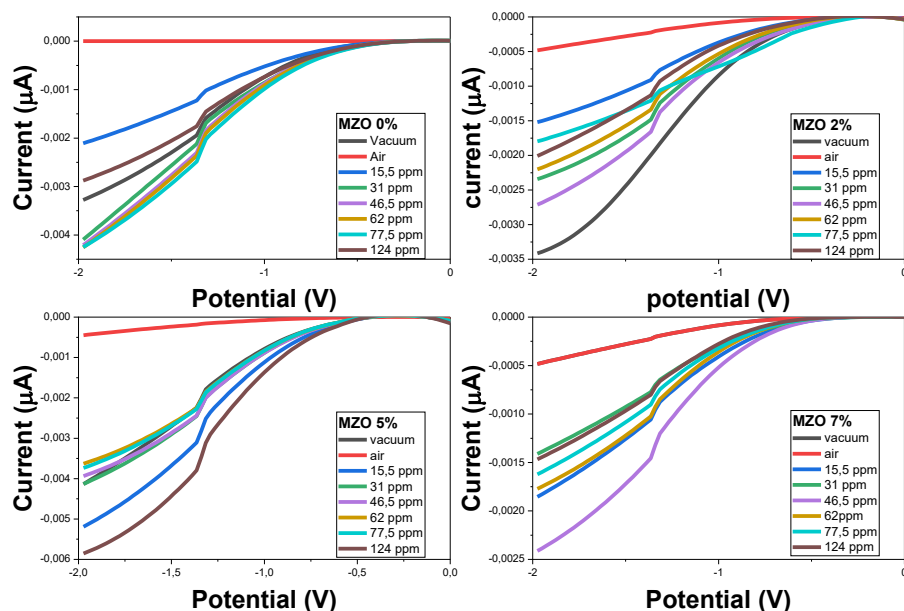


Figure V.1.6 I-V characteristics of the MZO 0%, MZO 2%, MZO 5%, and MZO 7% sensor toward CO₂ gas at a temperature of 25°C and different concentrations.

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This large improvement is likely due to the appropriate integration of Mg²⁺ ions, which boosts surface reactivity and increases the density of active sites for CO₂ adsorption while preserving sufficient charge carrier mobility. The evident nonlinear pattern in the 7% MZO curve, which is characterized by a sudden spike followed by a steady decline after 46.5 ppm, might be due to the saturation of active sites or restructuring effects at higher gas concentrations. These results demonstrate that fine regulation of Mg addition is important to optimize the performance of ZnO-based gas sensors and highlight 7% Mg as the ideal quantity of magnesium addition for extremely sensitive detection of carbon dioxide at ambient temperature.

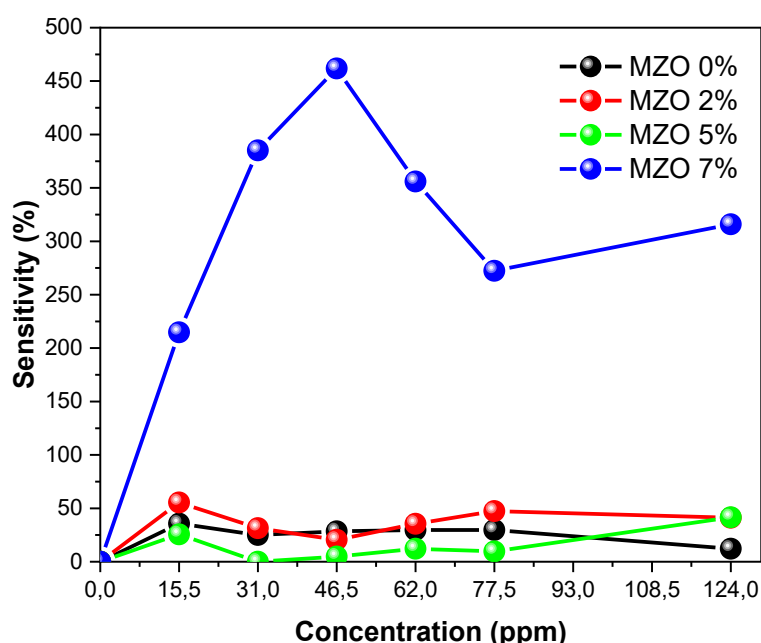


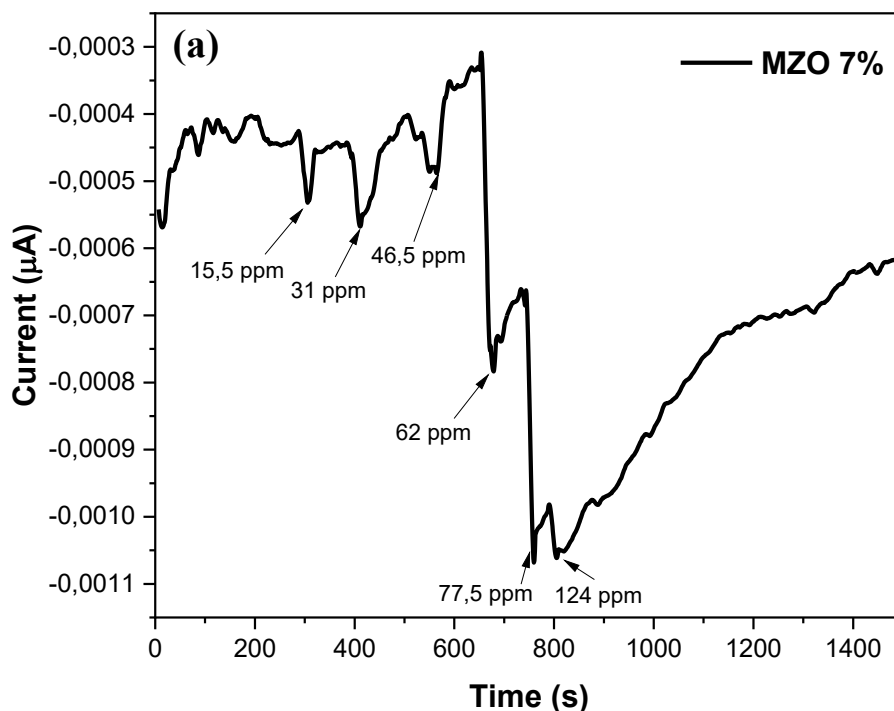
Figure V.1.7 S–C sensitivity of the MZO 0%, MZO 2%, MZO 5%, and MZO 7% sensor toward CO₂ gas at a temperature of 25°C and different concentrations. Bias potential 0.5 V.

Table V.1.3 Sensitivity of MZO thin films toward CO₂ gas 25°C under 0.5V bias.

Sensitivity (%)	MZO 0%	MZO 2%	MZO 5%	MZO 7%
15.5 ppm	35.68	55.47	25.60	214.82
31 ppm	25.00	31.38	0.05	385.14
46.5 ppm	28.46	20.55	4.79	461.76
62 ppm	29.78	35.52	12.18	355.90
77.5 ppm	29.77	47.34	9.62	272.31
124 ppm	12.19	41.18	41.56	315.87

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The dynamic current-time (I-t) response of the 7% MZO-based sensor under varied CO₂ gas concentrations at room temperature and 0.5 V applied bias is displayed in Figure V.1.8. The sensor demonstrates a rapid and steady response upon gas exposure, with a distinct rise in current when the gas is supplied (ON state), followed by a speedy return to baseline current when the gas is withdrawn (OFF state). Figure V.1.8 a depicts the dynamic response of the current (I-t) of the 7% MZO-based sensor under varying CO₂ concentrations at room temperature and an applied bias of 0.5 V. The sensor demonstrates a fast and steady response when exposed to gas, with a visible rise in current upon gas introduction (on state), followed by a rapid return to baseline current upon gas removal (off state). The reaction time and recovery time were recorded at 46.5 ppm, reflecting the time it takes for the sensor to achieve 90% of the final balanced output (baseline) following a change in the measured input. The reaction time and the time necessary for the sensor to return to 10% of the baseline constitute the recovery time (Kebaili et al., 2026), as illustrated in Figure V.1.8.b. It can be shown that the 7% MZO sensor has quick response/recovery times of 20/18 seconds, respectively. These results highlight the excellent sensing performance of the 7% MZO sample.



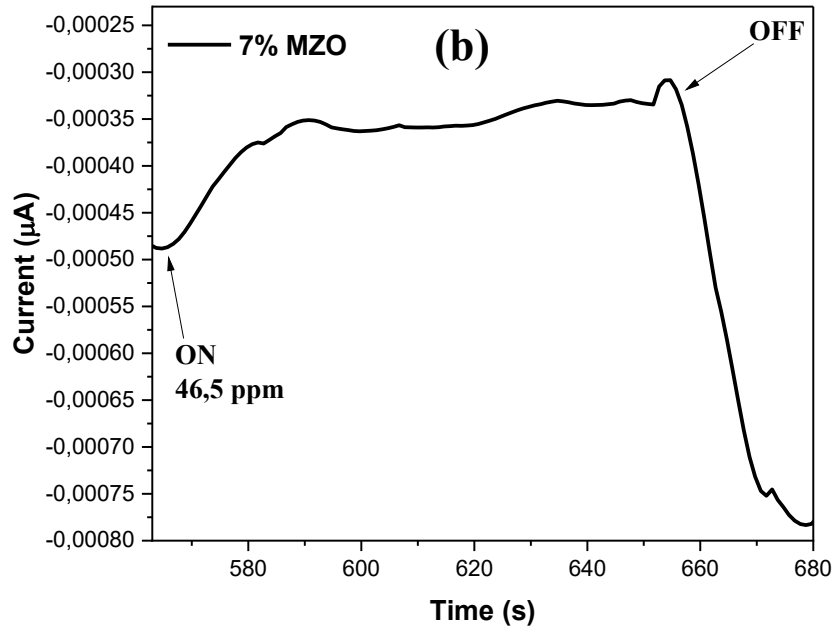


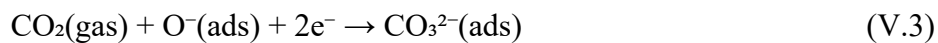
Figure V.1.8 (a) Dynamic response, (b) zoomed in view of on/off cycle of MZO 7% in different CO₂ gas concentrations at 0.5 V applied bias.

V.2.5 Sensing mechanism of MZO toward CO₂ Gas

The superior CO₂ sensing performance of the Mg-doped ZnO thin films, particularly the 7% Mg-doped sample, is governed by a surface-mediated electronic charge transfer mechanism. In ambient air, oxygen molecules adsorb onto the sensor surface and ionize by extracting electrons from the conduction band of ZnO, forming anionic species (O₂⁻, O⁻) (Amiri et al., 2020).



This process generates a low-conductivity electron depletion layer at the surface, leading in a high baseline resistance. Upon contact to CO₂, the gas molecules interact with these pre-adsorbed oxygen ions, resulting to the creation of surface carbonate species (CO₃²⁻) and the subsequent release of trapped electrons back into the conduction band. (Ziv et al., 2018)



The introduction of Mg²⁺ ions, which have a slightly smaller ionic radius than Zn²⁺, functions as an electronic sensitizer. It enhances the density of charge carriers and active adsorption sites on the film

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surface, altering the electronic structure, hence permitting more effective oxygen adsorption and charge transfer (Riahi et al., 2013). The ideal 7% doping level generates the most conducive surface environment for this reaction, accounting for the observed maximum sensitivity, whereas excessive doping may induce charge-scattering defects, as evidenced by the performance deterioration in the 5% Mg-doped sample.

V.2.6 Conclusion

This paper examines the prospective use of Mg-doped ZnO for detecting CO₂ gas at RT. For this, MZO thin films were synthesized via the dip coating sol-gel route with different concentrations of Mg (0%, 2%, 5%, and 7%), where Mg doping affects the structural, morphological, optical, and CO₂ gas sensing properties of ZnO. XRD, ATR-FTIR, and EDS analysis confirmed the successful doping of Mg in the ZnO structure. The SEM investigation indicated the changed crystallite size and surface shape. Optical research further indicated that the band gap fluctuates with Mg content. CO₂ sensing studies at RT demonstrated that all sensors exhibited a strong response at different concentrations of CO₂. The 0% MZO film demonstrated 35.68% sensitivity to 15.5 ppm. At the same concentration, 2% MZO recorded a 1.55 times greater response, estimated at 55.47%, then decreased by 0.72 times (25.60%) in 5% MZO film. 7% MZO film provided exceptional responses, with the highest being 461.76% for 46.5 ppm and the lowest 214.82% for 15.5 ppm. This response is significantly higher than many values reported for ZnO-based CO₂ sensors operating at room temperature. Our results demonstrated that Mg-doped ZnO thin films are a promising candidate for CO₂ gas sensing. This speaks well for additional study into its long-term stability and selectivity.

V.3 Section Two: Gas Sensing Performance of ZnO/CuO Multilayer Thin Films

In order to further improve the gas sensing characteristics of metal oxide semiconductors, multilayer structures based on different oxide materials have attracted significant attention. In this section, the sensing behavior of multilayer thin films composed of zinc oxide (ZnO) and copper oxide (CuO) is investigated. The combination of these two oxides is particularly interesting due to the formation of a p–n heterojunction between p-type CuO and n-type ZnO, which can enhance the charge transfer processes and improve the interaction with gas molecules. Therefore, the gas sensing performance of ZnO, CuO, ZnO/CuO, and CuO/ZnO thin films is studied and compared in order to understand the role of multilayer architecture in improving sensor response.

The experimental conditions used for the preparation of these films, including precursor solutions, deposition parameters, and annealing conditions, are the same as those described previously in Chapter II (Table II.1).

V.3.1 Structural Analysis

In order to investigate the structural characteristics of the prepared films, several complementary techniques were employed, including X-ray diffraction (XRD), Raman spectroscopy, and Fourier transform infrared spectroscopy (FT-IR). These techniques provide valuable information about the crystalline structure, phase composition, and chemical bonding of the deposited ZnO, CuO, and multilayer ZnO/CuO thin films.

The XRD patterns of ZnO, CuO, ZnO/CuO, and CuO/ZnO thin films are presented in Figure V.2.1. The diffraction spectra exhibit relatively broad and well-defined peaks, indicating the formation of polycrystalline oxide films. For the ZnO thin film, several diffraction peaks appear at 2θ values of 31.85° , 34.55° , 36.35° , 47.69° , 56.75° , 63.09° , and 68.16° . These peaks correspond respectively to the crystallographic planes (100), (002), (101), (102), (110), (103), and (112) of the hexagonal wurtzite structure of ZnO, in agreement with the standard data reported in JCPDS card No. 01-079-0205. The highest peak intensity is observed for the (101) plane, suggesting that the ZnO crystallites tend to grow preferentially along this orientation.

For the CuO thin film, the diffraction pattern reveals several peaks located at 2θ values of 32.63° , 35.66° , 38.85° , 48.95° , 53.61° , 58.54° , 61.73° , 65.98° , 66.59° , 68.36° , 72.78° , and 75.53° . These reflections are indexed to the planes (110), (-111), (111), (-202), (020), (202), (-113), (022), (-311), (220), (311), and (-222), confirming the formation of the monoclinic phase of CuO according to JCPDS card No. 03-065-2309.

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For the multilayer ZnO/CuO film, the diffraction pattern is mainly dominated by the peaks corresponding to the CuO phase, while the characteristic peaks of ZnO are not clearly observed. This behavior may be explained by the relatively larger thickness of the CuO layer deposited on top of the ZnO layer, which leads to the predominance of CuO diffraction signals. In contrast, the CuO/ZnO multilayer film exhibits diffraction peaks belonging to both ZnO and CuO phases, confirming the coexistence of the two oxide structures within the multilayer architecture.

The lattice parameters of the hexagonal ZnO and monoclinic CuO structures were calculated using Bragg's law together with the corresponding crystallographic relations (Bouhouche et al., 2018). For ZnO, the calculated lattice constants are $a = b = 2.84 \text{ \AA}$ and $c = 4.92 \text{ \AA}$, which are consistent with standard values reported for wurtzite ZnO. In the case of CuO-based films, the lattice parameters were found to be approximately $a = 4.62 \text{ \AA}$, $b = 3.4 \text{ \AA}$, and $c = 4.3 \text{ \AA}$, which correspond well to those reported for monoclinic CuO.

The average crystallite size (D) was estimated using the Scherrer equation (Chouk et al., 2020) based on the most intense diffraction peaks, namely the (101) reflection for ZnO and the (111) reflection for CuO. The calculated crystallite sizes are found to be in the nanometer range, with values of approximately 16.7 nm for ZnO, 14.4 nm for CuO, 12.3 nm for ZnO/CuO, and 11.7 nm for CuO/ZnO thin films.

In addition to crystallite size, the microstrain (ϵ) and dislocation density (δ) were evaluated from the peak broadening using the standard relations (Uddin et al., 2024) (Dandeneau et al., 2009). The obtained results, summarized in Table V.2.1, reveal negative microstrain values for all films, indicating the presence of compressive stress within the deposited layers. Such compressive strain may originate from lattice mismatch between the oxide film and the glass substrate, as well as from differences in thermal expansion coefficients between the substrate and the deposited layers (Lee et al., 2025).

For the single-layer films, the microstrain values remain relatively small, ranging from about 0.06% to 0.18%, whereas a significantly larger value (−1.37%) is observed for the CuO/ZnO multilayer film. This increase may be attributed to the structural mismatch and stress generated at the interface between the two oxide layers in the multilayer configuration (Samarasekara et al., 2018).

The dislocation density also shows a gradual increase from ZnO to CuO and then to the multilayer films. The calculated values are $0.35 \times 10^{-2} \text{ nm}^{-2}$ for ZnO, $0.48 \times 10^{-2} \text{ nm}^{-2}$ for CuO, $0.67 \times 10^{-2} \text{ nm}^{-2}$ for ZnO/CuO, and $0.74 \times 10^{-2} \text{ nm}^{-2}$ for CuO/ZnO. The higher dislocation density observed in CuO-containing films may be related to the monoclinic crystal structure of CuO, which facilitates the

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formation of structural defects compared to the hexagonal ZnO lattice. Moreover, the decrease in crystallite size leads to a larger proportion of surface atoms, which increases defect density and grain boundary formation (Uddin et al., 2024) (Gomathi, 2018).

It is well known that crystallinity is inversely related to dislocation density [(Gomathi, 2018). Accordingly, the ZnO film, which exhibits the lowest dislocation density, presents the highest degree of crystallinity among the prepared samples. This structural characteristic is particularly important since crystallinity strongly influences the electrical and sensing properties of metal oxide semiconductors, which may contribute to the enhanced gas sensing performance observed for ZnO-based films.

Table V.2.1 Structural and microstructural parameters of ZnO, CuO, ZnO/CuO, and CuO/ZnO films.

Films	Phase	Plane (<i>hkl</i>)	2θ ($^{\circ}$)	<i>FWHM</i> β ($^{\circ}$)	<i>D</i> (<i>nm</i>)	<i>Microstrain</i> ε (%)	$\delta \cdot 10^{-2}$ (<i>nm</i> ⁻²)	<i>Lattice</i> <i>Parameters</i> ($\text{\AA}$)
ZnO	ZnO	(101)	36.46	0.522	16.73	-0.18	0.35	a= 2.841; b= 4.923
CuO	CuO	(111)	38.90	0.56	14.43	-0.07	0.48	a= 4.620; b= 3.421; c= 4.343
ZnO/CuO	CuO	(111)	38.90	0.51	12.27	-0.06	0.67	a= 4.623; b= 3.441; c= 4.333
CuO/ZnO	CuO	(- 111)	35.70	0.63	11.68	-1.37	0.74	a= 4.621; b= 3.414; c= 4.326

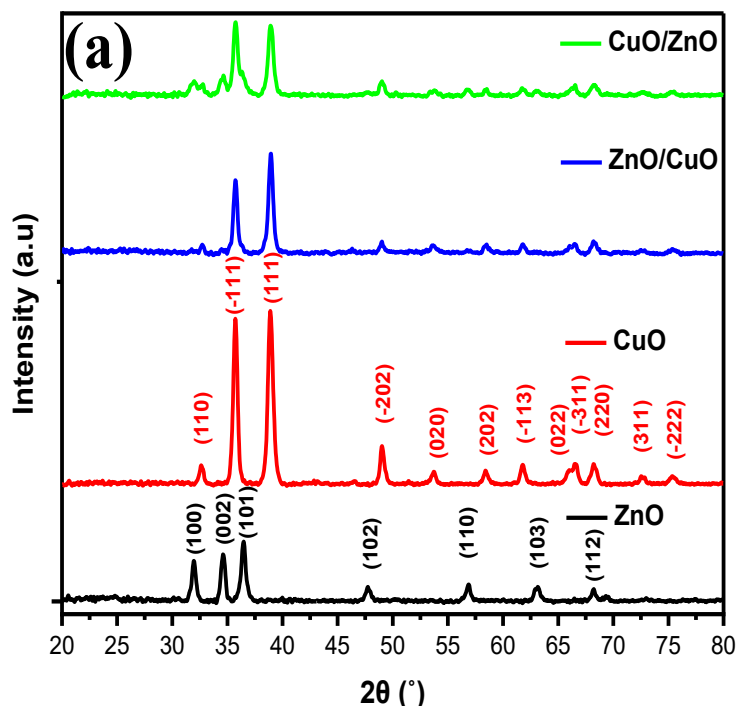


Figure V.2.1 XRD patterns of ZnO, CuO, ZnO/CuO, and CuO/ZnO films.

Further structural information was obtained from Raman spectroscopy, whose spectra are shown in Figure V.2.2. Raman spectroscopy is widely used to probe the vibrational modes of materials and provides valuable insights into crystal structure and structural defects. ZnO crystallizes in the hexagonal wurtzite structure belonging to the space group P6₃mc, which theoretically gives rise to several optical phonon modes, including A₁, E₁, E₂, and B₁ modes (Lupan et al., 2010).

In the Raman spectrum of ZnO film, three main peaks are observed at approximately 440, 557, and 576 cm⁻¹, corresponding respectively to the E₂(high), B₁(high), and A₁(LO) vibrational modes of ZnO. The E₂(high) mode located near 440 cm⁻¹ is considered a characteristic fingerprint of the wurtzite ZnO structure and is mainly associated with the vibration of oxygen atoms in the lattice. The presence of this peak confirms the formation of the hexagonal ZnO phase, in agreement with the XRD results. The sharpness and relatively small full width at half maximum (FWHM) of this band indicate a good crystalline quality of the ZnO thin film (Debbichi et al., 2012a).

The peak located around 576 cm⁻¹ corresponds to the A₁(LO) mode and is generally associated with lattice defects such as oxygen vacancies and zinc interstitials. The appearance of the B₁(high) mode near 557 cm⁻¹, which is normally Raman inactive, can be attributed to the presence of structural

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defects or disorder within the ZnO lattice (Dakhlaoui et al., 2009)(Dolai et al., 2017; Kunj & Sreenivas, 2016a; Zhou et al., 2007).

In the case of the CuO film, the Raman spectrum exhibits three characteristic bands located at approximately 279, 329, and 616 cm⁻¹, which correspond to the Ag, Bg(1), and Bg(2) vibrational modes of monoclinic CuO (Musa et al., 2017). A slight shift of these peaks toward lower wavenumbers compared to bulk CuO may be attributed to the quantum confinement effect in CuO nanostructures. For the multilayer films ZnO/CuO and CuO/ZnO, the Raman spectra reveal the coexistence of both oxide phases. A strong band near 279 cm⁻¹ confirms the presence of the CuO phase, whereas weaker bands around 441–445 cm⁻¹ and 572–574 cm⁻¹ indicate the presence of ZnO. However, the reduced intensity of ZnO Raman modes in the multilayer structures suggests a decrease in ZnO crystallinity after the deposition of the CuO layer.

Table V.2.2 Theoretical and experimental (results of this work) frequencies (in cm⁻¹) of the Raman modes of single- and bi-layered ZnO and CuO.

Modes	<i>ZnO</i> ²⁴ , <i>CuO</i> ⁴³ (cm ⁻¹)	<i>ZnO</i> (cm ⁻¹)	<i>CuO</i> (cm ⁻¹)	<i>CuO/ZnO</i> (cm ⁻¹)	<i>ZnO/CuO</i> (cm ⁻¹)
<i>E</i> ₂ ^{low}	101				
<i>A</i> ₁ (<i>TO</i>)	380				
<i>E</i> ₁ (<i>TO</i>)	407				
ZnO					
<i>E</i> ₂ ^{high}	437	440	1		445
<i>A</i> ₁ (<i>LO</i>)	574	576	2		574
<i>E</i> ₁ (<i>LO</i>)	583				
<i>B</i> ₁ ^{high} (<i>silent</i>)	552 ⁴²	557			557
CuO					
<i>A</i> _g	296		279	7	277
<i>B</i> _g ⁽¹⁾	344		329	7	339
<i>B</i> _g ⁽²⁾	629		616	5	616

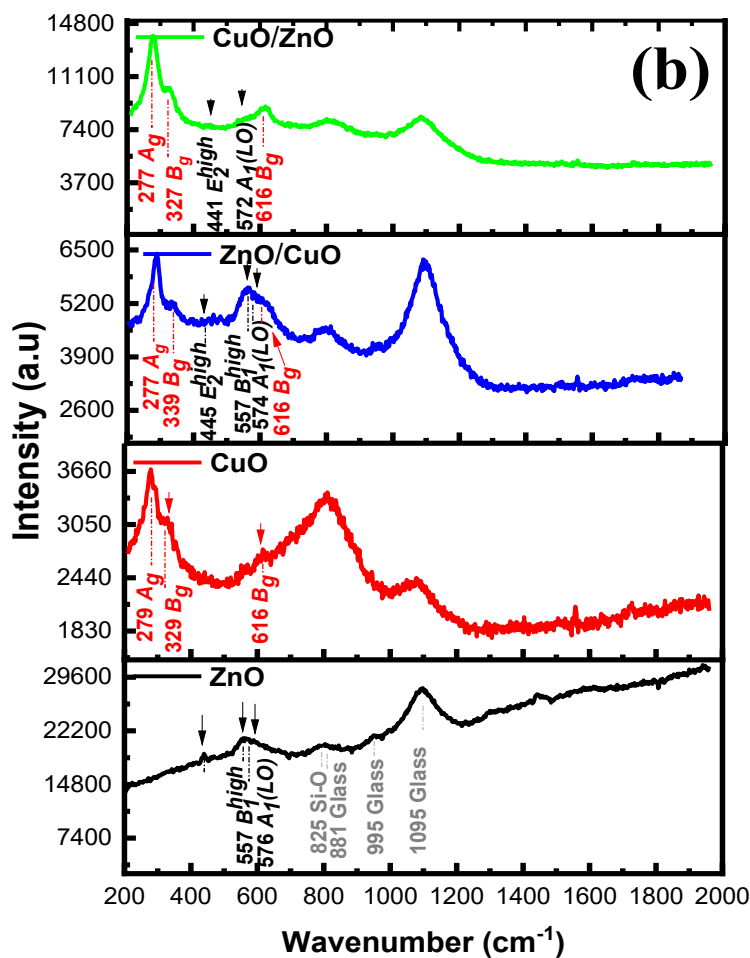


Figure V.2.2 Micro-Raman spectra of ZnO, CuO, ZnO/CuO, and CuO/ZnO thin films.

Additional structural confirmation was obtained from FT-IR spectroscopy, and the corresponding spectra are presented in Figure V.2.3. The FT-IR spectrum of the ZnO film shows a strong absorption band located around 447 cm⁻¹, which is attributed to the stretching vibration of the Zn–O bond (Calzolari & Nardelli, 2013) (Musa et al., 2017) (Iaiche et al., 2020) (Kunj & Sreenivas, 2016b). This band appears slightly shifted compared to bulk ZnO, which may be related to the nanoscale nature of the film.

For the CuO thin film, several absorption bands are observed at approximately 453, 493, 532, and 583 cm⁻¹, corresponding to the characteristic stretching vibrations of the Cu–O bond in the monoclinic CuO structure (Loiko et al., 2016), (Zhu et al., 2021), (Dey et al., 2021), (Ivanova et al., 2023). The absence of absorption bands associated with Cu₂O indicates that the deposited film consists predominantly of pure CuO phase.

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In the case of the ZnO/CuO multilayer film, a broad absorption band appears around 500 cm⁻¹, resulting from the overlap of the Zn–O and Cu–O vibrational modes. The slight shift of this band toward lower wavenumbers may be attributed to lattice mismatch and strain effects occurring at the interface between ZnO and CuO layers (Erdoğan, 2010).

Other absorption bands observed at higher wavenumbers are mainly related to residual species and environmental contributions. The broad band around 3440 cm⁻¹ and the band near 1636 cm⁻¹ correspond to the stretching and bending vibrations of adsorbed water molecules (Pillai et al., s. d.). The band near 1385 cm⁻¹ can be assigned to residual acetate groups originating from the precursor solution, while the bands observed near 2854–2956 cm⁻¹ are attributed to C–H stretching vibrations. A weak band around 2345 cm⁻¹ is associated with atmospheric CO₂, whereas the band near 1035 cm⁻¹ corresponds to Si–O vibrations from the glass substrate.

Overall, the combined XRD, Raman, and FT-IR analyses confirm the successful formation of ZnO and CuO phases in the deposited thin films and demonstrate the coexistence of both oxides in the multilayer structures.

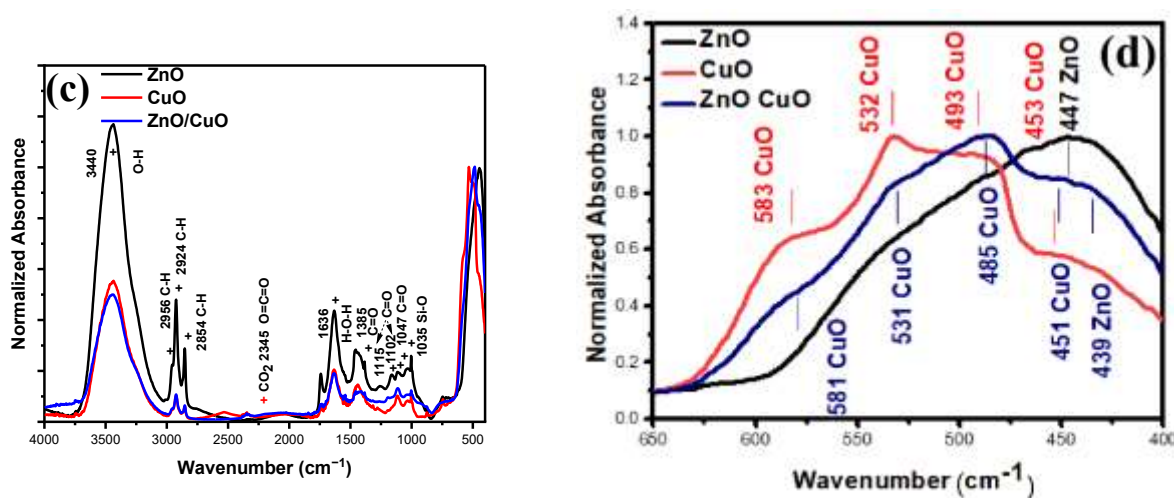


Figure V.2.3 FTIR spectra of the ZnO, CuO, and ZnO/CuO films.

V.3.2 Surface morphology and topography observations

To better understand the influence of surface structure on the sensing behavior of the prepared films, their morphology and surface topography were investigated using field emission scanning electron microscopy (FESEM) and atomic force microscopy (AFM). These techniques provide valuable information regarding grain distribution, surface roughness, and porosity, which are important parameters for gas sensing applications.

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The FESEM micrographs of the deposited films are presented in Figure V.2.4. The images reveal noticeable differences in the surface morphology depending on the oxide composition and the stacking sequence of the layers.

The ZnO thin film (Figure V.2.4.a) exhibits a relatively smooth and homogeneous surface composed of quasi-spherical nanoparticles uniformly distributed over the substrate. The grains appear to be very small and closely packed, forming a sponge-like porous structure. The average particle size is estimated to be in the range of 40–50 nm (Erdoğan & Güllü, 2010).

Such morphology generally leads to an increased surface area, which is beneficial for gas sensing applications since it provides more active sites for gas adsorption (Ungeheuer et al., 2022). In addition, a few micro-cracks can be observed on the surface, which are likely related to internal stress generated during the drying process of the sol-gel layer.

For the CuO thin film (Figure V.12b), the surface morphology appears more heterogeneous. The grains exhibit a broader size distribution with the coexistence of relatively large particles (around 250 nm) and smaller ones (around 100 nm). The particles still show a roughly spherical shape but with a less uniform arrangement compared to ZnO. This type of morphology is consistent with previous reports on CuO films prepared by similar methods (Debbichi et al., 2012b).

The morphology of the ZnO/CuO bilayer film (Figure V.12c) reveals a noticeable reduction in the size of CuO grains compared to those observed in the single CuO layer. This behavior may be related to the growth of the CuO layer on a previously crystallized ZnO surface, which can influence the nucleation process and lead to smaller grain formation. Similar observations were reported by Bhowmick et al. (Mejia-Bernal et al., 2025), who attributed this reduction in grain size to the deposition of a thin CuO layer over well-crystallized ZnO grains.

In contrast, the CuO/ZnO bilayer film (Figure V.12d) presents a different morphology. When the ZnO layer is deposited on top of the CuO underlayer, the grains tend to adopt a more flattened or plate-like structure rather than the quasi-spherical morphology observed for single ZnO films. Grain size analysis performed using ImageJ software indicates that the ZnO grains are randomly distributed with sizes ranging from 150 to 300 nm in the CuO/ZnO film. Meanwhile, the ZnO/CuO film exhibits a denser microstructure with smaller grain sizes distributed within the 60–200 nm range. This behavior may be attributed to the presence of additional nucleation sites provided by the Cu layer, which promotes the formation of a larger number of smaller grains (Saleem, Jabbar, et al., 2022).

Overall, the FESEM observations indicate that the multilayer structure significantly modifies the surface morphology of the films. The presence of porous regions and interconnected grains provides

a larger active surface area that can facilitate gas adsorption and improve the sensitivity of the sensing material.

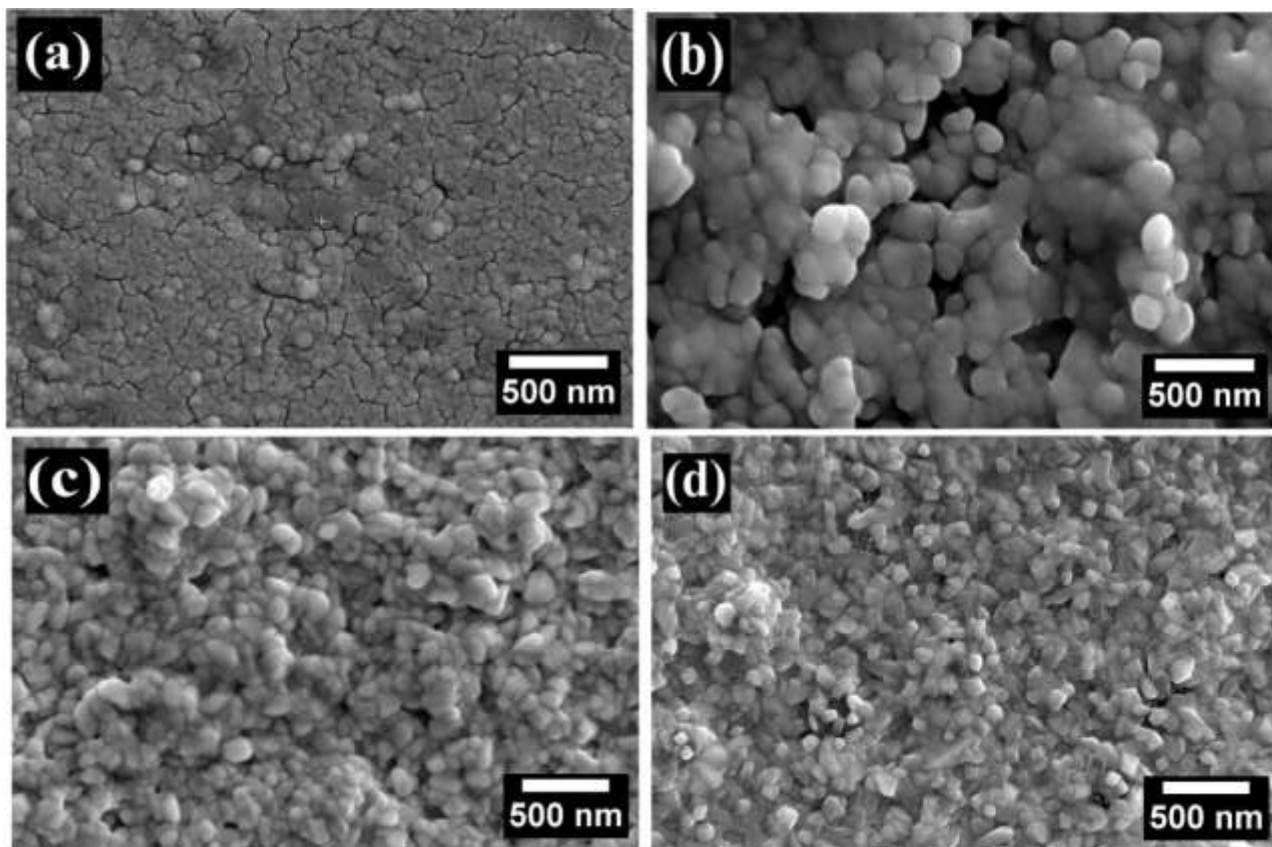


Figure V.2.4 FESEM images of (a) ZnO, (b) CuO, (c) ZnO/CuO, and (d) CuO/ZnO thin films.

Further information about the surface topography was obtained using AFM measurements performed in tapping mode. The three-dimensional surface images of the films are shown in Figure V.2.5, while the corresponding roughness values are summarized in Table V.1.3. The surface roughness was determined using the Gwyddion software package (Balık et al., 2019).

The AFM image of the ZnO thin film (Figure V.2.5.a) reveals a very smooth and uniform surface composed of fine grains with a relatively homogeneous distribution, in agreement with previously reported results (Alhumaimess et al., 2020). The measured surface roughness is very low, approximately 1 nm, indicating the formation of a compact and continuous film.

In contrast, the CuO thin film (Figure V.2.5.b) shows a significantly rougher and less uniform surface. The grains appear larger and more irregularly distributed, which leads to a higher surface roughness value of approximately 23 nm. The larger grain size contributes to the formation of a more discontinuous structure with increased porosity.

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For the multilayer structures, the surface topography strongly depends on the deposition sequence. The ZnO/CuO film (Figure V.2.5.c) exhibits grains whose sizes are intermediate between those of pure ZnO and pure CuO. On the other hand, the CuO/ZnO film (Figure V.2.5.d) presents a mixed morphology composed of both small and large grains.

Interestingly, the roughness and porosity levels differ between the two bilayer configurations. The ZnO/CuO film generally exhibits higher surface roughness compared to the CuO/ZnO structure. This observation indicates that the top layer plays a significant role in determining the final surface characteristics of the multilayer film. Similar behavior was reported by Vuong et al. (Narang et al., 1992), who showed that the presence of CuO can significantly influence the surface roughness of ZnO layers.

Overall, the AFM results confirm the observations obtained from FESEM analysis. Both techniques reveal that the prepared films consist of aggregated nanocrystals forming grains of various sizes separated by small voids. These structural features increase the available surface area and create active sites for gas adsorption, which is beneficial for improving the sensing performance of the films.

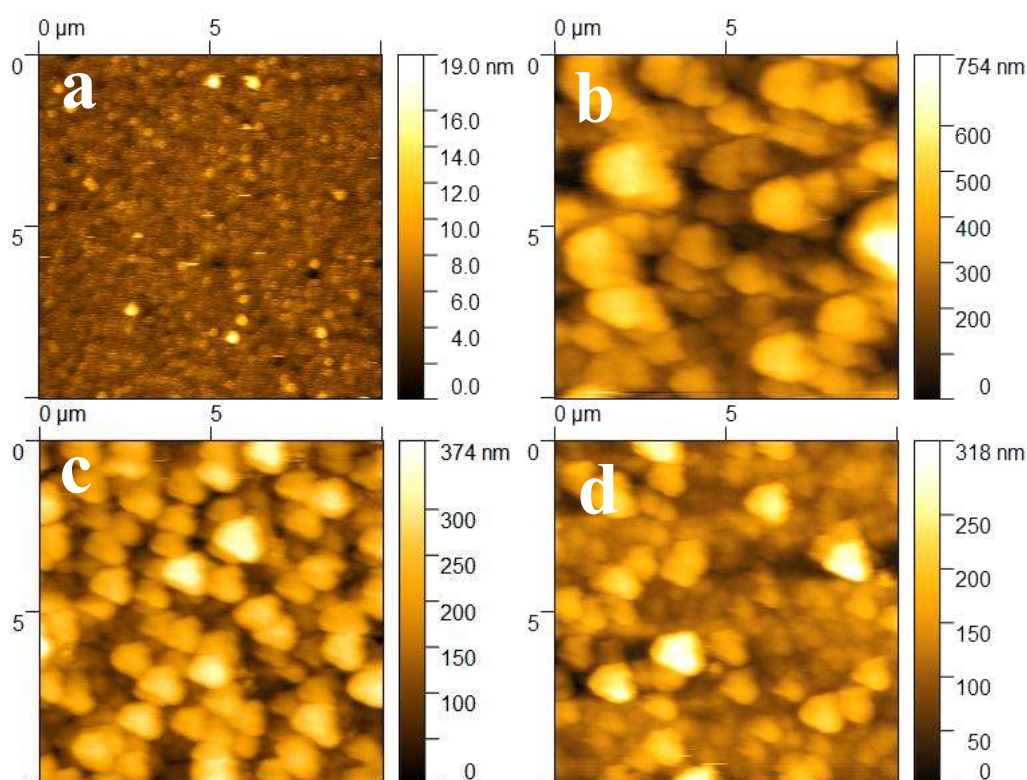


Figure V.2.5 AFM images of (a) ZnO, (b) CuO, (c) ZnO/CuO, and (d) CuO/ZnO thin films.

Table V.2.3 Analysis of the roughness parameters Ra (the arithmetic average roughness) and RRMS (the root-mean-square average roughness).

Films	R _a (nm)	R _{RMS} (nm)
ZnO	0.6	0.8
CuO	17.9	23
ZnO/CuO	17.6	21.3
CuO/ZnO	8.9	11.6

V.3.3 Optical properties

The optical behavior of the prepared thin films was investigated through optical transmittance measurements in the UV–visible spectral range. The transmittance spectra $T(\lambda)$ of ZnO, CuO, ZnO/CuO, and CuO/ZnO thin films are presented in Figure V.2.6.a.

The ZnO thin film exhibits a very high optical transparency in the visible region (380–780 nm), with transmittance values exceeding 90%. Such high transparency is typically associated with the good crystallinity and smooth surface morphology of ZnO films. In fact, AFM analysis revealed that the ZnO layer possesses a very low surface roughness of approximately 1 nm, which minimizes light scattering and allows efficient transmission of visible light.

In contrast, the CuO thin film shows a significantly lower optical transmittance of about 47% in the visible region. This reduction in transparency can be attributed to the rougher surface and larger grain size observed for the CuO film. Indeed, the AFM measurements indicate that CuO exhibits a much higher surface roughness (around 108 nm), which enhances light scattering and absorption, thereby reducing the transmitted intensity.

For the bilayer structures, namely ZnO/CuO and CuO/ZnO, the optical transmittance decreases further. The measured transmittance values at 800 nm are approximately 38% for ZnO/CuO and 42% for CuO/ZnO films. These results indicate that the stacking order of the layers does not significantly influence the overall transparency of the bilayer system, as both configurations exhibit relatively similar optical behavior.

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The optical band gap energy of the films was determined using the first derivative method of the transmittance spectra, as illustrated in Figure V.2.6.b. The band gap energy E_g was calculated using the following relation (Boudjouan et al., 2016):

$$E_g = \frac{hc}{\lambda_{max}} \quad (V.4)$$

where h is Planck's constant, c is the speed of light, and λ_{max} represents the wavelength corresponding to the maximum value of the first derivative of the transmittance curve ($dT/d\lambda$).

The calculated band gap energies are 3.30 eV, 1.58 eV, 1.578 eV, and 1.589 eV for ZnO, CuO, ZnO/CuO, and CuO/ZnO films, respectively. The obtained value of 3.3 eV for ZnO corresponds to the typical direct band gap of ZnO, while the value of approximately 1.58 eV for CuO is consistent with the reported indirect band gap energy of monoclinic CuO in the literature (Dabir et al., 2020).

Interestingly, the bilayer films (ZnO/CuO and CuO/ZnO) exhibit band gap values very close to that of CuO. This behavior suggests that the optical response of the bilayer structures is largely dominated by the CuO layer, which possesses the smaller band gap. In such heterostructures, the interaction between the electronic structures of the two oxides can modify the optical properties of the system, but the material with the narrower band gap generally governs the overall absorption behavior.

Figure V.2.6.c illustrates the evolution of the band gap energy as a function of the microstrain obtained from XRD analysis. It can be observed that the band gap energy tends to decrease with increasing microstrain. Microstrain represents small distortions within the crystal lattice that arise from structural imperfections, lattice mismatch, or internal stresses. These distortions may alter the atomic arrangement and modify bond lengths within the lattice, which in turn can influence the electronic band structure of the material.

In some cases, an increase in microstrain leads to a slight narrowing of the band gap due to the creation of defect states or modifications in the electronic energy levels. Therefore, the observed inverse relationship between microstrain and band gap energy may be attributed to structural distortions affecting the electronic properties of the films. Understanding this relationship is important for optimizing the optical and sensing performance of metal oxide thin films used in gas sensor applications.

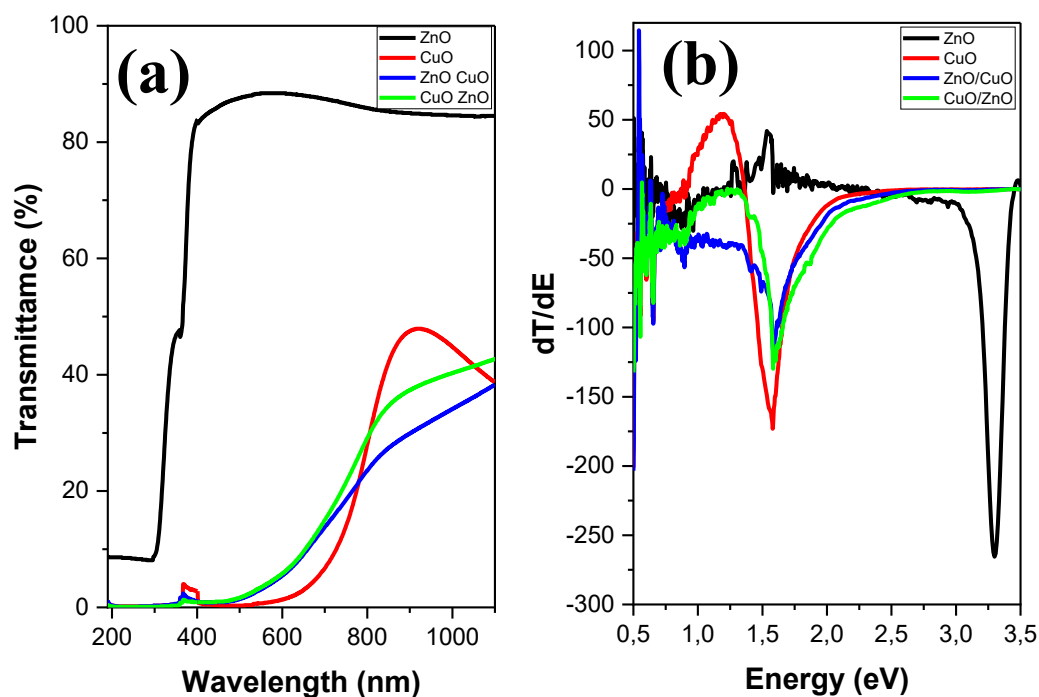


Figure V.2.6 a. Transmittance spectrum, b. First derivative ($dT/d\lambda$) plot of the transmittance spectra of ZnO, CuO, ZnO/CuO, and CuO/ZnO thin films.

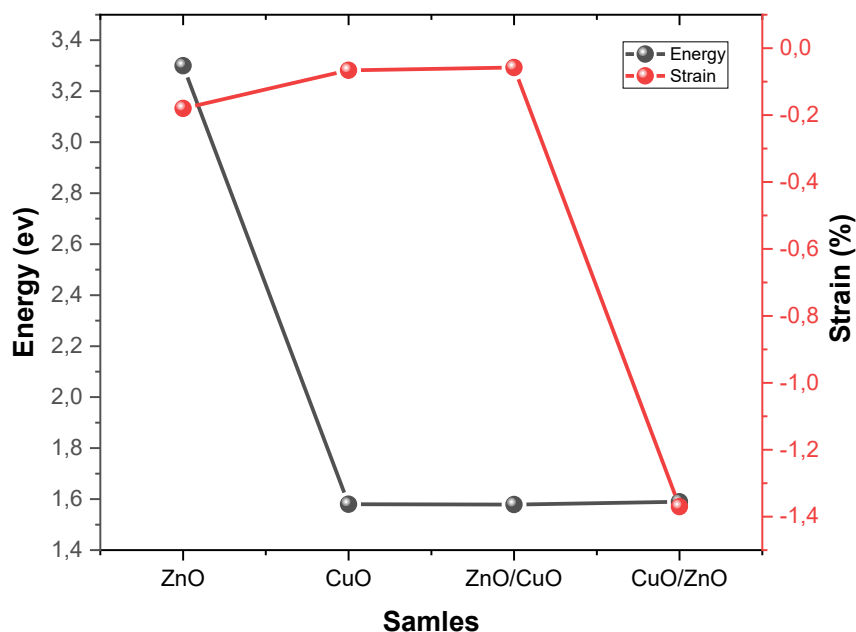


Figure V 2.6.c. Energy gap and Strain of ZnO, CuO, ZnO/CuO, and CuO/ZnO films.

V.3.4 CO₂ gas sensing measurements

Current-voltage characteristics

The electrical response of the fabricated sensing devices was first investigated through current–voltage (I–V) measurements. The I–V characteristics of the sensors based on ZnO, CuO, ZnO/CuO, and CuO/ZnO thin films are presented in Figure V.2.7. Measurements were carried out at room temperature under different environmental conditions, including vacuum, air, and CO₂ atmospheres with concentrations ranging from 15.5 to 124 ppm, while the applied voltage was varied between –1.5 V and +1.5 V.

The obtained I–V curves exhibit a linear relationship between current and applied voltage for all investigated samples. In addition, the curves are symmetric with respect to the applied potential, indicating that the sensing devices behave as ohmic resistive elements. This linear behavior suggests that the electrical conduction mechanism remains stable over the investigated voltage range.

A comparison between the measurements performed in air and those obtained in the presence of CO₂ reveals noticeable variations in the electrical current as the gas concentration changes. For a fixed applied voltage, the current tends to increase with increasing CO₂ concentration, particularly for the ZnO-based sensor, where a clear increase in current is observed as the gas concentration rises. This behavior indicates that the electrical response of the sensing device is strongly influenced by the presence of CO₂ molecules interacting with the film surface.

A closer examination of the I–V curves within the narrow voltage range between –1.5 V and –1.3 V (zoomed region in Figure V.2.7) shows a significant current variation upon CO₂ exposure. This observation highlights the enhanced sensitivity of the devices within this specific voltage region, suggesting that this bias range may be particularly suitable for sensing applications.

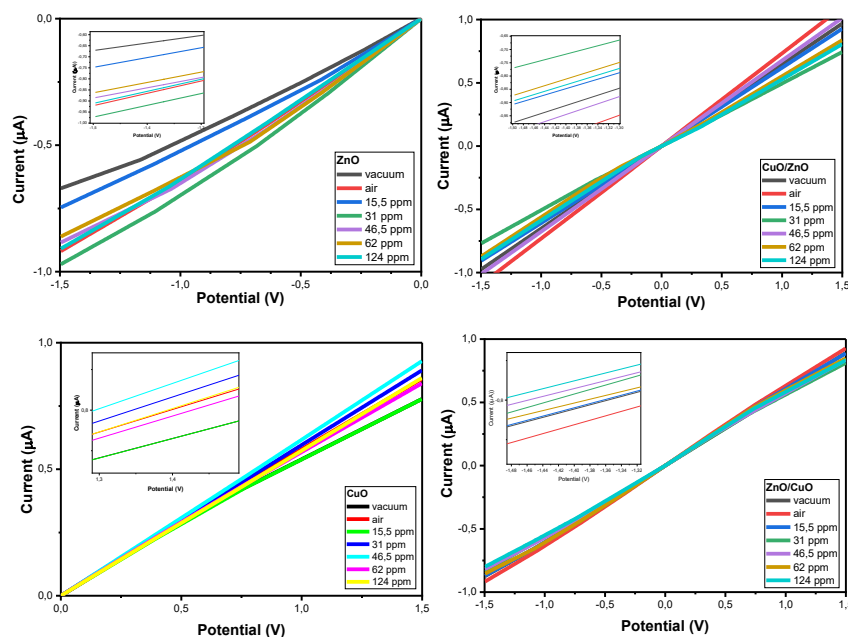


Figure V.2.7 I–V characteristics of the ZnO, CuO, ZnO/CuO, CuO/ZnO sensor toward CO₂ gas at a temperature of 25°C and different concentrations.

Sensitivity-Concentration dependence

The variation of sensor sensitivity as a function of CO₂ concentration is illustrated in Figure V.2.8 for all fabricated sensing structures. The measurements were carried out at room temperature using a constant bias voltage. For all investigated devices, the sensitivity initially increases with increasing CO₂ concentration until reaching a maximum value, after which it gradually decreases and tends to stabilize. This behavior is commonly observed in gas-sensing materials and is generally associated with the progressive occupation of available adsorption sites on the sensor surface.

Among the tested structures, the ZnO-based sensor exhibits the best sensing performance. A maximum sensitivity of approximately 44.77% is obtained at a relatively low concentration of 31 ppm. In comparison, the CuO sensor shows a lower sensitivity of about 20% at 46.5 ppm, indicating a less pronounced electrical response toward CO₂.

For the bilayer structures, the sensing performance strongly depends on the stacking sequence of the oxide layers. The CuO/ZnO sensor demonstrates a higher sensitivity (21% at 31 ppm) compared with the ZnO/CuO sensor, which reaches only 6.5% at 46.5 ppm. This result is consistent with the behavior observed for the single-layer sensors, where ZnO shows better sensing capability than CuO.

The superior performance of ZnO-based sensors can be explained by several intrinsic properties of ZnO, including its higher electron mobility, wider band gap, strong surface reactivity, and relatively

large specific surface area. These characteristics facilitate the adsorption of gas molecules and promote efficient charge transfer processes during gas detection.

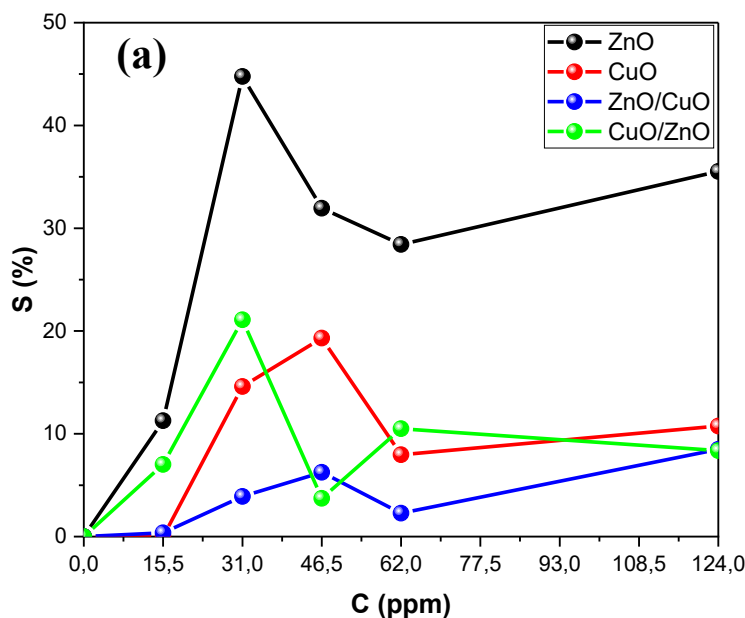


Figure V.2.8 S–C sensitivity of the ZnO, CuO, ZnO/CuO, and CuO/ZnO sensors toward CO₂ gas at a temperature of 25°C and different concentrations. Bias potential 0.5 V.

Response and recovery times

Another important parameter used to evaluate gas sensor performance is the response and recovery time, which characterizes how quickly the sensor reacts to changes in gas concentration.

The response time is defined as the time required for the sensor signal to reach 90% of its final value after exposure to the target gas. Conversely, the recovery time corresponds to the time needed for the sensor signal to return to 10% of its baseline value once the gas is removed from the chamber [9]. These two parameters are closely related to the adsorption and desorption processes of gas molecules on the sensor surface.

The dynamic response of the ZnO sensor at different CO₂ concentrations under an applied voltage of 0.5 V is shown in Figure V.2.9. When CO₂ is introduced into the chamber, the electrical current gradually increases until reaching a saturation level. After the gas supply is stopped, the current progressively returns to its initial value. This reversible behavior confirms that the sensor response is governed by adsorption and desorption processes occurring at the film surface.

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Figures V.2.10.a and V.2.10.b present a typical example of the response and recovery times measured for the ZnO thin film exposed to 46.5 ppm of CO₂. The ZnO sensor exhibits relatively fast dynamics with response and recovery times of 13.5 s and 9.8 s, respectively.

For the ZnO sensor, both response and recovery times decrease as the gas concentration increases, reaching minimum values around 62 ppm, and then slightly increase at higher concentrations. This trend is commonly reported in gas sensing studies and is generally attributed to the progressive saturation of adsorption sites on the sensor surface.

A similar behavior is observed for the CuO sensor, where the response and recovery times decrease until reaching minimum values near 62 ppm, followed by stabilization at higher gas concentrations. The response time of the CuO sensor is approximately 18.97 s, while the recovery time is around 8.1 s.

For the bilayer sensors, the sensing dynamics depend strongly on the top layer of the structure. In the ZnO/CuO configuration, the response and recovery times initially increase up to 31 ppm, then decrease rapidly up to 62 ppm, followed by a gradual reduction at higher concentrations. In contrast, the CuO/ZnO sensor exhibits an initial decrease in response and recovery times at 31 ppm, followed by a noticeable increase at higher gas concentrations.

These observations highlight the important role played by both intrinsic properties of the sensing materials and extrinsic factors related to the heterostructure configuration, which together influence the interaction between the sensor surface and the target gas molecules.

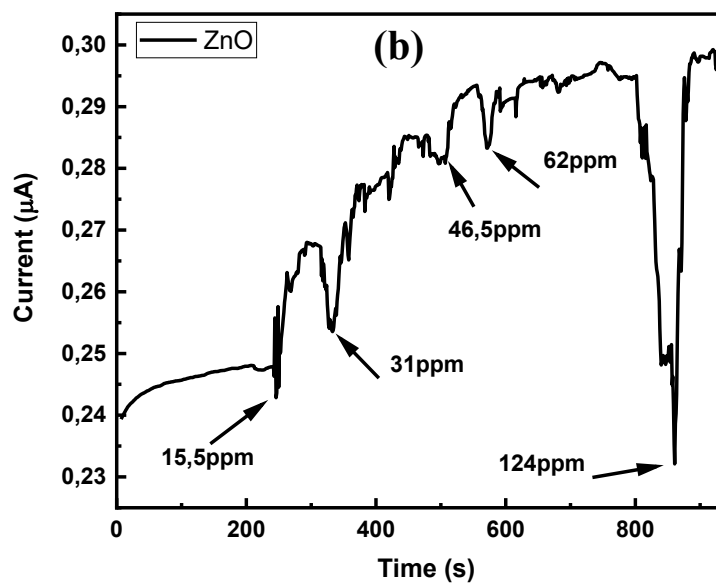


Figure V.2.9 Dynamic response of ZnO in different CO₂ gas concentrations at 0.5 V applied bias.

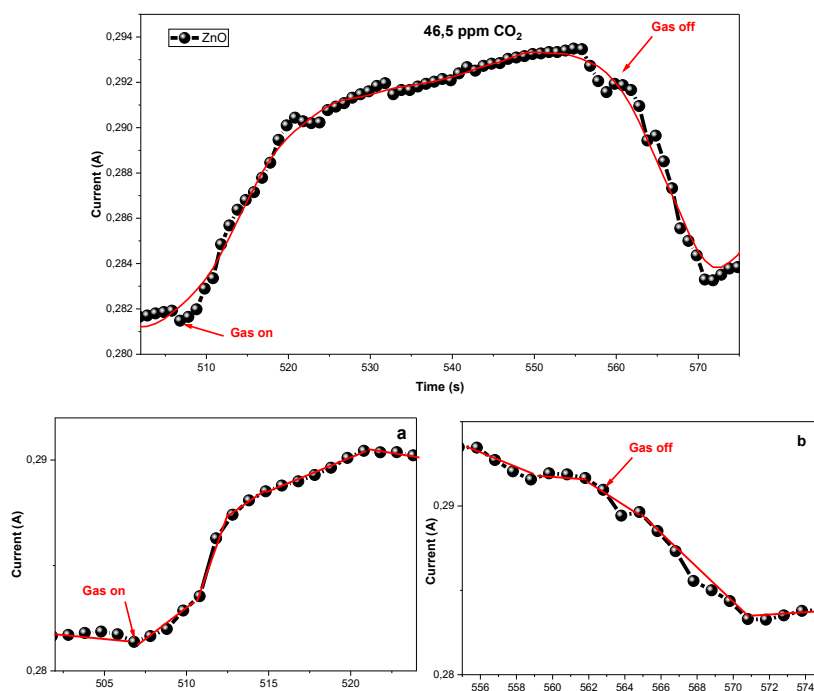


Figure V.2.10 a Response -time, b Recovery-time measurement of ZnO thin film for 45.6 ppm CO₂ concentration.

V.3.5 Sensing mechanism

The sensing behavior of metal oxide gas sensors is mainly governed by the adsorption and desorption processes occurring on the surface of the sensing material. These surface reactions lead to variations in the electrical resistance of the semiconductor, which are used as the detection signal for the target gas (Ghanbari Shohany et al., 2018). The sensing mechanism differs depending on whether the oxide behaves as an n-type or a p-type semiconductor.

For n-type semiconductors, such as ZnO, the sensing mechanism is primarily controlled by the interaction between atmospheric oxygen and the surface of the oxide. When the ZnO sensor is exposed to air, oxygen molecules are adsorbed on the surface and capture electrons from the conduction band of the semiconductor, forming ionized oxygen species such as O_2^- , O^- , or O^{2-} , depending on the operating temperature (González-Garnica et al., 2021) (Maier et al., 2024). At temperatures below 100 °C, which corresponds to the conditions used in this work, oxygen molecules generally capture only one electron according to the following reaction (Bhowmick et al., 2022):



These adsorbed oxygen ions modify the electronic structure near the surface by creating oxygen-related defects and charge redistribution within the lattice. The interaction affects the density and mobility of the charge carriers, leading to changes in the electrical conductivity of the sensing layer.

When the sensor is exposed to CO₂ gas, the gas molecules interact with the adsorbed oxygen species and the ZnO surface. CO₂ molecules may chemisorb on the surface and capture electrons from the semiconductor lattice, leading to the formation of carbonate species such as CO_3^{2-} . This process reduces the number of free electrons available in the conduction band, resulting in a decrease in electrical conductivity and consequently an increase in the sensor resistance. The variation in the electrical signal therefore indicates the presence of CO₂ in the surrounding environment.

Once the CO₂ supply is stopped and the sensor is returned to air, the carbonate species gradually decompose and release the trapped electrons back into the conduction band of the ZnO layer. As a result, the electrical resistance returns to its initial value, completing the sensing cycle.

For p-type semiconductors, such as CuO, the sensing mechanism follows the opposite behavior. When CuO is exposed to air, oxygen molecules adsorb on the surface and extract electrons from the semiconductor. This process leads to an increase in hole concentration near the surface, forming a hole accumulation layer. As holes are the majority charge carriers in p-type materials, the electrical resistance decreases under these conditions (Maki & Mahmoud, 2017).

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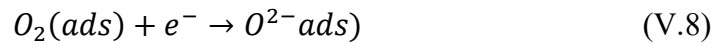
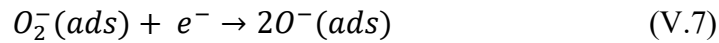
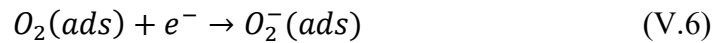
Upon exposure to CO₂ gas, the interaction between the gas molecules and the adsorbed oxygen species modifies the charge carrier concentration. The reactions occurring on the CuO surface reduce the number of available holes, which leads to an increase in the electrical resistance of the film.

Previous studies have reported similar behavior for CuO-based CO₂ sensors. For instance, Sameer Atta Maki et al. reported a sensitivity of approximately 14% for CuO films with a thickness of 200 nm at room temperature (Ashok et al., 2016). In another work, Bhowmick et al. prepared CuO thin films using the sol-gel technique and observed that the sensor response toward CO₂ became significant only at temperatures above 250 °C (Bhowmick et al., 2022).

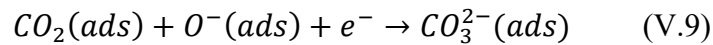
In the present study, the fabricated CuO sensor exhibits a response of about 21%, which demonstrates improved sensing performance under ambient conditions.

For the bilayer structures (ZnO/CuO and CuO/ZnO), the sensing mechanism becomes more complex due to the formation of p-n heterojunctions at the interface between the two oxides. The interaction between the n-type ZnO and the p-type CuO leads to charge transfer across the interface, which modifies the distribution of electrons and holes within the structure.

In air, oxygen molecules adsorb on the surface of both oxides and form ionized oxygen species according to the following reactions:



When the bilayer sensor is exposed to CO₂, the gas molecules interact with these adsorbed oxygen species through surface reactions such as:



These reactions consume electrons and modify the thickness of the depletion or accumulation layers at the oxide surface. In the ZnO/CuO configuration, where the n-type ZnO layer is located on top, electron withdrawal increases the depletion region, leading to an increase in the electrical resistance.

On the other hand, in the CuO/ZnO configuration, where the p-type CuO layer forms the surface, the interaction with CO₂ mainly affects the hole concentration and the potential barrier at the interface, which may result in a different variation of the electrical signal.

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Therefore, the sensing behavior of bilayer structures is strongly influenced by the heterojunction interface, band alignment, and charge transfer processes occurring between the two oxides. These interfacial effects play an important role in determining the overall sensitivity of the device.

V.3.6 Conclusion

In this work, single-layer (ZnO and CuO) and bilayer (ZnO/CuO and CuO/ZnO) metal oxide thin films were successfully fabricated using the sol–gel dip-coating technique for CO₂ gas sensing at room temperature.

Structural characterization performed by X-ray diffraction (XRD) confirmed the formation of polycrystalline ZnO and CuO phases. Additional investigations using Raman and FTIR spectroscopy further verified the presence of the characteristic vibrational modes associated with both oxides.

Surface morphology analysis revealed significant differences between the films. The ZnO thin film exhibited a very smooth surface with a roughness of approximately 1 nm, whereas the CuO film showed a much higher roughness of about 108 nm.

Gas sensing measurements demonstrated that the ZnO thin film sensor provides the best sensing performance among the investigated structures. The highest sensitivity of 44.8% was obtained at a CO₂ concentration of 31 ppm. The CuO/ZnO bilayer sensor showed the second-best performance with a sensitivity of 21.1% at the same concentration. In comparison, the CuO and ZnO/CuO sensors exhibited sensitivities of 19.3% at 46.5 ppm and 6.0%, respectively.

All sensors displayed relatively fast response and recovery times, ranging from 6.0 to 46.2 s and 0.86 to 33.55 s, respectively.

Although the bilayer structures were designed to enhance the sensing performance through heterojunction effects, their response did not exceed that of the single-layer ZnO sensor. This result suggests that the additional layer may partially limit surface activity or charge transport in the current configuration.

Nevertheless, the investigation of bilayer architectures remains important because it provides valuable insights into the influence of layer sequence, interface effects, and charge transfer mechanisms on gas sensing behavior. Further optimization of deposition parameters and material combinations may lead to improved sensing performance in future multilayer sensor systems.

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General Conclusion

General Conclusion

This thesis focused on the synthesis, characterization, and use of metal oxide-based thin films, namely zinc oxide (ZnO) and its modified structures, produced by an economical sol-gel dip-coating method. The main aim of this study was to explore the potential of these materials for environmental and optoelectronic applications, such as photocatalysis, UV photodetection, and gas sensing, while responding to the pressing demand for cost-effective, efficient, and sustainable technologies that can aid in environmental protection and pollution reduction.

The initial section of this study provided an extensive theoretical framework, emphasizing the essential physical, structural, and optical characteristics of metal oxides, specifically ZnO and CuO. Their extensive bandgap, chemical stability, abundance, and non-toxicity render them exceptionally appealing for environmental and energy-related applications. This thesis underscores the significance of these materials in tackling global environmental issues, including air pollution, water contamination, and greenhouse gas emissions, so providing a compelling impetus for the experimental research conducted.

The second chapter concentrated on the strategies of elaboration and the methods of characterization utilized in this study. The sol-gel dip-coating technique was chosen for its simplicity, cost-effectiveness, scalability, and capacity to generate homogeneous thin films with precise thickness control. Comprehensive experimental protocols were devised, encompassing precursor solution preparation, substrate selection and cleaning, and thin film deposition parameters. Structural, morphological, optical, and compositional characterization techniques—such as XRD, Raman spectroscopy, FTIR, AFM, SEM, UV-visible spectroscopy, and EDX—were systematically employed to gain detailed knowledge of the physicochemical features of the produced thin films. This scientific paradigm offered a solid foundation for linking material attributes with functional performance in the following chapters.

The third chapter was dedicated to the photocatalytic use of ZnO-based thin films. Thorough research was undertaken to examine the effect of major processing factors, including annealing temperature and duration, number of dip-coating cycles, and precursor molarity, on the photocatalytic degradation of methylene blue under UV irradiation. The results clearly revealed that these factors have a key role in affecting the structural quality, optical absorption, and photocatalytic performance of the films. Optimized annealing conditions resulted in better crystallinity and reduced defect density, which in turn promoted charge carrier mobility and reduced electron-hole recombination. Furthermore, doping and co-doping techniques, notably with urea and silver, dramatically increased the photocatalytic activity by altering the electrical structure and facilitating more efficient charge separation. These

findings demonstrate that controlled material engineering is a useful technique to enhance photocatalytic activity for environmental remediation applications. In the fourth chapter, the optoelectronic performance of Ag-doped ZnO thin films produced on silicon substrates was examined for UV photodetector applications. The structural and optical characterizations revealed the effective integration of silver into the ZnO matrix and its effects on grain size, surface morphology, and optical absorption. The constructed UV photodetector displayed a clear and repeatable response under UV irradiation, confirming the feasibility of Ag-doped ZnO thin films for UV sensing applications. This work demonstrates the promise of low-cost metal oxide thin films for optoelectronic devices that function under low power consumption, which is critical for portable and ecologically friendly technologies.

The fifth chapter addressed gas sensing applications, with specific attention on Mg-doped ZnO thin films and ZnO/CuO multilayer structures for CO₂ detection at ambient temperature. The results demonstrated that both doping and multilayer topologies greatly impact gas sensing performance by modifying surface morphology, band structure, and interfacial charge transfer processes. The development of n-p heterojunctions in ZnO/CuO multilayers boosted sensitivity and response characteristics, proving the usefulness of heterostructure engineering in gas sensor design. The ability to detect CO₂ at low concentrations at room temperature provides a crucial benefit for real-world environmental monitoring, as it decreases energy usage and simplifies device operation. Overall, the experimental results reported in this thesis reveal that metal oxide thin films generated by low-cost sol-gel processes may be efficiently customized for different environmental and optoelectronic applications. The tight link between synthesis parameters, material characteristics, and device performance underscores the need of rigorous optimization and material design. This work indicates that ZnO-based thin films, whether pure, doped, or mixed with other metal oxides, constitute diverse and promising materials for tackling environmental concerns. From a larger viewpoint, this thesis contributes to the development of sustainable technology associated with global environmental objectives and the United Nations Sustainable Development Goals. By addressing low-cost manufacturing processes, non-toxic materials, and energy-efficient operation, this study promotes the creation of accessible and ecologically responsible solutions for pollution control, environmental monitoring, and clean energy-related applications. In conclusion, our study gives useful insights into the design and optimization of metal oxide thin films for multifunctional applications. The discoveries not only increase scientific knowledge but also provide avenues for practical applications in environmental cleanup, sensing technologies, and optoelectronic devices. It is intended that the results provided in this thesis will stimulate additional

study and contribute to the ongoing efforts to develop sustainable, low-cost, and efficient solutions for a cleaner and healthier environment.

Perspectives

The conclusions of this work emphasize the significant potential of metal oxide-based thin films as effective and sustainable solutions for tackling contemporary environmental concerns. Given the rising concerns connected to air pollution, water contamination, and climate change, the development of low-cost, efficient, and environmentally friendly materials has become a crucial research goal. In this context, metal oxides such as ZnO and its derivatives offer potential possibilities because to their chemical stability, non-toxicity, and abundance.

One of the key aspects of this study is the advancement of environmental applications employing metal oxides produced by cost-effective procedures, such as the sol-gel dip-coating method. This technique has major advantages, including simplicity, low energy consumption, scalability, and decreased manufacturing costs, making it appropriate for large-scale environmental cleanup systems. Future work might focus on refining these synthesis pathways to further reduce costs while preserving or increasing material performance.

Another major aspect lies in increasing the functional features of metal oxide thin films for environmental applications such as gas sensing, photocatalytic destruction of organic contaminants, and environmental monitoring. By modifying factors such as doping concentration, annealing temperatures, and film design, it is feasible to increase sensitivity, selectivity, and efficiency under ambient circumstances, particularly at room temperature. This is a critical feature for lowering energy use and enabling real-time environmental monitoring.

Furthermore, the combination of several metal oxides into heterostructures or multilayer systems offers a viable path to increase charge separation and surface reactivity, which are critical for photocatalytic and sensing applications. Such structures can considerably enhance the interaction between the material surface and environmental contaminants, leading to enhanced degradation rates and detection limits.

In the long future, the integration of low-cost metal oxide thin films into practical environmental devices—such as portable gas sensors, photocatalytic reactors, and UV-assisted purification systems—could contribute to sustainable solutions for pollution management. These innovations connect with the worldwide purpose of minimizing environmental impact through green technology and offer a road toward inexpensive and accessible environmental protection measures, particularly in resource-limited places.