# An Investigation about Nano Structures of Zinc Sulfide Thin Layers Produced by Chemical bath deposition (CBD) Method

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## ABSTRACT

Zinc Sulfide thin layers with the same deposition conditions were deposited on glass substrates at 75 ℃ temperature by chemical bath deposition method. Different deposition times namely, 1 hour and 3 hours were used to produce ZnS thin layers. The nano-structure of layers were studied by using Atomic force microscopy (AFM) and X-ray diffraction (XRD) methods. Optical Transmittance, Reflectance and Absorbance were studied by spectrophotometer method. The layers were found to exhibit high transmittance (76%-84%), low absorbance and low reflectance when the wavelength over 370 nm. Correlation between nano-structures and optical properties versus thickness were discussed. The band gap energy values of ZnS thin layers decreased from 4 to 3.96 with increasing deposition time. There was a good agreement between structural and optical properties and calculated band gap energy.

**Keywords:** ZnS thin layers; Chemical bath deposition (CBD); Atomic force microscopy (AFM), X-ray diffraction (XRD).

## INTRODUCTION

Zinc sulfide (ZnS) belongs to the II-VI compound of semiconducting material. Nanocrystalline ZnS thin films with a wide direct band gap are promising for optoelectronic device applications，such as electroluminescent devices and photovoltaic cells. In optoelectronics，It can be used as light emitting diode in blue to ultra violet spectral region due to its wide band gap of 3.7 eV at room temperature [1]. Several techniques have been used to fabricate ZnS thin films such as molecular beam epitaxy (MBE) [2]，thermal evaporation [3]，spray pyrolysis [4]，sputtering [5]，electrodeposition [6]，and chemical bath deposition (CBD) [7].Among the various physical and chemical techniques the CBD is generally simple，efficient，economical，and convenient for largescale deposition at ambient temperatures and pressures [8，9]. This technique is also capable of growing thin film with nanocrystal，micro crystal and epitaxial structure under various growth conditions. The CBD process uses a controlled chemical reaction to achieve thin film deposition by precipitation. Substrates are vertically immersed in an alkaline solution containing the chalcogenide source，the metal ion，the added base，and a complexing agent. A complexing agent is used to control the speciation of the metal ion [10]. The deposition process requires the release of cations $Zn^{2+}$ and anions $S^{2-}$ in the solution:

$$[Zn(NH_3)_n]^{2+} \leftrightarrow Zn^{2+} + nNH_3 \tag{1}$$

$$SC(NH_2)_2 + 2OH^- \leftrightarrow S^{2-} + CN_2H_2 + 2H_2O \tag{2}$$

and then

$$Zn^{2+} + S^{2-} \rightarrow ZnS \tag{3}$$

Thu**s**，the film growth is decided by the releasing rate of $Zn^{2+}$ and $S^{2-}$ and the physical steps，such as diffusion and absorption [11].

In this paper we report the physical properties (structure, surface composition and optical properties) on chemical bath deposition of ZnS thin films from $NH_3/SC(NH_2)_2/ZnSO_4$ solution with various thicknesses and deposition time.

### Experimental Details

ZnS thin layers was prepared on microscope glass slides substrates by CBD method using prepared reagents ($ZnSO_4$, thiourea, 25% ammonia) as the study of Zhang et al [11]. But the concentrations of solutions and temperature of bath are different. Before the deposition，the glass substrates were cleaned in an ultrasonic cleaner using acetone followed by alcohol and deionized water for 15 min，respectively. ZnS thin film were prepared by

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first mixing 10.88 ml of 0.5M zinc sulfate ($ZnSO_4$)，8.4 ml ammonia ($NH_3$) secondly  8.25 ml of 2M thiourea was added under stirring condition. Thereafter deionized water was added to make the volume up to 200 ml. The solution pH was at 10.5-11. The mixture was stirred for several minutes to get a clear and homogeneous solution. The clean substrates were immersed vertically in the reaction vessel. The deposition was carried out at 75 ℃ temperature for 1 and  3 hours，respectively.

After completion of film deposition，the glass substrate were taken out from solution. The slides were thoroughly rinsed with acetone，ultrasonically cleaned white and loosely adherent precipitates during deposition，and blown dry with helium gas. The thin，uniform and colorless ZnS film were obtained [12]. The surface morphology and roughness were analyzed by means of AFM (Dual Scope $^{TM}$  DS 95-200/50) analysis. Nano structure of the films were investigated by using a Philips XRD X'pert MPD Diffractometer ($CuK_\alpha$  radiation) with a step size of 0.03 and count time of 1s per step. Optical Transmittance, Reflectance and Absorbance, spectra were obtained by using Perkin-Elmer Lambda 45 UV/VIS spectrometer. Band gap of  layers were calculated.

## RESULTS AND DISCUSSION



(a)

(b)

(c)

(d)
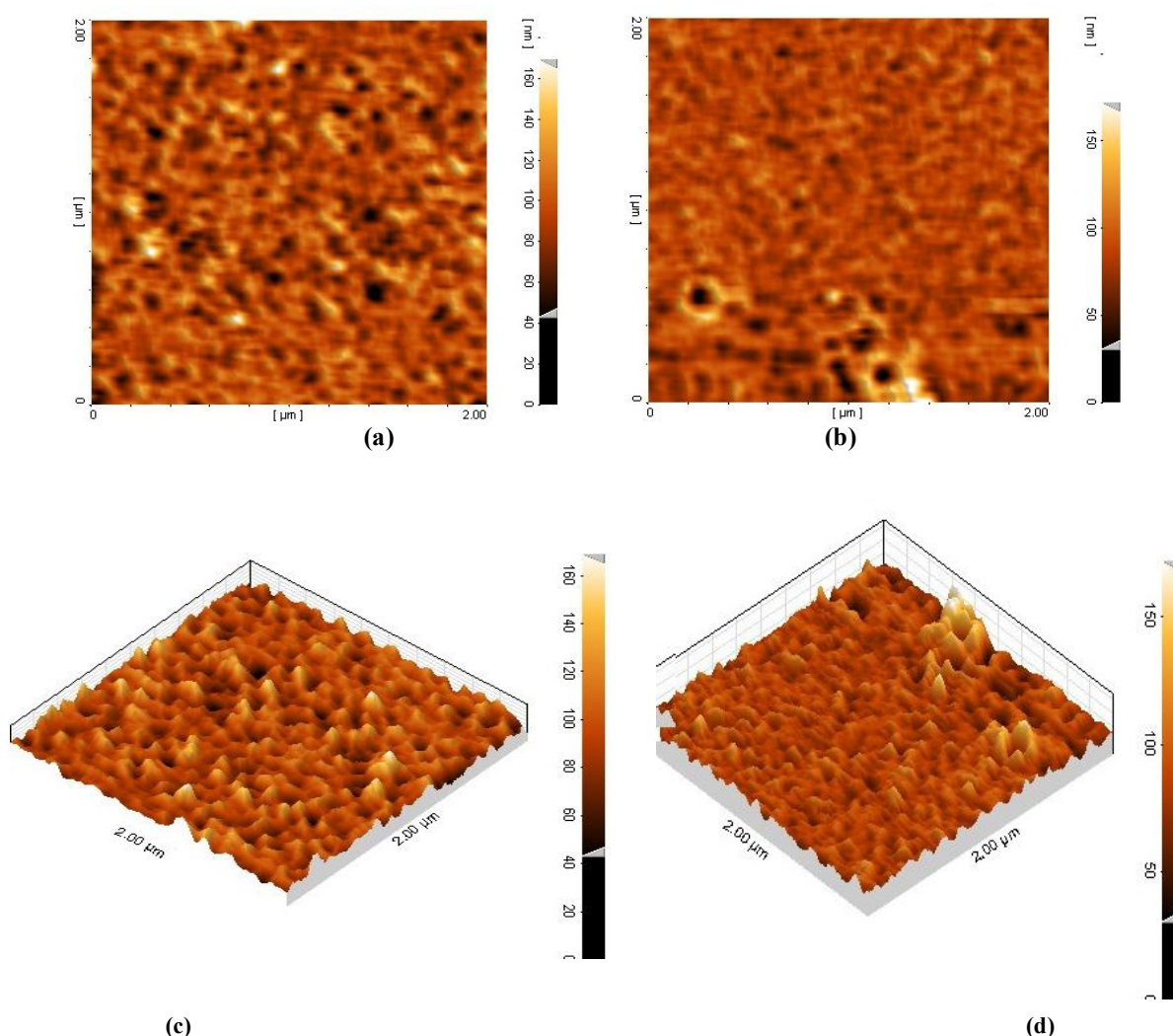
**Figure 1.** AFM images of ZnS/glass, a) two dimensional image,1 hour deposition time, b) two dimensional image, 3 hours deposition time, c) three dimensional image,1 hour deposition time, d) three dimensional image, 3 hours deposition time.

Figure 1 shows AFM images for the layers produced in this work. Figures 1(a) and 1(b), depends on, two dimensional AFM images of 1 hour (87 nm thickness) and three hours (143 nm thickness) deposited ZnS/glass layers, respectively. As it can be seen from figure 1(a) there are more voids on layer and by increasing thickness

fraction of voids decreases, and surface fill up with grains (figure 1(b)). Figures 1(c) and 1(d), show three dimensional AFM images for 1 hour (87 nm thickness) and three hours (143 nm thickness) deposited ZnS/glass layers, respectively. In figure 1(c) surface is full of domed grains with more fraction of voids between them and by increasing thickness in figure 1(d), fraction of voids decreases and surface is covered with bigger domed grains and layer gets denser and more completed. Some interesting observation on the nucleation stage may now be noted. It is seen that film growth proceeds by nucleation of islands, which subsequently coalesce to cover the entire substrate surface showing a dense structure.

Figure 2 shows roughness for the layers produced in this work. As it can be seen by increasing deposition time (increasing thickness), because of formation of bigger domed grains on layer roughness increases.
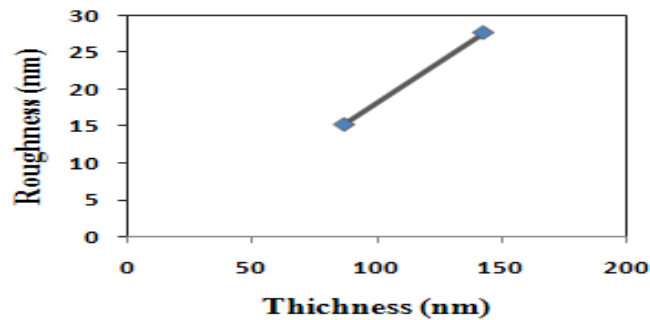


**Figure 2.** Roughness diagram of ZnS/glass layers with 1 hour and 3 hours deposition time.

Figure 3 shows XRD patterns for the layers produced in this work. As it can be seen from XRD patterns, 1 hour deposited layer (87 nm) is almost amorphous and there is no clear crystallographic peak for this layer. By increasing deposition time to 3 hours (143 nm), layer get crystalline and there are two crystallographic peaks as ZnS(220) and ZnS(331) also three zinc oxide (100), (002) and (101) peaks, there layer of 143 nm thickness is a combination of ZnS and ZnO crystals.
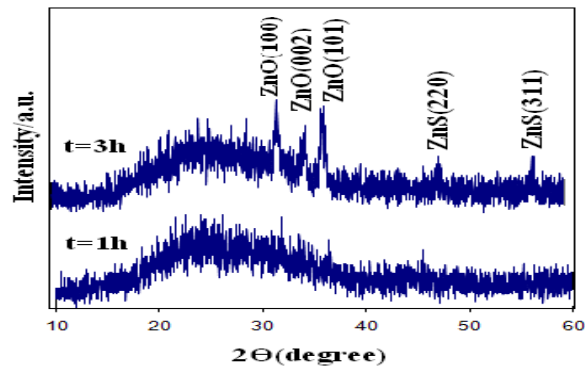


**Figure 3.** XRD patterns of ZnS/glass layers with 1 hour and 3 hours deposition time.

Figure 4 shows, optical spectra for the layers produced in this work. Figures 4(a), 4(b) and 4(c) depend to Transmittance, Reflectance and Absorbance versus wavelength for ZnS/glass layers produced in this work respectively. As it can be seen by increasing deposition time and thickness, Transmittance has a decreasing trend Reflectance has an increasing trend and also Absorbance has an increasing trend, the reason for all of them is because of increasing deposition time and thickness layer get more completed and fraction of voids decreases that tends to less Transmittance, more Reflectance and more Absorbance. In general there are high percent of Transmittance for layers produced in this work, that depends on low thickness of these layers.

**(a)**

**(b)**
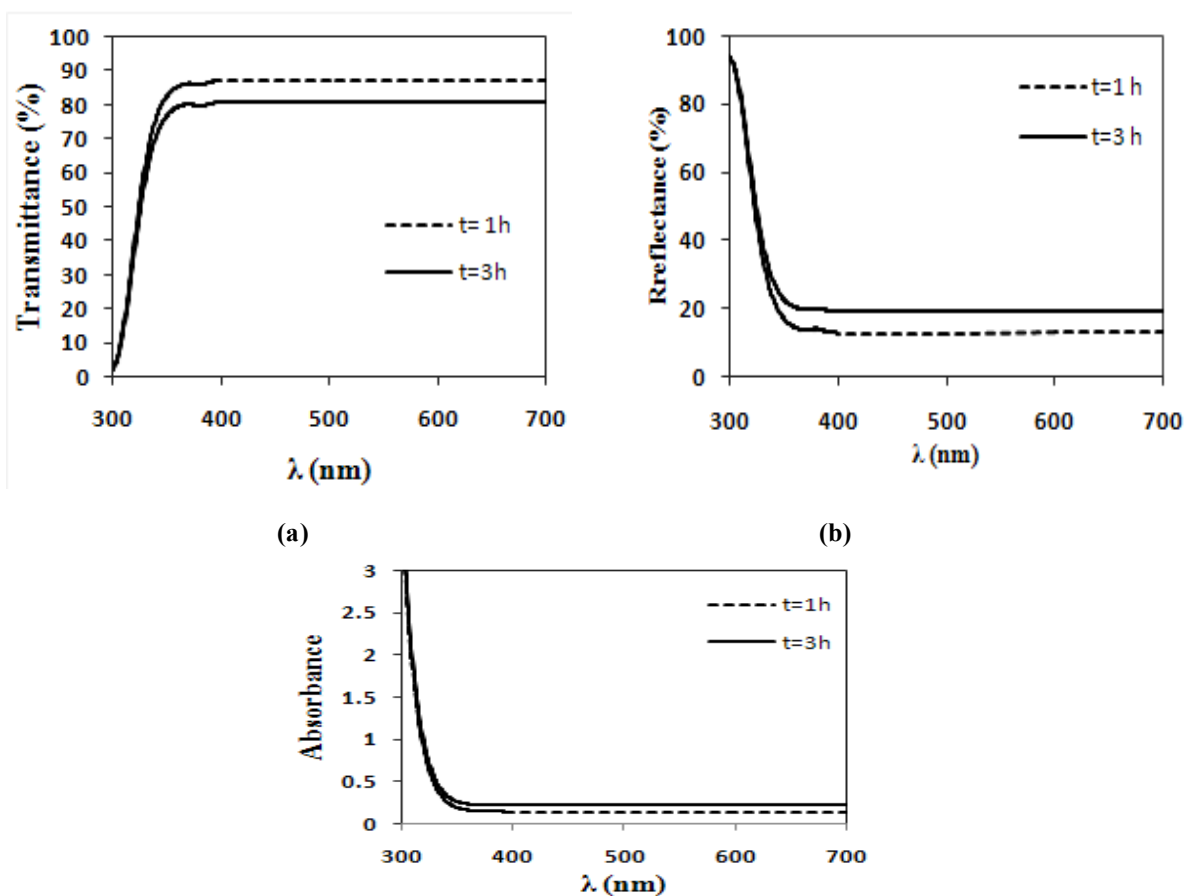
**(C)**

**Figure 4.** optical spectra, a) Transmittance, b) Reflectance and c) Absorbance of ZnS/glass layers with 1 hour and 3 hours deposition time.

The band gap of semiconductor could be obtained from the optical data. For a direct band gap material, the absorption coefficient $\alpha$ is related to the incident photon energy $h\upsilon$ by the relation:

$$A h\upsilon = A(h\upsilon - E_g)^{1/2} \tag{4}$$

Where A is the constant and $E_g$ is the band gap of semiconductor. The band gap was determined from the intercept of the straight-line portion of the $(\alpha h\upsilon)^{1/2}$ vs. the incident radiation energy $h\upsilon$ [11]. Figure 5 shows the band gap energy for the layers produced in this work. As it can be seen by increasing deposition time and thickness band gap energy decreases, that is because of effect of glass substrate on value of band gap for thicker layer. Table 1 shows values of band gaps and details of ZnS/glass layers produced in this work.
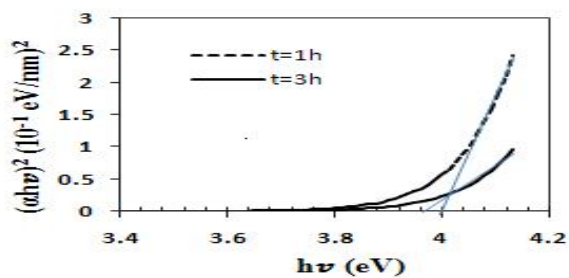


**Figure5.** Band gap energy of ZnS/glass layers with 1 hour and 3 hours deposition time.

**Conclusion**

ZnS/glass thin layers with two different deposition time and same other deposition conditions at 75 ℃ temperature, were produced by chemical bath deposition method. their nano structures and optical spectra were obtained by AFM, XRD and spectrophotometer methods. By increasing deposition time, morphology of layer changes bigger domed grains form, layer get more completed and fraction of voids decreases, roughness increases, Transmittance decreases, Reflectance and Absorbance increases. Also by increasing thickness (deposition time), structure of layer change from amorphous to crystalline structure. Band gap energy decreases by increasing thickness, for thick layer effect of substrate affect value of band gap. Structural changes and optical spectra were in agreement with each other.

**Table 1.** Band gap energy and details of ZnS/glass layers produced in this work.

| Deposition time ( h ) | Film thickness | Temperature of bath (C) | pH | Band gap (eV) |
|---|---|---|---|---|
| 1 | 87 | 75 | 10.5-11 | 4 |
| 3 | 143 | 75 | 10.5-11 | 3.96 |

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