CHARACTERIZATION OF ZNS AND ZNS: AL THIN FILMS

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ABSTRACT

Undoped and doped with Al ZnS thin films have been fabricated by vacuum evaporation technique under the vacuum of $10^{-5}$ Torr on glass substrate at room temperature and with different ratio of Al concentration of thickness (0.8 µm). The optical properties were revealed by UV-Visible transmittance spectra and the band gap energy was determined. Transmission spectra indicate a high transmission coefficient (>95%). The results showed that films have direct optical transition, and the values of energy gap were found to decrease with doping concentrations. Also the optical constants such as absorption coefficient, refractive index, extinction coefficient and dielectric constant have been calculated. The effect of doping concentration on the electrical properties has been studied.

Keywords: ZnS, Thin Films, Doping, Optical Properties, Structure Properties

I. INTRODUCTION

Zinc sulfide (ZnS) is a wide gap semiconductor. With the solution of chemical bath containing the metal consequently, it is a potentially important material to be and chalcogen ions. The film formation on substrate takes used as an antireflection coating for hetero junction solar place when ionic product exceeds solubility product. The cells is an important device material for the detection, precipitate formation in the bulk of solution is an inherent emission and modulation of visible and near ultra violet problem in CBD technique. This normally results light. With a large band gap, Zinc sulfide (ZnS) becomes unnecessary precipitation and loss of materials during film a highly efficient luminescent material, when doped deposition on glass substrate. In order to avoid such with manganese, copper or other ions. Owing to wide problem, proper optimization of chemical constituents of band gap value of 3.7 eV, it can be used for fabrication bath deposition is necessary.

The purpose of this work of optoelectronic devices such as blue light-emitting was to study the effects of the growth conditions, such as diodes, electroluminescent devices, electro optic deposition time on optical and structural properties of the modulator, optical coating, n-window layers for thin film chemical bath ZnS thin films [1]. Recent investigations have evoked considerable interest in
ZnS thin films due to their vast potential for use in thin film devices such as photo luminescent and electroluminescent devices and more recently as n-type windowlayer heterojunction solar cells [2]. The optical properties of the prepared film depend strongly on the manufacturing technique. Two of the most important optical properties; refractive index and the extinction coefficient are generally called optical constants. The amount of light that transmitted through thin film material depends on the amount of the reflection and absorption that takes place along the light path [3]. This class of new materials has not only provided many unique opportunities but also exhibited novel optical and transport properties, which are potentially useful for technological applications [4]. The study of the optical properties of doping material such as ZnS:Cu nanocrystals is important for the development of nanocrystal phosphors with efficient luminescence and the understanding of the impurity related optical transitions in semiconductor nanocrystals. A variety of methods have been deployed in order to synthesize and control the size of nanoparticles [5]. Many researchers investigated the structural, electrical and optical properties of ZnS films deposited at different temperatures evaporation for photovoltaic applications [6]-[12].

ZnS higher band gap energy (3.68 eV) [6] compared to that one of the CdS (2.42 eV) makes the ZnS wavelength range of transparency wider (above 330 nm) than the CdS one (above 520 nm). Many deposition techniques have been used to prepare ZnS thin films, such as sputtering, pulsed laser deposition, chemical vapor deposition, electron beam deposition, thermal evaporation, photochemical deposition and chemical bath deposition [3]. Among these methods, thermal evaporation is the most common method in producing thin film because the advantages of thermal evaporation are stability, reproducibility and high deposition rates. It is well known that the physical properties such as the structure and the surface are generally different from those of the same materials in bulk form[12]-[16]. In this work pure zinc sulfide and doped with Al are prepared by vacuum evaporation technique. The aim of this work is to preparing ZnS and ZnS:Al thin films and studying the effect of concentration of Al on the optical and electrical properties.

II. EXPERIMENTAL WORK

ZnS and ZnS:AL thin films with different Al concentration of thickness(0.8 μm)were prepared by vacuum evaporation technique under lower pressure (10^{-6} Torr) on Si and glass substrate by using Edward (E306A) coating system. The prepared films have been annealed at 400K. Spectrophotometer, type Shimadzu and UV-Visible recorder Spectrophotometer UV-160, is used to measure the transmittance and absorbance spectrum in the range (300-1100) nm region for ZnS thin films. The electrical resistance has been measured as a function of the temperature (T). The measurements have been done with used sensitive electrometer type of Keithly Digital Electrometer (616) and vacuum electric oven. The resistivity and conductivity as a function of Al concentration can be calculated from these measurements.

III. RESULTS AND DISCUSSION

A. Optical Properties

The study of optical absorption is important to understand the behavior of semiconductor nanocrystals. A fundamental property of semiconductors is the band gap-the energy separation between the filled valence band and the empty conduction band. Optical excitation of electrons across the band gap is strongly allowed, producing an abrupt increase in absorption at the wavelength corresponding to the band gap energy. This feature in the optical spectrum is known as the optical absorption edge [4]. The optical properties of un doped and doped ZnS thin films with Al were determined from transmittance measurement in the range 300-900 nm. Fig. 1 shows the optical absorbance of ZnS and ZnS:Al thin films at different Al concentration (pure, 1%, 2%) in the
wavelength range of 300nm to 900nm. The optical studies show that the absorbance of these films increases as Al concentration increases as in Table III. All the samples show very high absorption in UV region and low absorption in the VIS and NIR region. This make the material to be useful in windscreen coating and driving mirror to prevent the effect of dazzling light into driver’s eyes from oncoming vehicle and following vehicle [17]. It is observed that increasing of Al concentration shifts the peak of absorption spectrum to the red shift. The shift in the peak position films may be attributed to the crystallite of film structure by increasing the grain size which is confirmed by XRD results and AFM. Also the spectrum of transmittance has been studied; it is obviously that its behavior is opposite to that of the absorbance spectrum. From Table III the value of transmittance increases with increase of Al concentration, and it is quite clear that all films have excellent transparency in the visible range ≥95% transmission. The film is actually an efficient transmitting and antireflective material. Because of the high optical transmission and anti-reflective properties of ZnS film, ZnS may play an important role in photovoltaic devices. So they are useful as an antireflection coating for the optical transmission window. Similar behaviour was observed by researchers [15]-[18]. Also the values of reflectance are shown in Table I.

![Absorption spectrum of pure ZnS and ZnS-Al thin films at Al concentration of 1%, 2%](image)

**Fig. 1:** The absorption spectrum of pure ZnS and ZnS:Al thin films at Al concentration of 1%, 2%.

**TABLE I: SHOWS THE VALUE OF ATR FOR ZNS AND ZNS:AL THIN FILMS**

<table>
<thead>
<tr>
<th>Sample</th>
<th>A</th>
<th>T</th>
<th>R</th>
</tr>
</thead>
<tbody>
<tr>
<td>pure</td>
<td>0.279</td>
<td>0.554</td>
<td>0.0244</td>
</tr>
<tr>
<td>1%</td>
<td>0.433</td>
<td>0.363</td>
<td>0.2034</td>
</tr>
<tr>
<td>2%</td>
<td>0.765</td>
<td>0.116</td>
<td>0.1187</td>
</tr>
</tbody>
</table>

The absorption coefficient increases with increasing Al concentration and shifted to higher wavelength for all prepared samples as shown in Table II and Fig. 2. This is due to the decreasing value of energy gap with increasing Al concentration. The absorption coefficient (α) value varies between 1.4x10⁴ and 9.97x10⁴ cm⁻¹ with increasing of Al concentration from pure to 3% which are nearly agrees with [17]-[20]]. The energy band gaps were calculated with the help of the optical absorption spectral. To determine the energy band gap, we plotted (αhv)² against hv. Absorption
coefficient ($\alpha$) associated with the strong absorption region of the films was calculated from absorbance (A) and the film thickness (t) using the relation,

$$\alpha = \frac{2.303A}{t} \quad (1)$$

The theory of inter band absorption shows that at the optical absorption edge, the absorption coefficient $\alpha$ varies with the photon energy $h\nu$ according to:

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

where $E_g$ is the optical band gap, $A$ is a constant and the exponent $n = \frac{1}{2}, 1, 2, 3$, depending on the types of electronic transition in k-space. To determine the optical band gap of the ZnS and ZnS:Al thin films, taking $n = \frac{1}{2}$ gives the best fit for the films. The optical band gap, $E_g$, was determined by extrapolating the linear part of the optical absorption spectral. The band gap energy increases as Al concentration increases as in Table II. It could be observed that the optical band gap was decreasing with increasing Al concentration as shown in Fig. 3 and Table II. Also the decrease in band gap of the films could be attributed to improvement in the crystals and increases of the grain sizes of the films with increase Al concentration. This shift in the optical band gap may be attributed to the band shrinkage effect because of increasing carrier concentration [19] The ZnS is very useful as a window layer in heterojunction photovoltaic solar cells, because the high band gap energy will decrease the window absorption losses. This also leads to the improvement of the short circuit current. Similar results was observed by researchers [17]-[21]

<table>
<thead>
<tr>
<th>Sample</th>
<th>$E_g$(eV)</th>
<th>$\alpha \times 10^4 \text{ eV/cm}^2$</th>
<th>$B \times 10^5 \text{ cm}^{-1}\text{eV}^{-1}$</th>
<th>$\alpha \times 10^4 \text{ cm}^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>pure</td>
<td>3.8</td>
<td>0.31</td>
<td>1.4</td>
<td>0.465</td>
</tr>
<tr>
<td>1%</td>
<td>3.74</td>
<td>0.58</td>
<td>1.68</td>
<td>0.305</td>
</tr>
<tr>
<td>2%</td>
<td>3.45</td>
<td>0.81</td>
<td>9.97</td>
<td>0.277</td>
</tr>
</tbody>
</table>

**Fig. 2:** The absorption coefficient of pure ZnS and ZnS:Al thin films at Al concentration of 1%, 2%.
Fig 3: The \((ahv)^2\) as a function of photon energy of pure ZnS and ZnS:Al thin films at Al concentration of 1%, 2%

The coefficient \(A\) which is Tauc slope in the Tauc equation (2) has been obtained from the root square of the straight line slope in the Fig.(3). From this figure the value of \(A\) is increased with increasing Al concentration form pure to 3 wt% as shown in Table II. The factor \(A\) is inversely proportional to amorphosity and the width of the band tails [22]. This mean that amorphosity decreases with increasing Al concentration. The density of localize states in the band can be evaluated from the Urbach energy \((E_u)\) at \(\alpha <10^4\text{cm}^{-1}\) which is referred to absorption tails at energies smaller than the optical energy gap. In the exponential edge region, Urbach rule is expressed as [23]

\[
\alpha = \alpha_o \exp(hv/E_u)
\]

where \(\alpha_o\) is a constant, \(E_u\) is the Urbach energy, which characterizes the slope of the exponential edge. Equation (3) describes the optical transition between the occupied states in the valence band tail to the unoccupied states of the conduction band edge. By plotting \(\ln \alpha\) as a function of \(hv\), and the reciprocal slope of the linear part give the value of \(E_u\). It is obvious from Table II and Fig.(4) that \(E_u\) decreases from 0.645 to 0.2777 eV with increasing Al value from pure to 2%. This may be attributed to improvement in the structure by doping and decreasing the degree of amorphous films leading to decrease the localized states and fill all dangling bond
The refractive index is an important parameter for optical materials and applications. Thus, it is important to determine optical constants of the films Table III shows the variation of refractive index for prepared of pure ZnS and ZnS:Al thin films at Al concentration of 1%, 2%. It is obvious that n decreases with increasing Al concentration. This behavior is due to increase the crystalinity by adding Al which causes to expand the lattice and grow the grain size and decreases the defect (as in XRD and AFM) which means increasing the absorption and decreasing the reflection which the refractive index depend on it and this is an agreement with [17]. The behavior of extinction coefficient (k) is nearly similar to the corresponding absorption coefficient at different Al concentration; It is clear from Table V that k increasing with Al concentration. This attributed to the same reason, which mention previously in absorption coefficient [2]-[6]. The variation of real dielectric constant (ε₁) and imaginary dielectric constant (ε₂) with different Al concentration has been shown in Table III. The behavior of ε₁ is similar to refractive index because the smaller value of k comparison of n², while ε₁ is mainly depends on the k values, which are related to the variation of absorption coefficient [17].

<table>
<thead>
<tr>
<th>Sample</th>
<th>n</th>
<th>k</th>
<th>ε₁</th>
<th>ε₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>pure</td>
<td>2.46</td>
<td>0.047</td>
<td>6.05</td>
<td>0.23</td>
</tr>
<tr>
<td>1%</td>
<td>2.03</td>
<td>0.25</td>
<td>4.09</td>
<td>1.04</td>
</tr>
<tr>
<td>2%</td>
<td>2.015</td>
<td>0.41</td>
<td>3.89</td>
<td>1.65</td>
</tr>
</tbody>
</table>

B. Electrical properties

The physical properties of prepared films can be improved mainly by many parameters such as the substrate temperature, nature of the dopant, the amount of absorbed oxygen that appears during the deposition process, and the annealing process in controlled environments [24]. In this respect, in order to improve and control the electrical properties of ZnS films, they have been doped with Al. The incorporation of the impurity into the ZnZ lattice can increase the electrical conductivity. In order to study conductivity mechanisms, it is convenient to plot logarithm of the conductivity (ln σ) as a function of 1000/T for pure ZnS and ZnS:Al thin films at Al concentration of 1%, 2%.

as shown in Fig. 5. It is seen that resistivity decreases with temperature, indicating semiconducting nature of films. Also It is clear from these figures that there are two transport mechanisms, giving rise to two activation energies Eₐ₁ and Eₐ₂. This result is conform with [11]. At higher temperature range, the conduction mechanism is due to carrier excited into the extended states beyond the mobility edge and at lower temperature range; the conduction mechanism is due to carrier excited into localized states at the edge of the band[25]. Table VII shows the relation between the conductivity and film Al concentration. It is clear that the σᵣ T increases with increasing of Al concentration. This increase in conductivity is related to the improvement of crystallinity. The thermal activation energy was calculated using the relation

\[ \rho = \rho_o \exp(E_o/KT) \]
Fig. 5: The Ln $\sigma$ versus 1000/T for pure ZnS and ZnS:Al thin films at Al concentration of 1%, 2%

TABLE IV: SHOWS THE VARIATION OF D.C CONDUCTIVITY PARAMETERS

<table>
<thead>
<tr>
<th>Thickness (nm)</th>
<th>(293 – 453) K</th>
<th>(463 – 513) K</th>
<th>$\sigma_{R,T} \times 10^{-5} (\Omega \cdot cm)^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$E_{a1}$ (eV)</td>
<td>$E_{a2}$ (eV)</td>
<td></td>
</tr>
<tr>
<td>Pure</td>
<td>0.080</td>
<td>0.257</td>
<td>2.85</td>
</tr>
<tr>
<td>1%</td>
<td>0.085</td>
<td>0.216</td>
<td>3.25</td>
</tr>
<tr>
<td>2%</td>
<td>0.104</td>
<td>0.183</td>
<td>3.616</td>
</tr>
</tbody>
</table>

where, $\rho$ is resistivity at temperature $T$, $\rho_o$ is a constant, $K$ is Boltzmann constant ($8.62 \times 10^{-5}$ eV/K) and $E_o$ is the activation energy required for conduction. Table IV shows the variation in activation energy as a function of Al concentration. It is clear that the activation energies $E_{a2}$ decrease and $E_{a1}$ increases with increasing of Al concentration due to the tailing both of the conduction and the valence band is diminished thus moving the conduction into regions with higher density of states and mobility also may be the variation of crystallinity of film with increasing Al concentration. From the Hall measurement, the type of charge carriers, carrier concentration ($n_H$), Hall mobility ($\mu_H$) drift velocity ($v_d$) has been calculated as in Table V. It was noticed from this table that the films of all samples have a negative Hall coefficient. It can be observed from these calculations that both the conductivity increases with increasing of Al concentration, and the carrier's concentration, mobility and drift velocity increases with increasing of Al concentration.

TABLE V: SHOWS THE VARIATION of electrical parameters

<table>
<thead>
<tr>
<th>Thickness (nm)</th>
<th>$\sigma_{R,T} \times 10^{-5} (\Omega \cdot cm)^{-1}$</th>
<th>$R_H \times 10^5$ (cm$^3$/c)</th>
<th>$n_H \times 10^{15}$ (cm$^{-3}$)</th>
<th>$\mu \times 10^{-2}$ (cm$^2$/V.s)</th>
<th>$v_d \times 10^{-2}$ (cm/s)</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure</td>
<td>2.85</td>
<td>174.25</td>
<td>108.9</td>
<td>0.1636</td>
<td>1.635</td>
<td>n</td>
</tr>
<tr>
<td>1%</td>
<td>3.25</td>
<td>130.56</td>
<td>81.60</td>
<td>0.2489</td>
<td>2.489</td>
<td>n</td>
</tr>
<tr>
<td>2%</td>
<td>3.616</td>
<td>71.30</td>
<td>44.56</td>
<td>0.5071</td>
<td>5.071</td>
<td>n</td>
</tr>
</tbody>
</table>
For applications as transparent contacts, the films must have a low resistivity and a low absorption coefficient in the visible region. A way for evaluating this compromise is by means of the figure of merit (FOM), defined as:

$$\text{FOM} = \frac{1}{\alpha \rho}$$  \hspace{1cm} (5)

where $\alpha$ and $\rho$ are the visible absorption coefficient and the electrical resistivity, respectively. As the visible absorption coefficients of all the films were similar, the figure of merit was strongly dependent on electrical resistivity. As shown in Fig. 6, the variation of FOM shows the same trend with that of electrical conductivity, due to the variation observed in the electro-optical properties of films. The FOM increases with increasing of Al concentration and the highest figure of merit value was $3.15 \times 10^{-5} \, \Omega^{-1}$, which was obtained for the ZnS:Al (2%) film.

**Fig. 6:** Variation of figure of merit with the dopant concentration.

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CONCLUSION

Thin films of ZnS and ZnS:Al have been fabricated successfully by vacuum evaporation technique on glass substrate. The value of optical energy gap decreases with increasing Al concentration. The amorphosity decreases with increasing Al concentration. The width of tail decreases with increases Al concentration. The refractive index decreases with increasing Al concentration. The behavior of extinction coefficient is nearly similar to the corresponding absorption coefficient. The behavior of $\varepsilon_1$ is similar to refractive index, while $\varepsilon_1$ is mainly depends on the k values. The electrical resistivity and therefore activation energy are observed to be Al concentration dependent.

The Hall effect measurements confirm the n-type nature of ZnS and ZnS:Al thin films. Also the conductivity, Hall mobility, drift velocity and figure of merit increases with increasing Al concentration, whereas, the carrier concentration, decreased with increasing of Al concentration.
REFERENCES


