



Preparation and Characterization of ZnO:Al Thin Films Using Aqueous Solution Method

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Abstract. Transparent conducting oxide (TCO) thin films are widely used in modern optical and optoelectronic technologies, including solar cells, sensor displays, and light-emitting diodes. Among the various TCO materials, indium tin oxide (ITO) is the most commonly used. However, due to the increasing scarcity of indium metal in recent years, its high extraction cost, extensive water usage and pollution during mining, and toxic effects on human health, aluminum-doped zinc oxide (AZO) has been investigated as a potential alternative. By preparing AZO thin films in an aqueous environment under laboratory conditions, it becomes possible to produce low-cost and safer TCOs on an industrial scale while minimizing environmental pollution.

In this study, a total of four AZO thin films were fabricated using two methods: sol-gel and nanoparticle-based synthesis. Two of these films were thermally annealed at 500 °C for 2 hours. The optical properties of the films were analyzed using UV-Visible spectroscopy (UV-VIS), and surface morphology changes due to annealing were characterized using atomic force microscopy (AFM).

The AZO thin films prepared by both methods exhibited absorption in the ultraviolet (UV) region and transmittance of 70–80% in the visible region, with optical band gap energies ranging from 3.22 to 3.24 eV. In terms of surface morphology, the unannealed AZO films were relatively rough and non-uniform, whereas after annealing, the surface became smoother and more homogeneous. These results indicate that AZO thin films can be successfully fabricated using aqueous-based synthesis methods.

Keywords: AZO, ITO, Sol-gel, Nanoparticle

1 Introduction

Transparent conducting oxide (TCO) refers to a thin-film material that simultaneously exhibits optical transmittance exceeding 80% in the visible light region and an electrical conductivity of at least $10^3 \Omega^{-1} \text{cm}^{-1}$ CITATION KLC831 \l 1033 [1]. Although extensively studied in the 1940s, these materials were not widely adopted for commercial applications at that time. In recent years, however, transparent

conducting oxides have received increasing attention for use in optoelectronic devices, particularly in photoelectrochemical cells, solar cells, light-emitting diodes, and display technologies [2].

Among the various TCO materials, indium-doped tin oxide (ITO) is most commonly used due to its superior electrical and optical properties. With a wide band gap energy of approximately 3.5–4 eV, indium tin oxide is a highly transparent material in the visible light region, allowing minimal electron excitation and absorption. ITO thin films exhibit a high optical transmittance of about 85–90% and appear nearly colorless and transparent to the naked eye. Nonetheless, indium-bearing minerals are geologically scarce and typically do not form economically viable high-grade deposits. Furthermore, the extraction of indium involves the generation of substantial amounts of acidic waste, leading to increased production costs and significant environmental concerns [3].

Aluminum-doped zinc oxide (AZO) films are being extensively investigated as a potential replacement for ITO, owing to the abundance and low cost of their constituent elements. Moreover, AZO materials are considered environmentally benign and safer to handle during the fabrication process [4]. Zinc oxide (ZnO) thin films possess semiconducting properties; their intrinsic electrical conductivity is relatively low. When a small amount of Al^{3+} ions is introduced as a dopant into ZnO thin films, the sheet resistance of the film is significantly altered. Since the Al^{3+} ion has one more valence electron than the Zn^{2+} ion it replaces, the substitution results in an increase in the number of free electrons, thereby enhancing the charge carrier concentration. AZO thin films behave as n-type semiconductors, where the Al atoms act as donor impurities by contributing electrons to the conduction band. The typical free electron concentration in AZO films ranges from $10^{18} - 10^{20} \text{ cm}^{-3}$.

AZO thin films have been found to exhibit optical transmittance of approximately 80–90% in the wavelength range of 200–800 nm. The band gap energy of undoped ZnO thin films is approximately 3.267 eV, whereas the incorporation of aluminum increases the band gap to 3.325 eV [5].

Plasma-based techniques such as magnetron sputtering, along with pulsed laser deposition, atomic layer deposition, and chemical vapor deposition are widely employed at the industrial scale to fabricate high-quality AZO thin films. These methods typically achieve resistivities in the range of $10^{-3} - 10^{-4} \Omega \cdot \text{cm}$ and visible light transmittance exceeding 90%. However, the instrumental complexity and operational requirements of these vacuum-based techniques result in high capital costs and impose limitations on large-scale production. Consequently, there is significant interest in the development of low-cost, non-vacuum deposition methods for AZO thin film fabrication [5].

While low-cost aqueous methods have been proven to be viable for producing AZO films, a thorough comparison of these techniques to determine which is the most simple and straightforward has not been extensively explored. This study investigated various aqueous solution methods and found the sol-gel and nanoparticle-based methods to be particularly promising due to their simplicity, ease of use at room temperature, and low-cost nature. Therefore, the main objective of this research was

to compare these two methods and determine which produces a more uniform thin film layer.

In this study, AZO thin films were fabricated on glass substrates under laboratory conditions using both physical and chemical methods. The main objective was to investigate the optical and morphological properties of ZnO:Al thin films.

2 Methodology

First approach to this study, AZO thin films were synthesized via aqueous solution deposition using a metallic aluminum source immersed in an alkaline precursor. To ensure proper nucleation and film formation on the substrate, a ZnO seed layer was employed. Unlike conventional methods that rely on vacuum deposition or high-temperature sol-gel techniques, the seed layer in this work was prepared by synthesizing ZnO nanoparticles [5].

In the second approach, aluminum-doped ZnO (AZO) thin films were prepared via the sol-gel method and deposited onto glass substrates using spin coating. These experiments conducted under standard ambient temperature and pressure (25°C, 1 atm).

2.1 Synthesis of ZnO Nanoparticles by Co-precipitation Method

In this experiment, a 0.05 M zinc acetate solution and a 0.1 M sodium hydroxide solution were mixed in stoichiometric proportions. The reaction was allowed to proceed for 30 minutes, resulting in the formation of zinc oxide nanoparticles via the co-precipitation method. The obtained ZnO nanoparticles were then dispersed in ethanol at a concentration of 5 mg/mL and deposited onto glass substrates by spin coating.

2.2 AZO Aqueous Solution Deposition:

The thin films were fabricated using the chemical bath deposition (CBD) method. The precursor solution was prepared using diammonium citrate (1 mmol/L) and ZnO powder (10 g/L), which were dissolved and suspended in distilled water. NH_4OH solution (28 wt%) was added until the pH exceeded 11. The resulting mixture was stirred overnight, filtered through 1 μm glass fiber filters, and stored in polyethylene bottles at room temperature until use. 200 μm thick of aluminum foil was immersed in the precursor solution either before or during deposition, allowing precise control over the aluminum doping concentration in the resulting film. The deposition was carried out at 85 °C for durations ranging from 30 to 120 minutes, depending on the targeted film thickness. Subsequently, the deposited thin films were annealed at 500 °C for 2 hours to enhance crystallinity and improve the structural and optical properties of the AZO layers.

2.3 AZO Prepared by Sol-Gel Method

To AZO thin films via the sol-gel method, zinc acetate dihydrate was used as the main precursor, aluminum nitrate nonahydrate as the doping agent, ethanol as the solvent, and monoethanolamine (MEA) as the stabilizer. The molar ratio of MEA to zinc acetate was kept constant at 1.0, and the concentration of zinc acetate was fixed at 0.50 mol/L. The prepared solution was magnetically stirred at 60 °C for 2 hours to ensure complete homogeneity and clarity.





Using the spin coating technique, 1 ml of the prepared solution was deposited onto ultrasonically cleaned glass substrates at 3000 rpm for 30 seconds to form a uniform thin film. After each coating cycle, the deposited films were preheated on a hot plate at 220 °C for 10 minutes to evaporate residual solvents and remove organic compounds. This coating and preheating procedure was repeated 6 to 12 times, depending on the desired film thickness. Finally, the films were annealed at 500 °C for 2 hours to enhance crystallinity and produce high-quality, crystalline AZO thin films.

3 Results and Discussion

3.1 AZO thin films

In this study, a total of four AZO thin films were prepared to investigate the effect of temperature. The samples were characterized both before and after high-temperature annealing as shown in Table 1.

Table 1. Synthesized AZO thin films.

Method	Before Annealing	After Annealing
1st		
2nd		

3.2 =Optical properties of AZO

The optical measurements were performed using a UV-2500PC UV-Vis spectrophotometer in the 200-800 nm wavelength range. The optical band gap energy of the solid-state material was determined from the absorbance spectrum using the Tauc plot method.

$$\alpha h\nu = A(h\nu - E_g)^{n/2} \quad (1)$$

The transmittance of the sample was determined from its absorbance values using the Lambert-Beer law.

$$A = \varepsilon \cdot L \cdot c = \log_{10}\left(\frac{I_0}{I}\right) = \log_{10}\left(\frac{1}{\tau}\right) = -\log_{10}(\tau) \quad (2)$$

Optical properties of ZnO nanoparticle

The band gap energy of ZnO nanoparticles in the solid state was determined from the absorption spectrum using the Tauc plot method, as described by Equation (1). Depending on the type of electronic transition, the exponent r takes values of $1/2$ for allowed direct, $3/2$ for forbidden direct, 2 for allowed indirect, and 3 for forbidden indirect transitions. Since ZnO nanoparticles exhibit a direct allowed transition, a value of $r = 1/2$ was used in the calculation. The estimated band gap energy of the ZnO nanoparticles was found to be approximately 3.2 eV.

Optical properties of ZnO:Al thin films before temperature annealing

The optical band gap energy of the solid-state material was calculated from the absorbance spectrum, as shown in Figure 1 and Figure 2. The band gap energy for the nanoparticles was found to be 4.17 eV, while that of the sol-gel derived sample was 3.96 eV. Compared to the band gap energy of undoped ZnO nanoparticles, the band gap energy of the doped samples increased. This increase is attributed to the incorporation of Al into the ZnO crystal structure, which leads to an elevated free electron concentration. Such a change is known as a blue shift [6].

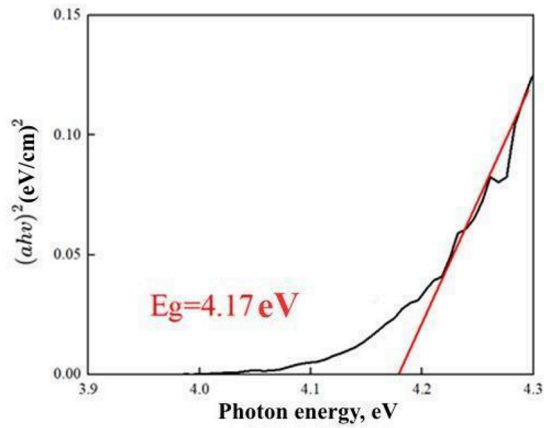


Fig. 1. Optical band gap energy of AZO thin films prepared by the sol-gel method.

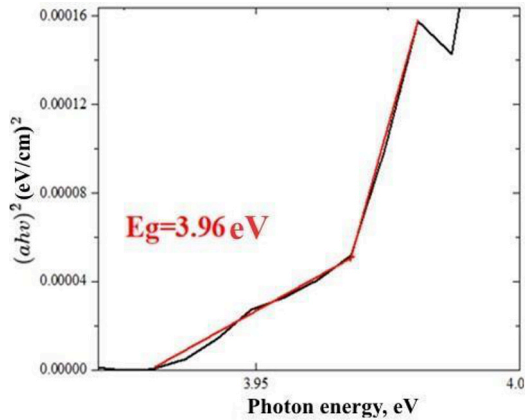


Fig. 2. Optical band gap energy of AZO thin films prepared by nanoparticle method.

Optical Properties of ZnO:Al Thin Films After Temperature Annealing

For ZnO:Al synthesized via the nanoparticle method, the band gap energy decreased from 3.96 eV to 3.24 eV. Similarly, for thin films prepared by the sol-gel method, this value decreased from 4.21 eV to 3.22 eV. Furthermore, when compared to the results from study [7], where the band gap energy was reported to be between 3.2–3.3 eV, our experimental results are consistent with and align well with theoretical predictions.

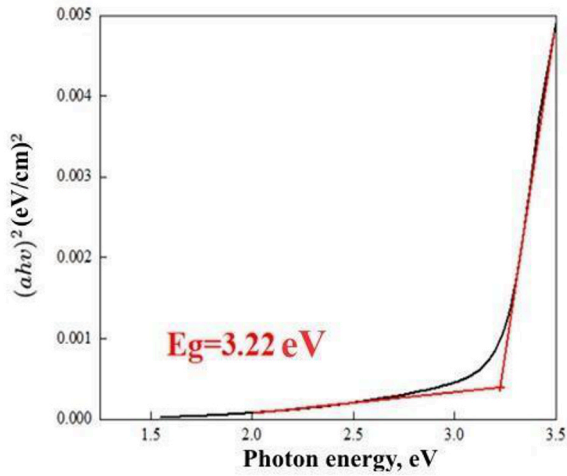


Fig. 3. Optical band gap energy of AZO thin films prepared by the sol-gel method.

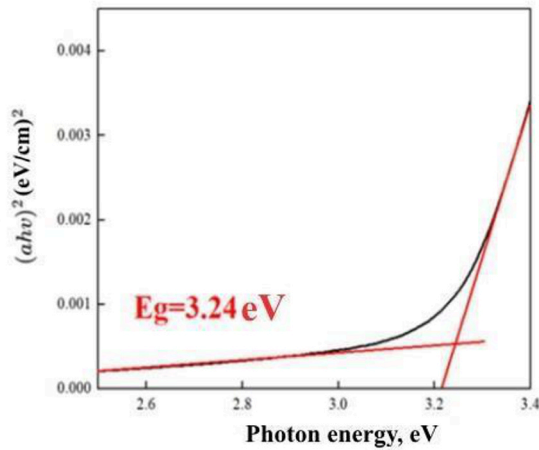


Fig. 4. Optical band gap energy of AZO thin films prepared by nanoparticle method.

Transmittance of AZO thin films

The optical transmittance of the samples was derived from their absorbance spectra utilizing the Lambert-Beer equation. In the visible light region, the sol-gel derived thin film exhibited a transmittance of 68%, whereas the nanoparticle-based thin film demonstrated a higher transmittance of 81%. This initial difference in transmittance is hypothesized to stem from the sol-gel process yielding a more compact and densely packed thin film microstructure, which inherently influences light propagation and absorption.

Subsequent to thermal annealing, the transmittance values exhibited a notable improvement, ranging from 70% to 85%. This enhancement is attributed to the thermal energy facilitating microstructural reorganization, including densification and the formation of a more uniform thin film. These processes typically involve the reduction of defects and voids, as well as an enhancement in crystallinity, all contributing to minimized light scattering and absorption within the film.

Table 2. Investigation of the optical properties of AZO thin films before and after annealing

Optical properties	Before doping	After doping				Literature review (after annealing)
		Sol-gel method		Nanoparticle method		
		Before	After	Before	After	
Bandgap (eV)	3.2	4.17	3.22	3.96	3.24	3.2-3.48 [5], [7]
Transmittance (%)	-	68	81	70	85	87 [7]

3.3 Morphological properties of AZO thin films

ZnO:Al thin films were investigated using atomic force microscopy. As depicted in Figure 5 (A), the sol-gel derived film exhibits a relatively non-uniform and irregular morphology, with a calculated average surface roughness of 12.25 nm. In contrast, Figure 5 (B) reveals the presence of agglomeration in certain regions of the nanoparticle-based film. Due to the incomplete formation of the thin film in these areas, the average roughness could not be accurately determined. The maximum peak height for the sol-gel film was 104 nm, whereas the nanoparticle-based film showed a significantly higher maximum peak height of 634 nm.

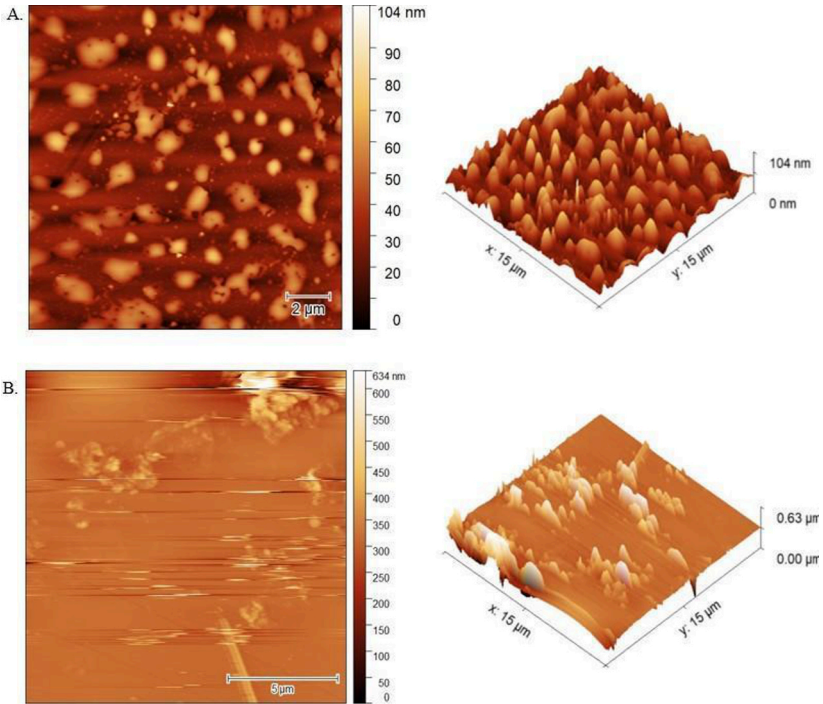


Fig. 5. Surface morphology of AZO thin films before annealing. (A) Sol-gel prepared film. (B) Nanoparticle-based film.

After high-temperature annealing, significantly less agglomeration was observed. Although the AZO was deposited on a glass substrate, a dense and uniform thin film had not initially formed.

Specifically, the as-deposited AZO thin film prepared by the sol-gel method exhibited large, agglomerated particles. However, following annealing, the surface roughness became relatively more uniform, the size of the smaller particles became more consistent, and a homogeneous thin film was formed. The measured average RMS roughness for the sol-gel film after annealing was 11.25 nm. This suggests that thermal treatment plays a crucial role in improving the film's microstructure, leading to better densification and reduced surface defects.

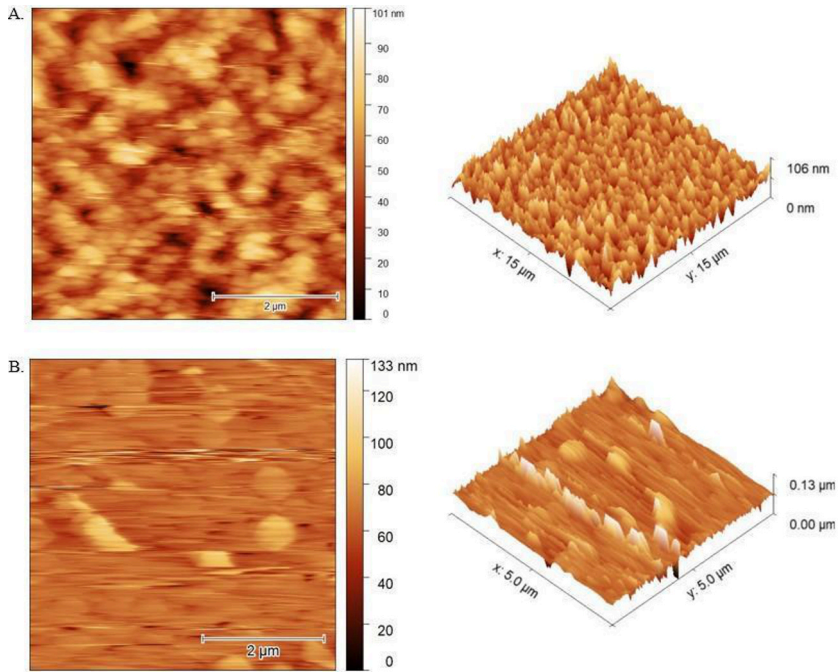


Fig. 6. Surface morphology of AZO thin films after annealing. (A) Sol-gel prepared film. (B) Nanoparticle-based film.

4 Conclusions

This study successfully synthesized AZO thin films using both sol-gel and nanoparticle-based methods, investigating their optical and morphological properties. Initially, as-deposited nanoparticle-based films showed superior transparency, reaching 85% compared to sol-gel films at 81%. This difference suggests the sol-gel process yields a more compact microstructure, which directly impacts the film's initial light transmission. For the synthesized ZnO nanoparticles, the optical band gap energy was found to be 3.2 eV.

High-temperature annealing significantly improved the optical properties of both film types. For nanoparticle-based films, the band gap energy decreased from 3.96 eV to 3.24 eV, while the sol-gel films' band gap reduced from 4.17 eV to 3.22 eV. This reduction in bandgap is primarily attributed to the elimination of internal defects and improved crystallinity. Following annealing, the transmittance also improved notably, ranging from 70% to 85%. This change indicates that thermal treatment enhanced the films' microstructure, leading to a more uniform and dense structure that minimizes light scattering.

AFM analysis further supported these results by revealing the films' surface morphology. Initially, as-deposited sol-gel films had a non-uniform, irregular surface with a roughness of 12.25 nm and a peak height of 104 nm. In contrast, the

nanoparticle-based films showed significant particle agglomeration, resulting in a much higher peak height of 634 nm. After annealing, both film types showed reduced agglomeration and smoother surfaces. Notably, the sol-gel films became more uniform and achieved a lower average roughness of 11.25 nm, confirming the crucial role of thermal treatment in improving film quality.

In conclusion, both the sol-gel and nanoparticle-based methods proved viable for synthesizing ZnO:Al thin films. However, based on the results, the sol-gel method produced a more uniform thin film, making it the more advantageous approach. This comparative study of the two methods demonstrates how simple and safe techniques can be used to produce thin films in large quantities, thereby contributing to future product development.

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