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A CYCLIC VOLTAMMETRIC SYNTHESIS OF ZnS THIN FILMS USING TRIETHANOLAMINE AS A COMPLEXING AGENT

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abstract: ZnS thin films have been synthesized by means of cyclic voltammetry technique. An aqueous solution of zinc chloride was used as Zn^{2+} source, sodium thiosulfate as S^{2-} source and triethanolamine as complexing agent for depositing ZnS thin films. The influence of complexing agent on the formation and properties of zinc sulphide thin films was investigated. Structure and surface morphology of thin films were characterized by X-ray diffraction and atomic force microscopy, respectively. The band gap energy and type of optical transition were determined from optical absorbance data. The band gap energy varies from 1.7 to 2.5 eV for the films prepared at different amounts of triethanolamine. XRD data indicate that the thin film deposited in presence of triethanolamine is polycrystalline in nature with cubic phase. Increase in amount of triethanolamine (5 ml) in electrochemical bath leads film is homogeneous, well covered to the substrate and exhibits higher absorption characteristic. We can conclude that the amount of complexing agent could affect the structure, surface morphology and optical properties of deposits. The good quality of zinc sulphide thin film could be prepared in the presence of triethanolamine.

key words: cyclic voltammetry; triethanolamine; thin film; zinc sulphide.

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Introduction

The semiconductor thin film deposition from aqueous solution [1-4] becomes increasingly popular because it has advantages of economical and capability of large area deposition. ZnS thin film is attracting considerable attention for possible application to UV light emitting diode, photocatalysis, solar cell and phosphors in flat panel displays. ZnS thin films are non toxic to human body, very cheap and abundant. Various techniques have been employed to prepare ZnS thin film including SILAR [5], electrodeposition [6], chemical bath deposition [7], spray pyrolysis [8], vacuum evaporation [9] and pulsed laser deposition [10]. The use of complexing agent is very common in the preparation of thin films. Many researchers use various complexing agents such as thiourea [11], ammonia [12],

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triethanolamine [13], disodium ethylene diamine tetra-acetate [14,15], nitrilotriacetic acid [16] and tartaric acid [17] during deposition of thin films.

In present study, we report for the first time the synthesis of ZnS thin film by means of cyclic voltammetry method at room temperature from an aqueous solution. In order to study the influence of complexing agent on the formation of films, the quantity of triethanolamine [TEA] added was varied from 0 to 5 ml to complex the zinc ions. The deposited thin films were characterized by X-ray diffraction and atomic force microscopy for their structural and surface morphological characteristics. We have also investigated the optical properties of ZnS thin film by UV-Vis spectrophotometer.

Experimental

The cyclic voltammetry was used to analyse the electrochemical bath. The electrochemical bath contains 0.05 M $ZnCl_2$ (25 ml), 0.05 M $Na_2S_2O_3$ (25 ml) and concentrated triethanolamine solutions. All the chemicals were of analytical grades. All the solutions were prepared in deionised water (Alpha-Q Millipore). The voltammetric study was performed using an Electrochemical Analyzer (BAS 100W, West Lafayette, Indiana, USA). The indium-doped tin oxide (ITO) glass was used as working electrode. The ITO glass was degreased by ethanol for 10 min, followed by distilled water rinse for 15 min in an ultrasonic bath. The saturated calomel electrode (SCE) and platinum wire were used as reference and counter electrodes, respectively. In order to study the influence of complexing agent on the formation of films, the quantity of triethanolamine added was varied from 0 to 5 ml to complex the zinc ions and the solution was stirred well. The pH of electrochemical bath was adjusted to 3 by addition of hydrochloric acid. All electrolyte solutions were bubbled with nitrogen for 15 min. The ZnS thin films were synthesized by cyclic voltammetry technique at room temperature in the potential range from -300 to -1500 mV versus SCE. The voltage scan rate of 10 mV/s was used in cyclic voltammetry. Then, the deposited films were tested for adhesion by subjecting it to a steady stream of distilled water and finally were kept for further analysis.

The structure of samples was studied by X-ray diffraction (Philips PM 11730 diffractometer) with CuK_α (λ=0.15418 nm) radiation. The morphology and thickness of thin films were examined with an atomic force microscopy (AFM) (Quesant Instrument Corporation, Q-Scope 250). The AFM was operated in contact mode, with a commercial Si_3N_4 cantilever. The absorption was recorded for the thin film in the range of 350-900 nm using Perkin Elmer UV/Vis Lambda 20 Spectrophotometer. The film-coated indium doped tin oxide glass was placed across the sample radiation pathway while the uncoated ITO glass was put across the reference path. From the analyses of absorption spectra, the band gap energy (E_g) was determined.

Results and discussion

Fig. 1 shows the cyclic voltammograms obtained from solutions of zinc chloride, sodium thiosulfate and triethanolamine at different amounts of TEA. In the forward scan, the cathodic current starts flowing at about –700 mV versus SCE for the sample prepared in presence of TEA (5 ml). This may be associated with the reduction of thiosulphate ions [18]. Further studies revealed the reduction of Zn^{2+} ion in an acidic solution to Zn at potential of –1000 mV [19]. In the absence of TEA, the sample shows that the hydrogen evolution starts at about –1000 mV. Zinc sulphide was formed from the combination of sulphide (S^{2-}) ions [20] and zinc (Zn^{2+}) ions and the rate of zinc sulphide formation increased with the more negatively potential applied [21]. In the reverse potential scan, the anodic peaks appear at –750, –600 and –500 mV for the films deposited with TEA (5 and 1 ml) and in the absence of TEA, respectively. As seen from the voltammograms, the anodic peak potential appears to shift towards more negatively values with increase in the amount of complexing agent. On the other hand, anodic peak current decreased markedly when the film prepared in the presence of TEA (5 ml), indicating minimal dissolution of the compound. We can conclude that the presence of TEA affects both cathodic and anodic peaks.

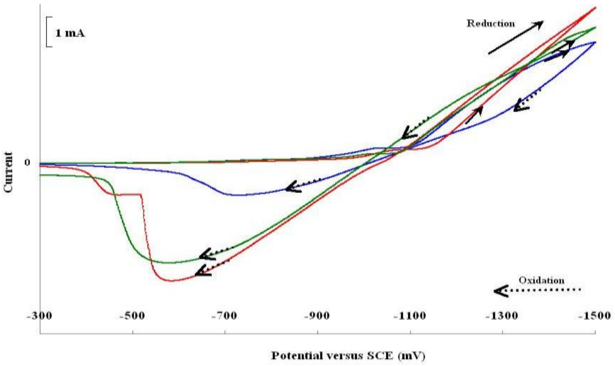

Fig. 1 *Cyclic voltammograms recorded in electrochemical bath contains $Na_2S_2O_3$, $ZnCl_2$ complexed with different amounts of TEA (🟩 0 ml, 🟥 1 ml, 🟦 5 ml) at pH 3. Scan range in -300 to -1500 mV versus SCE and scan rate was 10 mV/s.*

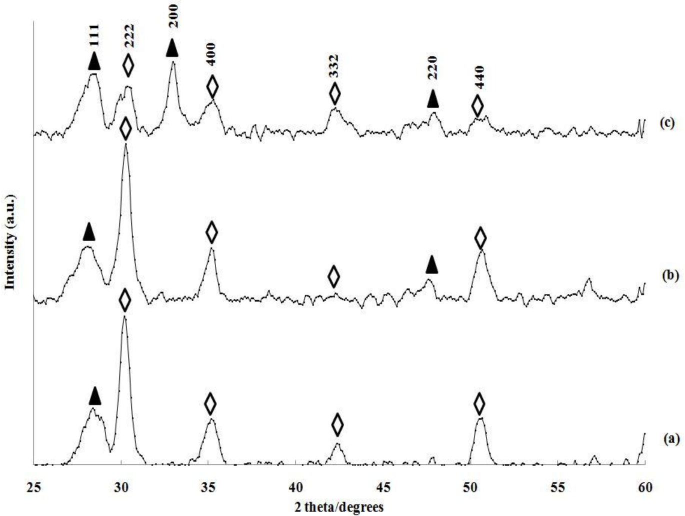

Fig. 2 *X-ray diffraction pattern of ZnS thin films deposited at different amounts of TEA* (a) 0 ml (b) 1 ml (c) 5 ml at pH 3. (▲ ZnS; ◊ $In_{1.875}O_3Sn_{0.125}$ (ITO)).

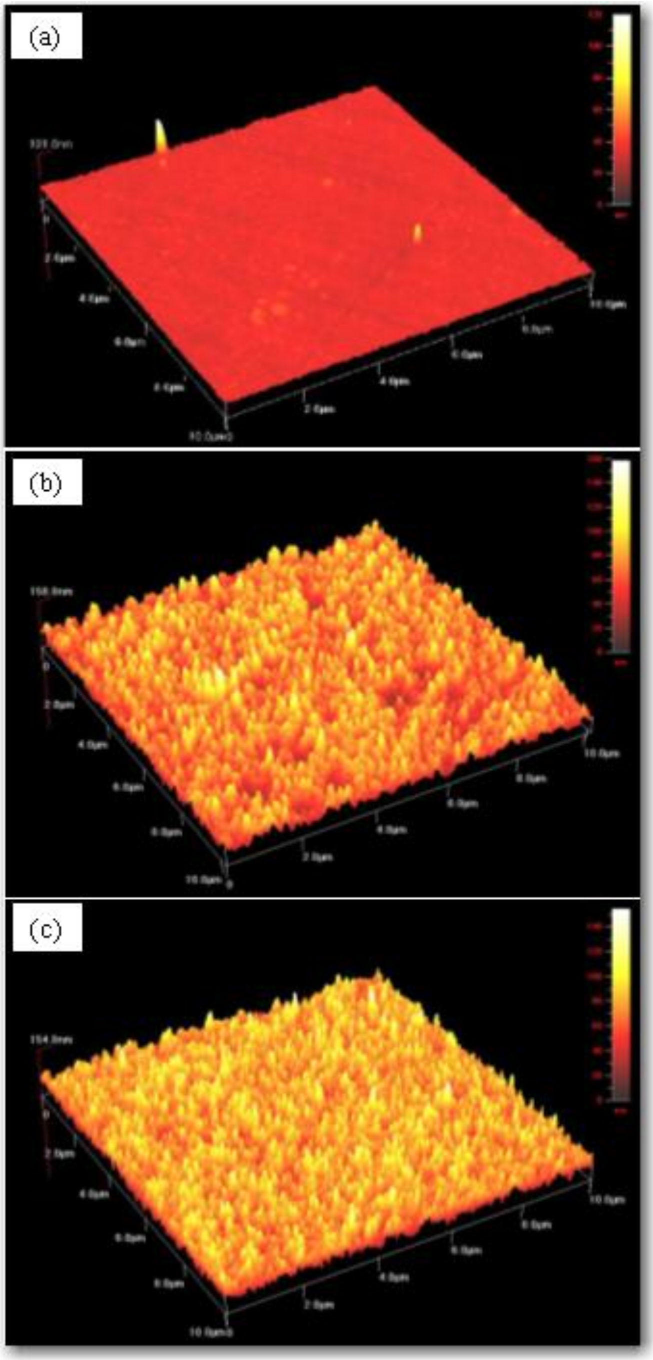

Fig. 3 *Atomic force microscopy images of ZnS thin films deposited at different amounts of TEA* (a) 0 ml (b) 1 ml (c) 5 ml at pH 3.

The structure of the samples has been investigated by X-ray diffraction (XRD). In Fig. 2, the XRD patterns for the samples deposited from aqueous solution with and without TEA are presented. The films show single phase and cubic structure as analysed by XRD. The XRD pattern in Fig. 2a corresponds to sample prepared in absence of TEA. There is only single peak corresponding to (111) plane was observed. This peak was identified by comparing the *d*-spacing value obtained from the XRD pattern with JCPDS (reference No.: 00-065-0309) data for ZnS [22]. The lattice parameters of the cubic structure are equal to a=b= c=5.4 Å. The XRD patterns of the samples deposited in presence of TEA show more peaks than the film prepared in the absence of TEA. The XRD data show an improvement in crystallinity for these films as shown in Fig. 2b and 2c. The presence of indium tin oxide [23] peaks (reference No.: 01-089-4597) comes from the substrates during deposition process. The intensity of ZnS peaks was higher than substrate peaks for the film prepared in the presence of TEA (5 ml). We have concluded that TEA has a significant influence on the crystallization of the film.

The three-dimensional atomic force microscopy images (10x10 μm) were taken on ZnS thin films deposited from aqueous solution with and without TEA in order to study the surface morphology as shown in Fig. 3. The film prepared without TEA (Fig. 3a) shows incomplete coverage of material over the surface of substrate. The root mean square (RMS) roughness and thickness of this film are 2.54 and 121 nm, respectively. The RMS value is used to evaluate the surface roughness. Fig. 3b shows the AFM image of ZnS thin film prepared in presence of TEA (1 ml). Increase in amount of TEA (5 ml) in electrochemical bath leads to more uniform, homogeneous and smoother film (16.74 nm). This material was found to cover the surface of the substrate completely (Fig. 3c). The thickness and grain size were estimated to be 155 nm and 0.1 μm, respectively.

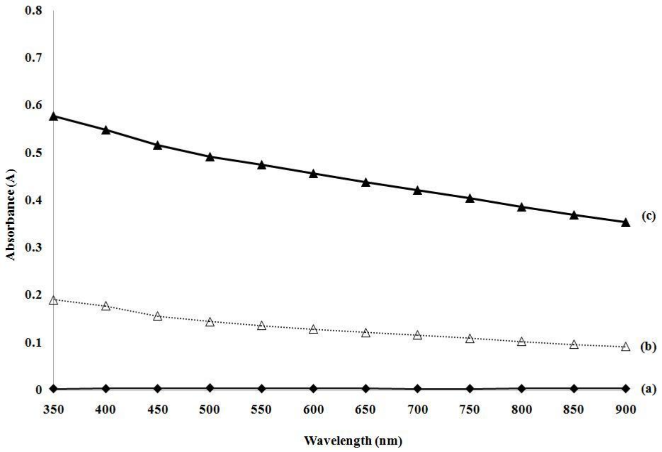

Fig. 4 *Absorbance versus wavelength spectra of ZnS thin films deposited at different amounts of TEA* (a) 0 ml (b) 1 ml (c) 5 ml at *p*H 3.

Optical properties of ZnS thin films were measured with UV-Visible Spectrophotometer in the range 350 to 900 nm. Fig. 4 presents the absorbance spectra of zinc sulphide thin films deposited at different amounts of TEA. The lowest absorbance is seen for the film deposited in the absence of TEA as shown in Fig. 4a. In contrast, the film prepared with TEA (5ml) exhibited the highest absorbance value in visible region. This is associated with more materials deposited onto surface of the substrate providing better absorption properties. This implies that the thin film has potential application in photoelectrochemical solar cell.

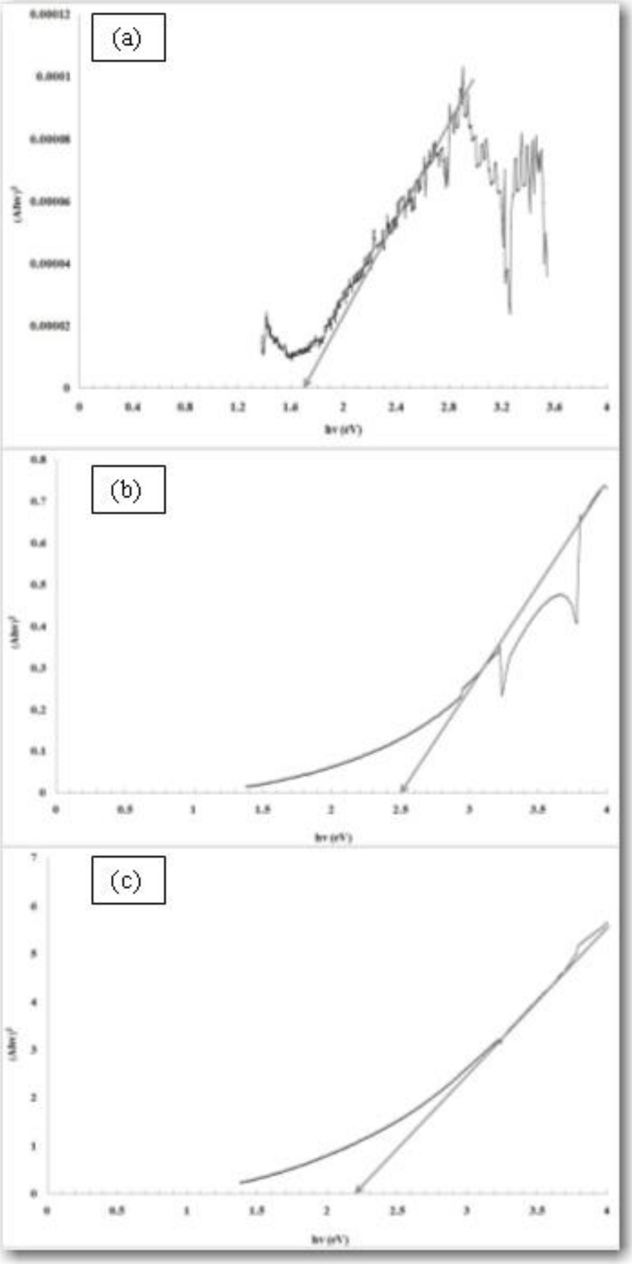

Fig. 5 *Plot of (Ahv)^2 versus hv of ZnS thin films deposited at different amounts of TEA:* (a) 0 ml (b) 1 ml (c) 5 ml at *p*H 3.

Band gap energy and transition type can be derived from mathematical treatment of data obtained from optical absorbance versus wavelength with Stern [24] relationship of near-edge absorption (Equation 1):

$$A = \frac{[k \;\; hv - E_g \;\; ^{n/2}]}{hv} \tag{1}$$

where v is the frequency, h is the Planck's constant, k equals a constant while n carries the value of either 1 or 4. The value of n is 1 for the direct transition and 4 for indirect transition, respectively. The band gap energy value was calculated via the $(Ahv)^2$ versus hv plot as shown in Fig. 5. It shows that the film deposited without TEA (Fig. 5a) has the lowest band gap (1.7 eV). On the other hand, the band gap energy decreases from 2.5 to 2.2 eV with increasing amount of TEA from 1 to 5 ml, respectively.

Conclusions

The ZnS thin films have been prepared by cyclic voltammetry technique from aqueous solutions containing $ZnCl_2$, $Na_2S_2O_3$ and TEA. XRD study indicated single phase with cubic structure. The band gap energy of the films deposited at different amount of TEA is in the range of 1.7-2.5 eV. The growth and quality of the thin films were found to be quite sensitive to TEA solution.

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