Structural Analysis of Sol-Gel ZnO Thin Films: Comparative Study of Dip Coating and Spin Coating Techniques

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Abstract—**In this study, we use dipping and spinning methods to coat glass slides with sol-gel ZnO thin films, composed of zinc acetate dihydrate, stearic acid, and ethanol. The effect of synthesis methods on structural properties of ZnO thin films was investigated. The crystallite size, dislocation density, microstrain, lattice strain, bond length, and morphological characteristics of the ZnO thin films were analyzed to evaluate the structural properties and surface morphology after deposition and thermal treatment. The lattice parameters of the ZnO thin films deposited using the dip coating method were calculated and found to be 5.1619 Å for the c-axis and 3.217 Å for the x-axis, indicating a hexagonal wurtzite crystal structure. These values are consistent with typical ZnO crystal dimensions, confirming the successful deposition and structural integrity of the thin films. The precise measurement of lattice parameters is critical for understanding strain effects, crystal quality, and the overall performance of the films in various applications.**

Index Terms—**ZnO, Sol-Gel, Dip coating, Spin Coating, Structural**

I. INTRODUCTION

Zinc oxide (ZnO) nanostructured thin films have garnered significant attention in the scientific community due to their remarkable versatility and exceptional properties, including wide bandgap (3.37 eV), large exciton binding energy (60 meV), and excellent optical transparency in the visible spectrum [1]. These characteristics make ZnO thin films particularly promising for diverse applications ranging from optoelectronic devices and solar cells to gas sensors and transparent conducting electrodes [2,3]. The method of thin film deposition plays a crucial role in determining the structural, morphological, and consequently, the functional properties of ZnO films. Among various deposition techniques, solution-based methods such as spin coating and dip coating have emerged as particularly attractive approaches due to their cost-effectiveness, scalability, and ability to produce high-quality thin films under ambient conditions [4]. These methods offer precise control over film thickness, composition, and morphology through the optimization of processing parameters [5,6]. However, a systematic comparative analysis of these two widely employed techniques and their impact on the resultant film properties remains essential for advancing their technological applications.

The present study undertakes a detailed investigation of nanocrystalline ZnO thin films synthesized via spin coating and dip coating methods, with subsequent thermal treatment at 575°C. By employing X-ray diffraction (XRD) analysis and field emission scanning electron microscopy (FESEM), we aim to establish a comprehensive understanding of how the deposition method influences the fundamental properties of ZnO thin films.

This comparative analysis is particularly significant as it provides crucial insights into the relationship between processing methods and resulting film characteristics, enabling informed decision-making in the selection of deposition techniques for specific applications. Furthermore, understanding these correlations contributes to the broader scientific knowledge base necessary for the rational design and optimization of ZnO-based devices, ultimately advancing their practical implementation in various technological applications.

II. EXPERIMENTAL METHOD

Sol-gel spin coating and dip coating techniques were used to deposit ZnO thin films on a glass substrate with a refractive index of 1.51. Zinc acetate dihydrate, stearic acid, and ethanol were used as the starting material, stabilizer, and solvent, respectively. A mixture of 1 g of zinc acetate, 0.5 g of stearic acid, and 30 ml of ethanol was stirred at 50°C and 500 rpm using a magnetic stirrer (Figure 1). The solution was aged for 24 hours to form a continuous gel structure, with the molar ratio of zinc acetate to stearic acid maintained at 1:2.

The glass substrates were cleaned sequentially with deionized water, methanol, and distilled water for 30 minutes each. For dip coating, the glass substrate was slowly dipped into the ZnO solution and then carefully withdrawn. For spin coating, the solution was dropped onto the glass substrate, which was spun at 3000 rpm for 30 seconds. The coated films were placed in a hot air oven at 250°C for 15 minutes to remove the solvent and organic residues. After cooling to room temperature, the films were annealed at 575°C for 2 hours in a high-temperature furnace.

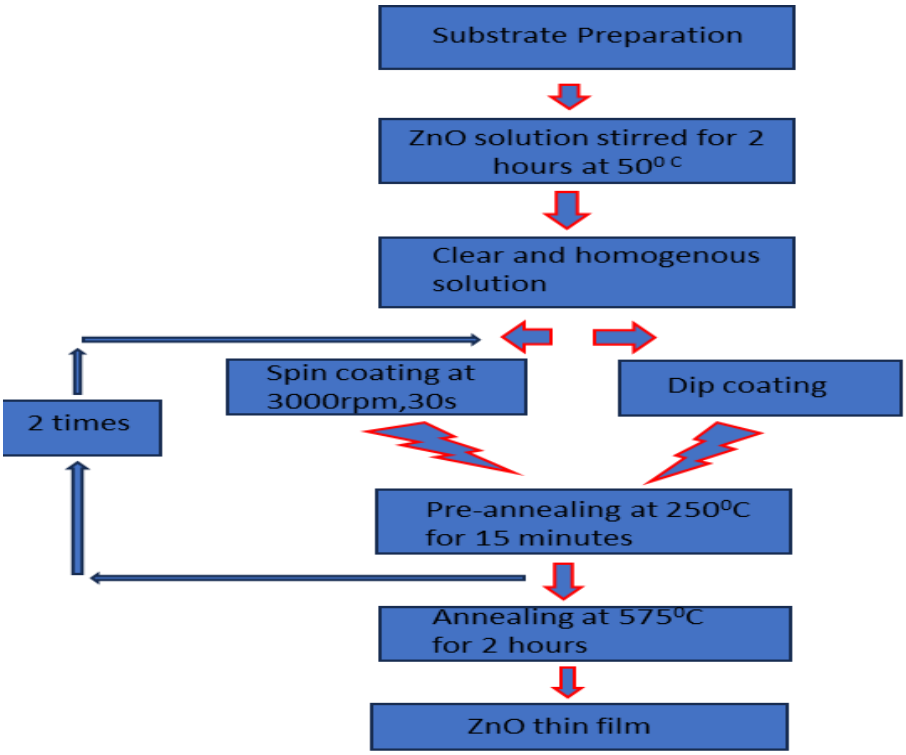

Figure 1 Flow chart of ZnO thin film deposition on glass substrate

III. RESULTS AND DISCUSSION:

A. Structural Properties

As shown in Fig. 2, the XRD patterns of nanocrystalline ZnO thin films, deposited on glass substrates and annealed at 575°C as well as not annealed, were obtained using sol-gel spin coating and dip coating methods. The analysis confirmed a hexagonal structure with distinct crystal orientations like (002), (101), (102), and (103), with the (002) plane showing preferential alignment [7]. The X-ray diffraction (XRD) patterns reveal the crystalline structure of ZnO samples prepared through spin coating and dip coating methods, compared against a non-annealed reference sample. The diffractogram displays several characteristic peaks corresponding to different crystallographic planes, with Miller indices (002), (101), (102), and (103) identified across the 2θ range of 20° to 80°. Both coating methods demonstrate successful crystallization of ZnO, with the spin coating method exhibiting notably higher peak intensities, particularly for the (002) peak reaching approximately 4800 cps compared to 2500 cps for dip coating. The predominant (002) peak in both patterns suggests preferential c-axis orientation of the crystallites [8]. The identical peak positions in both methods confirm similar crystal structures, corroborating the previously

observed lattice parameters. The sharp, well-defined peaks and stable background signal indicate good crystallinity in both coated samples, contrasting sharply with the minimal peaks observed in the non-annealed sample. The higher peak intensities in the spin-coated sample suggest it achieved slightly better crystallinity compared to the dip-coated sample, though both methods successfully produced crystalline ZnO structures.

S. No	$2\theta(Degree)$	D(nm)	Miller indices (hkl)	$\delta\times10^{-4}$ (nm^{-2})
1	34.733	40.99	(002)	5.95
2	36.55	33.72	(101)	8.79
3	47.844	32.18	(102)	9.66
4	63.151	42.37	(103)	5.57

Table 1 Various parameters of of ZnO thin film deposited by spin coating

S. No	$2\theta(Degree)$	D(nm)	Miller indices (hkl)	$\delta\times10^{-4}$ (nm^{-2})
1	34.729	37.14	(002)	7.25
2	36.57	32.16	(101)	9.66
3	63.13	38.83	(103)	6.63

Table 1 Various parameters of of ZnO thin film deposited by dip coating method

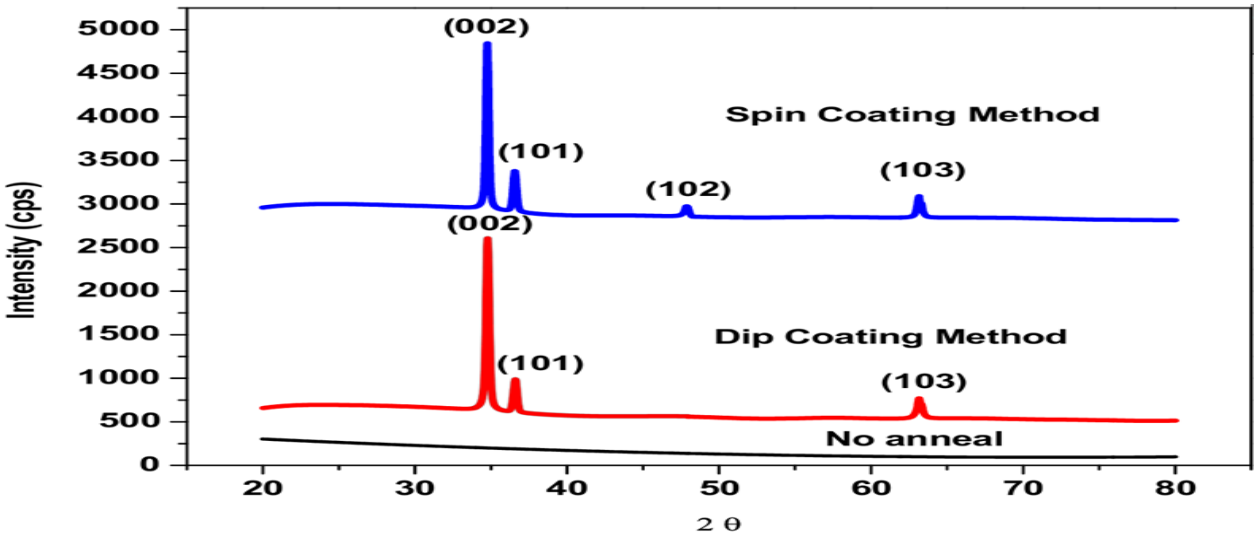

Figure 2 XRD plot of thin films synthesized by spin coating and dip coating method

Method	Average Crystallite Size (nm)	Lattice Parameter(Ă)		c/a	Unit Cell Volume ($Å^3$)
		a=b	c		
Spin coating	37.31	3.21	5.16	1.60	46.26
Dip coating	36.04	3.21	5.16	1.60	46.11

Table 3 Various parameters of of ZnO thin film deposited by spin coating and dip coating method

A. Lattice Parameters for Hexagonal Crystals

The lattice parameters a, b, and c of a hexagonal crystal can be calculated using the following relation between the interplanar spacing and Miller indices h, k, and l [7]:

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

1. Crystallite Size Calculation (Debye-Scherrer Formula)

The crystallite size D of a material can be estimated using the Debye-Scherrer formula [7]:

$$D = \frac{K\lambda}{\beta COS\theta}$$

Where notations have usual meaning.

The dislocation density δ is given by [1]:

$$\delta = \frac{1}{D^2}$$

2. Lattice Cell Volume for Hexagonal Crystals

The volume V of a hexagonal unit cell can be determined as [1]:

$$V = \frac{\sqrt{3}a^2c}{2} = 0.866a^2c$$

The analysis of crystallographic parameters for two different coating methods reveals interesting similarities and minor variations. The spin coating method resulted in a slightly larger average crystallite size of 37.31 nm compared to 36.04 nm for the dip coating method, showing a small difference of 1.27 nm. Both methods demonstrated identical lattice parameters with a=b=3.21 Å and c=5.16 Å, leading to the same c/a ratio of 1.60. The unit cell volume showed minimal variation, with spin coating yielding 46.26 Å³ and dip coating resulting in 46.11 Å³, a difference of just 0.15 Å³ (Table 1,2&3). These results indicate that both coating techniques produce highly similar crystallographic structures, with only marginal differences in crystallite size and unit cell volume, suggesting that either method could be suitable for applications requiring these specific structural parameters.

B. Morphological Parameters

The FESEM image of ZnO thin film prepared by spin coating method (Figure 3, Image a) at 30,000x magnification reveals a distinctive morphological structure characterized by uniformly distributed spherical nanoparticles. These particles have assembled into well-defined cauliflower-like agglomerates with clear grain boundaries, creating a notably porous structure throughout the film. The uniform distribution of particles and the consistent formation of these hierarchical structures demonstrate the effectiveness of the centrifugal force during the spin coating process in achieving homogeneous particle arrangement. The operating conditions were maintained at 15.0kV with a scale bar of 100nm, providing clear visualization of the surface features.

In contrast, the dip-coated ZnO film (Image b), observed at 60,000x magnification, exhibits a markedly different morphological arrangement. The surface shows larger, more densely packed agglomerates with smoother surfaces and less pronounced grain boundaries. The structure appears more compact with fewer visible pores between particles, suggesting a different growth mechanism influenced by gravitational forces during the dip coating process. This image, also captured at 15.0kV with a 100nm scale bar, highlights how the deposition method significantly influences the final film morphology, resulting in a more consolidated structure compared to the spin coating method.

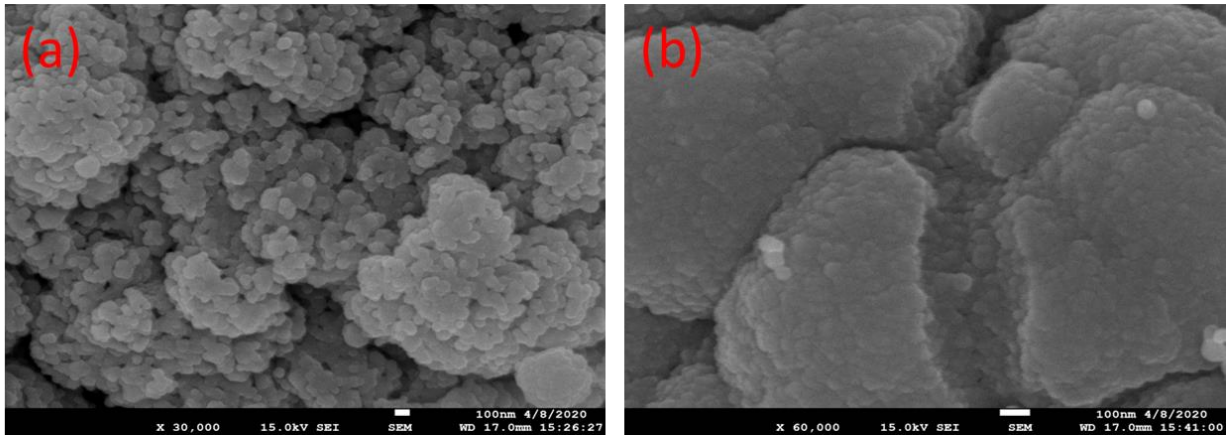

Figure 3 FESEM image of ZnO thin film deposited on glass substrate

IV. CONCLUSION

This study presents a comprehensive comparative analysis of ZnO thin films synthesized through spin coating and dip coating methods, with subsequent annealing at 575°C. XRD analysis confirmed the successful formation of nanocrystalline ZnO films with hexagonal crystal structure in both deposition techniques. The spin coating method demonstrated marginally superior crystallinity, evidenced by higher peak intensities, particularly for the (002) plane (4800 cps compared to 2500 cps for dip coating), indicating preferential c-axis orientation.

Crystallographic analysis revealed subtle variations between the two methods, with spin coating yielding slightly larger average crystallite sizes (37.31 nm versus 36.04 nm for dip coating). Both methods exhibited identical lattice parameters (a=b=3.21 Å, c=5.16 Å) and c/a ratios (1.60), while maintaining minimal difference in unit cell volumes (46.26 Å³ for spin coating and 46.11 Å³ for dip coating). These findings suggest that both techniques produce highly comparable crystallographic structures.

Morphological examination through FESEM revealed distinct surface characteristics for each deposition method. Spin-coated films exhibited uniformly distributed spherical nanoparticles arranged in cauliflower-like agglomerates with well-defined grain boundaries and pronounced porosity. In contrast, dip-coated films displayed larger, more densely packed agglomerates with smoother surfaces and reduced porosity, indicating the significant influence of deposition methodology on film morphology.

These results demonstrate that while both methods successfully produce crystalline ZnO thin films with similar structural parameters, they yield distinct morphological characteristics. This study suggests that the choice between spin coating and dip coating methods should be primarily guided by the specific morphological requirements of the intended application, as the crystallographic properties remain largely comparable between the two techniques.

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