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CHEMICAL SPRAY PYROLYSIS SYNTHESIS OF ZINC SULPHIDE (ZnS) THIN FILMS VIA DOUBLE SOURCE PRECURSORS

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We synthesized ZnS thin films by chemical spray pyrolysis method (CSPM) from a double-source precursor at temperatures of 300, 350, 400, and 450^{o}C. Studies on optical, structural and morphological properties were performed on the samples using UV-VIS spectrophotometer (UVS), X-ray diffraction (XRD), and scanning election microscope (SEM). XRD showed that the film is cubic and polycrystalline in nature with preferential orientation along (111) plane. The optical studies revealed energy band gaps of 3.90, 3.80, 3.70 and 3.60 eV for various temperatures 300, 350, 400 and 450^{o}C respectively.

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1. Introduction

Zinc sulphide (ZnS) is chalcogenide II-VI semiconductor material with wide direct bandgap [1, 2]. Among other chalcogenide semicinductors it has the highest bandgap of 3.70 eV at 300 K. These semiconductors (PbS, ZnS, CdS, CuS, Bi_2S_3) have attracted the attention of researchers in the recent times due to their special properties and potential uses in photovoltaics and opto-electronic devices [1-12]. ZnS can be used as an antireflection coating (n-window layers) in heterojuction in solar cells as the wide bandgap decreases the absorption losses and increases the short circuit current of the cell[1], a more environmental friendly option than CdS buffer layer [5], reflector in optics due to its high index of refraction (2.35) [1], in opto-electronics devices as electrolumescent display and light-emitting diodes (LED) in the blue to ultraviolet spectral region due to its wide band gap of 3.70 eV at 300 K[4,12], dielectric filter due to its high transmittance in the visible region [4]. ZnS has been prepared by various techniques such as chemical spray pyrolysis (CSP) [1], chemical bath method (CBD) [4,5], co-precipitation method (CPM) [6], chemical spray method (CSM) [7, 8], have been used to synthesize quality ZnS thin films [8], closed-space vacuum sublimation (CSVS) [9], resistive heating (RHT) [10], wet chemical method (WCM) [11] , vacuum evaporation technique (VET) [12]. Chemical spray pyrolysis techniques is very interesting method of depositing ZnS thin films due to the fact that it simple, convenient, cost effective, capable of producing uniform and homogeneous films that can produced to industrial scale [12].

In this work we report the influence of substrate temperatures on the optical and structural properties of ZnS thin films via doubl-source ($ZnCl_2$ and SC(NH2)2) precursors for applications in photovltaics and optoelctronics.

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2. Materials and Methods

The chemical precursors procured were of analytical grade and were used without further purification. The ZnS thin film were synthesized via 0.3M, 0.4M double-source precursors of zinc chloride and thiourea ($ZnCl_2$ & SC(NH2)2) which was sprayed directly in the ambient to the prepared substrates heated to temperatures of 300, 350, 400, and 450^{o}C, at the pressure of 4 bars, spray distance of 20 cm and time of 10 minutes. The deposited films were left in heating chamber for 10 minutes to react, then removed and dried in air. The suggested reaction is as follows:

$$ZnCl_2(aq) + SC(NH_2)_2(aq) + H_2O \rightarrow ZnS(S) + 2NH_3(g) + CO_2 \uparrow \quad (1)$$

The as deposited films were characterized for optical, structural and surface morphological properties using UV-VIS Spectrophotometery, X-Ray Diffraction using CuK$_\alpha$ irradiation ($\lambda = 1.518\overset{o}{A}$) and Scanning Electron Microscopy respectively.

3. Results and discussions

Fig.1 shows the diffraction patterns of polycrystalline ZnS films deposited at a 0.3M precursor concentration at substrate temperatures 400 and 450^{o}C. ZnS is cubic and polycrystalline in nature with (002) preferred orientation. The crystallite size (D) was estimated from the full width at half maximum (FWHM) of the X-ray diffraction line using Debye-Scherrer's formular [6]:

$$D = \frac{k\lambda}{\beta \cos\theta} \quad (2)$$

where β is the observed angular width at half maximum intensity, k is the dimensionless number which is 0.89, λ is the wavelength of X-ray radiation used (0.15406 nm for CuKα) and θ is the diffraction angle.

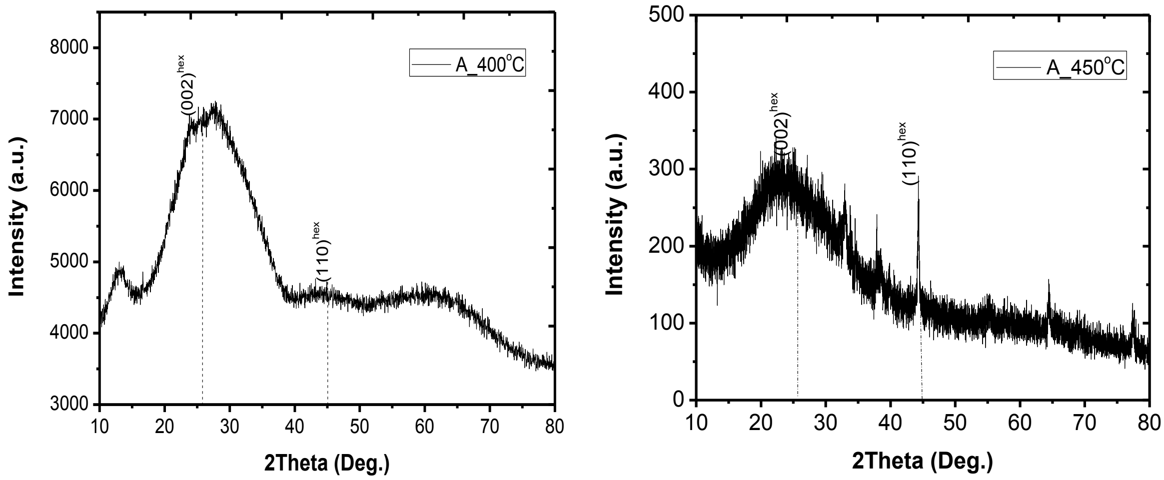

Fig. 1. The X-ray diffraction of ZnS thin films using precursor solution of 0.3M concentration at various substrate temperatures 400^{o}C and 450^{o}C respectively.

The optical band gap of the thin films was estimated using the Tauc Relation for direct band gap materials, which is given by:

$$\alpha h\upsilon = A(h\upsilon - Eg)^{\frac{1}{2}} \qquad (3)$$

where hυ, is the photon energy, Eg, the optical band gap and A is a constant.

From Fig. 2 (A, B), the direct E_g^d band gap for ZnS film estimated were found to lie in the range 3.50 – 4.25eV for different precursor concentrations (0.3, 0.4M). It was observed that the bandgap increased slightly with higher concentration of precursors. Also increase in substrate temperatures shifted the bandgap slightly higher.

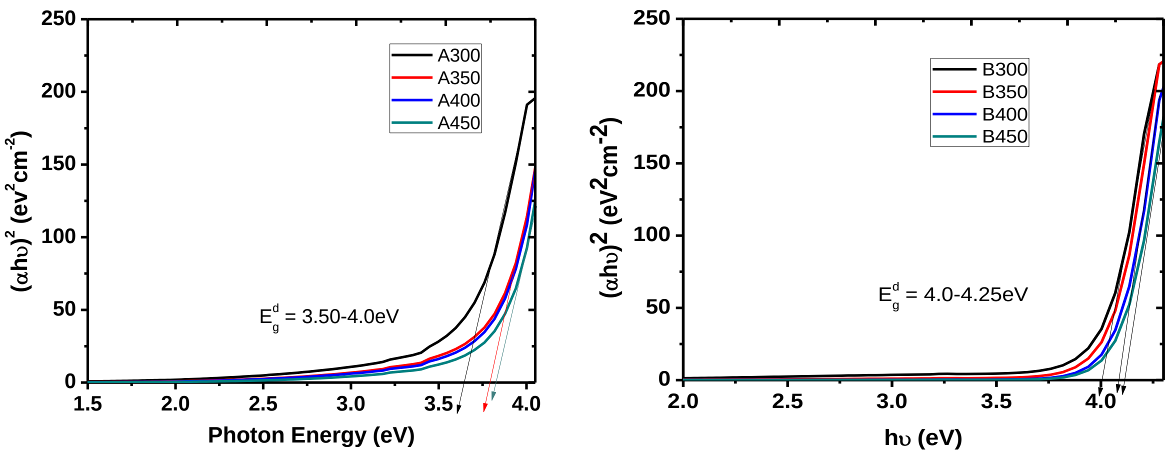

Fig. 2. Plot of $(\alpha h\upsilon)^2$ versus photon energy, hυ using precursor solution (A) 0.3M concentration (b) 0.4M, at 300, 350, 400, 450°C.

Fig. 3 (A, B, C, D) shows the SEM micrograph of the ZnS films prepared with a 0.3M precursor concentration at substrate temperatures (A) 300°C (B) 350°C (C) 400°C (D) 450°C. The films were dense, homogenous and polycrystalline.

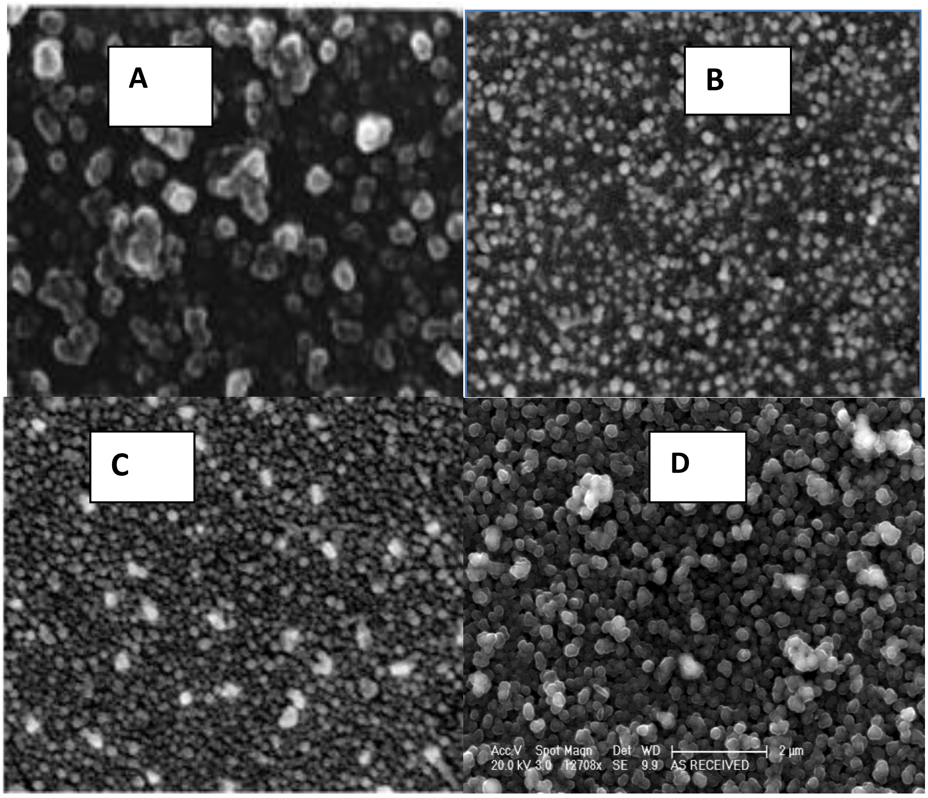

Fig. 3. SEM micrograph of as-deposited ZnS thin films at substrate temperatures (A) 300°C (B) 350°C (C) 400°C (D) 450°C

The films appear to be dense and composed of largely irregular shaped grains of diameter in the range of 300–500 nm. Fig 3 also shows that the films deposited at a substrate temperature of 450°C and 400°C are well adherent and more homogeneous with very little or no pores, but films deposited with a substrate temperature of 350°C and 300°C are less homogeneous and less adherent with more pores.

4. Conclusions

Chemical spray pyrolysis method (CSPM) was used successfully to synthesize ZnS thin films from a double-source precursor at substrate temperatures of 300, 350, 400, and 450°C. Studies on optical, structural and morphological properties were performed on the samples using UV-VIS spectrophotometer (UVS), X-ray diffraction (XRD), and sanning election microscope (SEM). XRD showed that the film is cubic and polycrystalline in nature with preferential orientation along (0023) plane. Optical study shows that the band-gap energy of ZnS thin films ranges 3.5-4.0 eV for 0.3M precursor concentration and 4.0- 4.25 eV precursor 0.4M respectively, showing dependence of bandgap on precursor concentration. The optical studies also revealed band gap dependence on substrate temperatures. The wide energy band gap Eg>3.50 and high transmittance make the ZnS film suitable for solar cell and opto-electronic applications.

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