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# Effects of annealing on optical properties of ZnS and ZnS:Mn thin films

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Zinc sulfide (ZnS) films were deposited by chemical bath deposition (CBD) method using zinc sulphate ($ZnSO_4$) and thioacetamide (TA) as starting materials. For doping the ZnS films, $MnCl_2$ was added to the solution. The changes in optical constants were studied as a function of annealing temperature. By annealing, the energy gap ($E_g$) values were seen to be reduced in both doped and undoped films. The Mn doped films were seen more resistant to the heat treatment than undoped films. The optical absorption coefficient changes were observed in the films.

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*Keywords:* Chemical bath deposition, ZnS, ZnS:Mn, Thin films, Optical properties

## 1. Introduction

Zinc sulfide thin films with a wide direct band gap ($E_g$=3.66 eV) [1] and n-type conductivity are promising material for optoelectronic device applications, such as electroluminescent devices and photovoltaic cells. ZnS thin films can be obtained by a variety of techniques: RF sputtering [2], chemical vapor deposition [3], spray pyrolysis [4], atomic layer deposition [5] and chemical bath deposition [6-9]. The chemical bath deposition method is largely attractive because the technique possesses a number of advantages over conventional thin-film deposition methods and the main advantages are low cost, low evaporation temperature and easy coating of large surfaces [10-12]. The energy band characteristics of the material are well documented: in the cubic form (lattice constant 5.410 Å) it possesses a direct bandgap of 3.68 eV at 295 K and in the hexagonal form (lattice constants $a_o$=3.822 Å and $c_o$= 6.260 Å) the direct band gap is 3.74 to 3.87 eV at 300 K. The optical properties refractive index ($n$) and extinction coefficient ($k$), of ZnS have been studied over a wide spectral range [13].

In this work, ZnS thin films were deposited at room temperature (27 $^oC$). Undoped and Mn doped ZnS films were annealed. The effect of annealing on the optical properties of these films are given with possible explanations.

## 2. Experimental details

The investigated ZnS thin films were grown on commercial microscope slides at room temperature (27 ºC). Zinc sulphate ($ZnSO_4$) was used as the zinc source, thioacetamide (TA) as the sulphur source, ammonia/ammonium chloride, $NH_3/NH_4Cl$, as buffer and triethanolamine (TEA) as complexing agent. The bath solution was prepared as an alkaline solution (pH=10.7). All the elements of the deposition bath were taken from 1M stock solutions. Manganese Chloride ($MnCl_2$) was used as Mn source for doping studies of ZnS. The glass substrates were cleaned with diluted hydrochloric acid (5 %), detergent and also with ultrasonic cleaner. After drying they were stored in desiccators. The prepared solution was mixed with magnetic stirrer, after obtaining clear homogenized bath, the stirrer was turned off and glass slides were placed in the bath vertically. Each deposition was carried for 24 hours at room temperature. For thicker films the samples were placed in new unused bath. This step was repeated for 24 hours periods until the required thickness obtained.

Optical properties of ZnS thin films were measured at room temperature by using Perkin-Elmer UV/VIS Lambda 2S Spectrometer in the wavelength range of 190-1100 nm. The thicknesses of the films were calculated using the following relation:

$$t = \frac{\lambda_1 \lambda_2}{2\left[n(\lambda_1)\lambda_2 - n(\lambda_2)\lambda_1\right]}$$

where $t$ is the film thickness, $n(\lambda_1)$ and $n(\lambda_2)$ are the refractive indices at the two adjacent maxima (or minima) at $\lambda_1$ and $\lambda_2$.

## 3. Results and discussion

### 3.1. The effect of various zinc sources

In the room temperature (27 ºC) zinc sulfide (ZnS) deposition study, four different zinc sources were used: zinc sulphate ($ZnSO_4$), zinc chloride ($ZnCl_2$), zinc acetate $Zn(CH_3COO)_2$ and zinc nitrate $(Zn(NO_3)_2$. The optical absorption properties of these films are given in Fig. 1. The ZnS films obtained by using zinc sulphate as zinc source gave the best results. They have lower optical absorption at sub band gap energies and higher optical absorption at and above the band gap energies. They adhered well to the substrates. Films deposited from the zinc acetate or zinc nitrate containing baths showed higher

optical absorption both below and above band gap energies. Films that resulted from zinc chloride containing baths were observed to have average values between previous groups mentioned. For doping and annealing studies which will be discussed in the proceeding sections, ZnS films from $ZnSO_4$ containing baths were used.

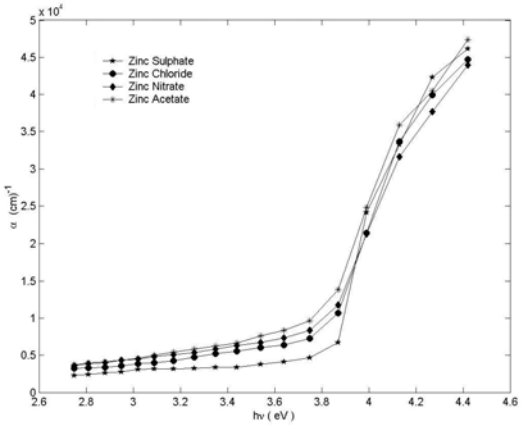


*Fig. 1. The α versus hv graphs of ZnS films deposited with different zinc sources at 27 ºC.*

### 3.2. Optical properties of ZnS and ZnS:Mn thin films

For the optical studies, ZnS films were deposited on clear microscope slides. Each film obtained after three consecutive dippings to the fresh baths. The energy gaps were determined from $\alpha^2$–energy graphs. The film thicknesses were deduced from the interface patterns at 500-800 nm wavelength interval of the optical absorption. The thicknesses of the films were 0.62 $\mu$m on the average and optical energy gap values were found to change between 3.70 eV and 3.88 eV and with an average value of 3.80 eV. These values are in good agreement with the literature [14]. All these data are given in Table 1.

*Table 1. Thickness and energy gap properties of ZnS thin films at 27 ºC.*

| Sample Number | Thickness t (μm) | Energy Gap $E_g$ (eV) |
|---|---|---|
| 1 | 0.61 | 3.86 ± 0.01 |
| 2 | 0.59 | 3.88 ± 0.01 |
| 3 | 0.58 | 3.86 ± 0.01 |
| 4 | 0.66 | 3.80 ± 0.01 |
| 5 | 0.64 | 3.80 ± 0.01 |
| 6 | 0.60 | 3.83 ± 0.01 |
| 7 | 0.68 | 3.74 ± 0.01 |
| 8 | 0.62 | 3.73 ± 0.01 |
| 9 | 0.67 | 3.70 ± 0.01 |
| 10 | 0.63 | 3.79 ± 0.01 |

The ZnS films were annealed in nitrogen at 100 ºC, 200 ºC, 300 ºC, 400 ºC and 500 ºC for one hour. The annealing effects in the optical absorption properties of the undoped ZnS films are given in Fig. 2. The optical absorption coefficients of as-deposited and 100 ºC annealed films are similar, no detectable changes occur with annealing at a nitrogen atmosphere for one hour annealing time at 100 ºC. As the annealing temperature increases the change in the absorption coefficient becomes more definite. Most of the changes occur at the optical band edge and with the annealing temperatures of 200 ºC and 300 ºC. By annealing, the optical absorption edge shifts towards the lower energies. A dramatic change occurs after annealing temperature reaches 400 ºC and higher values. This effect is due to the formation of ZnO in the film. Even though the annealing process was carried in an inert nitrogen atmosphere, ZnS films may contain some remnants from the bath, like water and $Zn(OH)_2$. These remnants act as oxidinging agents at temperatures 400 ºC and above. Similar results were obtained by other workers in the open air oxidation experiments [12-13]. The optical absorption coefficient of the annealed films increases at the measurement interval (2.8-4.5 eV). Increase in the optical absorption was seen as a common property for all the annealed ZnS samples.

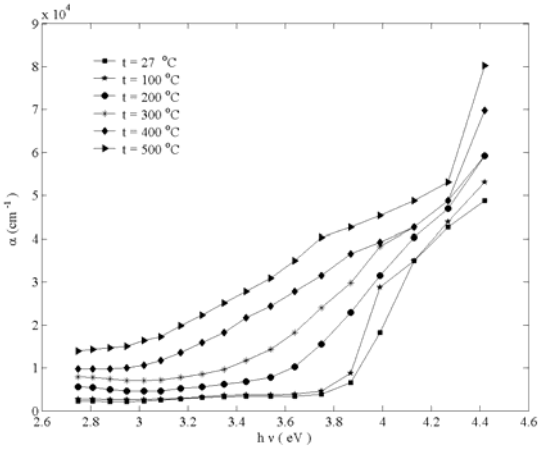


*Fig. 2. The α versus hv graphs of ZnS film as-deposited and annealed in nitrogene at different temperatures.*

The annealing effects in the optical absorption properties of the 1 % and 2 % Mn doped ZnS films are given in Figs. 3, 4. The annealing process has been taken place at 100, 200, 300, 400, 500 $^oC$ in % 1 and % 2 Mn doped ZnS films in the nitrogen medium. It is the similar process which was applied to undoped films. There is no significant change in absorption coefficient after annealing at 100 $^oC$. However, the absorption coefficient increased between 3.6 and 4.1 eV in the doped films which was tempered at 200 $^oC$. The increase of absorption coefficient vanished in the band. At the edge of the band (3.6-3.8 eV), we observed that the absorption coefficient increased remarkably. In addition, the absorption in the energy band gap also showed clear increase at 300 $^oC$. The fims whose annealing process was performed at 400 $^oC$ and 500 $^oC$

exhibited complete change and significant increase in absorption coefficient in the band edge. The increase of it observed at the band to band transition region as well.

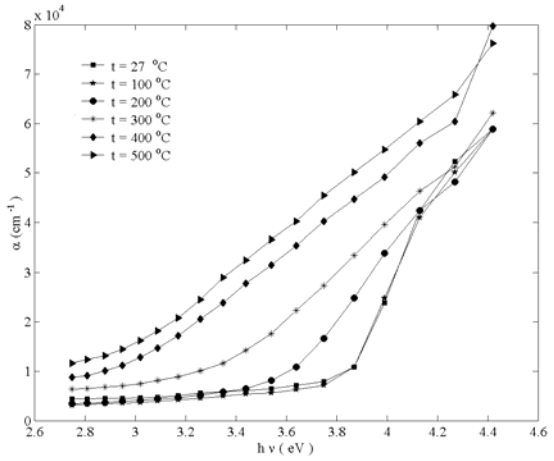


*Fig. 3. The α versus hν graphs of ZnS:Mn (1 % Mn) film as-deposited and annealed in nitrogene at different temperatures.*

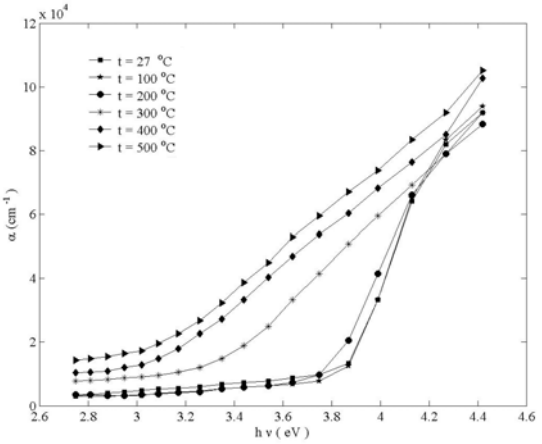


*Fig. 4. The α versus hν graphs of ZnS:Mn (2 % Mn) film as - deposited and annealed in nitrogene at different temperatures.*

The ratio of the absorption coefficients of annealed samples to as-deposited ZnS samples are given in Fig. 5. The maximum change in optical absorption ratio is seen near the optical absorption band edge. The peak of the annealed/unannealed ratio shifts to the lower energies as the annealing temperature increases. The optical absorption ratio peak is seen at ≈3.9 eV for the samples annealed at 100 ºC and for the 500 ºC annealed samples this peak shifts to 3.75 eV. Another feature which is clearly seen in this figure is that the rational change in the absorption coefficient is higher at the energies in the forbidden gap than the absorption ratio above the band gap energies.

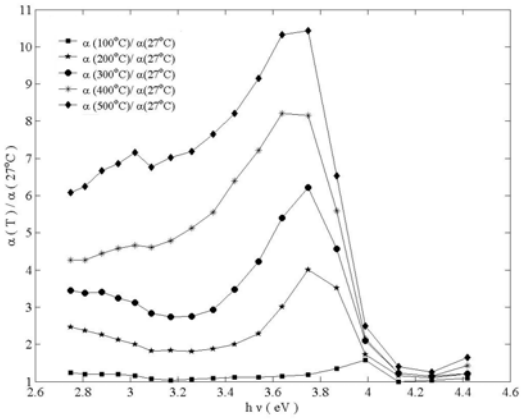


*Fig. 5. The ratio of the absorption coefficients of annealed samples to as-deposited ZnS film.*

Band edge steepness value $B$ and energy gap $E_g$ values were obtained from the plot of $\alpha^2$ versus energy gap graphs. The optical band gap energy was extrapolated from the most linear part of this graph and the slope of this graph was taken as $B$ value. The change of $E_g$ with annealing and the band edge steepness values are given in Table 2.

*Table 2. Annealing effect on B and $E_g$ values for 0.66 μm ZnS film.*

| Annealing Temperature (°C) | Band Edge Sharpness, B ($cm^{-2}$/eV) | Energy Gap, $E_g$ (eV) |
|---|---|---|
| As-deposited | $4.24 \times 10^9$ | 3.86± 0.01 |
| 100 | $4.71 \times 10^9$ | 3.83± 0.01 |
| 200 | $3.56 \times 10^9$ | 3.72± 0.01 |
| 300 | $3.10 \times 10^9$ | 3.60± 0.01 |
| 400 | $2.41 \times 10^9$ | 3.31± 0.01 |
| 500 | $2.45 \times 10^9$ | 3.28± 0.01 |

Optical energy gap values of the films decrease steadily from 3.86 eV to 3.28 eV with annealing. It has been reported that the band pap energy for ZnS thin films are decreasing with increasing annealing temperature [15,16]. An interesting feature in this table is a sudden drop of the $E_g$ value from 3.60 eV to 3.31 eV when annealed at 400 ºC for one hour. This change is due to the oxide formation as mentioned in the previous paragraphs of this subsection. The B value which is a measure of the band edge steepness value, fluctuates with annealing. Annealing of the ZnS samples gives more orderly therefore better films, but in the other hand evaporation of the absorbed/adsorbed bath remnants may give voids which act as a degrading factor for the optical properties of the films. Moreover at the temperatures above 400 ºC, oxidation occurs in the films. So the films become a mixture of ZnS and ZnO. This effect is believed to degrade the films. For the annealing studies in the Mn doped ZnS films, the same annealing process was repeated (nitrogen atmosphere, 100 ºC, 200 ºC, 300 ºC, 400 ºC,

500 ºC one hour annealing time) for the 1 % and 2 % Mn doped ZnS films. The results are given in Figs. 6, 7 for 1 % Mn doped and 2 % Mn doped films. One difference in the optical absorption coefficient change between the annealed and unannealed samples is that the doped samples are more stable to thermal processing than the undoped ones. The absorption band edge shifting to the lower energies by annealing is seen in these graphs but the change is smaller than the undoped ZnS samples annealed at these conditions.

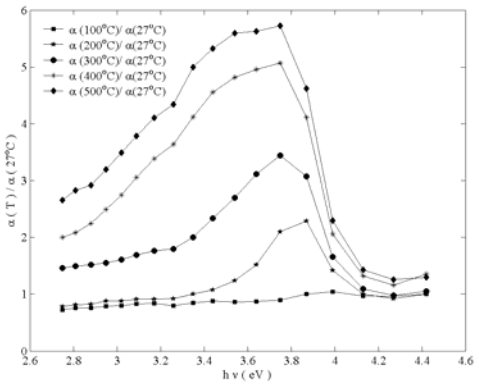


*Fig. 6. The ratio of the absorption coefficients of annealed samples to as-deposited ZnS:Mn film (1 % Mn).*

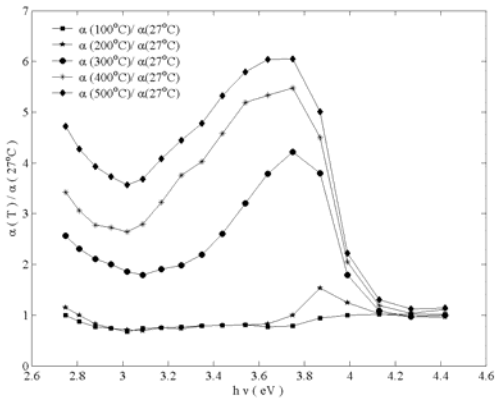


*Fig. 7. The ratio of the absorption coefficients of annealed samples to as-deposited ZnS:Mn film (2 % Mn).*

Annealing related optical absorption changes in the 2 % Mn doped ZnS films are similar to 1 % Mn doped films except high degree degradation starts at 300 ºC in 2 % doped films while in 1 % Mn doped films this change is taking place gradually. When the annealing temperature is 400 ºC and higher, changes due to oxidation are smoother in the doped films than undoped films. Optical energy gap values and band edge *B* parameters for the doped films are obtained from the $\alpha^2$ versus energy plots. The results are given in Tables 3 and 4. The $E_g$ values decrease from 3.84 eV to 3.26 eV in 1 % ZnS:Mn a jump from is seen 3.54 eV to 3.33 eV in seen when the annealing temperature changes from 300 ºC to 400 ºC. The band edge *B* parameters of doped films were seen clearly to be superior to the undoped films. The beneficial effect of the annealing process was observed as higher *B* values in this group of films.

*Table 3. Annealing effect on B and $E_g$ values for 0.44 μm (1 % Mn) ZnS:Mn film.*

| Annealing Temperature (°C) | Band Edge Sharpness, B ($cm^{-2}$/eV) | Energy Gap, $E_g$ (eV) |
|---|---|---|
| As-deposited | $4.87 \times 10^9$ | 3.84± 0.01 |
| 100 | $4.01 \times 10^9$ | 3.84± 0.01 |
| 200 | $4.01 \times 10^9$ | 3.67± 0.01 |
| 300 | $3.64 \times 10^9$ | 3.54± 0.01 |
| 400 | $3.87 \times 10^9$ | 3.33± 0.01 |
| 500 | $4.26 \times 10^9$ | 3.26± 0.01 |

*Table 4. Annealing effect on B and $E_g$ values for 0.24 μm (2 % Mn) ZnS:Mn film.*

| Annealing Temperature (°C) | Band Edge Sharpness, B ($cm^{-2}$/eV) | Energy Gap, $E_g$ (eV) |
|---|---|---|
| As-deposited | $5.69 \times 10^9$ | 3.81± 0.01 |
| 100 | $5.78 \times 10^9$ | 3.82± 0.01 |
| 200 | $4.24. \times 10^9$ | 3.70± 0.01 |
| 300 | $3.59 \times 10^9$ | 3.53± 0.01 |
| 400 | $4.31 \times 10^9$ | 3.40± 0.01 |
| 500 | $4.34 \times 10^9$ | 3.26± 0.01 |

Figs. 8, 9, 10 depict the optical density of ZnS, ZnS:Mn(% 1 Mn), ZnS:Mn(% 2 Mn) films, which were tempered at 27 °C and varies temperatures (100-500 °C), versus wavelength, respectively. As it is seen clearly from figures that a flat absorbation occurs inside the band it may be explained in terms of the scattering inducing a flat absorption related to the wavelength. However, at the edge of the band, the absorption increases rapidly. It is attributed to the fact that, increased temperature gives rise to increasing scattering rate inside and outside the band.

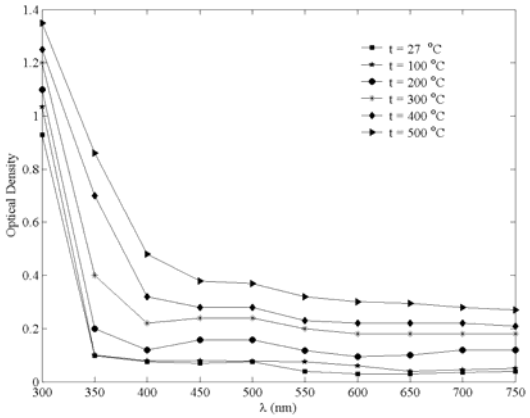


*Fig. 8. Optical density spectra of ZnS film as-deposited and annealed in nitrogene at different temperatures.*

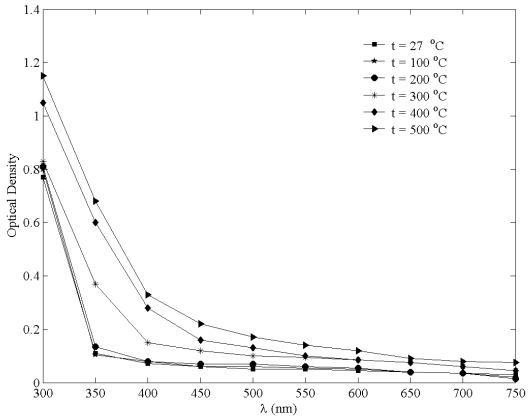


*Fig. 9. Optical density spectra of ZnS:Mn (1 % Mn) film as - deposited and annealed in nitrogene at different temperatures.*

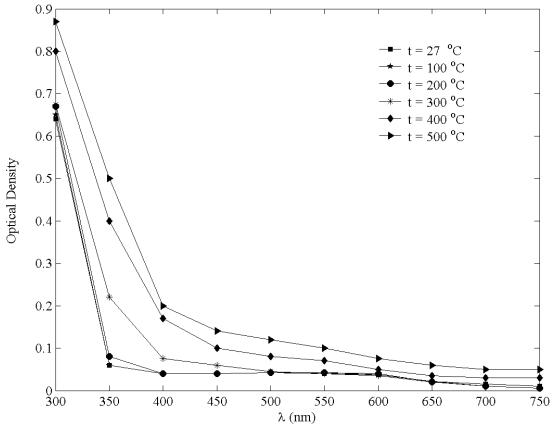


*Fig. 10. Optical density spectra of ZnS:Mn (2 % Mn) film as – deposited and annealed in nitrogene at different temperatures.*

## 4. Conclusions

Good quality ZnS films were obtained from the room temperature CBD bath method. Zn sources for the deposition were Zinc Sulphate, Zinc Acetate, Zinc Chloride and Zinc Nitrate. Among them Zinc Sulphate gave the best results. Doping of the ZnS film with Mn in the bath gives linear doping efficiency but the film formation rate was observed to decrease to its half of the previous value. Optical properties of the films were observed to change with annealing. Energy gap decreases steadily, shows a sharp jump when oxidation takes place at 400 ºC and higher temperatures.

Optical absorption increases in the entire region but most dramatic change is at the optical absorption band edge. Doped ZnS films were observed to be more resistant to the thermal process than undoped films. The optical band edge sharpness value oscillates with annealing due to the competing beneficial and detrimental effects. The healing and reordering effect of annealing is the beneficial one while oxidation at higher temperatures (>300 ºC) and possibly void formation by the evaporation were believed to be the detrimental effects of the annealing process.

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