SYNTHESIS AND STRUCTURAL CHARACTERIZATION OF NANO STRUCTURED ZINC SULPHIDE THIN FILMS GROWN ON GLASS SUBSTRATES BY CHEMICAL BATH DEPOSITION

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ABSTRACT
Nano Crystalline Zinc Sulphide thin films were prepared by chemical bath deposition technique using aqueous Zinc Sulphide and Thiourea solutions in a base medium (pH =10) at 90°C. The deposition was carried out on the glass substrate for various deposition periods from 30 to 120 min. The effect of different concentrations of complexing agent on the structural, morphological and optical properties of ZnS Nano particles was investigated. Other parameters such as solution pH, temperature and reactant concentration were kept constant for all the deposition. The Average diameter of the nano particle deposited were between 129 and 161nm, while the average roughness ranged from 58.5nm to 96.5nm. Atomic Force Microscope (AFM) images showed that the deposition time of 90min and concentration of 3M Ammonia Solution had a smooth deposition. The optical properties of ZnS thin films are found using UV-VIS Spectrophotometer. Using the transmittance spectra, the absorption coefficient is obtained as a function of photon energy and the ZnS band gap value was estimated in the range of 3.64eV – 3.96eV.

KEYWORDS: Zinc Sulphide, Chemical Bath Deposition, Optical properties.

1. INTRODUCTION
Researchers all over the world are aiming at enhancing the efficiency of solar cells in order to provide an environmental friendly energy source for the future generation. For improving the light harvesting in solar cells, it is important to lower the undesirable surface reflection losses at the interface between air and the top layer of solar cells for the complete range of the solar spectrum [1]. ZnS is an n-type II – VI compound with a wide gap of 3.5 – 3.7eV at room temperature. It is a promising material for various uses such as blue light emitting diodes, electro luminescent devices and photovoltaic cells [2 – 4]. The ZnS when coated in nano form with dimensions below Bohr diameter will show interesting optoelectronic properties for the reason such as quantum size defect.

There are a number of techniques available to prepare metal sulphide thin films, such as Chemical Bath Deposition (CBD) [5-10], Electrodeposition [11], Silar [12], Pulsed Layer Ablation [13], Metal Organic Chemical Vapour Deposition [14], Thermal and Photochemical Vapour Deposition [15]. Of these methods, CBD offers a very cheap and simple means of coating large area thin films of semiconductors and has gained more interest due to its high purity and quality of the deposited films. This technique has been used to coat PbS [16], CdO [17], CuSe [18], NiS2 [19]. In this paper, the deposition of ZnS thin films from aqueous solution using ammonia as a complexing agent and different deposition time has been reported.

The Chemical Bath Deposition of ZnS thin films have been done by various researchers in aqueous alkaline baths. Seghaier S et al [16] have reported on the influence of thermal treatment over the structural and optical properties of PbS films. Ezekoye B.A et al [17] have given a detailed investigation over the changes in the optical properties as well as resistivity of the films due to P Type Cu dopant on ZnS. Nagamani K et al [20] reported that the optical studies of CdO films have high average transmittance over 60% in the visible region. Trisodium Citrate has been used as a complexing agent in the deposition of ZnS thin films by Cheng et al [21] and Johnston et al [22].

In this paper, the deposition of ZnS nanoparticles by chemical bath deposition using Ammonia solution as a complexing agent have been focused and the synthesised samples were characterised using Scanning Electron Microscope [SEM], Atomic Force Microscope [AFM], X-Ray Diffraction [XRD], and UV–VIS Spectrophotometric Techniques. The surface morphology, the structure and the optical properties of ZnS films were analysed after annealing at 30°C in atmospheric condition for one hour after each deposition.

2. Experimental Methods
2.1. Preparation of Thin Films
The chemical used for the deposition were analytical grade (MERCK) and the solutions were prepared using double distilled water (MERCK- Emplura). The Zinc Sulphide thin films were prepared from aqueous solutions of Zinc Sulphate (ZnSO₄) and Thiourea (SC(NH₂)₂) acting as a source of Zn²⁺ and S²⁻ ions respectively.
The glass substrates used were micro slides (75mm x 25mm x 1.35mm). Before deposition, the glass substrates were degreased with ethanol for 10 min. Then it is ultrasonically cleaned with double distilled water for another 10min, further these substrates were dipped in chromic acid solution for 36 hours, rinsed in de-ionised water for 10 min and then dried. Then deposition of thin films was carried out in a hot alkaline medium in the following manner.

2.2. Chemical Bath Deposition
The chemical bath deposition starts with complexation of the zinc cations by the ammonia and the consecutive reaction with S²⁻ ions followed by the hydrolysis of thiourea. The chemical bath is prepared by mixing 20ml of 0.05 M zinc sulphate (ZnSO₄), 20 ml of 0.54 M Thiourea (SC(NH₂)₂) solution and 3M (NH₄OH) solution. While preparing the bath, first ammonia solution was mixed slowly with 20ml of 0.05M ZnSO₄ and stirred for several minutes in a magnetic stirrer until the solution becomes a colourless homogeneous solution. Then the solution was mixed with Thiourea with constant stirring. Finally, the mixture was placed in 50 ml beaker and kept in a water bath pot after sealing the beaker with a Teflon tape.
Four test samples were immersed inside the chemical bath and allowed to lean on the walls of the beaker. The reaction process for forming ZnS films is as follows:

\[
\text{ZnSO}_4 + 2\text{NH}_3\text{OH} \rightarrow \text{Zn(OH)}_2 + 2\text{NH}_4\text{SO}_4 \\
\text{Zn(OH)}_2 + 4\text{NH}_3\text{OH} \rightarrow \text{NH}_4\text{Zn(OH)}_6 \\
\text{NH}_4\text{Zn(OH)}_6 \rightarrow \text{NH}_4^+\text{HZnO}_2 + 3\text{OH}^- + \text{H}_2\text{O} \\
\text{SC(NH}_2)_2 + \text{OH}^- \rightarrow \text{CH}_3\text{N}_2 + \text{H}_2\text{O} + \text{SH}^- \\
\text{HZnO}_2^- + \text{SH}^- \rightarrow \text{ZnS} + \text{ZOH}^- \\
\]

The deposition was allowed to carry out for about 30, 60, 90 and 120 min and the temperature of the bath (T_b) was maintained at 90 °C. After each time interval of 3min, the samples were removed from the beaker and cleaned with deionized water to remove the white, loosely adhered powder precipitates, then the plate is annealed at 300°C for 1 hour.

3. Result and Discussion
3.1 Morphological Studies
In order to study the micro-structural surface topography, SEM images were taken on the ZnS deposited glass substrates. As shown in figure.1. ZnS thin films have grown on the substrate following the cluster by cluster deposition process.

The SEM image of ZnS nano particle prepared by CBD on the glass substrate with (NH4OH = 3M, ZNSO4 = 0.05M, Thiourea = 0.5M, t_d = 90 min, T_b = 90°C. The crystallinity structure obtained was for (NH4OH) concentration equal to 3 M and 4 M and the pH value of 12. The sample (a) in fig.1 shows the spherical structures compared to sample (b) in fig.2. These structures are formed by clusters of nano-particles whose size can be estimated from the line width of the (111) diffraction peak based on the schemer formula. The particles were measured to be around 55 – 78nm for 3 M concentration and 70 to 110 nm for 4M concentration. Also the sample (b) shows a widely dispersed nano-particles compared to sample (a). The ZnS nano particles grown on sample (a) showed best crystallinity.
The images obtained from Atomic Force Microscope (AFM) in figure 3, also show that the sample (a) has even deposition of nano ZnS particles than sample (b) in figure 4. The measurements are taken at different locations and the average of the roughness were measured. The average roughness (R_a) and Root Mean Square Roughness (R_q) values were 58.5 nm and 75.4 nm respectively for 3 M concentration and 74.7 nm and 96.5 nm for 4 M Concentration. This also showed that the sample (a) was better than sample (b). With the increase in deposition time the roughness of the sample increased since large sized grains which are closely packed are formed.

![AFM images](image1)

**Figure 4. AFM Images for Sample (b) t_d = 90 min, T_b = 90°C and 4 M concentration**

3.2 Optical Properties

The optical properties of ZnS thin films are found using the absorbance and transmittance spectrum with a UV-VIS Spectrophotometer. The transmittance spectra for ZnS film for dipping time 30, 60, 90, 120 min and at a temperature T= 90°C are given in fig 5. Transmittance was recorded for a range of 300 to 800 nm. The graphs show in figure 5., that the transmittance decreases with increase in deposition time. The average transmittance values for deposition time t_d = 30, 60, 90, 120 min are found as 99%, 98%, 97% and 95 % respectively. With the increase in deposition time, the thickness increases thereby decreasing the transmittance. This can also be explained as, the increase in grain size due to agglomeration has resulted in high surface roughness which reduced the transmittance. The graph showed a steep optical absorption feature, which is due to the good homogeneity in the coated ZnS samples.

![Transmittance Spectra](image2)

**Figure 5. Transmittance Spectra of ZnS Thin Film for Different Deposition Times.**

Using the transmittance spectra, the absorption coefficient is obtained as a function of photon energy and the figure 6 was plotted. The band gap energy obtained was used to plot figure 7. The linearity in the graph shows that ZnS is a direct band gap material. The band gap energy was found to vary between 3.64 eV – 3.96 eV. For different deposition
time this closely agrees with the results reported for ZnS coatings by CBD method. The band gap obtained by CBD prepared ZnS coatings are higher than the typical band gap for ZnS (3.6eV) at 300K. The band gap values for 120min deposition time is 3.64eV and 30min deposition time is 3.96eV.

**CONCLUSION**

ZnS films were deposited on glass substrates by CBD Method. The Structural, Morphological and Optical properties were found by varying the deposition time from 30 – 120min. The SEM images showed that the particle size were uniform for 90min deposition time. The AFM showed even deposition of ZnS nanoparticles over the glass substrate for 90min deposition time. The AFM showed even deposition of ZnS nanoparticles over the glass substrate for 90min deposition time. The concentration and dipping time were optimized and a good anti-reflective layer of ZnS nanoparticles was coated by CBD method which can be used for solar cell applications.

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**REFERENCES**


