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Effect of bath temperature on morphological and optical properties of ZnS films prepared by electrochemical deposition technique

Jitendra Borse, Arun Garde

Department of Physics, Late Pushpadevi Patil Arts and Science College, Risod, India

Department of Physics, S P H Arts, Science and Commerce College Nampur, Nashik, India

jaborse@gmail.com, arungarde@yahoo.co.in

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Zinc sulfide thin films were synthesized by means of cyclic voltammetry technique onto stainless steel substrate. The electrolyte bath of aqueous solution containing 0.1 N Zinc sulfate ($ZnSO_4 \cdot 7H_2O$) and 0.1 N sodium thiosulfate ($Na_2S_2O_3.5H_2O$) with 0.1 N Triethanolamine was used as complexing agent. Cyclic voltammetry was employed to measure its ranges of deposition voltages and thickness of ZnS thin films can be controlled by number of voltage cycles applied during deposition. Also we obtained hysteresis curve that imply its potential application. The bath temperatures were varies from 30°C to 60°C. The Influence of bath temperatures on optical properties and morphology has been investigated in details. The electrochemical deposited ZnS thin films were characterized by UV-visible spectroscopy and the field emission scanning electron microscopy (FESEM). The UV-visible spectroscopy analysis showed that energy gap varied between 3.99 to 3.79 eV depending on bath temperatures. The FESEM analysis showed that ZnS thin film deposited at various bath temperatures are polycrystalline nature, homogenous, uniform with randomly oriented nanoflakes and nanorods. The good quality of zinc sulphide thin film could be prepared in the presence of triethanolamine.

Keywords: electrodeposition, bath temperature, ZnS-thin film, morphological and optical properties.

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1. Introduction

Zinc sulfide (ZnS) is one of the direct II–VI semiconductor compounds with large band gap energy of ~ 3.65 eV at room temperature exhibits a wide optical transparency from the ultraviolet to the infrared region [1]. The material crystallizes in both cubic and hexagonal forms and it is used a material of reference to test several theoretical models in condensed material physics [2]. Most of the times it shows mixed phase crystal structure. While cubic structure of ZnS has been reported to have a wide direct band gap of ~ 3.6 eV at optimum temperature, hexagonal structure of ZnS has been reported to have a bandgap of ~ 3.91 eV [3]. The material has been huge potential application in both thick and thin film form in various photovoltaic and optoelectronic devices [4] This optical transparency combined with chemical and thermal stability makes zinc sulfide used as key material for solar control coating, window layer solar cell, electroluminescence devices, optoelectronic devices, sensors and others [5]. Zinc sulfide is a promising material to be used in solar cell as passivation layer for better photovoltaic properties [6]. Due to its high refractive index of material (~ 2.3), it can be used as an antireflective coating [7]. Zinc sulfide is also an important phosphor host lattice material used in preparation of electroluminescent devices (ELD). This is because of its large band gap that is enough to emit visible light without absorption and the efficient transport of high energy electrons [8]. Recently, investigation has shown that, layered type semiconducting cadmium chalcogenides group (CdSe, CdS,ZnS, CdTe) which absorb ultraviolet and near infrared light. These materials are particularly promising materials for photo electrochemical solar energy conversion [9]. Various types of physical, chemical and growth techniques have been used to deposit ZnS thin films on to different substrates. While physical deposition methods such as physical vapor deposition, sputtering, molecular beam epitaxy, pulsed laser deposition atomic layer epitaxy, cathodic arc deposition and metal organic chemical vapor deposition demand the use of either vacuum conditions or complex equipment. Growth methods such as layer by layer, layer plus island etc are used for thin film deposition. Chemical techniques are simpler, inexpensive and cost effective. Thus they have become more popular in recent times. ZnS thin film has been grown by using electrodepositon and various chemical techniques [10] such as Sol-gel [1], Spin coating [5], Spray Pyrolysis [11], chemical vapor deposition and chemical bath deposition [12] etc. The technique of electrodepositon is simple, inexpensive and can be adaptable to large area processing with low fabrication cost. The ZnS thin films have been deposited by two electrode or three electrode cyclic voltammetry electrochemical deposition techniques [13]. Using chemical bath deposition techniques, many researchers have reported different characterization results for thin films with different temperatures [14]. The deposition of ZnS thin film on the substrate as cathode is given by following reaction:

$$\mathrm{Zn}^{+2} + 2e^- + S \rightarrow \mathrm{ZnS\ (Thin\ Layer)}. \tag{1}$$

Cyclic voltammetry is a very important electrochemical and linear sweep technique. It is used potentiodynamic electrochemical measurement and to study the redox behavior of compounds and to determine mechanisms and rates of oxidation/ reduction reaction. Also it is generally used to study the electrochemical properties of an analyte in solution or of a molecule that is adsorbed onto the electrode. In a cyclic voltammetry experiment, the working electrode's potential is ramped in the opposite direction to return to the initial potential. These cycles of ramps in potential may be repeated as many times as needed. The current at the working electrode is plotted versus the applied voltage (that is, the working electrode's potential to give the cyclic voltammogram trace. In the present study we report the synthesis of ZnS, three electrodes potentiostatic electrodeposition technique with different electrolyte bath temperature was employed to prepare ZnS thin films and their morphological and optical properties [15, 16].

2. Experimental work

The deposition of ZnS on stainless steel substrate by three electrode cyclic voltammetry technique.The electrolyte was prepared by mixing solution of AR grade Zinc Sulfate ($ZnSO_4$), Sodium Thiosulfate ($Na_2S_2O_3$) of 0.1 N in the volume ratio of 1:1 respectively, with 2 % of total volume of electrolyte bath. Here 0.1 N Triethanolamine was taken as a complexing agent [17].

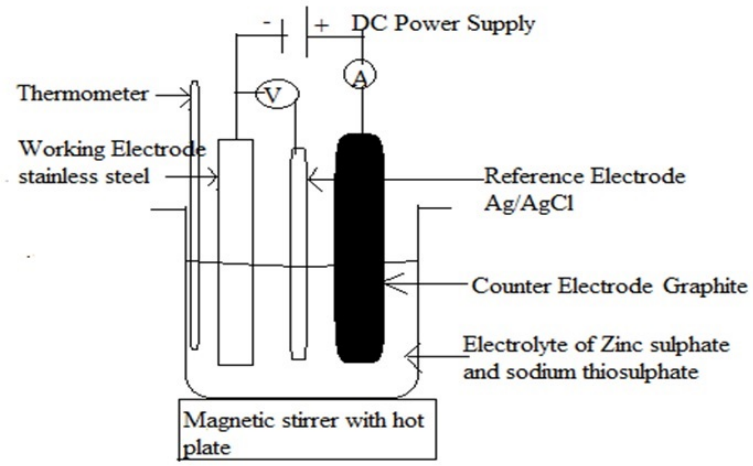

FIG. 1. Schematic of Electrodeposition method used in the present study of deposition of ZnS thin films with various bath temperatures

Figure 1 show a standard cyclic voltammetry experiment consists of a cell with three electrodes such as reference electrode, working electrode and counter electrode. This combination is sometimes referred to as a three-electrode setup. Electrolyte was added to the sample solution to ensure sufficient conductivity. The solvent, electrolyte, and material composition of the working electrode will determine the potential range that can be accessed during the experiment. It was employed to measure its ranges of deposition voltages [13]. Distilled water was used for preparation of aqueous solution of above precursor chemicals. The pH of electrolyte solution was maintained fixed at 3.5 by dilute hydrochloric acid. By using magnetic stirrer with hot plate while other parameters being kept constant, the electrolyte bath temperatures were adjusted from 40 to 65 °C. Before deposition the substrate was thoroughly cleaned with double distilled water and acetone. The distance between the working electrode and counter electrode was kept constant as 1 cm during deposition of materials. The deposition parameters were adjusted such as deposition time 20 min and bath temperatures adjusted 30 – 60 °C. It was observed that a formation of uniform and well adherent black ZnS films were obtained on the substrate. The film was dried under IR lamp for 10 min. We obtain that thickness of ZnS films was controlled by number of voltage cycles applied during deposition. The thicknesses of films with different bath temperatures were measured [18]. Also we obtained hysteresis curve that imply its potential application. We conclude that, the variation of bath temperatures do affect the structure, surface morphology and optical properties of thin films.

3. Results and Discussion

3.1. Cyclic Voltammetry

In a cyclic voltammetry experiment, for reaction mechanisms that involve the transfer of electrons, the working electrode's potential was ramped in the opposite direction to return to the initial potential. These cycles of ramps

in potential may be repeated as many times as needed. Accordingly this process was repeated. The current at the working electrode was plotted versus the applied voltage (that is, the working electrode's potential) to give the cyclic voltammogram trace.

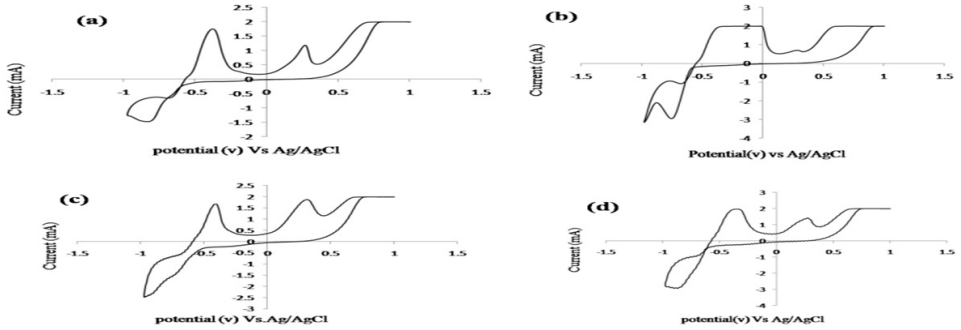

FIG. 2. Cyclic voltammogram of measured current versus applied potential of mixed electrolyte bath of 0.1 N $ZnSO_4$ and 0.1 N of $Na_2S_2O_3$ with different scan speed at a) 25 mV/s, b) 50 mV/s, c) 75 mV/s, d) 100 mV/s

Figure 2 shows variation of the cyclic voltammetry of mixed electrolyte bath with different scan speeds at different electrode potentials. The cyclic voltammetry of these mixtures were performed at different scan speeds to find suitable deposition potential for ZnS film [19].The first and second anodic peak $+0.25$, $+0.80$ V was found at scan speed 25 mV/s indicating dissolution of sulphide and zinc ions in to the solution respectively. At that time, cathodic potential reached -0.80 V against the Ag/AgCl (Reference Electrode) and deposition of ZnS occurred [20]. Anodic potential at range $+0.55$ to $+0.99$ V was found at scan speed 50 mV/s due to dissolution of deposited materials in to the solution and materials deposited at -0.743 V against Ag/AgCl (Reference Electrode). Anodic potential peaks were found at $+0.29$, $+0.75$ V at scan speed 75 mV/s due to the dissolution of sulfide and zinc ions in to the solution respectively. That times the cathodic potential reached at -0.94 V the material deposition take place. However, Fig. 2(d) The anodic potential peaks were found at $+0.23$, $+0.63$ V at scan speed 100 mV/s indicating the dissolution of sulfide and zinc in the solution respectively, When the deposition take place at cathodic potential -0.85 V versus Ag/AgCl (Reference Electrode), the film deposited at cathodic potential range from -0.74 to -0.94 V against Ag/AgCl shows optimized value of deposing potential [20]. Fig. 3 shows linear sweep voltammetry of mixed electrolyte bath. The potential increases with small increase in current. After 0.74 volts, potential continuously increases with saturated peak current.

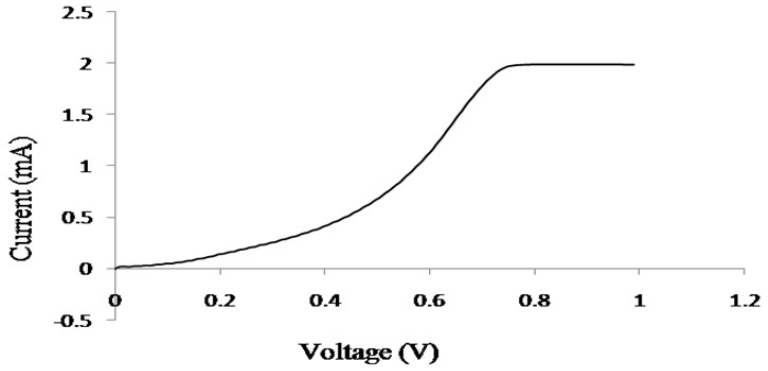

FIG. 3. Linear Sweep Voltammetry measured current versus applied potential of mixed electrolyte bath of 0.1 N of $ZnSO_4$ and $Na_2S_2O_3$

Figure 4 shows the chronoamperometry of mixed electrolyte bath. The variation of current with time of solutions indicated that the current increases linearly as a function of time. After 20 seconds, the current was saturated with continuously increase in time.

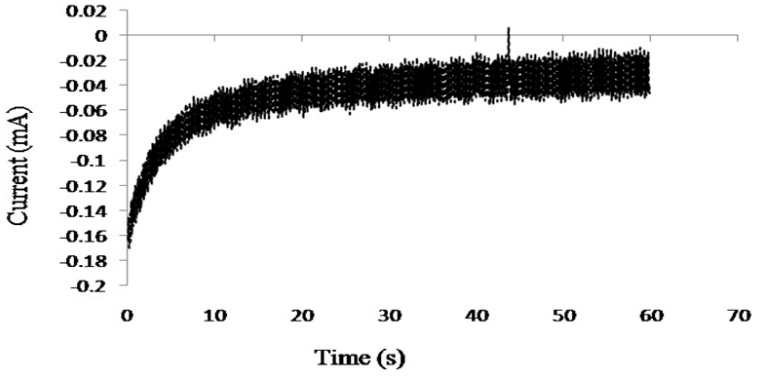

FIG. 4. Chronoamperometry of mixed electrolyte bath of 0.1 N of $ZnSO_4$ and $Na_2S_2O_3$

3.2. Film thickness estimation

The thickness variation of ZnS deposited by using electrodepositon was measured by using mass difference method [21, 22].

$$t = \frac{\Delta m}{\Lambda \rho}, \tag{2}$$

where Δm is mass difference of before deposition and after deposition, t is thickness of film, Λ is area of deposition, ρ is density of deposited material.

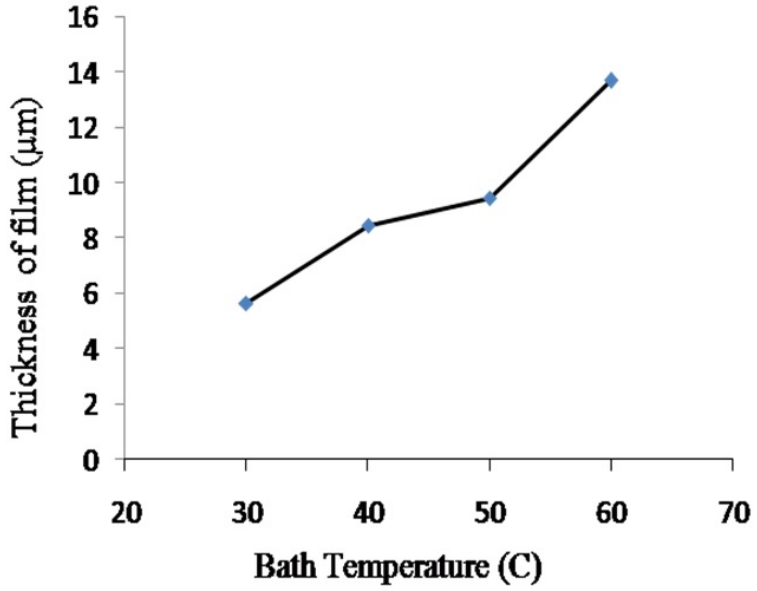

FIG. 5. Thickness Variation of ZnS thin films deposited at different bath temperatures

The variation of film thickness as a function of electrolyte bath temperature is shown in Fig. 5. The ZnS film thickness linearly increases with an increase in bath temperature. The thickness of films increased from 5.65 to 13.69 μm when bath temperature rose from 30 to 60 °C. However, in this technique, we have controlled the thickness of ZnS film by adjusting the bath temperature.

3.3. UV- visible spectroscopy

The optical absorption measurement was carried out by using UV visible spectrophotometer (BSR-UV-1900) in the range of 190–400 nm.

Figure 6 shows the absorption band edge was found at 311, 317, 322 and 327 nm at bath temperatures 30, 40, 50, and 60 °C respectively. The band gaps of ZnS films were found to be 3.99, 3.91, 3.85, 3.79 eV at 30, 40, 50, and 60 °C

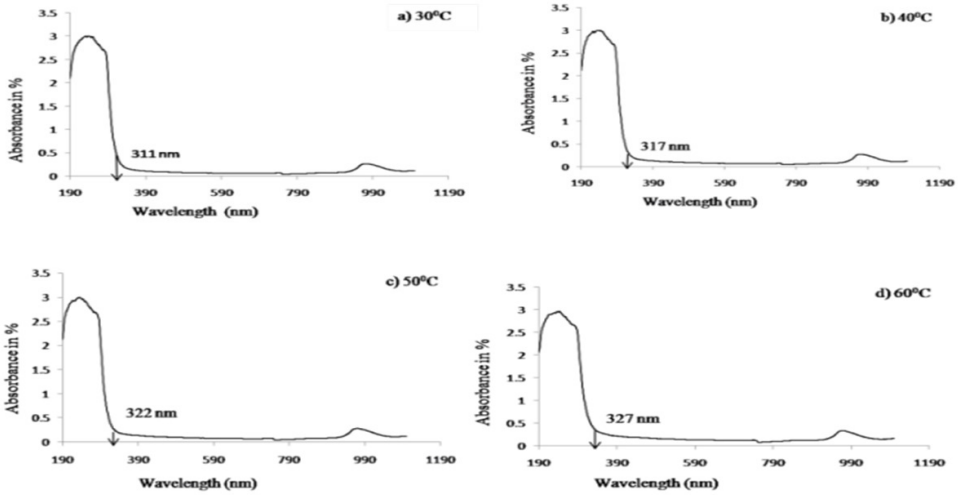

FIG. 6. UV-Visible absorption spectra of ZnS thin film at Bath temperatures a) 30 °C, b) 40 °C, c) 50 °C and d) 60 °C

respectively. The UV visible absorption spectra show the band gap energy varies inversely with crystallites sizes. As a result, it was found that band gap energy of ZnS decreased with increased bath temperature [14].

3.4. Energy dispersive analysis by X-ray spectroscopy

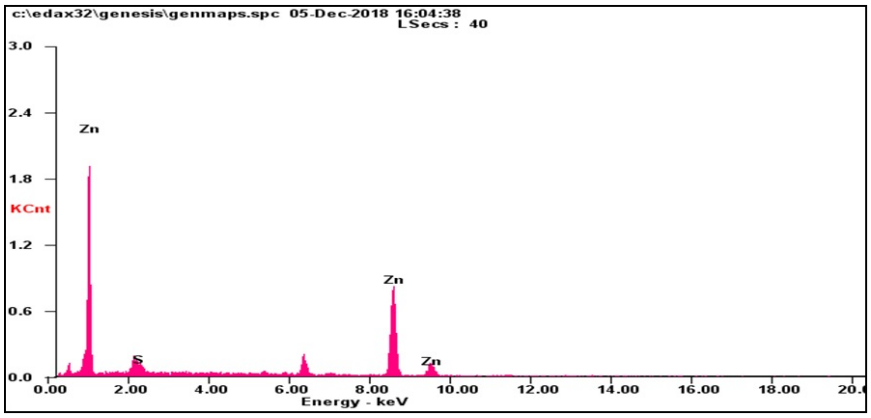

FIG. 7. Energy Dispersive analysis by X-ray Spectroscopy of ZnS thin film

EDS spectra of deposited ZnS thin film shows in Fig. 7. It confirm the successful formation of ZnS. That grown thin film composed of only Zn and S elemental composition. No impurity peaks are observed in this spectrum.

3.5. Field emission scanning electron microscopy

The FESEM was carried out to study the effect of different bath temperature on the surface morphology of ZnS thin films.

Figure 8 FESEM photographs shows ZnS films at bath temperatures 30, 40, 50 and 60 °C. The surface morphology of ZnS thin films changes significantly with increasing bath temperature [20]. The ZnS films' morphologies also show the size of ZnS nanorods was increased with an increase in bath temperature [23]. The crystallinity of ZnS thin film is higher at bath temperature 60 °C indicated that the film was dense and pinhole free. The crystallinity of ZnS thin films layer is increases with increase in bath temperature [24]. The variation of average crystallite size of the film sample with bath temperatures are listed in Table 1.

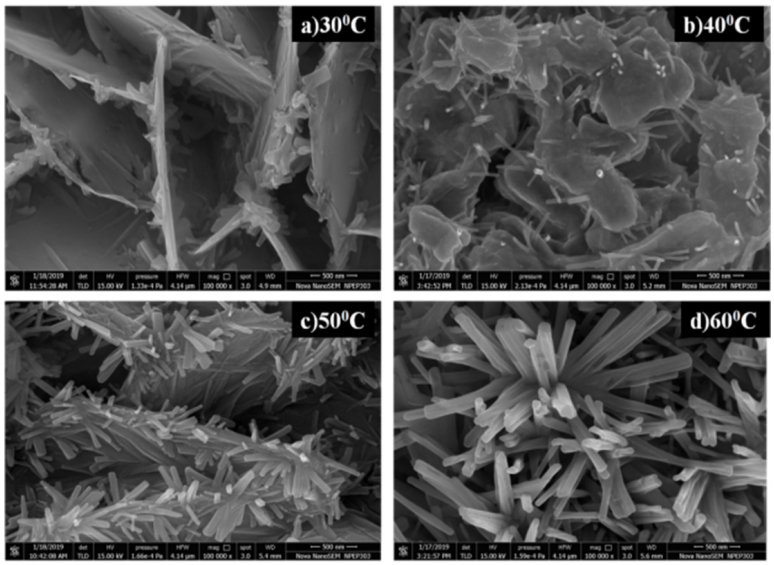

FIG. 8. FESEM micrograph of the ZnS thin films at bath temperatures a) 30 °C, b) 40 °C, c) 50 °C, d) 60 °C

TABLE 1. Estimated values of Average crystallite size and band gap of ZnS at different bath temperatures

Bath temperature (°C)	Average Crystallite size (nm)	Energy Band gap (eV)
30 °C	40.15 nm	3.99
40 °C	60.10 nm	3.91
50 °C	80.08 nm	3.85
60 °C	160.06 nm	3.79

4. Conclusion

The synthesis of ZnS films has been carried out by cyclic voltammetry technique. ZnS has been successfully deposited on stainless steel substrates. The influence of bath temperature on optical properties has been investigated systematically. The ZnS film thickness linearly increases with increase in bath temperature. The ZnS films shows absorption band edges 311 to 327 nm with band gap varies in the range between 3.99 to 3.79 eV. The UV visible absorption spectra show the band gap energy varies inversely with crystallites sizes. The surface morphology of the films shows that films are smooth and uniform with randomly oriented nanorods. The crystallinity of ZnS films layer is increases with increase in bath temperature.

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