

Structural and optical properties of nanocrystalline ZnS thin films grown by successive ionic layer adsorption and reaction method

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Abstract: Zinc sulphide (ZnS) thin films of the II-VI group is a favorable alternative buffer layer for replacing the toxic CdS material, have been deposited on glass substrate by successive ionic layer adsorption and reaction method by using urea as a complexing agent. The structural and optical properties of the ZnS thin films were characterized by X-ray diffraction (XRD) and UV-VIS-NIR spectrophotometer techniques. The XRD study reveals that the formation of nanocrystalline ZnS thin films of cubic structure. The particle size was found to be in the range of 1.63-1.91 nm for (111) planes. The direct band gap values of deposited ZnS thin films are decreased from 3.42 to 3.38 eV with number of SILAR cycles. These ZnS thin films may be used as buffer layer for solar cells.

Keywords: ZnS, SILAR, XRD, Optical

I. INTRODUCTION

The utmost comprehensively used buffer layer in thin film solar cells (TFSC) based on the use of CuInSe₂ (CIS), CdTe (CT) and CuInGa(S,Se)₂ (CIGS) absorber layers is CdS. However, there are toxic hazards in the production of CdS layer and it will cause environmental pollution. One possible replacement for the CdS is zinc sulphide (ZnS), which is non-toxic. Unpolluted ZnS thin film has received great attention in recent years in the optoelectronics applications [1, 2]. ZnS is an important semiconductor compound of II-VI groups with wide band gap 3.4 -3.70 eV at room temperature [3] and high transmittance in the visible region [4]. ZnS thin films have been developed on different substrates like glass, silicon, FTO,ITO and GaAs [5, 6]. There has been rising interest in developing methods to deposit semiconductor ZnS thin films. Several methods such as MOCVD [7], molecular beam epitaxy [8], chemical bath deposition [4], electrodeposition [9], successive ionic layer adsorption and reaction (SILAR) [1, 2], spray pyrolysis [10] have been used to produce ZnS thin films. Among these methods, SILAR has several advantages with other methods such as control of thickness, uniform film deposition, simple and inexpensive [1]. In addition, the preparative parameters such as pH, concentration, temperature, nature of complexing agent, etc. are easily controllable. Nicolau [11] introduced the SILAR technique

in the 1985. The method has been employed to grow selected II-VI compounds, particularly CdS and ZnS.

The SILAR technique is an exclusive method in which thin films of compound semiconductors can be deposited by sequential immersion of a substrate into separately placed cationic and anionic precursors. Between every immersion it is rinsed in ion exchange or distilled water. For deposition of ZnS thin films, zinc sulphate was used as zinc ion releasing source (cations) and sodium sulfide was used as sulphur ion releasing source (anion). Both anionic and cationic precursors were kept at room temperature.

In the present work, ZnS thin films were deposited by successive ionic adsorption and reaction method on glass substrate at room temperature using (0.1M) ZnSO₄ and (0.1M) Na₂S solutions with urea as a complexing agent. These films were characterized for their structural and optical properties by using X-ray diffraction and optical absorption studies.

II. EXPERIMENTAL

All chemical reagents zinc sulphate, sodium sulfide and urea are of analytical grade (AR) and used further without purification. Before the deposition of ZnS thin films, microscopic glass slides were cleaned as earlier report [1]. The cationic precursor was 0.1M ZnSO₄ and to make it alkaline, aqueous ammonia was added. The anionic precursor was 0.1M Na₂S, formed by dissolving the sodium sulfide (Flakes) in distilled water. In this study, urea was used as complexing agents to control the free ion concentration. One SILAR cycle involved the following three steps; (1) well-cleaned glass substrate was immersed in the aqueous cationic precursor of (0.1M) ZnSO₄ with urea for 10 sec. where Zn²⁺ ions were adsorbed on the glass substrate, (2) the substrate with adsorbed Zn²⁺ was immersed in an anionic precursor of (0.1M) Na₂S with urea for 15 sec. where S²⁻ ions were reacted with Zn²⁺ ions to form ZnS, and (3) finally the substrate was immersed in the rinsing bath for 10 sec. to remove loosely bound ZnS material. This completes one SILAR cycle of ZnS.

The schematic set up used for the synthesis of ZnS by SILAR technique is demonstrates in Figure 1. By repeating such SILAR cycles 20, 40, 60 and 80 times, we obtained white, uniform, weakly adherent ZnS thin films on glass substrate. The preparative parameters used for the deposition of ZnS thin films are summarized in Table 1. The ZnS thin films prepared with 20, 40, 60 and 80 SILAR cycles are denoted by ZS20, ZS40, ZS60 and ZS80 respectively and used for further characterizations.

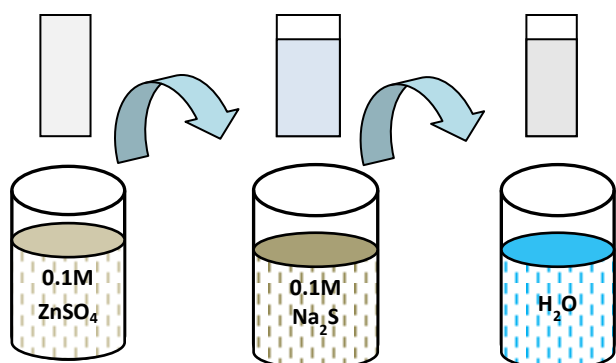


Figure 1 Schematic representation of SILAR method

The study of optical properties of ZS20, ZS40, ZS60 and ZS80 were carried out within wavelength range 300-700 nm using JASCO UV-VIS-NIR spectrophotometer, Model :V-670. To study the structural property of ZS20, ZS40, ZS60 and ZS80 thin films, X-ray diffraction (XRD) patterns were obtained from Bruker axe D8 Advance diffractometer with CuK α ($\lambda = 0.15406$ nm) target.

Table 1Preparative parameters for the deposition of ZnS thin films

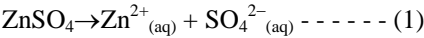
Parameters	Precursors solutions	
	ZnSO ₄	Na ₂ S
Concentration (M)	0.1	0.1
pH	~ 10.5	~ 11.2
Immersion time (s)	10	15
Number of SILAR cycles	20, 40, 60, 80	20, 40, 60, 80
Temperature (°C)	Room temperature	Room temperature

III. RESULTS AND DISCUSSION

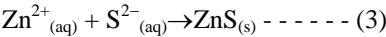
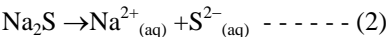
3.1 Growth mechanism

The SILAR method is based on the successive reaction at the surface of glass substrate. The formation of ZnS may involve the following steps:

1. The glass substrate was immersed into cationic precursor where Zn²⁺ ions get adsorbed on the glass substrate.



2. After rinsing in distilled water substrate was immersed into anionic precursor where Zn²⁺ ions react with S²⁻ to form ZnS.



Here, it is necessary to control the free Zn²⁺ and S²⁻ concentrations by using suitable complexing agent, which release small concentration of ions. In this study, urea is used as a complexing agent.

3.1 Structural studies

A weakly adherent ZS20, ZS40, ZS60 and ZS80 thin films can be scratched from the substrate and obtained ZnS powder was subsequently washed repeatedly in distilled water and heating the powder at 70°C for 60 min. X-ray diffraction (XRD) with CuK α radiation ($\lambda=0.15406$ nm) was made for structural characterization of the synthesized powders of ZS20, ZS40, ZS60 and ZS80 in the 2 θ range 20-80 degree. Figure 2 shows the XRD patterns of the ZS20, ZS40, ZS60 and ZS80 powder. The leading diffraction peaks centered at 28.97°, 48.50° and 56.43° are indexed to (111), (220) and (311) planes of cubic structure of ZnS [PDF#800020]. Other peaks of ZnS did not appear in the spectrum.

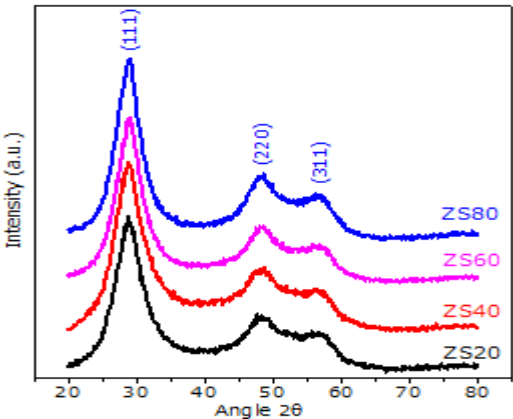


Figure 2 XRD pattern of ZS20, ZS40, ZS60 and ZS80

Table 2 Standard and observed ‘d’ values, FWHM, D and δ of ZS20, ZS40, ZS60 and ZS80 thin films for (111) plane

Plane→	For (111) plane			
Parameter ↓	ZS20	ZS40	ZS60	ZS80
Standard ‘d’ (Å ⁰)	3.0859	3.0859	3.0859	3.0859
Observed ‘d’ (Å ⁰)	3.0882	3.0983	3.0802	3.0803
FWHM (β)	5.0472	4.7915	4.5169	4.2905
D (nm)	1.63	1.71	1.82	1.91
δ in (nm) ⁻² (x10 ⁻¹)	3.782	3.410	3.028	2.723

The crystallite size of ZnS thin films was calculated from XRD patterns by using Debye Scherrer’s equation [1], $D = 0.9\lambda/\beta.\cos\theta$, where D is the grain size, β is the angular line width of half-maximum intensity in radians, λ is the X-ray wavelength used, and θ is Bragg’s angle. The calculated crystallite size of ZS20, ZS40, ZS60 and ZS80 was found to be 1.63, 1.71, 1.82 and 1.91 nm respectively. The observed and standard d values, crystallite size, dislocation density and FWHM of ZnS thin film for (111) plane have been given in Table 2. Lesser value of dislocation density directs better crystalline nature of ZnS thin films.

3.2 Optical studies

The optical properties of ZS20, ZS40, ZS60 and ZS80 thin films have been determined from absorbance measurement in the range 300-700 nm. Figure 3 (A) shows the absorbance spectra of ZS20, ZS40, ZS60 and ZS80 thin films.

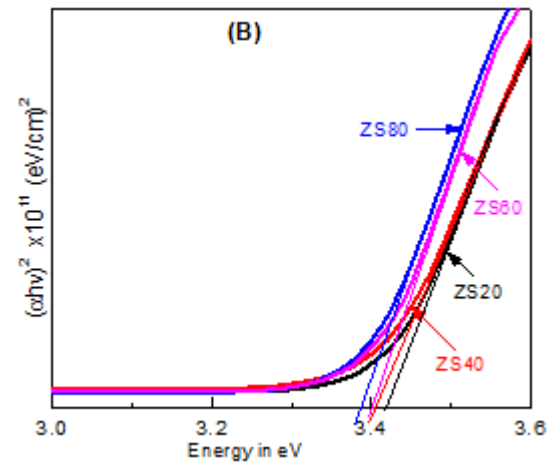
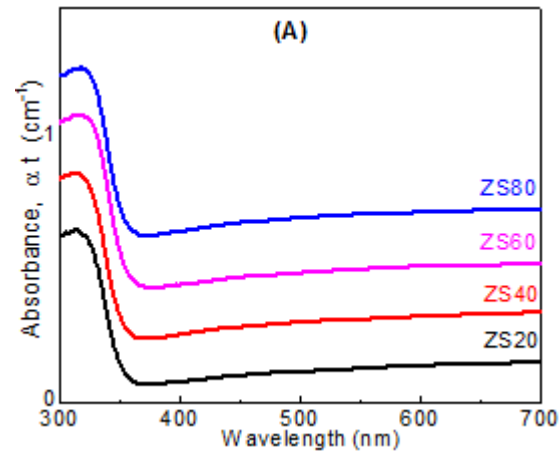


Figure 3 Variation of absorbance vs wavelengths (A) and $(\alpha h\nu)^2$ vs $h\nu$ (B) of ZS20, ZS40, ZS60 and ZS80 thin films

The variations of $(\alpha h\nu)^2$ versus $h\nu$ for ZS20, ZS40, ZS60 and ZS80 is shown in Fig. 3(B). The band gap energy determined by extrapolating the straight line portion to the energy axis at $\alpha=0$ and is found to be 3.42, 3.41, 3.40 and 3.38 eV which are in good agreement with the band gap values reported by other researchers [6, 12, 13]. The decrease in band gap of ZS20, ZS40, ZS60 and ZS80 thin films could be attributed to improvement in the crystallite size of the films with SILAR cycles as supported by XRD studies [12, 14]. Similar effect has been observed for CBD grown ZnS films [6].

IV. CONCLUSION

Nanocrystalline ZnS thin films have been grown by successive ionic layer adsorption and reaction (SILAR) method using a novel complexing agent, urea. The X-ray diffraction (XRD) and UV-VIS-NIR spectrophotometer techniques were used for the study of structural and optical properties of the ZnS thin films. The XRD study reveals that the formation of nanocrystalline ZnS thin films of cubic structure. The particle size was found to be in the range of 1.63-1.91 nm for (111) planes. The optical band gap decreased from 3.42 to 3.38 eV with increasing number of SILAR cycles. These films can be used as buffer layers in the fabrication of heterojunction thin film solar cells.

REFERENCES

- [1] S. G. Deshmukh, Akshay Jariwala, Anubha Agarwal, Chetna Patel, A. K. Panchal, Vipul Kheraj, AIP Conference Proceedings 1724 (2016) 020033
- [2] M. S. Shinde, P. B. Ahirrao, I. J. Patil, R. S. Patil, Indian J. Pure Appl. Phys. 49 (2011) 765-768
- [3] M. S. Shinde, P. B. Ahirrao, R. S. Patil, Archives Applied Sci. Research 3 (2011) 311-317
- [4] F. Gode, Physics B 406 (2011) 1653-1659
- [5] J. Diaz-Reyes, R. Castillo-Ojeda, J. Martinez-Juarez, O. Zaca-Moran, J. E. Flores-Mena, M. Galvan-Arellano, Inter. Jr .of circuits, systems and signal processing 8 (2014) 15-21
- [6] S. D. Sartale, B. R. Sankapal, M. Lux-Steiner, A. Ennaoui. Thin Solid Films 480–481 (2005) 168–172
- [7] C. W. Wang, T. J. Sheu, Y. K. Su, M. Yokoyama, Appl. Surf. Sci. 113/114 (1997) 709-713.
- [8] Ichino K, Onishi T, Kawakami Y, Fujita S., J Crystal Growth 28 (1994) 138
- [9] H. M. M. N. Hennayaka, Ho Seong Lee, Thin Solid Films, 548 (2013) 86-90.
- [10] M. A. Hernandez-Fenollosa, M. C. Lopez, V. Donderies, M. Gonalez, B. Mari, J. R. Ramos-Barrado, Thin Solid Films 516 (2008) 1622.
- [11] Nicolau Y. F., Appl. Surf. Sci. 22-23 (1985) 1061-1074
- [12] Jie Cheng, DongBo Fan, Hao Wang, BingWei Liu, YongCai Zhang and Hui Yan, Semicond. Sci. Technol. 18 (2003) 676–679
- [13] S. Thirumavalavan, K. Mani, S. Sagadevan, Int. Jr. Physical Sciences, 10 2015 204-209
- [14] Aytunc Ates, M. Ali Yıldırım, Mutlu Kundakci, Aykut Astam, Materials Science in Semiconductor Processing 10 (2007) 281– 286.