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Effect of Varying Deposition Time on the Microstructural Properties of ZnS Thin Films

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ABSTRACT
Zinc sulfide (ZnS) thin films were deposited on glass substrates using the chemical bath deposition method with varying deposition times of 7, 14, and 21 hours. Structural characterization was performed using X-ray diffraction (XRD) to investigate the effect of deposition time on crystallite size and preferred orientation. The results confirmed that all films exhibited a polycrystalline cubic (Zinc blende) structure, with prominent diffraction peaks corresponding to the (111), (220), and (311) planes. Crystallite size, calculated using Scherrer's formula, showed a decreasing trend with increased deposition timefrom 34.06 nm at 7 hours to 26.84 nm at 21 hours for the (111) planeindicating enhanced nucleation and grain refinement over time. Peak broadening and reduced intensity at longer durations further supported the formation of finer grains. The (111) orientation remained dominant across all samples, suggesting a consistent growth direction. These findings highlight the significant influence of deposition time on the microstructure of ZnS thin films, offering tunable properties for potential use in optoelectronic applications.

Keywords: Zinc sulfide (ZnS), Chemical bath deposition (CBD), Deposition time, Crystallite size, X-ray diffraction (XRD), Microstructure.

I. INTRODUCTION

Zinc sulfide (ZnS) is a II–VI group semiconductor material that has garnered significant attention due to its wide direct bandgap (approximately 3.6 eV at room temperature), high transparency in the visible range, and strong photoluminescence characteristics [1]. These properties make ZnS thin films suitable for various optoelectronic applications such as photodetectors, solar cells, electroluminescent devices, and light-emitting diodes (LEDs) [2].

The structural and microstructural properties of ZnS thin filmssuch as crystallite size, lattice strain, dislocation density, and preferred orientation are critical parameters that influence the material's electronic and optical performance.[3] These properties are highly sensitive to deposition conditions including substrate temperature, solution concentration, pH, and particularly, deposition time [4]. Deposition time controls the film thickness and affects the nucleation and growth mechanisms, which in turn determine the crystallinity and structural integrity of the films [5].

Several techniques such as chemical bath deposition (CBD), thermal evaporation, sputtering, and spray pyrolysis have been used to fabricate ZnS thin films. Among them, CBD stands out as a cost-effective and low-temperature technique for producing uniform and adherent films over large areas [6][7]. Previous studies have demonstrated that varying the deposition time in CBD significantly alters the film morphology, crystallite orientation, and microstructure, ultimately impacting its functional properties [8], [9].

Despite extensive research on ZnS films, a systematic investigation into how varying deposition time influences their microstructural evolution remains an important area of interest [10]. This study aims to fill this gap by analyzing the effect of deposition time on the microstructural characteristics of ZnS thin films deposited via CBD. The findings are expected to provide insights into the optimization of film growth parameters for enhanced device performance.

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II. LITERATURE REVIEW

Hassan et al., (2021) in their study,deposited ZnS thin films on glass substrates at 473 K using thermal evaporation under a vacuum of 4×10^{-6} mbar for varying durations (10, 20, and 30 minutes). The impact of deposition time on the films' thickness, structural, morphological, and optical properties was examined. XRD analysis confirmed a cubic β-ZnS structure, with crystallite size increasing from 7.05 to 12.28 nm as deposition time increased. AFM revealed surface roughness dependence on deposition duration, while UV–Vis spectroscopy indicated high transparency and zero absorption in the visible and infrared regions. Optical parameters, including band gap, refractive index (fitted with Cauchy's relation), and dielectric constants, were determined.

Hennayaka and Lee 2013 in their workdeposited ZnS thin films on indium–tin-oxide (ITO) coated glass using pulsed electrodeposition to study the influence of deposition temperature on their structural and optical properties. All films exhibited a polycrystalline cubic structure. Films grown below 70 °C were less dense with visible agglomeration, while those deposited above 70 °C were denser with well-defined grains. As temperature increased, film thickness and particle size increased, leading to reduced optical transmittance and bandgap. Notably, ZnS films grown at 90 °C showed strong (200) orientation, n-type conductivity, and a wide bandgap of 3.75 eV.

Babatunde et al., 2019 discovered that the influence of deposition time on the optical and morphological properties of ZnS thin films was studied using the chemical bath deposition method at 50 °C. Films were synthesized on glass substrates for 1, 2, and 3 hours using a precursor solution of zinc sulfate (Zn source), thiourea (S source), and ammonia as a complexing agent. Film thickness was determined by the double weighing method, while morphology and optical properties were analyzed using SEM and UV-Vis spectroscopy. Results showed that transmittance increased in the visible range (400–800 nm) and decreased in the infrared region (>800 nm). The 2-hour sample exhibited the highest transmittance (70%), followed by the 1-hour (55%) and 3-hour (37%) samples. The estimated optical band gap ranged from 3.6 to 3.8 eV. SEM images revealed dense grain structures, with smoother and more clustered surfaces for the films deposited at 2 and 3 hours compared to the 1-hour sample.

Erken et al., 2017 deposited ZnS thin films on glass substrates at 80 °C using chemical bath deposition for varying durations (4, 6, and 8 hours) to investigate the effects of deposition time on their optical and electrical properties. Film thickness ranged from 210 to 1375 nm, determined via gravimetric analysis. UV–Vis spectroscopy (300–1100 nm) revealed transmittance values between 51–90% and refractive indices from 1.40 to 2.45. The optical band gaps were found to range from 3.61 to 3.88 eV, with sharp band edge transitions. Electrical measurements showed specific resistivity values between 1.08×10^{5} and 1.01×10^{6} Ω·cm, confirming n-type conductivity through Hall effect analysis.

III. MATERIALS AND METHOD

A. Materials

The precursor chemicals used for the synthesis of ZnS thin films include:

- Zinc sulfate ($ZnSO_4 \cdot 7H_2O$) – used as the zinc source
- Thiourea ($CS(NH_2)_2$) – used as the sulfur source
- Ammonia solution (NH_4OH) – used as a complexing agent and pH regulator
- Distilled water – used as the solvent
- Glass microscope slides – used as substrates for film deposition

All chemicals were of analytical grade and used without further purification.

B. Substrate Preparation

Glass substrates were cleaned using a sequential process involving detergent washing, rinsing with distilled water, ultrasonication in acetone and ethanol for 10 minutes each, and finally air drying. This ensured proper adhesion and uniform growth of the ZnS thin films.

C. Thin Film Deposition

ZnS thin films were deposited using the chemical bath deposition (CBD) technique at a fixed temperature of 50 °C. The chemical bath was prepared by mixing 0.1 M zinc sulfate and 0.1 M thiourea in 100 mL of distilled water. Ammonia was added dropwise under continuous stirring until the pH of the solution was adjusted to approximately 10. The cleaned glass substrates were vertically immersed in the solution.To study the effect of deposition time, the films were deposited for 1 hour, 2 hours, and 3 hours respectively. After deposition, the samples were removed, rinsed thoroughly with distilled water to eliminate loosely adhered particles, and dried at room temperature.

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D. Film Thickness Measurement

The thickness of the deposited films was determined using the double weighing method, where the weight difference before and after deposition was used to calculate film thickness based on the film density and surface area.

E. Characterization Techniques

X-Ray Diffraction (XRD):

XRD analysis was carried out using a [specify model] diffractometer with Cu-Kα radiation (λ = 1.5406 Å) to determine the crystal structure, crystallite size, lattice constant, dislocation density, and microstrain of the films.

IV. RESULTS AND DISCUSSION

The structural analysis of ZnS thin films is carried out by varying the deposition time. The XRD pattern of the deposited ZnS thin film at 7 hours, 14 hours and 21 hours onto glass substrates is as shown in fig. 1-3 respectively. The crystallite size was estimated by using Scherrer's formula (Monchi et al.,2012)

$$D=\frac{0.9\lambda}{\beta\cos\theta} \quad (1)$$

Where:

D = Crystallite size (in nanometers)

K = Shape factor (0.9)

λ = Wavelength (1.5406Å)

β = Full width at half maximum (FWHM) in radians and

θ = Bragg's angle

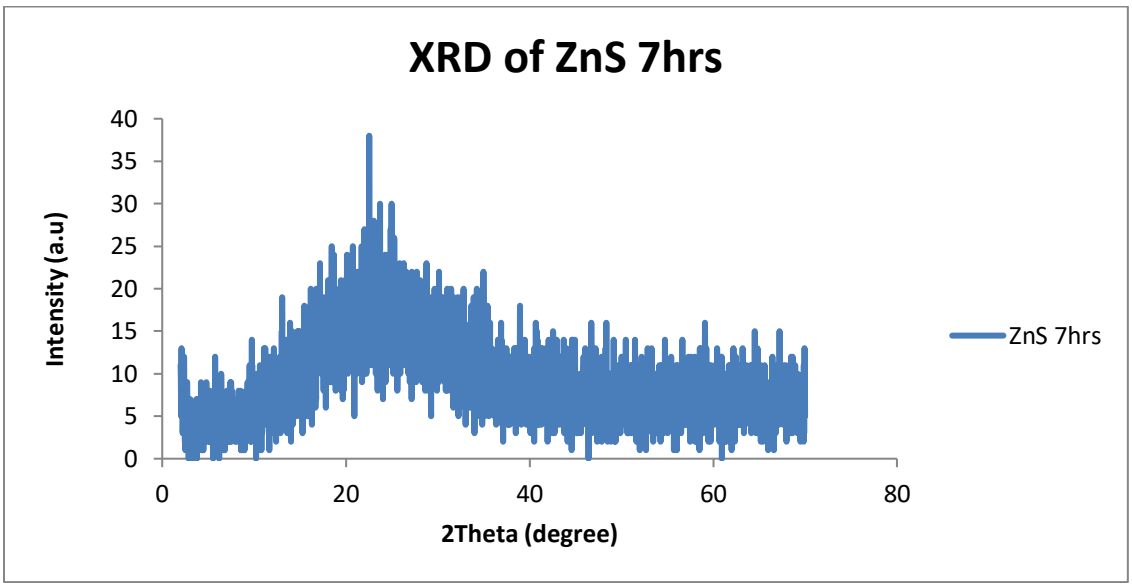

Fig. 1: XRD pattern for ZnS thin film deposited at 7 hours

Different diffraction peaks in the XRD pattern displayed in figure 1 indicate polycrystalline ZnS thin film. Especially around 2θ at 28.5^0, 47.5^0, and 56.3^0 which corresponds to the (111), (220), and (311) planes respectively, these peaks fit well with the standard planes of cubic (Zinc blende) ZnS structure. Usually, the most intense peak for cubic ZnS, the peak at $2\theta = 28.5^0$ is ascribed to the (111) plane. This reveals the preferred orientation in crystal development. For the several planes (111), (220), and (311), crystallite sizes are 34.06 nm, 28.91 nm, and 34.92 nm respectively. ZnS thin film is polycrystalline based on the different diffraction peaks shown in figure 1. These coordinate well with the cubic (Zinc blende) standard planes.

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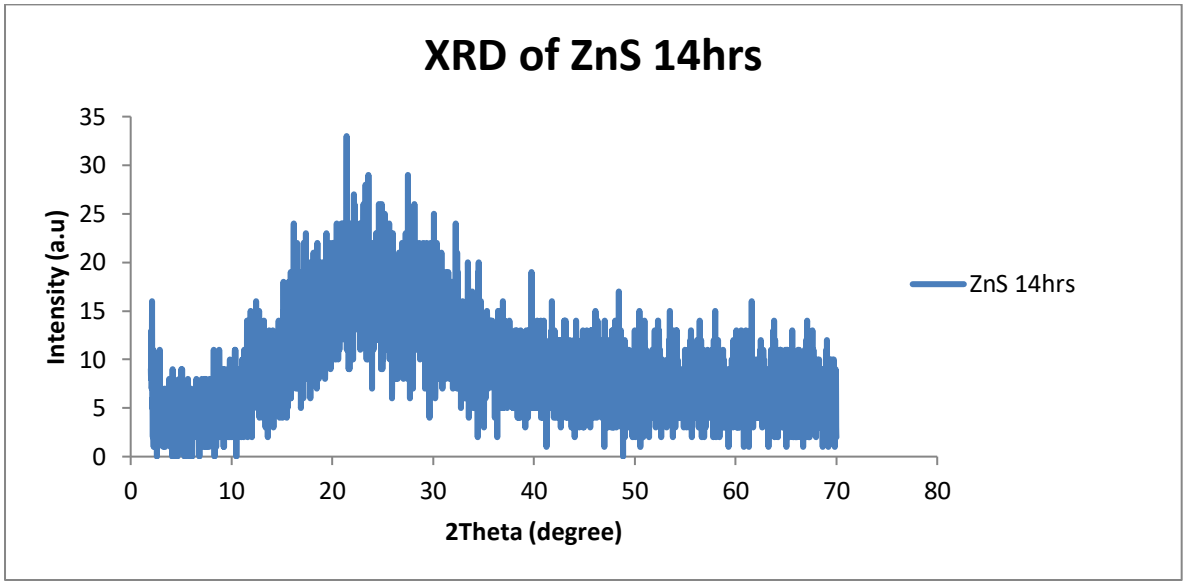

Fig. 2: XRD pattern for ZnS thin film deposited at 14 hours

Corresponding to the (111), (220), and (311) planes, the XRD pattern as displayed in figure 2 shows three major peaks at $2\theta = 28.66^0$, 47.60^0, and 56.40^0. These peaks confirm the phase purity of the film by matching nicely with the normal data for cubic (Zinc Blende) ZnS. Though slightly broader than a shorter deposition period (7 hours), the clear and sharp peaks indicate that the film is polycrystalline. This behavior is supported by Chabouet.al (2020).This leads to moderate crystallinity with either a slight lattice disorder or a decrease in grain size brought on by prolonged deposition. The strong intensity at (111) and the relatively large crystallite size at the (311) plane indicate that (111) is still the preferred orientation even though the growth is becoming multidirectional. The various planes (111), (220), and (311), have calculated crystallite sizes of 30.94 nm, 27.10 nm, and 32.10 nm, respectively.

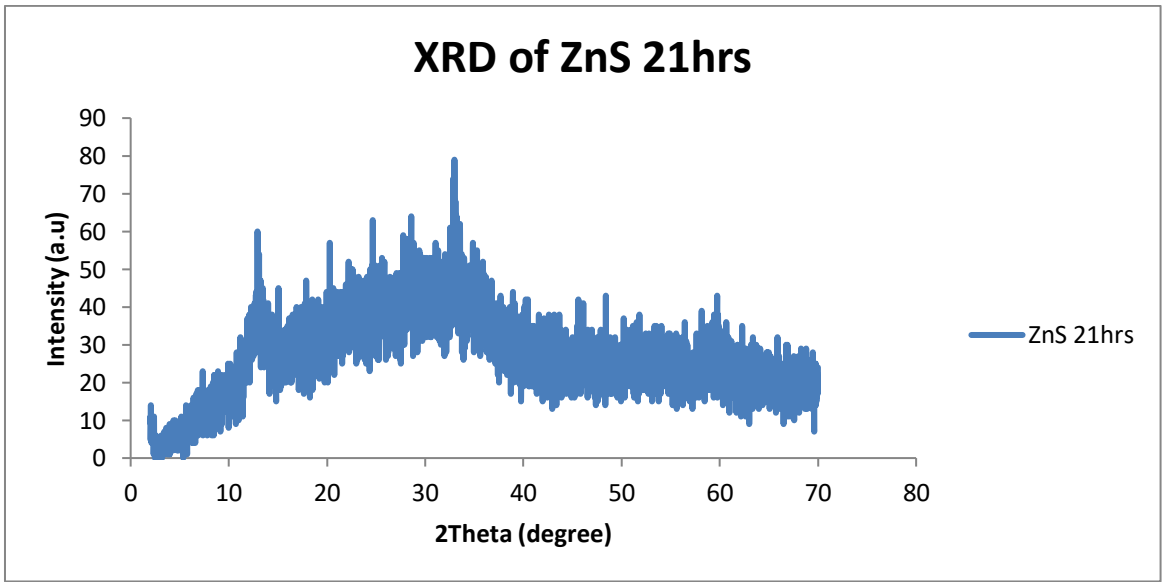

Fig. 3: XRD pattern for ZnS thin film deposited at 21 hours

The peaks at $2\theta = 28.76^0$, 47.64^0, and 56.44^0, which correspond to the (111), (220), and (311) planes, are visible in the XRD pattern in Figure 3. These reflections verify that there is no

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indication of secondary phases and that the film maintains the cubic (Zinc blende) ZnS phase. Despite extended deposition, this suggests a good purity phase. A decrease in crystallite size is suggested by the peaks' broader and less intense appearance. The various planes (111), (220), and (311) have calculated crystallite sizes of 26.84 nm, 25.44 nm, and 29.81 nm, respectively. The film may be appropriate for uses where uniform thin films and a large surface area are desired due to the decreased crystallite size at 21 hours.

Table 1: Summary of X-ray diffraction data for all the deposited ZnS thin films

Samples	**Planes (hkl)**	**2θ(Degree)**	**FWHM(Degree)**	**Crystallite size, D(nm)**
7 hours	(111)	28.58	0.240	34.06
	(220)	47.50	0.280	28.91
	(311)	56.32	0.230	34.92
14 hours	(111)	28.66	0.260	30.94
	(220)	47.60	0.300	27.10
	(311)	56.40	0.250	32.10
21 hours	(111)	28.76	0.300	26.84
	(220)	47.64	0.320	25.44
	(311)	56.44	0.270	29.81

As the deposition time increases, the crystallite size decreases as demonstrated in table 1. This implies that a longer deposition time might result in more nucleation sites, which would lower the average crystallite size and possibly raise the film's density. The largest crystallite size is consistently displayed in the (111) plane, indicating that this orientation is still the preferred one for growth. Decreased crystallite size is indicated by a trend of peak broadening (higher FWHM) as deposition time decreases.

V. CONCLUSION

The structural characterization of ZnS thin films deposited at varying durations (7, 14 and 21 hours) via XRD confirms the formation of a cubic (Zinc blende) phase across all samples. The films exhibited polycrystalline nature with prominent diffraction peaks corresponding to the (111), (220) and (311) planes. Aclear trend of decreasing crystallite size was observed with increasing deposition time from 34.06 nm at 7 hours to 26.84 nm at 21 hours (for the (111) plane, indicating that prolonged deposition promotes the formation of smaller, more compact grains. This behaviorsuggests an increase in nucleation density and a potential saturation of crystal growth over time. This trend aligns with the findings from Gode et al.(2023)who reported that extended deposition time in CBD processes leads to increased nucleation sites, resulting in finer grain structures and reduced crystallite sizes.

The formation of a cubic (Zinc blende) phase in all samples is confirmed by the structural characterization of ZnS thin films deposited at different times (7, 14, and 21 hours) using XRD. The films' prominent diffraction peaks, which corresponded to the (111), (220), and (311) planes, demonstrated their polycrystalline nature. For the (111) plane, there was a noticeable trend of decreasing crystallite size as the deposition time increased, going from 34.06 nm at 7 hours to 26.84 nm at 21 hours. This suggests that longer deposition encourages the formation of smaller, more compact grains.This behavior points to a possible saturation of crystal growth and an increase in nucleation density over time, which is consistent with the findings of Arsad et al. (2023), who found that longer deposition times in CBD processes result in more nucleation sites, which in turn lead to smaller crystallites and finer grain structures.

The findings suggest that deposition time has a significant impact on ZnS thin-film microstructure, with shorter durations favoring larger crystallites and higher crystallinity and longer durations potentially producing films with finer grain structures and possibly improved surface uniformity. These deposited thinfilm properties are useful in optoelectronic applications.

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