Effect of Deposition Temperature on Structural and Optical Properties of Chemically Sprayed ZnS Thin Films

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Abstract

Zinc sulfide (ZnS) thin films have been successfully deposited via spray pyrolysis using an aqueous solution of thiourea and zinc acetate onto glass substrate. The effect of varying substrate temperature (150, 200, 250 and 300°C) on structure and optical properties is presented. The films have been characterized by X-ray diffraction (XRD), UV-Vis-NIR spectrometry, photoluminescence (PL) spectroscopy and field emission scanning electron microscopy (FESEM). All the deposited ZnS films exhibit a cubic structure, while crystallinity and morphology are found to depend on spray temperature. PL analysis indicates the presence of violet and green emissions arising from Zn and S vacancies. The value of bandgap of ZnS films is found to decrease slightly with increasing substrate temperature; varying in the range 3.52–3.25eV, most probably associated with the formation of Zn(S,O) solid solution.

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1. Introduction

The exceptional and unique characteristics of Zinc sulfide (ZnS) make it among the most interesting semiconducting materials, in particular its nontoxicity and its high bandgap (~3.7 ev)\(^1\). Therefore, it has been considered as potential candidate in the fabrication of electronic devices, such as light-emitting diodes (LEDs)\(^2\), field-effect transistors (FET)\(^3\), gas sensors\(^4\), thermal sensors\(^5\), biosensors\(^6\), and solar cells\(^7\). Several methods have been proposed for the preparation of ZnS films, including pulsed laser deposition \(^8\), chemical vapor deposition\(^9\), atomic layer deposition (ALD), molecular beam epitaxy (MBE)\(^10\), chemical bath deposition (CBD)\(^11\), etc.

However, the above methods differ significantly in terms of film’s quality and cost, which are considered the most important criteria for the fabrication of any devices. In addition, some synthesis methods require high cost and complex apparatus. In this regard, the aim of this research work consists on adopting an approach for the preparation of ZnS films at relatively low cost and using simple/easy operating apparatus, while exhibiting high film’s quality. Therefore, spray pyrolysis has been identified as a very promising technique that has been successfully used for the deposition of ZnS films and other related materials.

This research paper is devoted to the synthesis of ZnS films by using spray pyrolysis, because of its simplicity and cost-effectiveness. In addition, the films are expected to have a better homogeneity, high crystallinity without further annealing after deposition and coverage of a relatively large area of the substrate. The study consists on investigating the effect of varying substrate temperature at relatively low range (150-300°C) on phase stability, crystallinity, surface morphology and topography as well as optical properties.

| Nomenclature | Definition |
|--------------|------------|
| ZnS | Zinc sulphide |
| XRD | X-ray diffraction |
| EDX | Electron dispersive x-ray spectrometer |
| PL | Photoluminescence spectroscopy |
| FESEM | Field emission scanning electron microscopy |

2. Experimental Part

During chemical spray pyrolysis, the solution was sprayed onto a hot glass substrate (prior to deposition, the substrates were subjected to cleaning). In this work, zinc acetate dehydrate (Zn(CH\(_3\)COOH)\(_2\).2H\(_2\)O) and thiourea (CH\(_4\)N\(_2\)S) (R & M Chemical) precursors were used as source for Zn\(^{2+}\) and S\(^{-2}\) ions, respectively while deionized water was used as a solvent. The molar ratio Zn:S was fixed 1:1. The solution was sprayed with a steel needle at a spray rate of 4ml/min on to the glass substrate and the air was used as a carrier gas at a pressure of 3 bars. The substrate temperature was varied from 150 up to 300°C using electronic temperature controller.

The crystal structure of ZnS thin films was characterized by X-ray diffraction (XRD) using X-ray Philips X-Pert diffractometer equipped with Cu-K\(_{\alpha}\) radiation source (\(\lambda_{Cu}=1.5418\) Å). Surface morphology of the deposited films were observed by field emission scanning electron microscopy (FESEM) using FEI Nova Nano SEM 450. The chemical composition (Zn/S ratio) was checked by electron dispersive spectroscopy (EDS). Optical properties were determined by recording absorbance spectra using Shimadzu UV-Vis 1800 double-beam UV-VIS spectrophotometer and photoluminescence spectroscopy using JobinYvon HR 800 UV equipped with He-Cd laser at325 nm excitation source.
3. Results and Discussion

3.1 Structural Analysis

Figure 1 shows the evolution of XRD patterns of ZnS films deposited at various (150, 200, 250 and 300°C) substrate temperature. Only single well-defined intense peak can be detected around 2θ=29°, which can indexed as (111) reflection of the cubic (zinc blende) ZnS phase, in agreement with JCPDS card No. 01-080-0020. No major changes can be easily observed with varying substrate temperature, except slight change in peak (111) position (the values lattice parameter are reported in Table 1) and broadening (usually associated with crystallite size and microstrain). However, it can be concluded that the as-grown ZnS films show a strong preferred orientation along (111) direction. The average crystallite size (D) is calculated from Scherer formula:

\[ D = \frac{0.9 \lambda}{\beta \cos \theta} \]  

(1)

Where, \( \lambda \) is the wavelength of X-ray radiation used, \( \theta \) is the Bragg angle and \( \beta \) is the full-width at half-maximum (FWHM) measured in radian. The average crystallite size (Table 1) is found to increase slightly with increasing substrate temperature, i.e. 13.8-16.6 nm with varying substrate temperature in the range 150-300°C. The increase in reaction temperature (substrate temperature) results in grain growth thereby an increase in crystallite size. The lattice parameter (a) of cubic zinc blend type structure can be calculated by the following formula:

\[ \frac{1}{d_{hkl}^2} = \frac{h^2 + k^2 + l^2}{a^2} \]  

(2)

Where \( d_{hkl} \) is the inter planar spacing (distance) corresponding to Miller indices h, k, and l. The calculated lattice parameter (Table 1) is found to slightly decrease with increasing substrate temperature, i.e. 0.53286-0.53364 nm for150-300°C. This can be attributed to better chemical homogeneity (stoichiometry) all over the deposited ZnS films as well as to the possible dissolution of some O within ZnS lattice by occupying S sites (O\(^2\) has lower ionic radius than that of S\(^2\): 0.140 and 0.184 nm). The microstrain (\( \varepsilon \)) attributed to the mismatch between the lattice parameter of the deposited film and the substrate, can be estimated by the following simple equation:

\[ \varepsilon = \frac{a - a_0}{a_0} \]  

(3)

Where \( a_0 \) represents the value of lattice parameter of unstrained ZnS and a the value of lattice parameter of
strained ZnS. It can be seen that the value of microstrain (Table 1) increases with increasing substrate temperature; i.e. -0.15 to -0.31% for 150-300°C. With increasing substrate temperature, ZnS film adheres much more to the glass substrate and due to the lattice mismatch, as reported earlier, this will induce some lattice strain within ZnS film.

Table 1. Structural (lattice parameter) and microstructural parameters (crystallite size and microstrain) obtained from X-ray diffraction patterns of ZnS thin films deposited at different substrate temperatures.

| Sample | T °C | 2θ (deg) | D(nm) | a (nm) | \(\varepsilon = \frac{a - a_0}{a_0}\) |
|--------|------|----------|-------|--------|----------------------------------|
| 1      | 300  | 29.0250  | 16.6  | 5.3286 | -0.31%                           |
| 2      | 250  | 29.0241  | 14.2  | 5.3290 | -0.30%                           |
| 3      | 300  | 29.0059  | 13.9  | 5.3300 | -0.24%                           |
| 4      | 150  | 28.9823  | 13.8  | 5.3364 | -0.15%                           |

3.2. UV-vis Absorption Analysis

![Fig. 2.](image)

Fig. 2. UV-Vis absorption spectra of ZnS synthesis at different substrate temperatures (a) 150°C; (b) 200°C; (c) 250°C and (d) 300°C.

![Fig. 3.](image)

Fig. 3. Tauc plot of ZnS deposited at different substrate temperatures (a) 150°C; (b) 200°C; (c) 250°C and (d) 300°C.

The optical absorption of the deposited ZnS films is shown in Figure2. The ZnS film deposited at 150°C exhibited the minimum absorption, which increases with increasing substrate temperature up to 300°C. This might be associated with better crystallinity and larger grains (increase in crystallite size). Tauc’s relation (4) was applied to determine the bandgap (E_g) of the as-deposited ZnS films. The value of m is taken as \(\frac{1}{2}\), because ZnS is a direct band gap material as mentioned by many researchers 13:
\[ a\hslash \nu = A(h\nu - E_g)^m \] (4)

Where \( A \) is a constant which is different for different material, \( \alpha \) is the absorption coefficient, \( \hslash \nu \) is the energy of incident photon, and the exponent \( m \) indicates the type of transition. The energy bandgap is determined by extrapolating the linear region of the curve toward X-axis (\( h\nu \)), \( E_g \) represents then the intercept, as shown in Figure 3. It can be seen that the value of bandgap energy \( E_g \) decreases with increasing substrate temperature; 3.52 eV for 150°C compared to 3.25 for 300°C, see Table 2.

| Substrate temperature (°C) | 150  | 200  | 250  | 300  |
|----------------------------|------|------|------|------|
| Band gap(eV)               | 3.52 | 3.50 | 3.45 | 3.25 |

These results are very consistent with some previous studies; the reported energy gap was found around 3.5 eV\(^{14}\). The reason for the observed inverse relationship between the value of energy gap and the deposition temperature, can be explained as follows: the higher the temperature of the substrate, the more likely that the deposited ZnS film interacts with oxygen (from substrate material, glass) resulting in the formation of Zn(S,O) solution (O will dissolve into ZnS host lattice). This will lead to a reduction in the bandgap energy to lower values; the bandgap energy of ZnO is around 3.2 eV\(^ {15}\).

### 3.3 Photoluminescence Study

Fig. 4. Photoluminescence measurements for a film deposited at different substrate temperatures (a) 150°C; (b) 200°C; (c) 250°C and (d) 300°C.

Figure 4 shows the photoluminescence (PL) spectra of ZnS films grown at different substrate temperatures. Two main broad peaks can be observed at 418 and 514 nm, in good agreement with some previous studies reported in literature. Kumar et al. observed similar PL properties with an intense peak located at 412 nm ascribed to the optical activation of S vacancies while the peak centred at 518 nm was considered to be caused by Zn vacancies\(^ {10}\). Also, it can be noticed that there is a direct correlation between the intensity of emission and temperature of the substrate, which is most probably due to a better homogeneity of the chemical composition over the entire film, improved crystallinity and less defects.
3.4. Morphological Observations

Figure 5 shows the evolution of surface topography of ZnS films grown onto glass substrate at different temperatures. It can be clearly observed that the surface of the films looks smooth covering the entire substrate. In addition, the formed particles are homogeneously distributed and within the nanoscale regime, but the average size of particles seem to increase with increasing substrate temperature, indicating that the crystallization (grain growth) process occurs.

Figure 6. Zn and S atomic ratio of ZnS films as function of deposition temperature (a) 150°C, (b) 200°C, (c) 250°C and (d) 300°C.
Figure 6 illustrates the ratio Zn/S of ZnS films at different substrate temperatures. It can be seen that Zn/S ratio varies with substrate temperature; the sulfur (S) content decreases with increasing temperature. This can be explained, as previously reported, by the inverse relationship between the amount of sulfur and the deposition temperature: the higher the temperature the more likely ZnS film interacts with oxygen (from substrate) forming Zn(S,O), O will replace S hence its content is reduced.

4. Conclusion

ZnS thin films were successfully grown by chemical spray pyrolysis technique onto glass substrate at different substrate temperature (150-300°C). X-ray diffraction analysis confirms the formation of single ZnS phase with strong preferred orientation along (111) plane. Both crystallite size and microstrain increase with temperature; i.e. 13.8-16.6 nm and 0.15-0.31%. From PL study, it emerged that Zn and S vacancies are formed. Based on UV-visible spectra, the energy gap decreases with temperature (3.52-625 eV), associated with the possible formation of Zn(S,O) solid solution and point defects. EDS analysis reveals a reduction in S content, confirming the formation of Zn(S,O) solid solution.

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