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Optimization of the Properties of ZnO Films Produced by the SILAR Technique

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Abstract. Zinc oxide (ZnO) is a promising semiconductor material for optical and gas sensors. This study examines the influence of film thickness and solvent choice on the performance of ZnO thin films generated by SILAR at room temperature and atmospheric pressure. Ethanol and distilled water (DW) were used as solvents. Thin films of varying thicknesses were analyzed using X-ray diffraction (XRD), scanning electron microscope (SEM) atomic force microscopy (AFM), and Hall effect measurements to evaluate their morphology, crystal structure, and optical and electrical properties. X-ray diffraction analysis showed that films created using ethanol or DW have a hexagonal ZnO structure with a predominant growth orientation along the (002) plane. Films prepared with ethanol exhibited crystallinity comparable to films prepared with DW. ZnO films prepared with ethanol showed low resistivity (10^{-2} Ω cm) and high electron mobility (750 cm^2/Vs). This highlights the potential of the SILAR method using ethanol to create high-quality ZnO thin films suitable for various applications. Thus, the study highlights the importance of thickness and solvent selection in the SILAR deposition process to optimize the properties of ZnO thin films for optical and gas sensors.

Keywords: zinc oxide, SILAR method, semiconductors, distilled water and ethanol, optical and electrical properties.

Introduction

Various techniques for preparing thin film ZnO coatings such as spin coating, salt-gel, spray pyrolysis, electrochemical and chemical deposition, and magnetron sputtering are widely used to create such films [1]. Over the past three decades, SILAR has become one of the popular solution methods for thin film deposition [2]. The main advantages of SILAR include high layer growth rate, control of adsorption and reaction time, and low process temperature, which prevents oxidation and corrosion of the substrate [3]. To obtain a high-quality thin film, it is important to optimize the preparation conditions, such as the concentration of precursors, the nature of the complexing agent, the pH of the solutions, the reaction time and the deposition cycle.

The SILAR method is inexpensive, simple, and suitable for deposition over large areas, including a variety of substrates such as insulators, semiconductors, metals, and temperature-sensitive materials. It is based on sequential reactions between a substrate and a solution, where semiconductor materials are grown by immersion in various aqueous solutions [4].

The SILAR method has enabled the creation of various ZnO nanostructures such as nanorods and nanoflowers. Recent studies have created ultraviolet detectors based on ZnO nanorods and oriented nanorod films without a grain layer. The hydrophobic properties of flower-like ZnO and their excellent performance as gas sensors are also investigated [5]. The morphology and properties of the films are controlled by reaction parameters such as concentration, temperature, pH and number of deposition cycles.

The influence of the immersion cycle on the properties of thin ZnO layers has been discussed in many articles [6]-[8]. Precursors and annealing temperature play an important role. Studies show the influence of different precursors and annealing conditions on the performance of ZnO films. However, most studies used aqueous media to form ZnO films.

In some studies, solvents such as ethylene and isopropyl alcohol were used in the SILAR process, but water remained the main solvent [9]. This study reports the fabrication of ZnO thin films on glass substrates using pure ethanol as a solvent. The functionality of ZnO films grown from aqueous and alcoholic solutions was also compared, which provided new data on the effect of film thickness and solvent on surface morphology.

1. Materials and methods

ZnO films were deposited onto glass substrates using the SILAR method at room temperature and atmospheric pressure. The glasses were cleaned in an ultrasonic bath (first in a soap solution, then in distilled water and a 1:1 mixture of water and ethanol), and then dried in a nitrogen atmosphere for an hour and a half. Zinc chloride ($ZnCl_2$, Sigma Aldrich purity ≥ 98%) was used as a source of zinc. A 0.1 M $ZnCl_2$ solution was prepared by dissolving 1.363 g of $ZnCl_2$ in 100 ml of distilled water or ethanol, adding ammonia solution (25-30% NH_4OH, Sigma Aldrich) drop by drop until pH 10.5 was reached.

To deposit the film, the glass substrate was immersed in a solution of zinc and ammonia for 15 seconds, then in hot (90°C) distilled water for 7 seconds. The zinc-ammonia complex was adsorbed in hot water, forming zinc hydroxide ($Zn(OH)_2$) on the substrate. After air drying for a minute, the samples were washed with distilled water for 30 seconds. The cycle was repeated 30, 40, 50 and 60 times to obtain films of different thicknesses. All deposition steps and SEM images of the various cycles are shown in Figure 1.

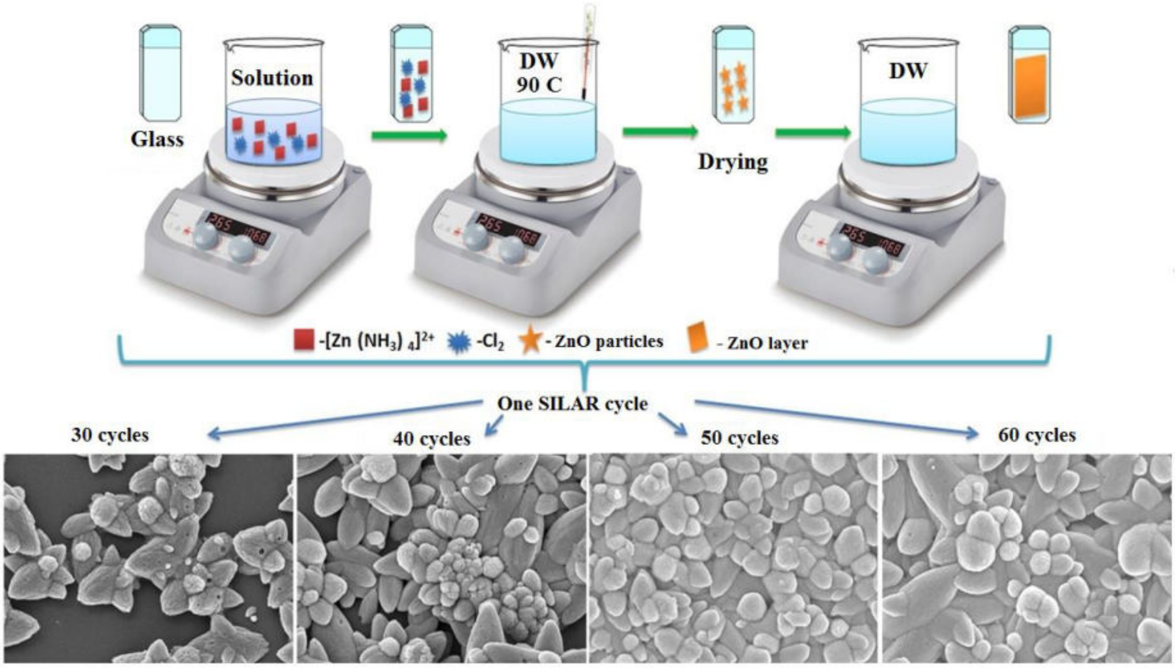

Fig. 1. – Steps for preparing ZnO thin film using SILAR and SEM images

After deposition, the ZnO samples were dried at room temperature and annealed in an N_2 atmosphere at 500 °C for 2 hours. The samples were designated as ZnO: 30 (DW or ethanol), ZnO: 40 (DW or ethanol), ZnO: 50 (DW or ethanol), ZnO: 60 (DW or ethanol). The detailed procedure for deposition of films using the SILAR method was described in a previous studies [10,11]. Film thickness was measured by spectroscopic ellipsometry using SEN research 4.0 ellipsometer, fixing the incident angle at 70° and scanning the wavelength range from 330 to 1100 nm in 0.5 nm steps.

***2.* Results and their discussions**

Srtuctural properties.

To study in more detail the influence of thickness and reaction environment on the growth of zinc oxide nanostructures, structural analysis of deposited ZnO thin films on glasses was performed using X-ray diffraction (XRD). The structural properties of ZnO films were studied using XRD on a SmartLAB Rigaku system (using Cu Kαλ = 1.5406 Å radiation). Figure 2 shows the X-ray diffraction patterns of ZnO thin films with different deposition cycles (30, 40, 50 and 60) that were grown using DW (Figure 2a) and ethanol (Figure 2b) solvents.

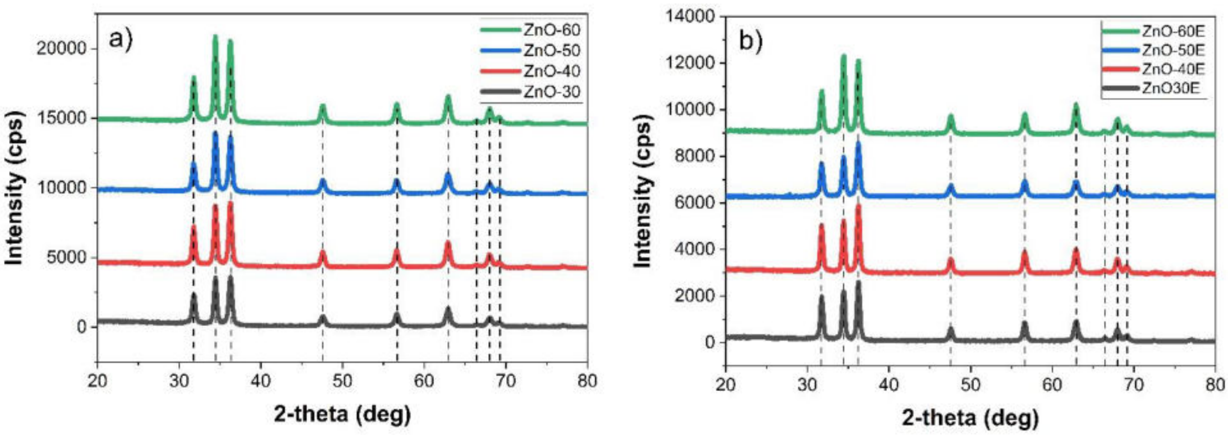

Fig. 2. – XRD patterns of ZnO thin films with different SILAR cycles: a) DW solvent and b) ethanol solvent.

All ZnO thin films exhibited high crystallinity with clear peaks corresponding to the hexagonal wurtzite crystal structure of ZnO, such as (100), (002), and (101). An increase in peak intensity was observed, especially along the c axis along the (002) plane, with increasing film thickness, regardless of the use of water or alcohol in the process. This trend is consistent with published work [12] and data from the ICSD PDF-2 database (No. 03-065-0726).

Despite the differences in SILAR cycles and the use of various precursors, the calculated lattice parameters (a=3 Å, c=5.2 Å) and interplanar spacing (d=2.6 Å) of the ZnO hexagonal structure remained consistent across all samples. This suggests that using ethanol as a solvent for ZnO does not compromise its crystalline structure and can be considered a suitable alternative to the conventional aqueous solution.

Table 1. Effect of the number of SILAR cycles on the crystallite size, half-maximum width (FWHM), dislocation density (δ), lattice strain (ε), interplanar distance (d) and lattice constants (a,c) of ZnO films along the diffraction peak (002)

Name	2θ (deg)	D (nm)	FWHM	δ $(Å)^{-2}\times10^{-6}$	ε (10^{-3})	d (Å)	Lattice constant (Å)		Thickness (nm)
							a=b	c	
DW									
ZnO:30	34.42	22.720	0.3695	19.372	11.81	2.603	3.006	5.2069	192±7
ZnO:40	34.41	23.182	0.3621	18.608	11.31	2.604	3.007	5.2087	217±9
ZnO:50	34.42	20.502	0.4095	23.791	10.66	2.603	3.005	5.2063	329±12
ZnO:60	34.42	21.395	0.3924	21.846	10.45	2.603	3.006	5.2067	498±16
Ethanol									
ZnO:30	34.44	23.289	0.3605	18.437	10.62	2.602	3.007	5.2040	136±6
ZnO:40	34.44	23.191	0.3620	18.593	10.43	2.602	3.005	5.2044	191±9
ZnO:50	34.45	22.773	0.3687	19.282	10.39	2.601	3.004	5.2033	284±9
ZnO:60	34.44	23.529	0.3568	18.063	10.28	2.602	3.005	5.2041	354±14

Morphological properties.

Particle size in distilled water (Fig. 3a) shows small shifts, but no dependence on cycles is observed, while the particle size of films grown in ethanol (Fig. 3b) increases with the number of cycles.

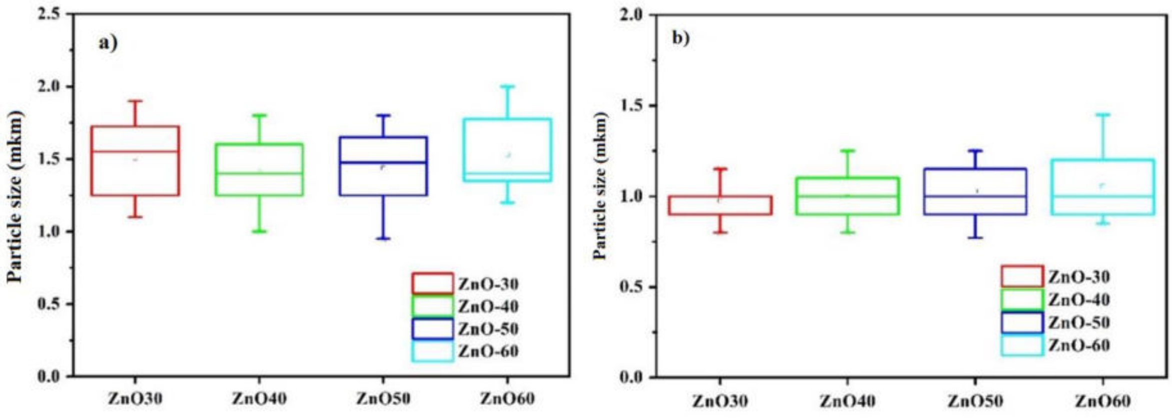

Fig. 3. – Film particle sizes calculated from AFM images for ZnO thin films grown in (a) DW and (b) ethanol.

Electrical properties.

The electrical parameters of the thin films were assessed using Ecopia Hall measurements at room temperature. Hall effect measurements were carried out to obtain the electrical parameters such as resistivity – ρ (Ω*cm), Hall mobility – μ (cm^2/Vs) and carrier concentration – n (cm^{-3}) listed in Figure 4.

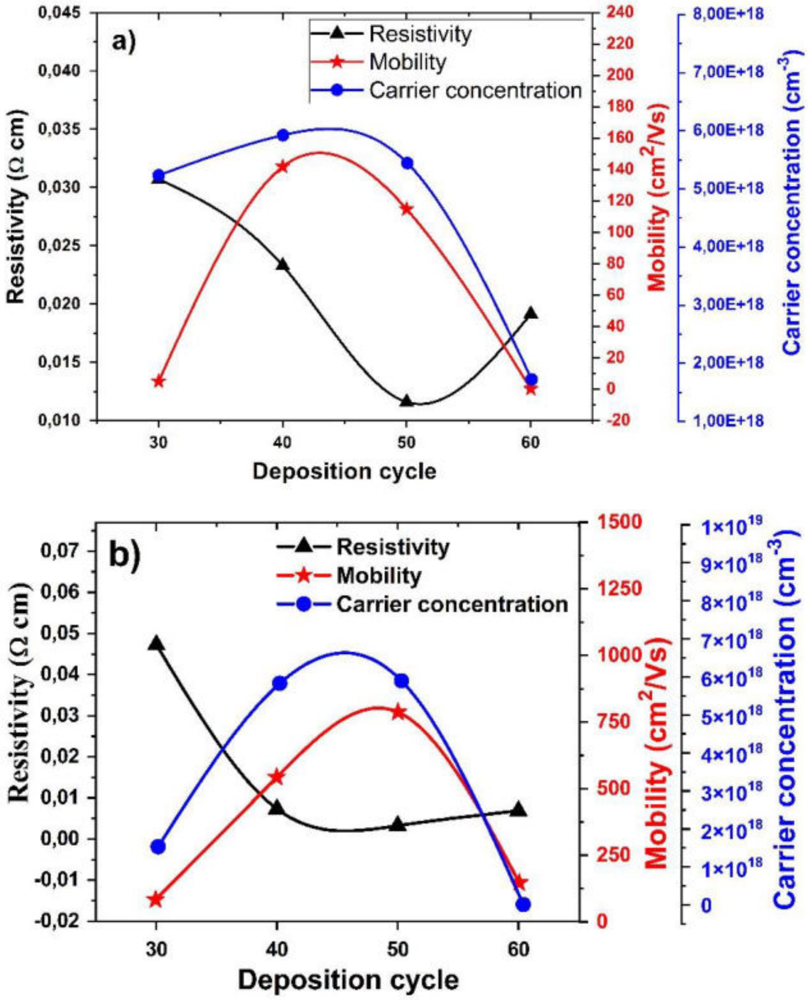

Fig. 4. – Hall measurements results of ZnO thin films grown in a) DW, and b) in ethanol.

According to these results, the carrier concentration of ZnO samples increased to a maximum at 50 deposition cycles. Then it decreased with further increase in the deposition cycle.

Conclusion

In this study, ZnO thin films of various thicknesses were prepared on glass substrates using the SILAR method and solvents of distilled water and ethanol. The use of ethanol instead of distilled water in the SILAR method to produce ZnO thin films on glass substrates resulted in higher crystallinity and smaller grain size. Films produced with more SILAR cycles had a dense coating of nanostructures on the surface. ZnO thin films produced using ethanol also had a wider band gap and the highest charge carrier mobility. This offers potential for applications in gas sensors and dye-sensitive solar cells. Further research will be aimed at studying the gas-sensitive properties of these ZnO films.

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