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Preparation and Characterization of ZnO Thin Films using Liquid Phase Technique Deposition (LPD)

A graduation project submitted to the Department of physics in partial fulfillment of the requirements for the degree of Bachelor of Science in Applied physics

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Abbreviation & Acronym

- ZnO: Zinc Oxide

- LPD: Liquid Phase Deposition

- XRD: X-ray Diffraction

- SEM: Scanning Electron Microscopy

- UV-Vis: Ultraviolet-Visible Spectroscopy

Acknowledgement

I would like to express my sincere gratitude and appreciation to my research supervisor, Dr. Nawal Ahmed Madkhali, whose leadership and guidance enabled me to successfully complete this project. Furthermore, I would like to express my gratitude to Imam Muhammad ibn Saud Islamic University and its faculty and staff for the opportunity to collaborate with and learn from leading researchers. Last but not least, I would like to express my sincere appreciation to my family and friends for their continuous support and encouragement throughout this endeavor.

Abstract

This study explores the preparation and characterization of Zinc Oxide (ZnO) thin films using the Liquid Phase Deposition (LPD) technique. The objective was to develop a cost-effective and efficient method for fabricating ZnO thin films with desirable structural and optical properties. The LPD process was employed to deposit ZnO films on glass substrates, and the films were characterized using X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM) and Ultraviolet-Visible (UV-Vis) spectroscopy, and. The results indicate that the LPD method is effective in producing high-quality ZnO thin films with potential applications in optoelectronics and photovoltaics.

الملخص

تهدف هذه الدراسة إلى إعداد وتوصيف الأغشية الرقيقة لأكسيد الزنك (ZnO) باستخدام تقنية ترسيب الطور السائل .(LPD) والتي تعتبر طريقة فعالة من حيث التكلفة وذات فعالية جيده وواعدة في تصنيع الأغشية الرقيقة ZnO ذات الخصائص الهيكلية والبصرية المرغوبة. تم استخدام عملية LPD لإيداع أفلام ZnO على ركائز زجاجية، وتم تمييز الأفلام باستخدام حيود الأشعة السينية (XRD) والمجهر الإلكتروني الماسح (SEM) ومطياف الأشعة فوق البنفسجية المرئية (UV-Vis) تشير النتائج إلى أن طريقة LPD فعالة في إنتاج أفلام رقيقة عالية الجودة من أكسيد الزنك مع تطبيقات محتملة في الإلكترونيات الضوئية والضوئية .

Introduction

The liquid phase deposition (LPD) technique is an advantageous method for producing zinc oxide (ZnO) thin films due to its simplicity, low cost, and suitability for large-area coatings. This method typically involves immersing a substrate in an aqueous solution containing zinc salts, such as zinc nitrate or zinc acetate, and a complexing agent. The complexing agent helps to control the release of zinc ions, which gradually precipitate onto the substrate, forming a uniform ZnO thin film. One of the primary advantages of LPD is that it allows precise control over the deposition conditions, including temperature, pH, and precursor concentrations, which directly influence the film's properties. The deposition occurs at relatively low temperatures, often below 100°C, making the process energy-efficient and compatible with flexible or heat-sensitive substrates [1]. Once the ZnO thin films are deposited, their structural, optical, and electrical properties must be characterized to assess their quality and suitability for various applications. X-ray diffraction (XRD) is commonly used to examine the crystallinity of the films, confirming the formation of the hexagonal wurtzite ZnO structure and determining the preferred orientation of the crystals [2]. Scanning electron microscopy (SEM) provides information about the film's surface morphology, revealing features such as grain size and surface uniformity. Studies have shown that ZnO films produced through LPD typically exhibit a smooth surface with good coverage, although the precise morphology can vary depending on the deposition parameters [2]. In addition to structural analysis, the optical properties of ZnO thin films are crucial, particularly for applications in optoelectronics and photovoltaics. UV-visible spectroscopy is used to measure the films' transparency and band gap energy. ZnO is a wide-bandgap semiconductor (approximately 3.37 eV), and thin films produced by LPD often display high transparency in the visible range, making them suitable for use in transparent electronics and solar cells [1, 2]. Electrical characterization, including the measurement of resistivity and carrier concentration, is also essential for applications such as gas sensors and transistors. The electrical properties of ZnO thin films can be tailored by modifying the deposition parameters or by doping the films with other elements to enhance their conductivity [2].

Chapter 1

1.1.1 Thin film preparation

Thin film preparation involves depositing a thin layer of material, typically ranging from a few nanometers to several micrometers, onto a substrate. This process is crucial for creating various electronic and optoelectronic devices, including semiconductors, optical coatings, solar cells, and sensors. The specific properties of the thin films, such as their structural, optical, electrical, and mechanical characteristics, can vary significantly depending on the deposition method and the conditions used during the process [3,4].

1.1.2 Key Methods of Thin Film Preparation

1. Physical Vapor Deposition (PVD):

- Evaporation: Material is heated until it vaporizes, and the vapor condenses onto a cooler substrate, forming a thin film. This method is commonly used for metal coatings, semiconductors, and optical layers.
- Sputtering: Ions from a plasma dislodge atoms from a target material, which then deposit onto the substrate. This technique is used for depositing magnetic materials, hard coatings, and decorative films.

2. Chemical Vapor Deposition (CVD):

- CVD involves gaseous precursors that chemically react on the substrate surface to form a solid film. This process typically requires high temperatures and is ideal for depositing films with complex compositions, such as those used in semiconductor devices, photovoltaic cells, and cutting tool coatings [4].

3. Atomic Layer Deposition (ALD):

- ALD is a variant of CVD where materials are deposited one atomic layer at a time through a series of self-limiting surface reactions. This technique offers precise control over film thickness and composition, making it suitable for applications like high-k dielectrics and nanoscale coatings [3].

4. Sol-Gel Process:

- In this process, a solution containing precursors undergoes hydrolysis and polymerization to form a gel that can be applied to a substrate. After drying and heat treatment, a solid thin film is produced, which is commonly used in optical coatings, anti-reflective coatings, and catalysts [4].

5. Electrochemical Deposition (ECD):

- ECD involves depositing a thin film onto a conductive substrate through the reduction of metal ions from an electrolyte solution. This technique is selective and is often used for metal films in applications such as electroplating, battery electrodes, and corrosion-resistant coatings [7].

6. Liquid Phase Deposition (LPD):

- LPD is a method where thin films are deposited from a liquid solution onto a substrate. The substrate is immersed in the solution, and as the material precipitates out, it adheres to the substrate, forming a thin film. This method is particularly used for depositing oxide films like ZnO, TiO2, and SiO2, which have applications in optics and electronics [5].

7. Spin Coating:

- In spin coating, a liquid precursor is deposited on the center of a substrate, which is then rapidly spun to spread the liquid evenly. The film solidifies upon drying and is used in applications like photoresists in photolithography and organic solar cells.

8. Dip Coating:

- The substrate is dipped into a solution containing the film material and then withdrawn at a controlled speed. As the solvent evaporates, a thin film forms on the substrate, which is used in anti-corrosion coatings, hydrophobic layers, and optical films [7].

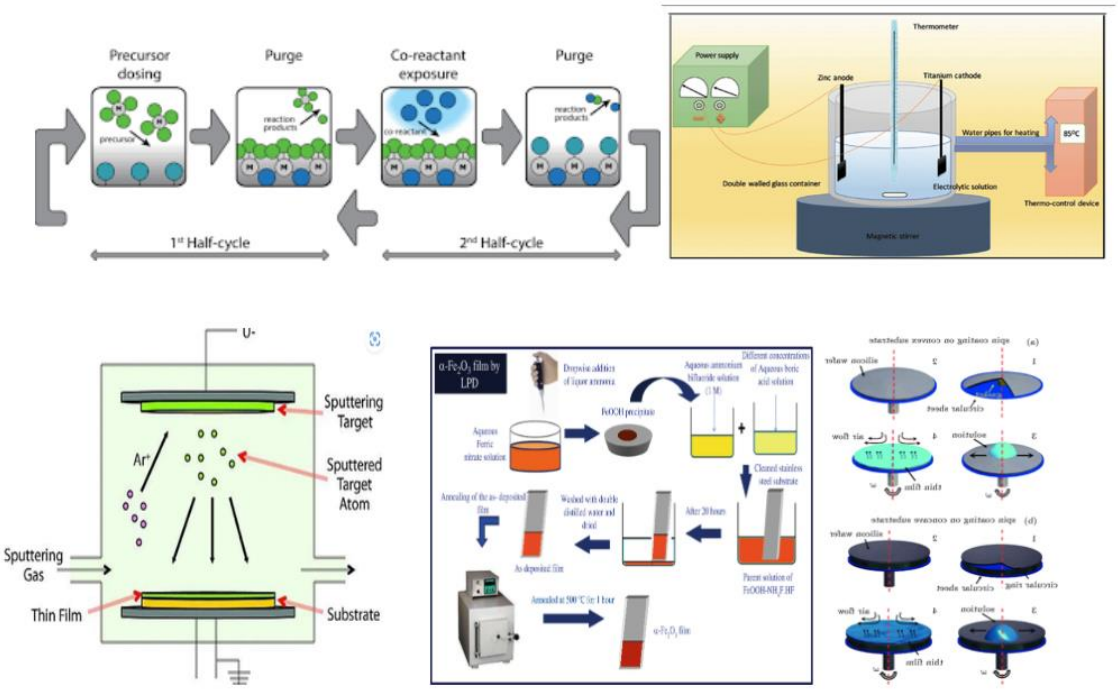


Figure (1.1): Some methods of Thin Film Preparation.

1.1.3 Factors Influencing Thin Film Properties

The properties of thin films are influenced by several factors, including:

- Substrate Material: The type of substrate (e.g., glass, silicon, metal) affects the film's adhesion, stress, and crystallinity [3,4].
- Deposition Rate: The rate of material deposition impacts the film's thickness, uniformity, and microstructure [5].
- Temperature: The deposition temperature is critical in determining the crystalline structure, grain size, and density of the thin film.
- Pressure: In vacuum-based methods like PVD and CVD, chamber pressure affects the mean free path of the depositing species and can influence film morphology and uniformity [6].
- Ambient Conditions: The presence of oxygen, moisture, or other reactive gases during deposition can lead to oxidation or contamination of the thin film [7].

1.1.4 Characterization Techniques

After deposition, thin films are characterized using various techniques to assess their properties:
- X-ray Diffraction (XRD): Analyzes the crystal structure and phase composition of the thin film.
- Scanning Electron Microscopy (SEM): Provides high-resolution images of the surface morphology.
- Optical Spectroscopy (UV-Vis, FTIR, PL): Analyzes optical properties, such as absorbance.

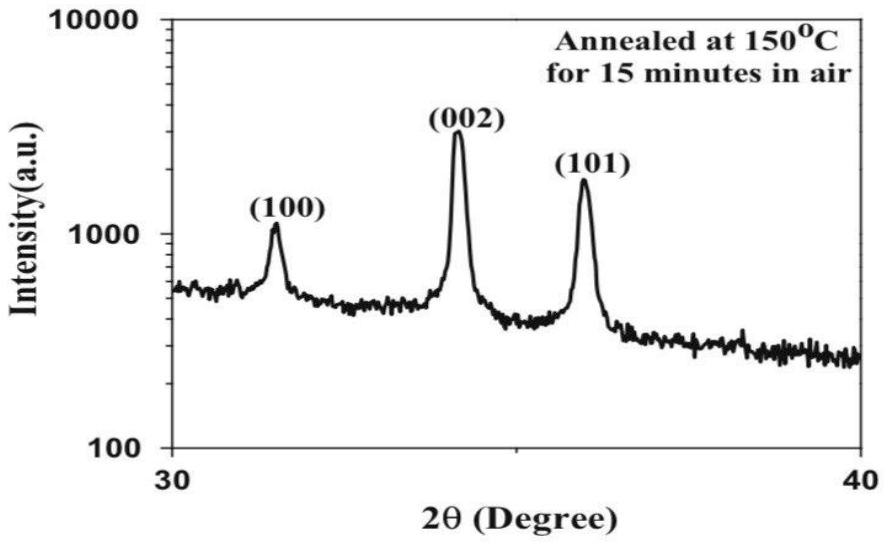


Figure (1.2): XRD spectra of ZnO thin film.

1.1.5 Applications of Thin Films

Thin films have a wide range of applications across various industries:

- Semiconductors: They are essential in the manufacturing of integrated circuits and transistors.
- Optics: Used in anti-reflective coatings, mirrors, and lenses.
- Energy: Thin-film solar cells represent an emerging technology in the photovoltaic industry.
- Sensors: Employed in gas sensors, biosensors, and pressure sensors due to their sensitivity to environmental changes.

- Protective Coatings: Applied as hard coatings, corrosion-resistant layers, and decorative films to enhance the durability and appearance of materials [8.9].

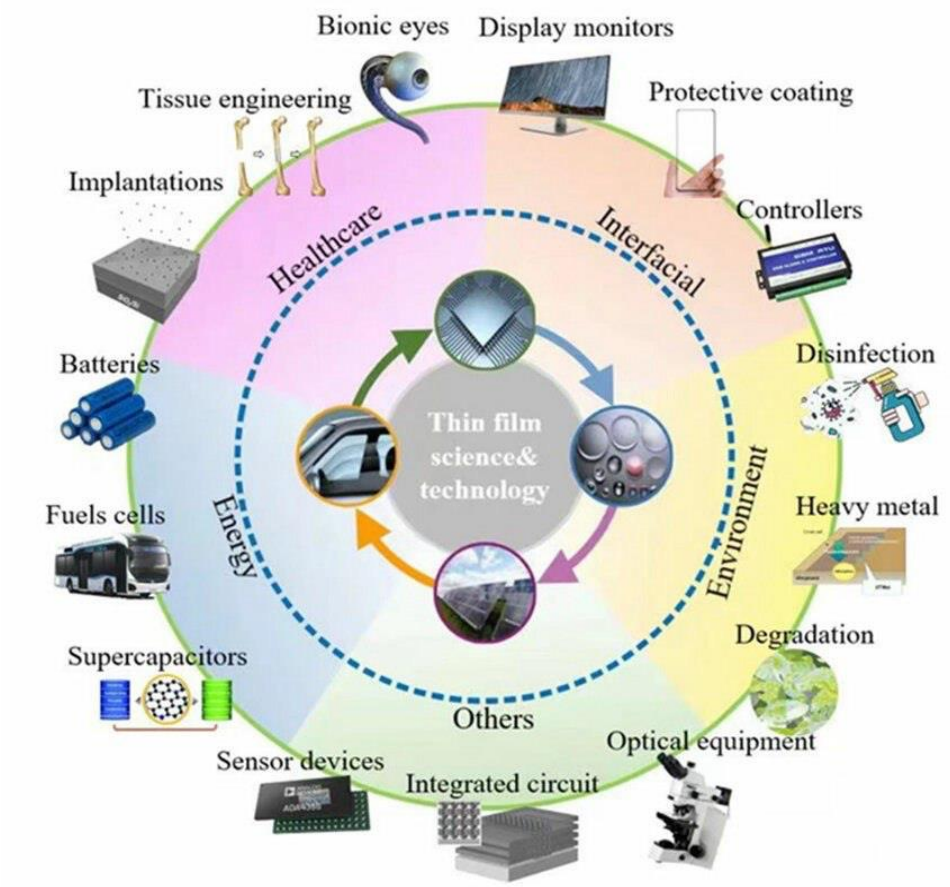


Figure (1.3): Applications of Thin Films.

1.2 zinc oxide

1.2.1 Structure of Zinc Oxide

Zinc oxide is a compound of zinc and oxygen with a wide range of physical and chemical properties. Zinc oxide typically crystallizes in two main forms:

- *Wurtzite Structure:*
    - This is the most thermodynamically stable structure of zinc oxide under ambient conditions. It has a hexagonal crystal structure with lattice parameters of a = 3.25 Å and c = 5.2 Å.
    - The wurtzite structure belongs to the space group P6_3mc and is characterized by tetrahedral coordination, where each zinc ion is surrounded by four oxygen ions and vice versa.
- *Zinc Blende Structure:*
    - Zinc oxide can also adopt a cubic zinc blende structure under specific conditions, although it is less common than the wurtzite form. This structure is typically stabilized under high pressure.
    - The zinc blende structure is similar to that of diamond, where each atom is tetrahedrally coordinated.
- *Rocksalt Structure:*
    - Under extreme pressures, zinc oxide can transform into the rocksalt (NaCl) structure, which has a cubic crystal symmetry [5].

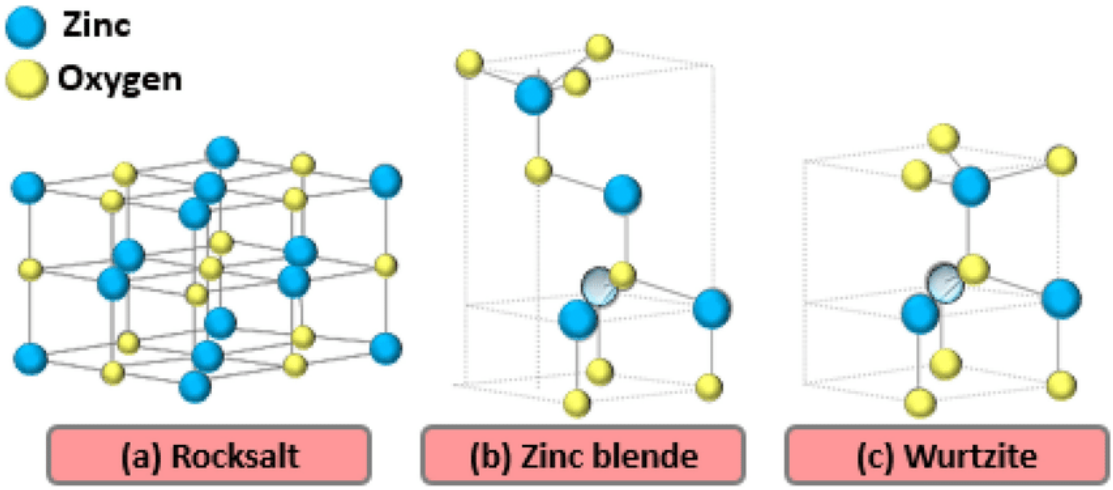


Figure (1.4): Structures of Zinc Oxide.

1.2.2 Properties of Zinc Oxide

- Electrical Properties:
    - Zinc oxide is a wide bandgap semiconductor with a bandgap energy of about 3.37 eV at room temperature, which makes it suitable for optoelectronic applications such as UV light emitters and photodetectors.
    - It also exhibits high electron mobility, low electrical noise, and good transparency in the visible region, making it an ideal material for transparent conducting films.
    - Optical Properties:
    - Zinc oxide has a high exciton binding energy (~60 meV), which allows for efficient excitonic emission at room temperature.
    - Zinc oxide is also highly transparent to visible light, making it useful in transparent electrodes for display technologies and solar cells.
    - Mechanical Properties:
    - Zinc oxide has a relatively high Young's modulus (140 GPa) and hardness (5 GPa), which contribute to its durability and mechanical strength.
    - The material is also piezoelectric, meaning it can generate an electric charge in response to mechanical stress, which is useful in sensors and actuators
    - Chemical Properties:
    - Zinc oxide is chemically stable, with good resistance to chemical corrosion. It is often used as a protective layer in various applications.
    - It can also act as a catalyst or photocatalyst in chemical reactions, such as the degradation of organic pollutants under UV light [4.6].

1.2.3 Applications of Zinc Oxide

1. Electronics and Optoelectronics:

- Thin-Film Transistors (TFTs): Zinc oxide is used as a semiconductor in thin-film transistors, which are critical components in display technologies.

- Light-Emitting Diodes (LEDs) and Lasers: Due to its wide bandgap and high exciton binding energy, zinc oxide is used in ultraviolet light-emitting diodes and laser diodes.

- Transparent Conductive Oxides (TCOs): Zinc oxide is used as a transparent electrode in solar cells, flat-panel displays, and touchscreens.

2. Sensors:

- Gas Sensors: Zinc oxide's surface conductivity changes in the presence of different gases, making it useful for gas sensing applications.

- Biosensors: Zinc oxide nanostructures are used in biosensors for detecting biomolecules due to their high surface area and biocompatibility.

3. Energy Devices:

- Solar Cells: Zinc oxide is used as a buffer layer in thin-film solar cells, improving their efficiency by enhancing light absorption.

- Piezoelectric Generators: The piezoelectric properties of zinc oxide are exploited in devices that convert mechanical energy into electrical energy, such as in energy harvesting applications.

4. Catalysis and Photocatalysis:

- Zinc oxide is used as a catalyst in chemical reactions, particularly in the degradation of organic pollutants through photocatalysis, making it valuable in environmental cleanup technologies [6].

5. Medical Applications:

- Antibacterial and Antimicrobial Agents: Zinc oxide nanoparticles are incorporated into coatings and textiles to provide antibacterial properties [4].

- Drug Delivery: Zinc oxide nanoparticles are being explored for use in targeted drug delivery systems due to their biocompatibility and ease of functionalization.

6. Cosmetics:

- Zinc oxide is a common ingredient in sunscreens due to its ability to block UV radiation. It is also used in skin care products for its soothing and protective properties [6].

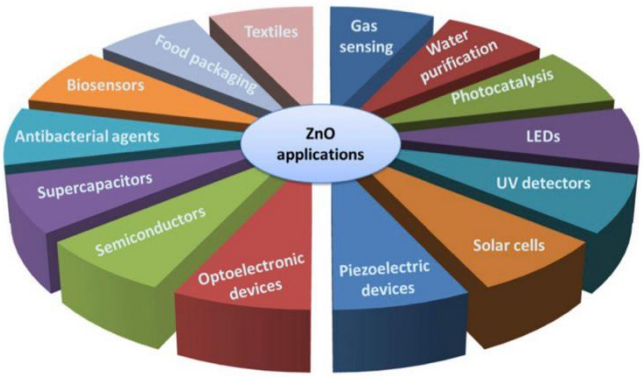


Figure (1.5): Applications of ZnO in different fields.

Chapter 2

Sample and Devices

2.1 Sample preparation

Electrodeposition (electroplating) involves the reduction of metal ions in solution to form a solid metal layer on the surface of a conductive material (cathode). In the case of zinc chloride, Zn^{2+} ions in the electrolyte are reduced at the cathode to form a metallic zinc layer. This process is widely used for corrosion protection (galvanization), enhancing surface properties, or for decorative purposes.

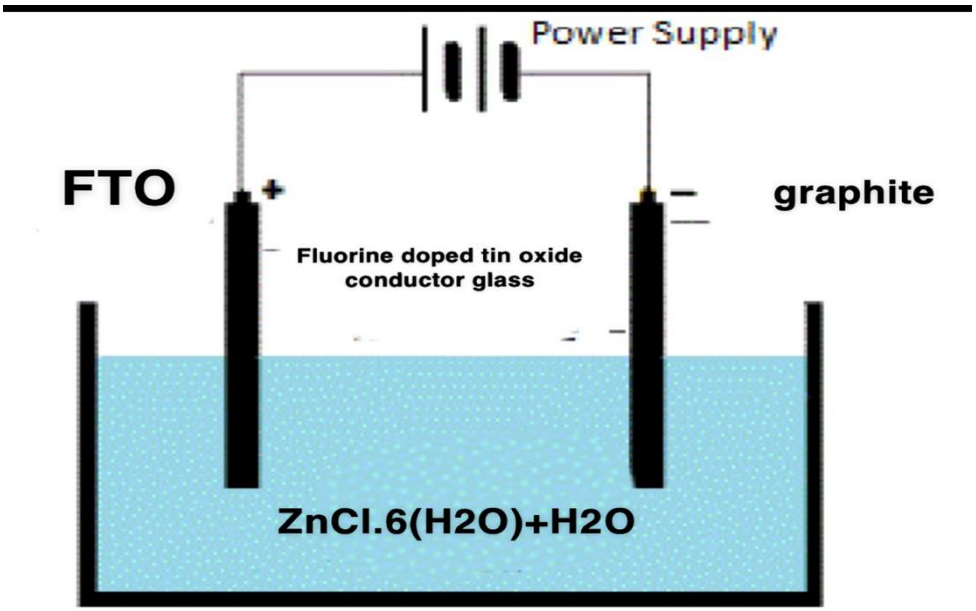


Figure (2.1): Electrochemical deposition of Zinc Oxide thin film.

Materials:

- Electrolyte: Zinc chloride ($ZnCl_2$) solution
- Zinc Anode
- Cathode
- DC Power Supply
- beaker
- Connecting Wires with Alligator Clips: To connect electrodes to the power supply
- Distilled Water: For dissolving $ZnCl_2$ and rinsing electrodes
- Gloves and Safety Goggles: For personal protection
- Stirring Rod: For dissolving $ZnCl_2$ in water

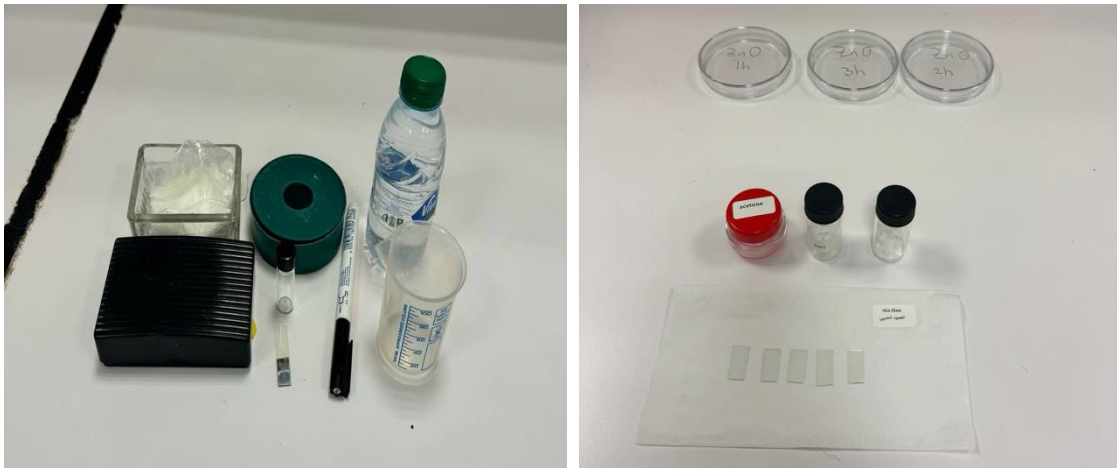


Figure (2.2): Electrodeposition experiment tools.

Procedure:

1. Preparation of the Electrolyte:

- Dissolve approximately 1 g of $ZnCl_2$ in 100 mL of distilled water for two hours at 65°C to prepare a zinc chloride solution.

(A) **(B)**

Figure (2.3) Sample preparation: (A) zinc chloride solution under 65°C in Ultrasound device, (B) 1g of NaCl dissolved in 100ml distilled water.

2. Surface Preparation:

- Clean the cathode thoroughly with acetone to remove any oxide layer or contaminants. This step is critical for achieving good adhesion between the deposited zinc and the metal surface.
- After cleaning, rinse the cathode with distilled water to remove dust or particles.

3. Electrolytic Cell Setup:

- Fill the three beakers with the $ZnCl_2$ solution.
- Immerse the zinc anode into the solution and connect it to the positive terminal of the DC power supply.
- Immerse the prepared cathode (gravit) into the solution and connect it to the negative terminal of the power supply.
- Ensure the electrodes are not touching and are positioned parallel to ensure uniform current distribution.

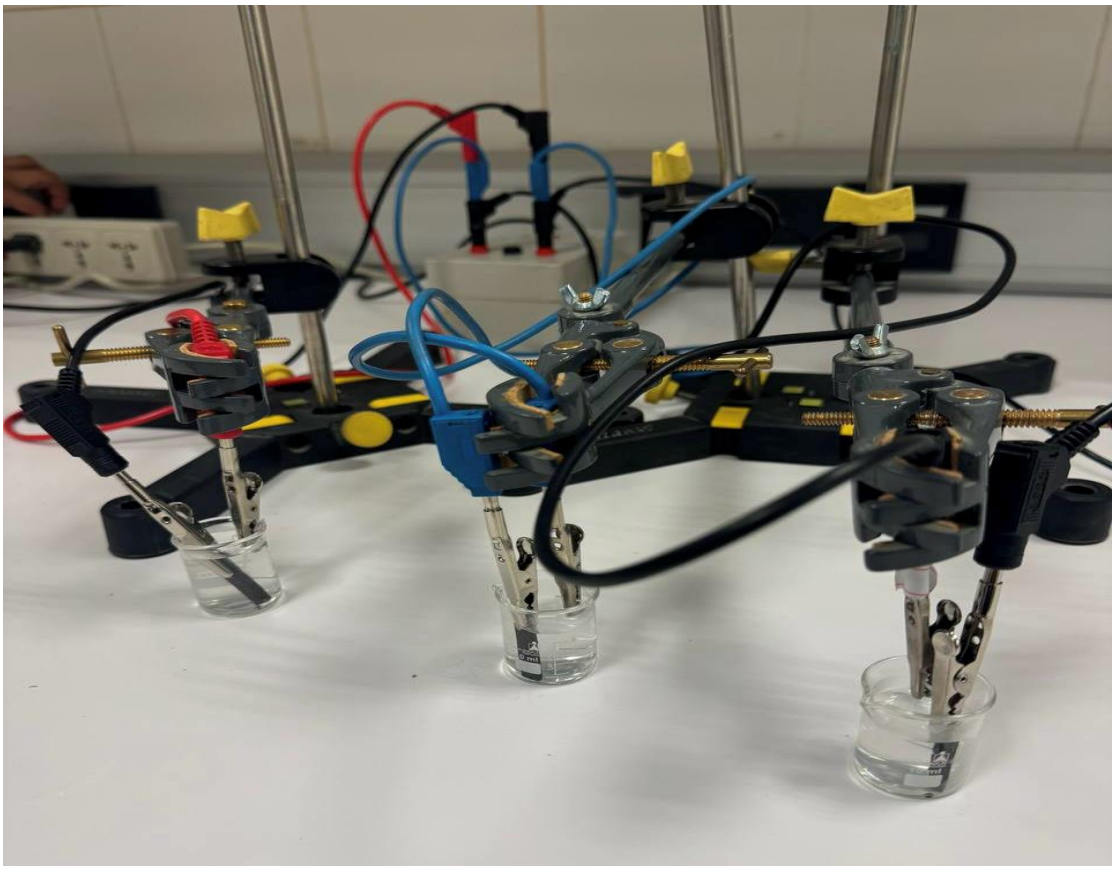


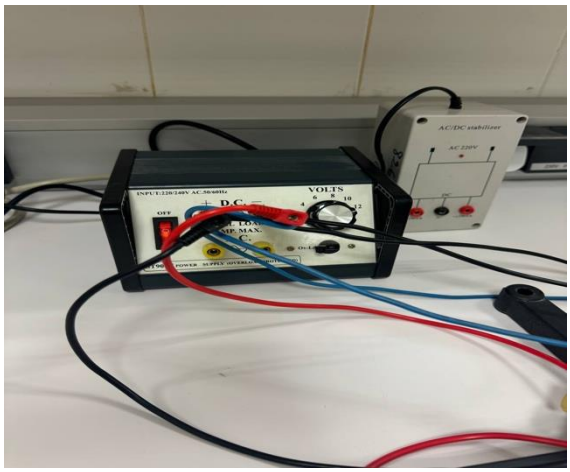
Figure (2.4) Electrolytic Cell Setup: three beakers with ZnCl solution, zinc anode in positive terminal and gravit cathode in negative terminal.

4. Electrodeposition Process:

-Turn on the power supply and set the voltage to 12V. Apply the current to the connected side of the Fluorine-doped tin oxide (FTO) conductive glass (coated on one side), ensuring the current is directed at a specific point on the coated surface R=15K Ω

- Observe the gradual deposition of zinc on the cathode. The reaction at the cathode will form a zinc coating, typically a shiny or matte silver-gray layer depending on the deposition conditions.

- During the process, zinc gradually deposits on the cathode. The deposition is observed for a period of 90 to 120 minutes, depending on the desired thickness of the zinc layer.



(A)

(B)

(C)

Figure (2.5) Electrodeposition Process: (A) Power supply at 12V, (B) Adjust the current, (C) Thin film after electrodeposition process.

5. Post-Deposition Steps:

- After the desired time has elapsed, turn off the power supply.

- Remove the cathode from the solution and rinse it with distilled water to remove any traces of electrolyte.

- Dry the coated cathode with a cloth or allow it to air dry.

6. annealing thin film:

The first thin film was annealinged for one hour at a temperature of 450°C, the second for two hours at 450°C, and the third for three hours at 450°C. A layer of zinc oxide was produced as a result of the annealinging process.

(A) (B)

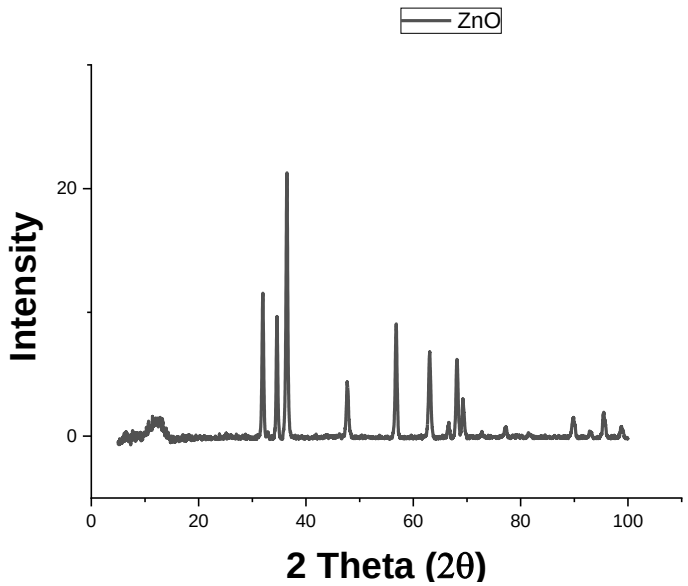
Figure (2.6) annealing thin film: (A) thin film before annealinging, (B) the thin film become ZnO after annealinging.

Chapter 3 : Results and Discussion

In this chapter, we will discuss the results obtained from our study. We will begin by examining the characterization of the deposited material using X-ray diffraction to ascertain its nature. Subsequently, we will explore the effects of increasing annealing duration on the properties of the material and how this influences its size characteristics. Finally, we will investigate the optical properties of thin films.

3.1 XRD diffraction

Figure (3.1) illustrates the typical XRD patterns of pure ZnO synthesized via LPD technique for thin film deposited for 1hour (1h). The peak positions in this figure indicate that all the samples were nanocrystalline powder with hexagonal wurtzite structures, which is in good agreement with the reports[10]. The peak corresponding to the (100) plane, usually around 31.7° and the peak for the (002) plane, found near 34.4° 2θ. The (101) plane appears at approximately 36.2° 2θ. Another notable peak, for the (102) plane, occurs around 47.5° 2θ. The (110) plane shows a peak near 56.6° 2θ the (103) plane is observed around 62.9° 2θ. Finally, the (112) plane appears at about 68.0° 2θ.



3.2 Optical Properties:

In the experiment involving the electrodeposition of zinc from $ZnCl_2$ solution, UV-Vis spectroscopy was used to analyze the process. The spectrophotometer was set to measure absorbance across a wavelength range of 330 nm to 980 nm, with readings taken every 50 nm. The absorbance was plotted on the y-axis, and the wavelength (in nm) was plotted on the x-axis.

Figure (3.2): UV Spectrophotometer and wavelength range display.

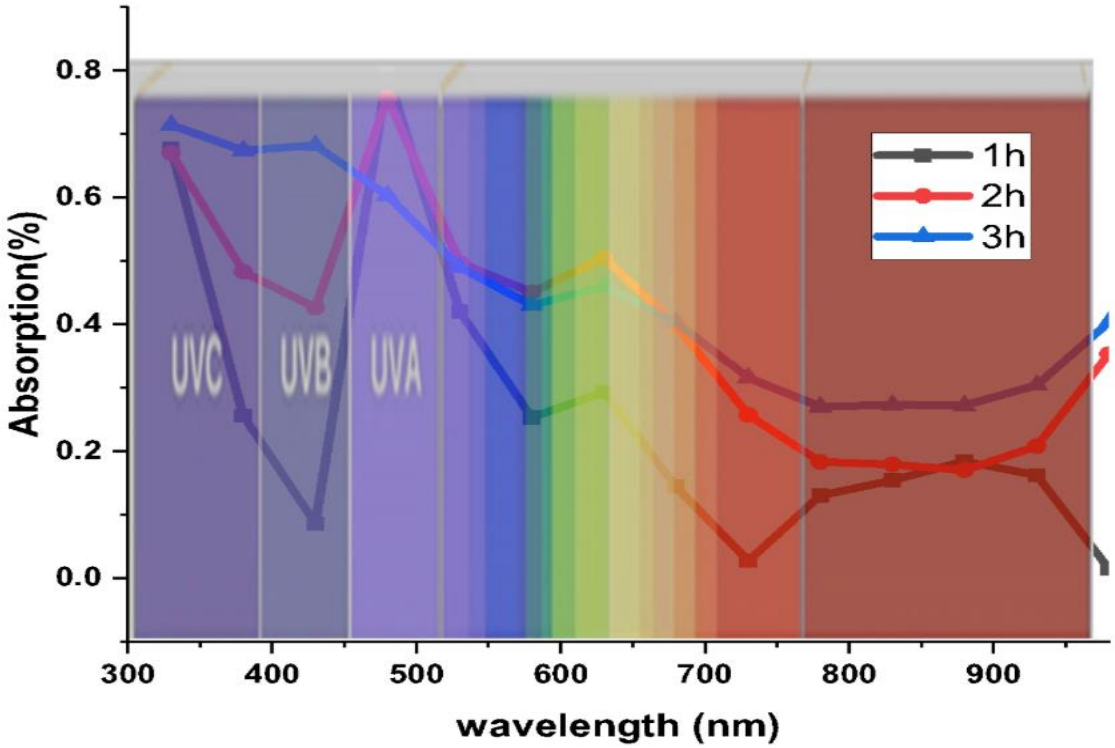


Figure (3.3): The relationship between absorption rate (%) and wavelength (nm).

The figure (3.3 shows an absorption spectrum graph with absorbance on the y-axis and wavelength on the x-axis.

- Absorbance Trend for 1 Hour (Black Line):
  - The absorbance starts high, near 0.6%, at around 350 nm in the UVC range, then drops significantly to approximately 0.2% at around 400 nm in the UVB range. There is a small peak near 450 nm in the UVA range, and from 600 nm to 900 nm, the absorbance remains relatively stable, with a slight downward trend.
- Absorbance Trend for 2 Hours (Red Line):
  - The absorbance begins at approximately 0.5% at around 350 nm and decreases more sharply to about 0.2% at around 400 nm. This is followed by a small peak near 450 nm. Between 500 nm and 700 nm, the curve shows some fluctuation, and beyond 700 nm, the absorbance steadily increases, reaching up to 0.6% by 900 nm.
- Absorbance Trend for 3 Hours (Blue Line):
  - The absorbance starts higher at around 0.7% at 350 nm and drops to about 0.3% at 400 nm. It then rises again, peaking between 500 nm and 600 nm. From 700

nm to 900 nm, the absorbance stabilizes, with a slight increase towards the higher wavelengths.

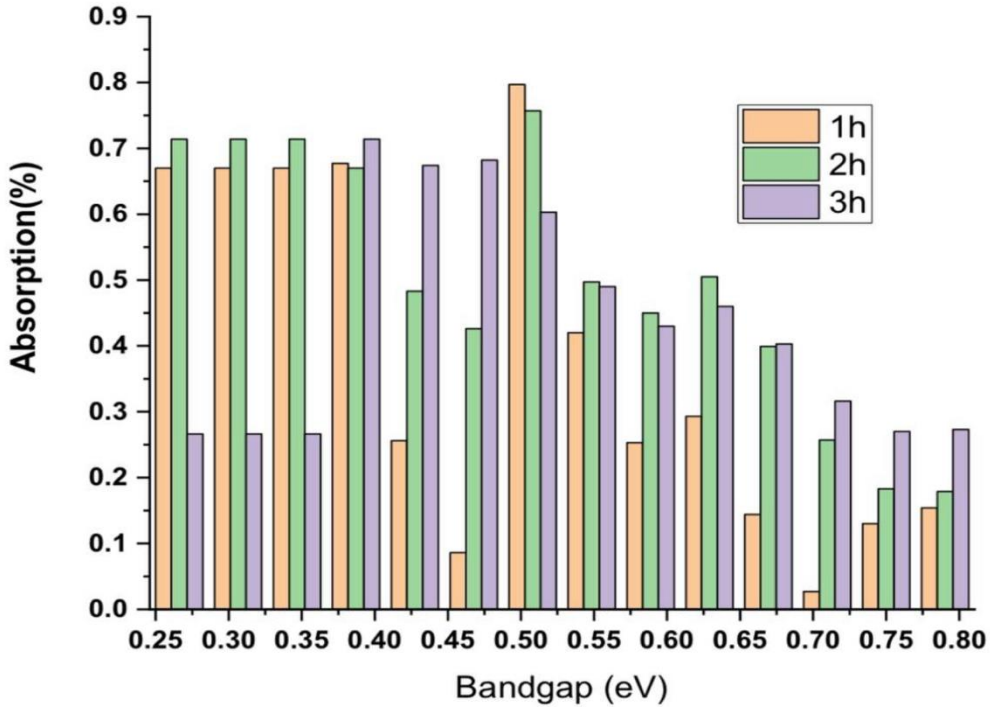


Figure (3.3): Absorption Percentage as a Function of Bandgap Energy (eV) at Different Time Intervals (OriginLab).

The figure (3.3) depicts a bar chart illustrating the absorption percentages of materials at various bandgap energy levels (eV), measured after 1 hour, 2 hours, and 3 hours of treatment (represented by the different colored bars: orange for 1h, green for 2h, and purple for 3h).

- After 1 hour, the peak absorption, approximately 0.7%, occurs at a bandgap of 0.50 eV. The material shows a consistent absorption of around 0.6% for lower bandgaps ranging from 0.25 eV to 0.45 eV. However, once the bandgap exceeds 0.55 eV, the absorption sharply drops to below 0.5%, and this downward trend continues as the bandgap increases further.
- After 2 hours, the peak absorption, which remains at approximately 0.7%, also occurs at a bandgap of 0.50 eV. For lower bandgaps, ranging from 0.25 eV to 0.45 eV, the absorption is slightly reduced compared to the 1-hour data, with values close to 0.6%. The absorption starts to decline after the bandgap surpasses 0.55 eV, following a gradual decrease at higher bandgaps, similar to the pattern observed at the 1-hour mark.
- After 3 hours, the peak absorption still occurs at approximately 0.7% at a bandgap of 0.50 eV, but the overall absorption levels are lower compared to the previous two time

intervals. For lower bandgaps between 0.25 eV and 0.45 eV, the absorption is around 0.5%. The absorption continues to decrease at higher bandgaps (above 0.55 eV), reaching its lowest value during the 3-hour interval.

3.3 Scanning Electron microscopy (SEM)

The surface of the zinc oxide films deposited at different time intervals 1hr, 2hr, and 3hr) was characterized using a scanning electron microscope (SEM). The magnified images at 10 micrometers reveal that the zinc oxide grains exhibit a spherical shape, with an increase in their uniformity as the annealing time increases. This indicates an improvement in the structural properties of the film surface because of the extended annealing time.

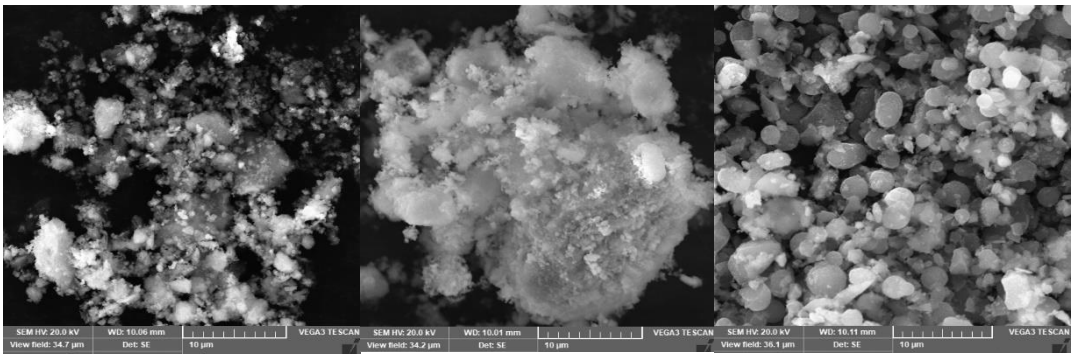


Figure (3.3): SEM images of ZnO at various annealing times (1h,2h and 3hr -from left to right)

3.2 Conclusion

In this research, we successfully fabricated thin films of zinc oxide using the liquid chemical deposition (LPD) method. The X-ray diffraction (XRD) results demonstrated a good agreement of the produced material with zinc oxide. The (LPD) technique proved to be an effective method for producing uniform zinc oxide (ZnO) thin films. Through the experimental procedure, which involved electrodeposition of zinc from a $ZnCl_2$ solution followed by controlled annealinging at 450°C for different durations (1, 2, and 3 hours), the ZnO thin films exhibited distinct changes in their absorbance characteristics over time. The UV-Vis spectrophotometric analysis revealed a clear relationship between the deposition time and the absorbance of the ZnO thin films. Films that were annealinged for three hours exhibited higher absorbance in the UV region, specifically between 350 and 400 nm, and showed stability in absorbance at higher wavelengths. These variations in absorbance, observed across different wavelengths and annealing durations, The

results of the surface characterization using scanning electron microscopy (SEM) also showed that the thin films becomes more organized in the form of spherical grains and homogeneous, as the annealing time increases. The films deposited through this method demonstrated good structural, optical, and electrical properties, which are essential for various optoelectronic applications

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