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An Experimental Investigation of Optical Properties of ZnS Thin Films Prepared by Chemical bath Deposition Method for Solar Energy Application

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Abstract

Due to the rising competition for fossil fuels as an energy source, a photovoltaic device couple that harvests renewable energy (solar energy) has emerged as an alternative. The crucial components of this device are thin film semiconductors, hence it is necessary to create zinc sulphide thin films utilizing a variety of molar concentrations ranging from 0.5M to 2M onto a plate of stainless steel using a chemical bath deposition approach at a deposition temperature of 333K. After the deposition, the thickness of the samples was determined using a meta electronic balance technique. Structural, Morphological and optical characterizations of the films were made using XRD, SEM, UV-Visible and photoluminescence spectroscopy. Microstructural Parameters deduced from XRD profile exhibits an increase in grain size with an increase in molar concentration (4M to14M). Optical analysis shows, that the band gap energy values of ZnS film decreased from 3.960eV to 3.840eV with an increase in deposition time. The photoluminescence studies showed that the prominent peak is shifted towards a longer wavelength region indicating loss of sulfur at high concentration: The excellent properties obtained show that this thin film material is good for photovoltaic device fabrication.

1. Introduction

In modern technology, there has been a lot of interest in metal chalcogenide semiconducting material because the physical and chemical properties change rapidly with particle size. These materials are attracting considerable attention due to their fundamental electronic and optical properties, high performance and low production cost. They are important semiconductor materials because of the matchable band gap with solar spectrum synthesis of these materials in terms of thin films is responsible for the wide range of dominant effects on the development of recent science. Nowadays, nanocrystalline materials with wide band gap has many applications as they are important in opto-electronic devices. Depending on the method of synthesis and physic-chemical properties of these materials.

Recently the nano and polycrystalline ZnS thin films have attracted researchers as they play a crucial role in photovoltaic technology and opt-electronics device [1]. In the area of optics, ZnS can be used as a reflector and dielectric filter because of its high transmittance in the visible range respectively [2,3],ZnS thin films are synthesized by different methods such as thermal evaporation, spray pyrolysis [4], Sputtering [5], Chemical vapour deposition [6], Successive ionic layer absorption and reaction [7] and the metal organic vapour phase epitaxy [8], ZnS transmits more high-energy photons to the junction and enhance the blue region and provides better lattice matching with absorber having energy band gaps in the range of 1.3 – 1.5V [10]. Also, in the area of optics, ZnS can be used as a reflector and dielectric filter because of its high refractive index and high transmittance in the visible range respectively. In optoelectronic, it can be used as light emitting diode in the blue to ultraviolet spectral region. Among the several techniques used to produce zinc sulphide thin films, the chemical bath deposition method is highly attractive since the technique possesses a number of advantages over conventional thin films deposition methods.

The main advantages of this method are low cost, low deposition temperature and easy coating of large surfaces. The method is based on slow controlled precipitation of the desired compound from its ions in a reaction bath solution. In this study, the preparation of ZnS thin films by chemical bath deposition using different molar concentration (0.5m to 2m) at the deposition temperature of 333K.

2.0. Materials and Method

Our major activity for this study is to deposit ZnS thin film on a polish, sheet stainless steel to observe and if possible, modify the optical and structural properties of the thin film for technological advancements purposes as discussed in the preceding section of this report. The method used is the chemical bath method (CBD), list and discussions on materials, equipment and apparatus used to perform the research experiment are described in the following sections:

2.1. Materials

The materials used for the study are in two categories:

a. Instruments and Accessories
  i. Analytical chemical balance
  ii. pH Meter (Corning pH meter 220)
  iii. Thermometer (10^oC – 300^oC)
  iv. Beaker (250 mL)
  v. Retort stand
  vi. Spatula
  vii. Plain sheet of stainless steel (7.5 x 7.5 x 0.1cm)
  viii. Petri dish
  ix. Gauze sponge
  x. Transparent surgical gloves
  xi. Magnetic stirrer / hot plate

b. The chemicals and solvent material
  i. ZnS
  ii. NH 20% aqueous ammonia
  iii. SC^3 $(NH_2)_2$
  iv. Zn $(cH_3C00)_2$ Solution
  v. Deionized water
  vi. $Zncl_2$
  vii. Emery paper
  viii. Vim polish powder
  ix. Detergent

2.2.Method

2.3.Plain Stainless Steel Cleaning:

In order to obtain good adherence and uniformity for the films, it is necessary to use pre-cleaned stainless steel (75mm x 75mm x 1.0mm) in the chemical bath system. The stainless steel cleaning steps were as follows

i. Polished with emery paper of grit number 100, 200.0 and 320 respectively
ii. Washed with Vim polishing powder until mirror finishes is obtained
iii. Washed with detergent and a piece of gauze sponge
iv. Rinsed many times in distilled water, so as to ensure no dirt on it
v. Ultrasonic cleaning of stainless sheet substrates in Isopropyl Alcohol

2.4.Experimental

Thin films of ZnS are obtained by chemical deposition technique. The initial aqueous solution is prepared from zinc acetate at 0.5M, 1.0M and 2.0M concentrations in 25ml of de-ionized water. Ammonia solution added slowly to zinc solution and stirred for about two minutes using a magnetic stirrer until a clear solution is obtained.

$$Zn\,(cH_3Coo)_2 \rightarrow Zn^{2+} + 2cH_3\,Coo^- \quad (1)$$

$$0H \rightarrow NH_4^+ + 0H^- \quad (2)$$

Initially $Zn(0H)_2$ precipitates, but this re-dissolved in excess ammonia to give the zinc ammine complex.

$$Zn^{2+} + 4NH_3 \rightarrow Zn\,(NH_3)_4^{2+} \quad (3)$$

$$SC(NH_2)_2 + 0H^- \rightarrow SH^- + CH_2N_2 + H_2O \quad (4)$$

The solution is heated to 333K and equal volume of (0.5M, 1.0M and 2.0M) thiourea solution is added as S^{2-} source and solution is stirred for 5-6 minutes.

$$SH + OH \rightarrow S + H_2O \quad (5)$$

The pH of the final solution is raised to 9. The mixed solution is kept at 333K temperature. And finally Zinc sulphide films were formed according to the relation.

$$Zn^{2+} + S^{2-} \rightarrow ZnS \quad (6)$$

After about 45 minutes the stainless steel slides were covered with white deposit. The substrate is removed and rinsed with de-ionized water. The thickness of the deposited film was determined using weight difference method. The structural studies of the chemical deposited zinc sulphide thin film samples were done by using Schimadzu XRD-600 X-ray diffractometer with a Cuka radiation. (X = 1.5406A). The morphological analysis of film was carried out using JEOL mode TSM 6390 SEM and optical studies of the samples were done using spectrophotometesJasco Corp. V-570 in the spectral range 300-2500mm with 1nm resolution. The photoluminescence studies have been carried out using Cary Eclipse WinFLR photoluminescence device.

3.0.Results and Discussion

As shown in Figure 1 (a, b, c) the XRD pattern of ZnS films on stainless sheet substrate was prepared using different molar concentrations (0.5M, 1.0M and 2M) at the deposition temperature of 333K. The XRD pattern shows preferential orientation at 2θ equals to 28.3° indicating monocrystalline nature. The diffraction peaks become slightly sharper and their intensity is relatively enhanced on increasing the molar concentration, while the location did not change significantly.

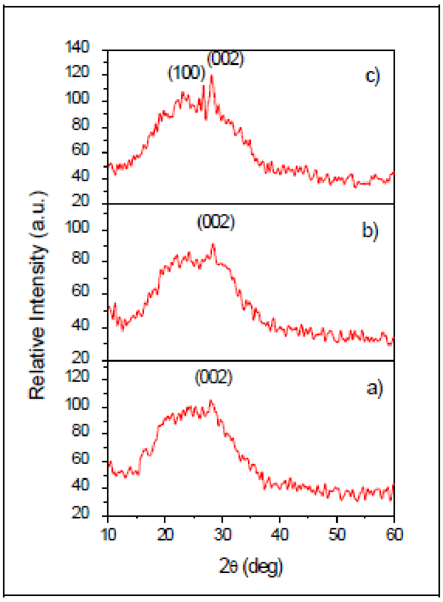

Figure 1. XRD Spectrum of ZnS thin films of molar concentration a) 0.5M b) 1M c) 2M.

Optical Analysis

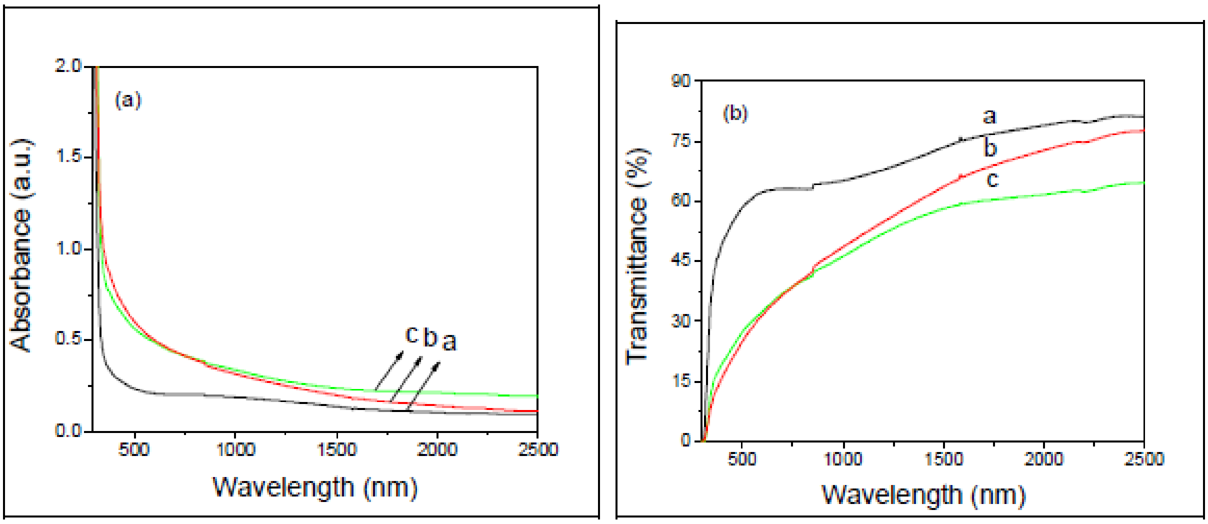

Figure 2. Absorbance and (b) Transmittance Spectra of ZnS thin films of molar concentration a) 0.5M b) 1M c) 2M.

Figure 2 (a and b) shows the optical absorption and transmittance spectra recorded in the spectral range of 300 – 2500nm for ZnS films of different molar concentrations prepared at 333K. It is observed that the absorption onset slightly shifts towards the high energy region indicating the improvement in crystalline. From the transmittance spectral, the maximum transmission observed are 80% 77% and 65% for 0.5M, 1.0M and 2.0M respectively. The band gap energy was evaluated based on the recorded optical spectra. The best fit to the experimental data was obtained for n = 0.5. This is in agreement with the literature data according to which Zinc is a semiconducting material with a direct band gap. In fig. 3 the dependence of $(\propto hv)^2$ versus (hv) for ZnS thin film is presented. The ZnS films are characterized by band gap energy of 3.96 ev, 3.9ev and 3.84ev. From available literature reported values for band gap energy of bulk ZnS are 3.6eV. The higher calculated values of the band gap are presumably due to quantum size effect [1]. In particular, it is well known that the optical band gap of thin film materials, which are characterized by a length scale less than 10nm, is higher than that of bulk material. As the molar concentration increases, the absorption edge shifts gradually towards a longer wavelength and shifts the band gap. This absorption edge shifts are associated with a decrease in band gap with an increase in molar concentration. All the films demonstrated the basic optical properties of ZnS films ie, the transmittance increased rapidly at 350nm. The transmittance of ZnS films deposited at the temperature o 333K is 50-80% when the wavelength is higher than 1000nm.

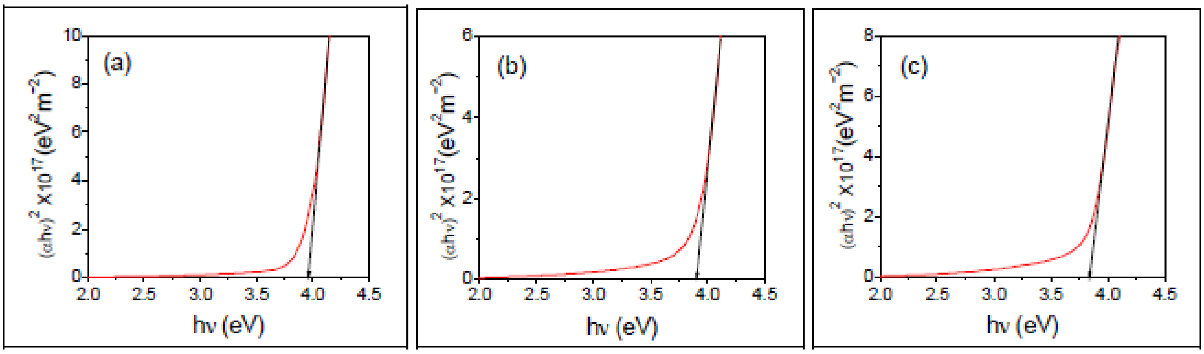

Figure 3.Plot of $(\alpha hv)_2$ versus (hv) of ZnS thin films of molar concentration a) 0.5 M b)1 M c) 2 M

Photoluminescence Studies

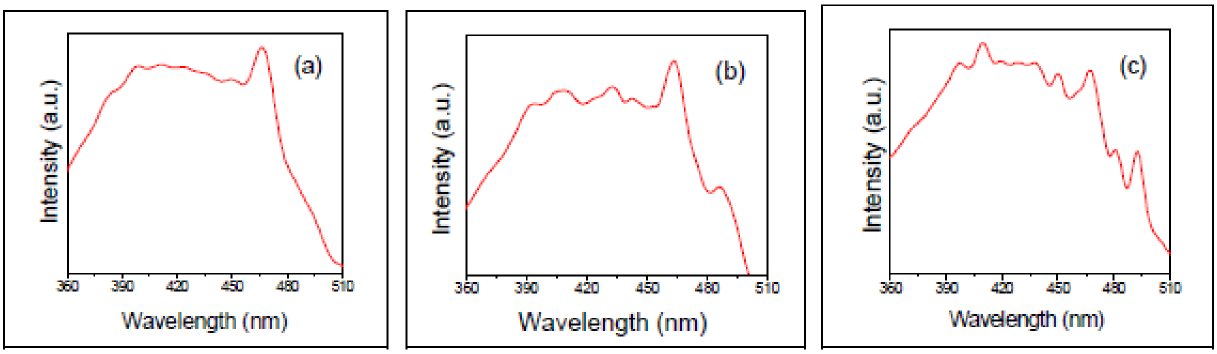

Figure 4.PL Spectra of ZnS thin films of molar concentration a) 0.5M b) 1M c) 2M

Figure 4 shows the PL spectra of ZnS thin film prepared at a bath temperature of 333K varying the molar concentration (0.5M, 1.0M and 2.0M). It is inferred from the spectral that the maximum intensity of the emission peak is around 466nm for 0.5M and 463nm for 1M. On increase of concentration to 2.0M, the intensity of the peak centred around 466nm as observed in 0.5M and 1M decreases and two more peaks at 409nm and 493nm are observed. The decrease in intensity of the peak of 466nm may be due to the loss of sulphur atoms and increase of Zn atom. The relative higher wavelength peak of 492nm may be due to the atmospheric oxygen impurity present on the surface of the film or may be assigned to the emission from the impurity either of the precursor of Zn or sulphur, which incorporate during the deposition process. This shows that there is a gradual shift from blue to green region at higher concentration and this may be due to the transmission transition from the conduction band to an acceptor level or due to interstitial sulphurs.

4.0.Conclusion

The study gives details of the preparation of ZnS thin film using chemical bath deposition method: ZnS thin films of different molar concentrations (0.5M, 1.0M and 2.0M) are prepared using Zinc acetate and Thiourea at a bath temperature of 333K. The XRD analysis shows that all grown films are nanocrystalline. The lattice parameters calculated are in good agreement with the standard data confirming that the ZnS films are hexagon structure. From the optical studies, band gap energy decreased from 3.96eV to 3.84eV with the increase in molar concentration. Shifting of prominent peak to longer wavelength region indicates the loss of sulphur at a higher concentration as evident from PL studies.

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