Effect of the Sulfur Concentration on the Optical Band Gap Energy and Urbach Tail of Spray-Deposited ZnS Films

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**Abstract**

Zinc Sulfide (ZnS) films were deposited through a simple and low cost spray pyrolytic technique by using mixed aqueous solutions of zinc nitrate and thiourea. The structural and optical properties of films were investigated as a function of initial (Zn:S) molar ratio in the precursor solution which varied between (1:1) and (1:3). X-ray diffraction (XRD) analysis revealed that wurtzite Zinc Oxide (ZnO) and cubic ZnS phases formed in the prepared film by the equal molar ratio of zinc to sulfur ions and only single cubic ZnS phase was appeared by increasing sulfur content in the precursor solution. The transmittance spectra was measured by UV-Vis spectrophotometer indicated that by increasing the sulfur content, the transmittance of the films increased in the visible and near-infrared regions about 50% and the absorption edges shifted to the shorter wavelengths. As a result, the band gap energy (E_g) increased from 3.43 to 3.72 eV and the band tail width (E_u) decreased from 553 to 259 meV due to the phase composition and the decrement of structural defects. By extracting a linear relevance between the band gap energy and width of the band tail of ZnS, the optical band gap was estimated to be 3.977 eV at E_u ≈ 0.

**1. INTRODUCTION**

Many research efforts have been pointed to the film deposition techniques and different types of materials that can often induce dramatic changes in the optical and electrical properties for using in various modern technologies of solid-state devices [1-3]. As a prominent functional II–VI compound semiconductor with a wide band gap (≈ 3.7 eV) [4], zinc sulfide (ZnS) has witnessed an explosion of interest over the last decade because of advances in controlled synthesis and unrivaled optical properties [5]. Under ambient conditions, ZnS crystallizes in two forms; zinc blend (cubic phase) and wurtzite (hexagonal phase) which have wide and direct band gaps about 3.54–3.6 and 3.74–3.87 (eV), respectively. Thus the wurtzite ZnS has large potential applications in electronics and optoelectronics. The cubic phase is stable at room temperature whereas the hexagonal phase is stable above 1020 °C at atmospheric pressure and metastable as a macroscopic phase. Also, ZnS possesses significantly large exciton binding energy (approximately 40 MeV) compared to the low thermal energy (25 MeV at 273 K) that can be utilized for designing efficient room temperature exciton devices [6-9]. ZnS, in both bulk and film forms, is receiving ever increasing attention due to its broad spectrum of diverse application such as in photovoltaic technology [10], electroluminescence devices [11] and photocatalysts [12] for a long time. In the optics area, ZnS can be used as an environmentally benign buffer layer for thin film solar cells, antireflective coating material in photovoltaic devices [13] and a dielectric filter due to its high transmittance in the visible range. In optoelectronics, it can be used as a light emitting diode in the blue to ultraviolet spectral region due to its direct wide band gap at room temperature [14, 15]. During the past decades, production of controlled and cost-effective materials is the key to employ them in practical applications. There are several advanced techniques for preparing ZnS films with unprecedented properties, such as chemical bath deposition (CBD) [16], thermal evaporation [17], radio frequency reactive sputtering [18], atomic layer deposition (ALD) [19], molecular beam epitaxy (MBE) [20], pulsed laser deposition (PLD) [21] and metal organic chemical vapor deposition (MOCVD) [22]. However, most of these techniques require vacuum conditions, precision instruments and also are not affordable. The technique

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of chemical spray pyrolysis is considered as a cheap technique to produce large area films. Many studies have been done over about three decades on spray pyrolysis processing and preparation of films since the pioneering work by Chamberlin and Skarman on cadmium sulfide (CdS) films for solar cells [23]. Therefore, due to the simplicity, ambient operating environment, relatively low cost and good productivity of this technique on a large scale, it offered a most attractive way for the formation of films of noble metals, metal oxides, spinel oxides, chalcogenides and superconducting compounds [13, 24]. As well as it has been successfully applied in preparing functional materials such as ZnO [25], MgO [26], SnO₂ [21] and MnIn₅S₄ [27] etc. Up to now, ZnS films deposited by spray pyrolysis have been investigated via several groups [28-32]. Primary studies on ZnS films by spray pyrolytic technique were performed by using ZnCl₂ and thiocarbamide (Tu) at fixed (Zn:S) molar ratio of (1:1) [2, 23, 33, 34]. Later, studies on the spray-deposited ZnS films prepared at different molar ratios of (Zn:S) in spray solution were appeared. They were introduced [29-32] that films grown from solution with same molar ratio of (Zn:S)= (1:1) had a cubic structure and band gap (Eg) values were 3.3–3.5 (eV). López et al. had considered that the zinc to sulfur molar ratio in the films grown at 500 °C increased from 0.8 to 0.92 varying the (Zn:S) in solution from (1:1) to (1:6) [30]. According to the Poornima et al. the ZnS films prepared at 450 °C were not well crystallized and ZnO phase was detected in the films grown from (1:0.5) and (1:1) solutions [32]. The researches on the ZnS films properties and formation, dependent on the molar ratio of precursors in solution at different deposition temperatures, remains still an important issue. So in this present research we have done a systematic study on the effect of the precursor’s molar ratio on the structural and optical properties of sprayed ZnS layers deposited at a fixed temperature, 400 °C, without any capping agent for producing the films. It is expected that increasing sulfur content in the precursor solution causes a remarkable change on phase composition, structural defects, band gap energy and Urbach tails of ZnS films. To our best knowledge this is the first report considering Urbach tails in absorption spectra of ZnS films under affected of sulfur concentration.

2. MATERIALS AND METHODS

2.1. Materials and specimens preparation

Analytically pure zinc nitrate (Zn(NO₃)₂.4H₂O) and thiourea (SC(NH₂)₂) were used directly as received from Merck. All the chemicals were of analytical reagents grade and used as received without further purification. Deionized water was used throughout the process as a reaction medium in all the synthesis steps for dilution and sample preparation. The substrates used in this work were commercial soda-lime glass slides that were cleaned ultrasonically in ethanol for 10 min then washed with deionized water and finally dried.

2.2. Preparation of ZnS films

A home-made spray pyrolysis set-up had been used to prepare ZnS films. With spray pyrolysis, the solution was sprayed directly onto the clean substrates. A stream of gas (compressed air) was used for atomization of the solution through the nozzle. To preparing the precursor solutions, zinc nitrate and thiourea in three different molar ratio (Zn:S) of (1:1), (1:2) and (1:3) were dissolved in deionized water. Such solutions were used for the spray pyrolysis onto the pre-heated glass substrate maintained at 400 °C. The gas pressure and aqueous solution flow rate were kept constant at 3.5 bars and 4 ml.min⁻¹, respectively. Also, the nozzle to substrate distance was 25 cm. During spray pyrolysis process, when precursor solution droplets arrived close to the preheated substrates, the droplets decomposed thermally, which resulted into the forming a highly adherent ZnS film. No post-deposition annealing was given to these films and all the characteristics were studied in as-deposited samples. The different pyrolytic process parameters in film deposition are listed in Table 1. The schematic of the spray pyrolysis set-up applied in this study is presented in Fig. 1.

![Figure 1. The schematic of the spray pyrolysis set-up](image)

### TABLE 1. Process parameters for the spray deposition of the films

<table>
<thead>
<tr>
<th>Spray parameters</th>
<th>Optimum value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Substrate</td>
<td>Glass</td>
</tr>
<tr>
<td>Nozzle–substrate distance</td>
<td>25 (cm)</td>
</tr>
<tr>
<td>Zinc nitrate solution</td>
<td>Deionized water</td>
</tr>
<tr>
<td>concentration</td>
<td>0.5 M</td>
</tr>
<tr>
<td>Solvent</td>
<td>Compressed air</td>
</tr>
<tr>
<td>Solution flow rate</td>
<td>4 ml.min⁻¹</td>
</tr>
<tr>
<td>Carrier gas</td>
<td>400 °C</td>
</tr>
<tr>
<td>Substrate temperature</td>
<td></td>
</tr>
</tbody>
</table>
2.3. Characterization of films
The crystalline structure of the films was confirmed by using high-resolution X-ray diffraction (XRD) with Cu Kα radiation (Kα = 1.54056 Å) (X’Pert PRO MPD, PANalytical, Netherlands) and the scanning angle 2θ was varied ranging 10° to 90°. Surfaces and cross-section morphologies of the films were observed by a field emission scanning electron microscope (FE-SEM, MIRA3, TESCAN, Czech). The chemical compositions of sprayed films were examined on the surface of the deposited films by using an energy dispersive spectrometer (EDS, OXFORD) equipped to the SEM. Optical absorbance spectrum was recorded by using UV–Vis spectrophotometer (Lambda25, Perkin Elmer, US) in the wavelength range of 300-1100 nm. All the measurements were performed at the room temperature.

3. RESULT AND DISCUSSION
3.1. Micro-structural and compositional properties
The effects of the molar ratio of sulfur to zinc ions on the crystallinity of the obtained films were studied by XRD. Fig. 2 shows XRD patterns of ZnS films prepared with diverse molar ratios of sulfur to zinc. The same amounts of the solution were used to deposit films with thicknesses of about 600 nm. The films grown from solutions with the molar ratio of (Zn:S)= (1:1) and (1:2) demonstrate poor crystallinity and contain zinc oxide (ZnO) as a secondary phase. The observed diffraction peaks at 31.9°, 34.5° and 36.4° match well with the wurtzite phase of ZnO crystal (JCPDS card No. 01-079-0205) for their intensity and peak position. For all the patterns, the results exhibit broad diffraction peak at the 2θ position of 29.5° related to the (111) refraction of the ZnS cubic phase. The peak has been indexed with the JCPDS card No. 01-079-0043. As obvious, increasing the amount of sulfur in ZnS lattice during deposition caused to increase the intensity of (111) peak and the observed peaks related to the ZnO phase slightly disappear. So, films produced from solution with the molar ratio of (Zn:S)= (1:3) introduced the single cubic phase of ZnS. As well as increasing the sulfur content in the structure draws on improving the crystallinity of the films. It is considered that diffraction peaks are significantly broadened essentially due to extremely small crystallite size. The mentioned findings prove that sufficient sulfur concentration is necessary for forming single phase of ZnS in spray pyrolysis process from aqueous solutions of zinc nitrate and thiourea complexes without using any capping agent. The observed results are in accordance with the data published earlier [29, 35-37].

SEM micrographs are indicated in Fig. 3 (a-b) for investigating the morphology and elemental composition of deposited ZnS film at 400 °C using Sulfur-rich solution.

Figure 2. X-Ray diffraction patterns of ZnS films deposited at 400 °C with various molar ratios of (Zn: S)= (1:1), (1:2) and (1:3).

Figure 3. (a) SEM image and (b) Typical EDS spectra of deposited ZnS film at 400 °C with a molar ratio of (Zn: S)= (1:3)

Fig. 3a reveals uniform surface and dense structure. As well as ZnS film consists of smaller grains with the size about 4-5 nm. According to EDS analysis in Fig. 3b, the film contains low amount of oxygen due to the conditions of spray pyrolysis process. The flat area of film contains Zn and S that were found in a near-stoichiometric ratio with little sulfur deficiency. So S2− /Zn2+ atomic ratio is 0.97 in the film deposited at 400
°C. It could be concluded that ZnS film from (1:3) solution has only cubic ZnS phase as shown in Fig. 2. EDS results are in accordance with that recorded by XRD as the film from S-rich solution contain crystalline cubic phase of ZnS.

### 3.2. Optical studies

The optical properties of ZnS films prepared by spray pyrolysis technique depend on the chemical composition of the precursor. Usually, an improved stoichiometry of precursor results in preparing of films with better optical transmission.

Fig. 5 shows the transmittance spectra against wavelength ranging from 300 to 1100 nm of sprayed ZnS films with different molar ratio of zinc to sulfur ions. It can be observed that transmittance of the films prepared from both solutions contained (1:1) and (1:2) of zinc to sulfur ions molar ratio have lower values varied from 15% to 35% in the visible and near-infrared regions. It is appeared due to the composed mixture of the ZnS and ZnO phases in their structure that proved by XRD results. Whereas obtained films from sulfur-rich solution (1:3) possess high specular transmittance around 65% in the visible and near-infrared spectral region, these observations are in good agreement with results found by other researchers [2, 38, 39]. Also from Fig. 5, it can be concluded that all the films have high absorption around the ultra-violent regime (320-360 nm).

Fig. 6 illustrates the relation between the absorption coefficient ($\alpha$) and the photon energy ($h\nu$) of ZnS deposited films at 400 °C with various molar ratios of (Zn: S) = (1:1), (1:2) and (1:3).

For calculating the value of optical band gap energy, the relationship between the absorption coefficient ($\alpha$) and the energy of the incident light ($h\nu$) is given by Tauc equation:

$$ (\alpha h\nu)^{1/n} = \alpha_0 (h\nu - E_g) $$

Where, $E_g$ is the optical band gap energy, $\alpha_0$ is the edge width parameter and $n$ is equal to 2 for the direct band gap semiconductors, such as ZnS. The direct optical band gap values of the ZnS films have been estimated by plotting a graph between $(\alpha h\nu)^2$ versus $h\nu$ shown in Fig. 7. The band gap energy has been evaluated by extrapolating the straight line portion of the graph to the $h\nu$ axis (maximum transmission, i.e. $\alpha = 0$). The
estimated values of the optical band gap energy of the films are listed in Table 2. Apparently, the calculated band gap values for preparing films from both (Zn:S) molar ratios of (1:1) and (1:2) have minimum values. Also, obtained band gap energies for both solutions are lower than the bulk crystal (E_g = 3.65 eV); which can be ascribed to the sulfur deficiency [40]. This result can be associated with the presence of zinc oxide (as proved by XRD profiles) in which an energy gap is very close to the ZnS (E_g = 3.24 eV) [41]. The general trend of the band gaps for ZnS deposited films from solutions with different molar ratio increase as sulfur content of the solution increased.

As realized from Fig. 7, the band gap energy of the obtained film from solution with the excess amount of the sulfur is approximately equal to the band gap energy of the ZnS cubic phase which obtained in XRD analysis. The increment in the transmittance and band gap energy with increasing sulfur concentration is possible due to the changing of phase morphology, the improving of crystallinity and stoichiometry of the films. It is important to mention that the effect of thickness on the transmittance of the films is less important than the effect of chemical composition (as summarized in Table 2).

TABLE 2. The values of the optical band gap energy (E_g) and the band tail width (E_u) of ZnS deposited films at 400 °C with various molar ratios of (Zn:S)=(1:1), (1:2) and (1:3)

<table>
<thead>
<tr>
<th>molar ratio of (Zn:S)</th>
<th>Thickness (nm)</th>
<th>Wavelength of absorption edge (nm)</th>
<th>E_g (eV)</th>
<th>E_u (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1:1)</td>
<td>615</td>
<td>360</td>
<td>3.43</td>
<td>553</td>
</tr>
<tr>
<td>(1:2)</td>
<td>628</td>
<td>343</td>
<td>3.59</td>
<td>396</td>
</tr>
<tr>
<td>(1:3)</td>
<td>636</td>
<td>332</td>
<td>3.72</td>
<td>259</td>
</tr>
</tbody>
</table>

In the semiconductors and insulators, the spectral dependence of the absorption edge on the low photon energy range follows the empirical Urbach rule given by:

\[ \alpha = \alpha_0 \exp \left( \frac{h\nu}{E_u} \right) \]

(3)

Where \( \alpha_0 \) is a constant, \( E_u \) is often interpreted as the width of the tail of localized states in the band gap. The exact cause of the Urbach exponential tails has phonons, impurities, excitons and structural disorders in the materials [42-44]. In the near absorption edge, the variation of \( \ln \alpha \) against the photon energy is induced in Fig. 8 for ZnS obtained films in various molar ratios of zinc to sulfur. The width of Urbach tail (E_u) for all the films was computed from the reciprocal gradient of the straight line and presented in Table 2. It is considered that increasing of sulfur content in ZnS lattice draws on decreasing E_u values. The behavior of E_u can be attributed to the decreasing disordered atoms and defects in the structural bonding and improving the structural crystallinity along that increasing amount of sulfur in deposited films. The disorder and defects can introduce localized states at or near the conduction band level leading to increasing the Urbach energy [45].

Figure 7. The variation of (αhν)^2 as a function of photon energy (hν) for determining of the optical band gap energy for ZnS deposited films at 400 °C with various molar ratios of (Zn: S)=(1:1), (1:2) and (1:3)

Figure 8. The variation of ln \( \alpha \) against the photon energy (hν) of ZnS deposited films at 400 °C with various molar ratios of (Zn: S)=(1:1), (1:2) and (1:3).

Furthermore, to study of the Urbach tail of the films, the relationship between the band gap energy and the width of Urbach tail was investigated for the first time in the case of ZnS films with diverse molar ratio of the zinc to sulfur. According to the Fig. 8, it can be confirmed that the Urbach tail decreases as the optical band gap increases. Also, there is a linear correlation between band gap and Urbach tail, therefor a linear fit was extracted. The experimental equation from this linear fitting is presented as:

\[ E_g = 3.977 - 0.987 E_u \]

(4)
The average value of the constant parameter ($\alpha_0$) of equation 3 can be evaluated from the linear fitting of Fig. 9. As well as the equation introduce the band gap energy in the absence of band tailing which in the case of the ZnS films, optical band gap ($E_g$) is equal to 3.977 (eV) at $E_u=0$. Such a linear relation between band gap energy and the Urbach tail was found for other semiconductors [43, 46, 47].

**Figure 9.** The relationship between the band gap energy ($E_g$) and the width of Urbach tail ($E_u$) of ZnS deposited films at 400 °C with various molar ratios of (Zn: S)= (1:1), (1:2) and (1:3)

4. CONCLUSION

In summary, a low-cost, continuous, easy-controllable spray pyrolysis method has been used to deposit ZnS films. A systematic study on the impact of main spray pyrolysis technological parameter such as molar ratio (Zn:S) of precursor, (1:1), (1:2) and (1:3), at the fixed substrate temperature about 400 °C, on structural and optical properties of ZnS films was presented. Relatively good crystallinity and ZnS cubic single phase in sulfur-rich solution was obtained at spray rate of 4 ml min⁻¹. The band gap energy was computed through the absorption coefficient and found that by increasing sulfur concentration up to three times of zinc content in the ZnS lattice, the transmittance and values of the band gap energy slightly increased due to improving of crystallinity and producing the single ZnS cubic phase. From the plot of the natural logarithm of the absorption coefficient against the incident photon energy, it was observed that this tailing confirms Urbach rule. The width of the tail decreased by increasing sulfur content because of the reduction of impurities and disorders. Finally, a linear dependence between the band gap energy and the width of Urbach tail was appreciated for the first time in the case of ZnS deposited films in different molar ratios of zinc to sulfur.

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