Structural and Optical Properties of ZnS Thin Films by SILAR Technique obtained by acetate Precursor

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Abstract: In the group of II-VI compound semiconductor, zinc sulphide (ZnS) has numerous potential applications in optoelectronic devices. In this effort, we have prepared ZnS thin films on glass substrates by Successive Ion Layer Adsorption and Reaction (SILAR) method. Zinc acetate and sodium sulphide were used as cationic and anionic precursors for the films. The crystal structure and surface morphology of the films were studied by X-ray diffractometer (XRD) and Scanning electron microscope (SEM). The deposited ZnS thin films showed polycrystalline with cubic phase. The increment in grain size is an effect of the increase in thickness of the films in accordance with the immersion cycles. The SEM images of the films confirmed that films were uniformly distributed in substrates and pin hole free. The band-gap of the films was estimated.

Keywords: Semiconductor, Thin films, SILAR, Band gap.

1. Introduction

In the current development, the wide band gap semiconductor of zinc sulphide (ZnS) thin films are auspicious for optoelectronic device applications, such as electroluminescent devices and solar system [1]. Among the various sulphides, zinc sulphide (ZnS) have been broadly studied from both experimental and theoretical points of view [2, 3]. Epitomizing the results from the literature, it is found that ZnS thin films have been deposited by physical methods like thermal evaporation [4], pulsed laser deposition [5], sputtering [6], and chemical methods like Metal organic chemical vapour deposition [7], electrodeposition [8], sol gel [9], spray pyrolysis [10], chemical bath deposition [11, 12], SILAR [13] etc.

Among these techniques, SILAR (Successive Ionic Layer Adsorption and Reaction) technique is simple and economical because of the utilisation of environment production conditions. SILAR technique, introduced by Nicolau [14], is a unique method in which thin films of compound semiconductors can be deposited by alternate immersing of a substrate into the solutions containing ions of each precursors. This method is improved version of Chemical Bath Deposition. But in this method, the precursor solutions are kept in different beakers. Hence it is easy to control the growth of the film. From the growth cycles, the

controlled thickness can be possible [15, 16]. By tuning the experimental parameters, i.e., deposition cycles, dip duration, etc., the growth rate can be controlled. SILAR offers a quick operation to deposited thin films from an aqueous solution of precursors at room temperature. The tedious dipping process has motivated the development of many automatic deposition apparatus [17].
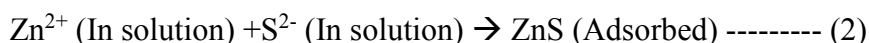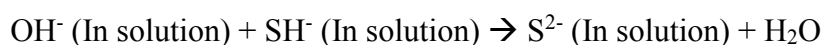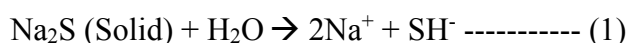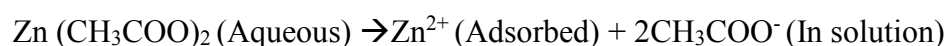
In the current work, the effects of immersion cycles on the structural and optical properties of SILAR deposited ZnS have been analysed.

2. Experimental details

ZnS thin films were prepared by SILAR method using glass substrates. Before deposition substrates were cleaned in dilute hydrochloric acid, and then in acetone. Later they were rinsed with double distilled water.

For this deposition, cationic precursor used as zinc acetate ($Zn (CH_3COO)_2$) and anionic precursor as sodium sulphide (Na_2S). Well cleaned glass substrates were dipped into aqueous solution of zinc acetate. The surface of the substrate was absorbed by zinc ions. Then substrate was rinsed by double distilled water to expulsion of loosely bound Zn^{2+} ions. Next to this, the substrates were dipped into aqueous solution of sodium sulphide. The sulphide ions reacted with adsorbed zinc ions. Finally, to avoid precipitation the substrates were rinsed with distilled water. This is the growth cycle of SILAR method. To obtain desired thickness of the films, these growth cycles have been replicated.

The reactions involved were:

$$Zn (CH_3COO)_2 \text{ (Aqueous)} \rightarrow Zn^{2+} \text{ (Adsorbed)} + 2CH_3COO^- \text{ (In solution)}$$

$$Na_2S \text{ (Solid)} + H_2O \rightarrow 2Na^+ + SH^- \text{ ------------ (1)}$$

$$OH^- \text{ (In solution)} + SH^- \text{ (In solution)} \rightarrow S^{2-} \text{ (In solution)} + H_2O$$

$$Zn^{2+} \text{ (In solution)} + S^{2-} \text{ (In solution)} \rightarrow ZnS \text{ (Adsorbed)} \text{ --------- (2)}$$

In this work, the prepared ZnS thin films were characterized to study structural and optical properties with the effect of immersion cycles. Powder X-Ray diffraction analysis studied the crystal structure of the films. The surface feature of the films was analysed by a scanning electron microscope. The UV - VIS spectrophotometer was used to measure the absorbance in the wavelength range 300 - 600nm and from these measurements, the band gap of the films was calculated.

3. Results and discussion

ZnS thin film deposited by varying the number of immersion cycles. The thickness of the film was estimated by gravimetric method and verified by cross-sectional SEM. The thickness of the film increased from 210 nm to 400 nm with number of immersion cycles.

The XRD patterns of the ZnS films are shown in Figure 1. which influenced by immersion cycles. The patterns show polycrystalline with cubic phase and peaks corresponds to (111), (220) and (311) planes.
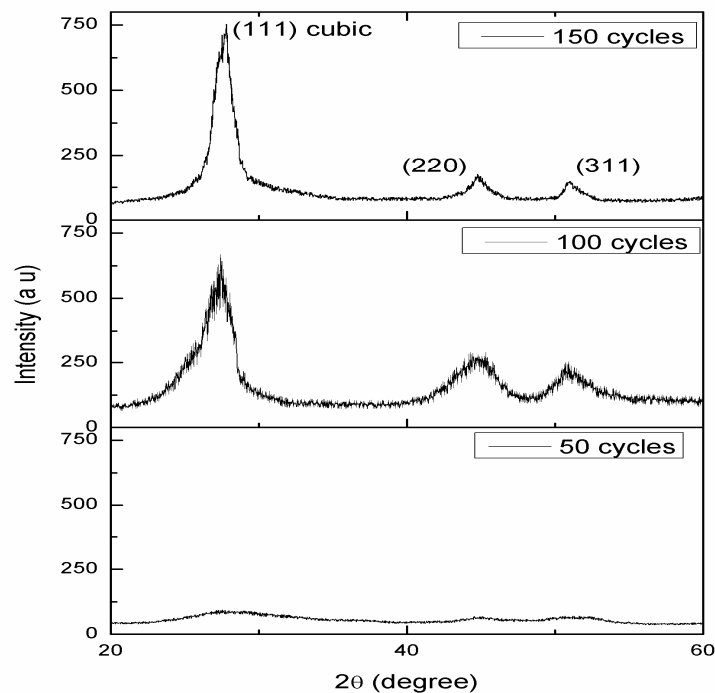

Figure 1. XRD patterns of ZnS thin films with different number of immersion cycles

From Scherrer formula, the grain size 'D' of the films was calculated were shown in Table 1.

$$D = \frac{0.9\lambda}{\beta \cos\theta}$$

Where λ is the wavelength of the x-rays used, β is the full-width-at-half maximum (FWHM) at Bragg angle θ.

Table 1. Grain size of the films with respect to the number of immersion cycles

Immersion cycles	Grain Size (Å)
50	15
100	36
150	49

The deposited films were attributed to the significant improvement in the crystallinity of the films. For lower immersion cycles 50 and 100, the growth rate of ZnS has been slightly lower.

So, broad peak observed for 100 cycles. For 150 immersion cycles, there was sharp peak observed with increase of crystallinity.

The deposited films were uniform substrate coverage and no void, pin hole free clearly showed in Figure 2.
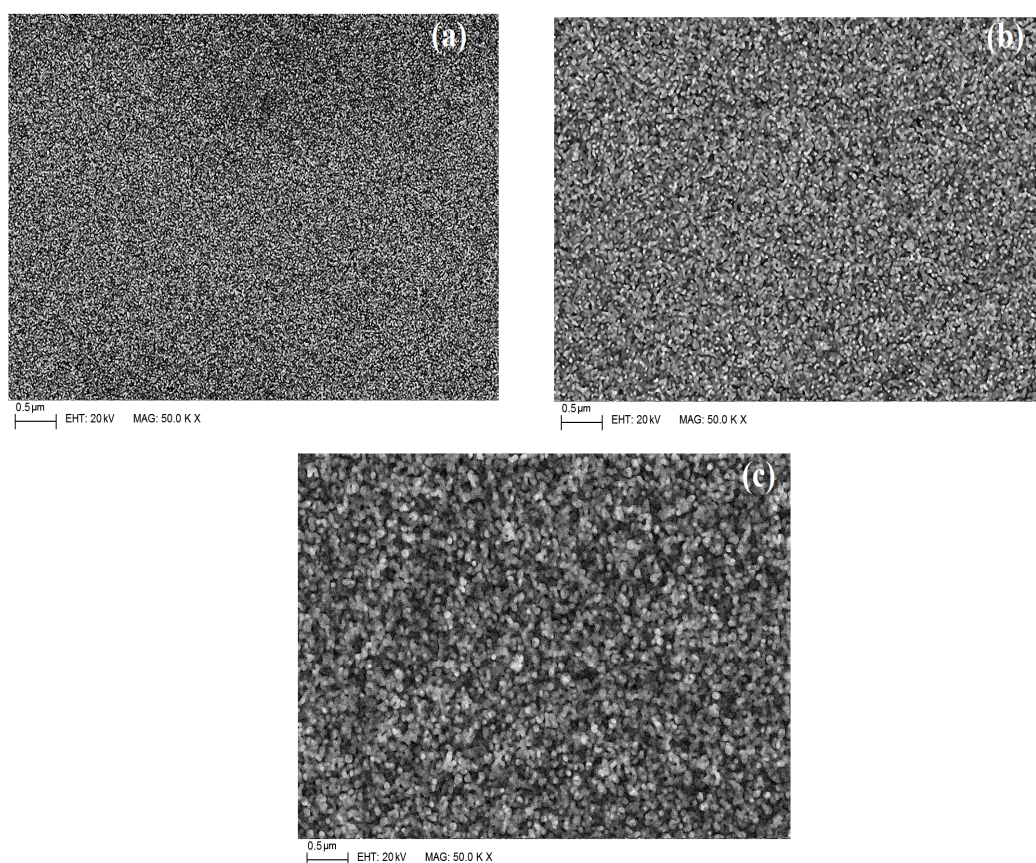

Figure 2. SEM images of ZnS thin films with different number of immersion cycles (a) 50 (b) 100 (c) 150 cycles.

The growth in the grains are visible in the SEM images. The optical properties of the ZnS films were estimated from the wavelength measurements in the range 300–600 nm shown in Figure 3.
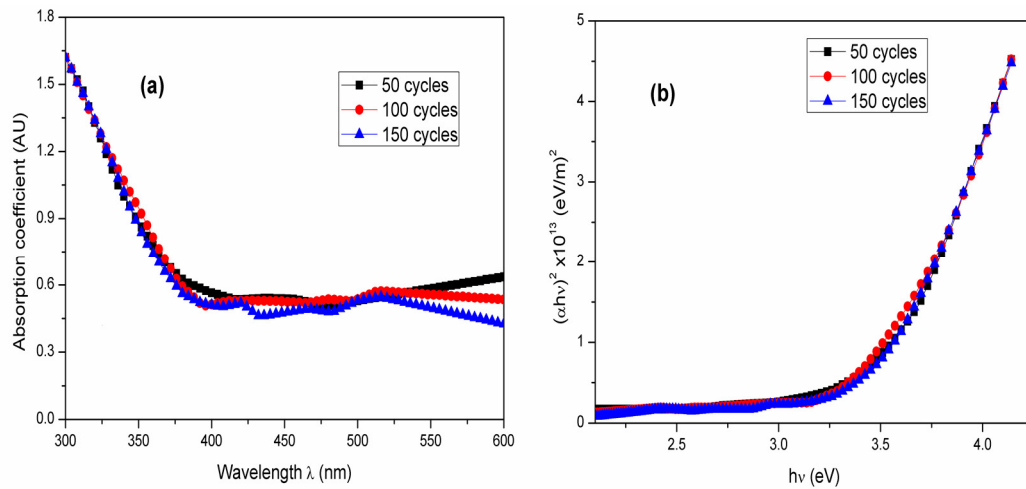
Figure 3. The optical properties of ZnS films deposited for different numbers of immersion cycles: (a) absorbance (b) Tauc plots

The films show high absorption for wavelengths below visible region and band gap of the films observed closer to 3.5 eV.

4. Conclusion

ZnS films were deposited by SILAR technique showed uniform substrate coverage. The thickness of the films can be controlled by the number of immersion cycles. The deposited films showed uniform substrate coverage. Increase in the grain size was observed with the increase in deposition cycles. The bandgap of the films obtained 3.5 eV.

Acknowledgment

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