

## **EFFECT OF ANNEALING TEMPERATURE ON OPTICAL AND STRUCTURAL PROPERTIES OF ZnS THIN FILMS PREPARED BY CBD TECHNIQUE**

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### **ABSTRACT**

Zinc sulfide thin films were deposited on optical glass substrates by using chemical bath deposition (CBD) technique. The chemical bath contains the solutions of thiourea, zinc acetate, ammonia and sodium citrate. The effect of annealing temperature on the deposited films has been studied at different temperatures from 200 °C, 250 °C, 300 °C and 350 °C in 24 hours. SEM, XRD and UV-Vis were used to characterize the samples. XRD shows development of well-crystallized film with pure wurtzite structure after annealing. XRD spectrum indicates that the films are amorphous and have cubic zinc blend structure. SEM shows that the film are thicker and have bigger grains size at 350 °C compared to the film at 200 °C with the grain size between 360.0 – 392.7 nm and 329.4 – 385.0 nm respectively. UV-Vis spectra showed that the deposited ZnS thin films have more than 93% transmittance in the visible region and direct band gap of deposited films are in range of 3.01 eV to 3.90 eV. The transmittance of the film increases slightly with the increase of annealing temperature. Therefore, ZnS thin films are suitable for coating onto CIS layer as solar cell application.

### **INTRODUCTION**

Zinc sulfide (ZnS) is a wide band gap semiconductor with a band gap value of 3.6eV. Consequently, it is an important material to be used as an antireflection coating for hetero-junction solar cells. It is an important device material for the detection, emission and modulation of visible and near ultra violet light. Due to a large band gap, which becomes a highly efficient luminescent material, when doped with manganese, copper or other ions. It can be used for fabrication of optoelectronic devices such as blue light-emitting diodes, electroluminescent devices, electro optic modulator, optical coating, n-window layers for thin film hetero junction solar cells, photoconductor and especially photovoltaic devices. ZnS films can be prepared by different techniques such as molecular beam epitaxy sputtering, metal-organic chemical vapour deposition, electro deposition or chemical bath deposition (CBD). Chemical bath deposition is a very attractive method for producing ZnS thin films due to its specific advantages. This method has been successfully used in the obtaining of other metal chalcogenide thin films. The purpose of this work was to study the effects of the growth conditions, such

as annealed temperature on optical and structural properties of the chemical bath ZnS thin films. In this paper, we focus on effect of the annealing temperature on optical and microstructure of zinc sulfide by a simple CBD technique.

### EXPERIMENTAL DETAILS

All experiments were carried out initially at room temperature for this experiment, 2.5 ml of 1M  $\text{Zn}(\text{CH}_3\text{COO})_2$ , 0.5 ml of 3.75M triethanolamine (TEA), 2.5 ml ammonia ( $\text{NH}_3$ ), 0.8 ml of 0.66M trisodium citrate ( $\text{C}_6\text{H}_5\text{Na}_3\text{O}_7$ ), and 2.5 ml of 1M thiourea were employed as starting materials. First of all, solution of zinc acetate and trisodium citrate were mixed and stirred for about 30 minutes. After the formation of clear solution, thiourea was added slowly along with ammonia as buffer solution. TEA was then added into the solution and stirred for about another 30 minutes until a stable solution has formed. The substrates were immersed in the solution and put into the microwave oven at temperature range of  $80^\circ\text{C} - 86^\circ\text{C}$  for 24 hours. After deposition, the ZnS thin films were washed by distilled water and dried in air. The deposition takes place on glass substrates where it was cleaned with detergent, dried and degreased with ethanol in an ultrasonic cleaner and kept immersed in distilled water prior to the deposition. The glass substrates were placed vertically in the reaction solution to deposit the film. The coated substrates were removed at the end of the chosen duration of deposition, washed in running tap water, rinsed in deionized water and dried in air. Various samples were obtained when annealed at different temperatures of  $200^\circ\text{C}$ ,  $250^\circ\text{C}$ ,  $300^\circ\text{C}$  and  $350^\circ\text{C}$ .

### RESULTS AND DISCUSSION

Zinc sulfide exists in sphalerite, cubic and hexagonal forms. The cubic form is stable at room temperature, while the less dense hexagonal form is stable above  $102^\circ\text{C}$  at atmospheric pressure. The films obtained by this technique were white in colour and adhere very well. The structure properties of this film were characterized by X-Ray Diffraction. Figure 1 shows X-Ray spectra made for ZnS thin films with different annealed temperature of  $200^\circ\text{C}$ ,  $250^\circ\text{C}$ ,  $300^\circ\text{C}$  and  $350^\circ\text{C}$ . From Figure 1, ZnS appears almost in amorphous form. The difference annealing temperature does not look any obvious different in XRD pattern. There was only one peak at 2 Theta scale of 30.1 at (1 1 1) that occurred in XRD pattern. As the annealing temperatures increases, the diffraction peaks of samples become sharper due to the coarsening of grains.

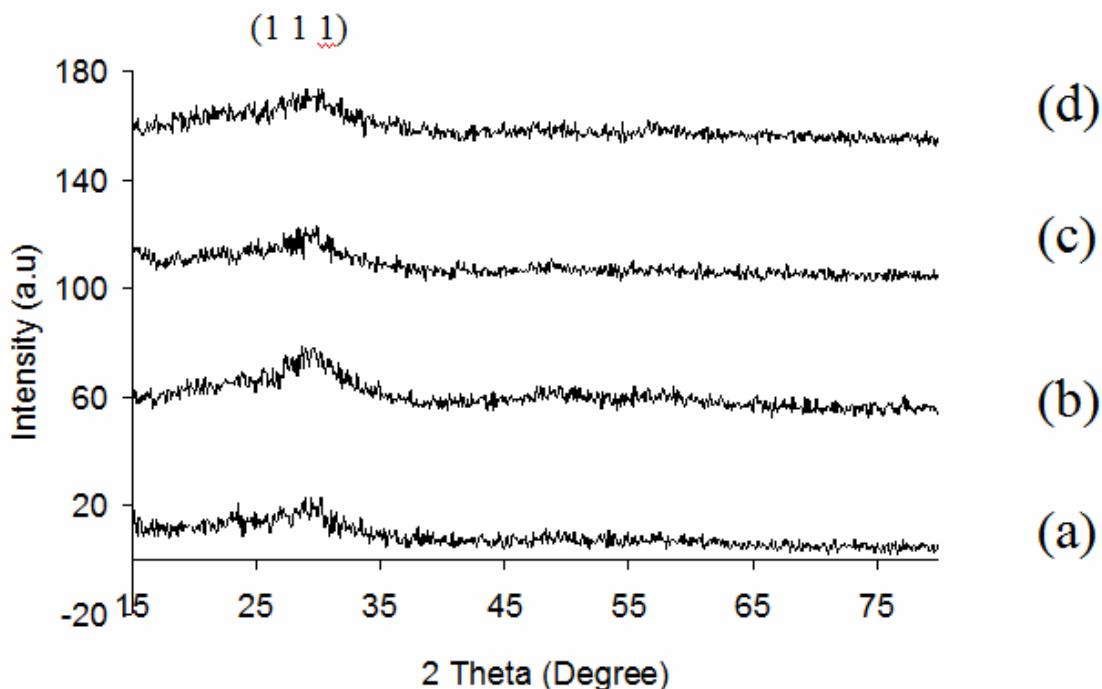


Figure 1. X-Ray diffraction pattern of ZnS thin films on glass substrates with annealed temperature of (a) 200 °C, (b) 250 °C, (c) 300 °C and (d) 350 °C

The optical properties of the films deposited on glass substrates were determined from the transmission measurements in the range of 200 – 800 nm. Figure 2 shows the transmission spectra of ZnS thin films which have more than 93 % in the visible range for deposited films. The thickness of the film was about 35.22 nm, 42.25 nm, 55.99 nm, 72.3 nm for each annealing temperature. The increase of the annealing temperature follows the increase of the optical transmission.

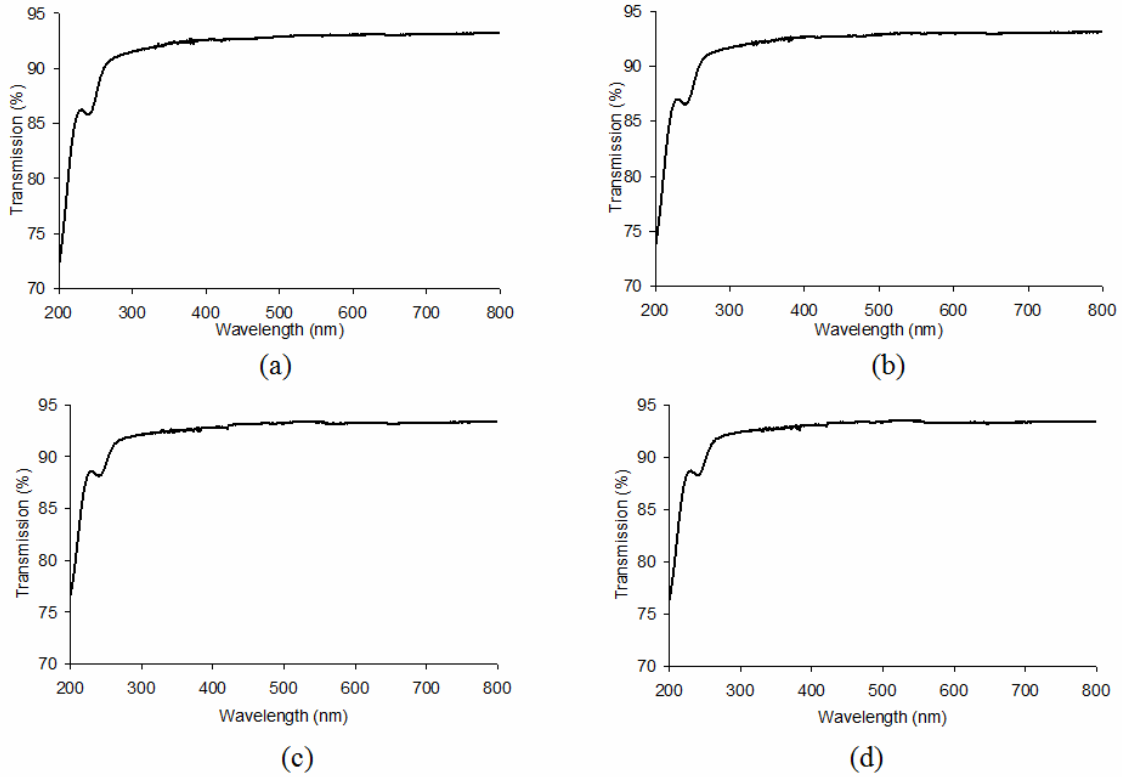


Figure 2: Optical transmission spectra of ZnS thin films on glass substrates with annealed temperature of (a) 200 °C, (b) 250 °C, (c) 300 °C and (d) 350 °C

Based on the obtained optical transmittance, the square of optical absorption coefficient,  $(\alpha h\nu)^2$  is plotted as a function of photon energy ( $h\nu$ ) in Figure 3. It can be seen that the films have a steep optical absorption feature indicating good homogeneity in the shape and size of the grains and lower defects density near band edge. As can be seen,  $(\alpha h\nu)^2$  varies almost linearly with  $h\nu$  above band gap energy ( $E_g$ ). Accordingly, the following equation for a direct inter-band transition can be applied.

$$(\alpha h\nu)^2 = A (h\nu - E_g) \quad (1)$$

where  $A$  is a constant. The band gap is obtained by extrapolating the straight portion of the curve to zero absorption coefficient. The determined band gap values are listed in Table 1. The band gap values of ZnS thin films annealed at 200 °C, 250 °C, 300 °C and 350 °C are in the range of 3.01 eV to 3.90 eV which is larger than the typical value of the bulk ZnS (~3.6 eV) probably due to the quantum size effect as expected for nanocrystalline nature of the films. Figure 4 shows that band gap (eV) plotted against deposition time for ZnS thin films deposited on glass substrates. It is clearly shows that increasing annealed temperature will increase the band gap.

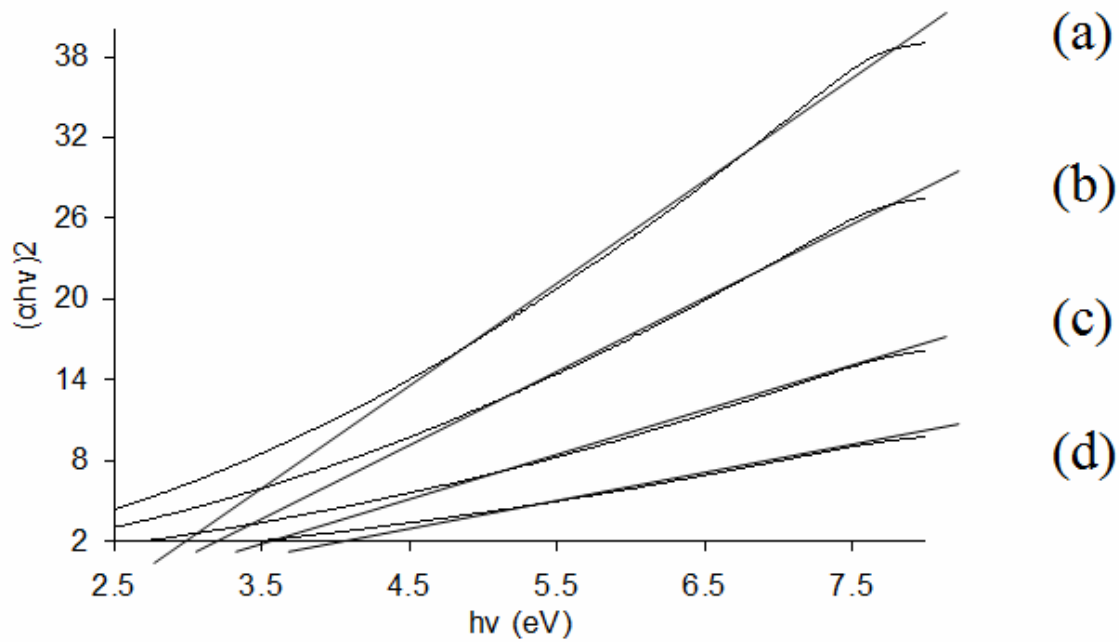


Figure 3: Plot of  $(\alpha h\nu)^2$  against  $h\nu$  for ZnS thin films on glass substrate with annealed temperature of (a) 200 °C, (b) 250 °C, (c) 300 °C and (d) 350 °C

Table 1: Effect of deposition time on optical band gap of the ZnS thin films deposited on glass substrates.

| ANNEALED<br>TEMPERATURE (°C) | OPTICAL BAND GAP<br>(eV) |
|------------------------------|--------------------------|
| 200                          | 3.01                     |
| 250                          | 3.29                     |
| 300                          | 3.52                     |
| 350                          | 3.90                     |

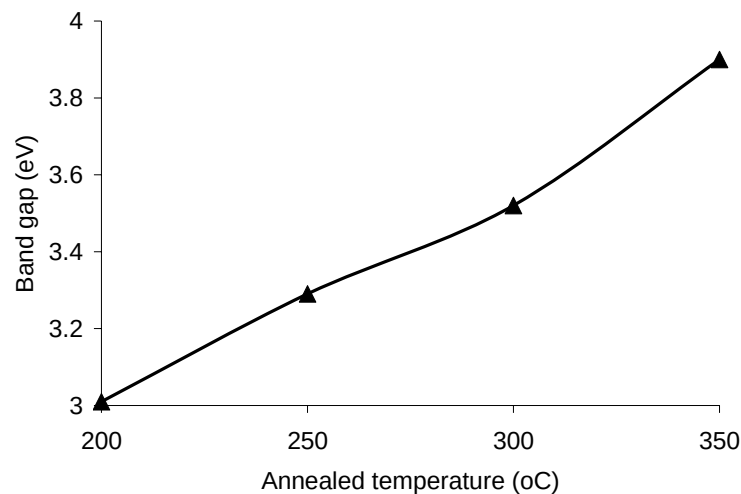


Figure 4. Plot of band gap (eV) against annealed temperature ( $^{\circ}\text{C}$ ) for ZnS thin films deposited on glass substrates.

SEM image has been obtained for ZnS thin film deposited on glass substrate in order to study thin film surface. SEM brings microscopic information of the surface structure and roughness. It appears to be a helpful technique to specify the growth mode via the study of a surface roughness, and to determine the effect of the different annealing temperature on the film morphology. Figure 5 shows the surface of ZnS layers obtained at four different annealing temperatures. A slight increase of the grain size follows the increase of the annealing temperature but does not improve the surface roughness. Concerning the nucleation stage film growth proceeds by nucleation of crystallites then formed grains which coalesce to cover the entire substrate surface and to show a dense structure.

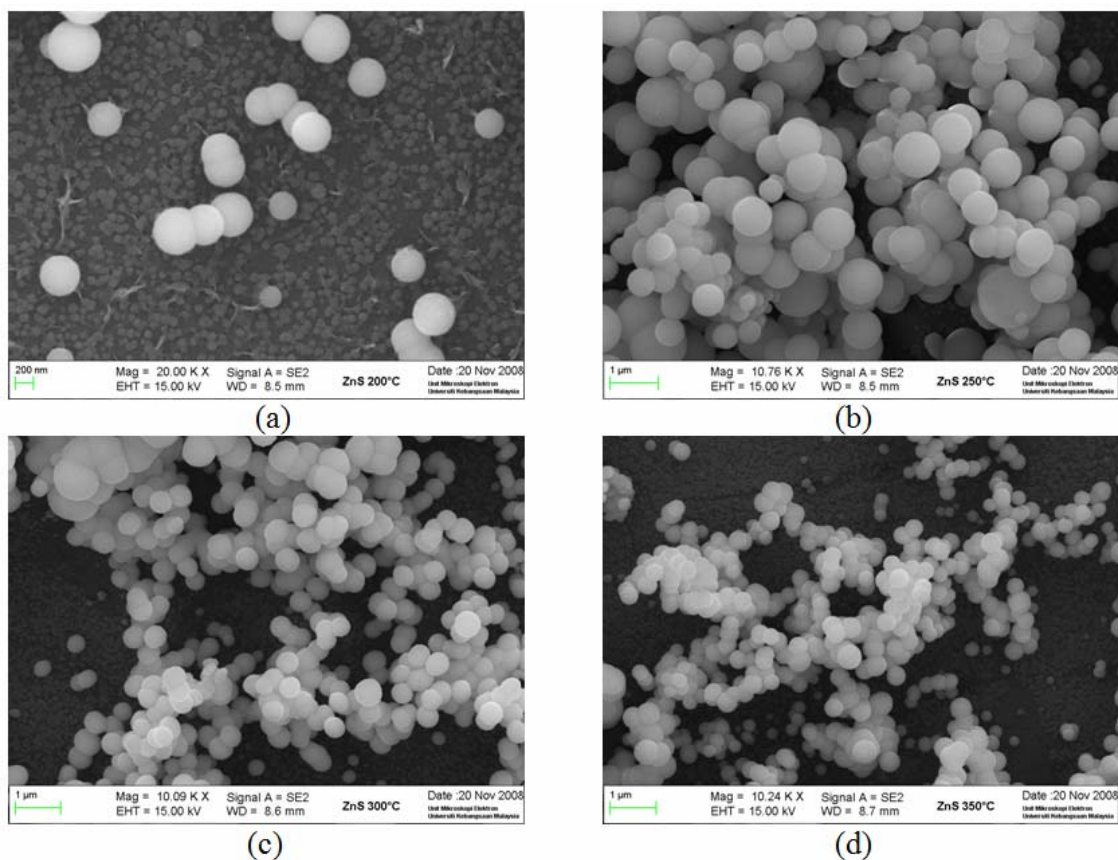


Figure 5: SEM image of ZnS thin films grown with annealed temperature of (a) 200  $^{\circ}\text{C}$ , (b) 250  $^{\circ}\text{C}$ , (c) 300  $^{\circ}\text{C}$  and (d) 350  $^{\circ}\text{C}$

## CONCLUSION

Zinc sulfide thin films are prepared on glass substrates by the CBD technique. The films are in good quality, adherent and uniform. The films are in good quality, adherent and uniform. There is a good agreement between XRD, SEM, and optical results. These

studies show that the annealed temperature contributes to the growth structure of deposited films. It is particularly observed that the best crystallinity of the ZnS thin films is obtained at 350 °C. ZnS thin film prepared with 350 °C shows a high transmission coefficient (93%) and direct band gap in range of 3.01 eV to 3.90 eV. The increase of the annealing temperature follows the increase of the optical transmission.

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