Synthesis and characterization of ZnS nanostructured thin films using chemical spray pyrolysis

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Abstract - *Zinc Sulfide (ZnS) nanostructured thin films were prepared by spray pyrolysis technique using aqueous of Zinc nitrate and Thiourea at a molar ratio 1:1. The depositions were carried out on substrate temperature at 400^{0}C. The structural, optical, morphological and elemental composition of the deposited films were characterized by X- ray diffraction (XRD), Photoluminescence (PL), UV-visible spectroscopy, Field Emission Scanning Electron Microscope (FESEM) with Energy Dispersive Analysis (EDAX). XRD result showed that the obtained sample had cubic phase with the average crystallite size of 3.84 nm. The surface morphology of the deposited film showed that the particles were in sphere like shape. The optical properties showed that the obtained ZnS nanostructured thin film were having the band gap energy of 3.5 eV and the PL gave the emission in the wavelength range of 350 nm. These results indicate that ZnS material is suitable for optoelectronic device application.*

Key Words: **ZnS, Spray pyrolysis, XRD, FESEM, Optoelectronic application**

1. INTRODUCTION

Zinc sulfide is a semiconducting material with II-VI group compound, having the wide direct band gap energy of 3.65 eV [1]. Also ZnS semiconductor has n-type conductivity and is a promising material for optoelectronic devices, such as solar cells, antireflective coating, electroluminescent displays, optical sensors devices [2-5], UV-light emitting diodes, blue light emitting diode and emission flat screens [6,7].

Various techniques including both physical and chemical methods have been employed to prepare ZnS thin films. The physical methods including thermal evaporation [8], RF sputtering [9], pulsed laser deposition [10], atomic layer deposition [11] and these methods require expensive high vacuum systems for the deposition. The non vacuum based chemical methods are chemical bath deposition [12], spray pyrolysis [13][18], chemical precipitation [14], sol-gel and solvothermal method [15-16]. Among these, spray pyrolysis is the most popular deposition method because simple, low cost, minimal waste product, ability to coat large surface area and easy to include in an industrial production line [17]. The present study report the deposition of ZnS nanostructured thin films have been carried out using chemical spray pyrolysis techniques. The influence of substrate temperature at 400 ˚C on the surface of the deposited film is studied using X-ray diffraction (XRD), field emission scanning electron microscope (FESEM) with energy dispersive spectrometer (EDS), UV- Visible and Photoluminescence (PL) spectroscopy.

2. EXPERIMENTAL DETAILS

2.1 Materials

The chemical reagents were purchased from Merck Company and used without further purification for the preparation of ZnS thin films. Zinc nitrate heptahydrate ($ZnNO_3.7H_2O$) and thiourea ($(SC(NH_2))_2$ were prepared Zinc nitrate, thiourea and deionized water were the materials and solvent respectively.

2.2 Experimental Procedure

Thin films of ZnS were deposited on to the glass substrate using Spray pyrolysis technique. Glass substrates were cleaned by sonication for 15 min each in soap solution followed by dilute HCl and finally with double distilled water. After the cleaning process, the substrates were dried completely in air and placed on the plate to start the deposition process. The precursor solution was prepared using molar concentration 0.1M (0.89247g) of zinc nitrate ($ZnNo_3.7H_2O$) and 0.1M (0.2283g) of thiourea ($(SC(NH_2)_2$) in deionized water. The solution was kept for stirring 30 min to dissolve all the particles completely and to obtain a clear solution. The obtained clear solution was used for the deposition of nanostructured ZnS thin films at a temperature of 400˚C and continuous coating had been taken place. The spray pressure was 1.4 bars and the distance between the spray nozzles to the substrates was around 20-25cm.

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2.3 Characterization Tools

The deposited ZnS thin films were characterized by powder X-ray diffraction (XRD, Rigaku) equipped with a Cu Kα - 1.5406 Å radiation. The surface morphology and chemical composition of the obtained films were determined by field emission scanning electron microscope with energy dispersive spectrometer (M/s FE-SEM with EDS, Carl Zeiss, Germany). To study the optical properties, UV-Visible spectroscopy using Perkin Elmer (Model Lambda 35) and the room temperature Photoluminescence were taken with a Perkin Elmer (Model Lambda 45).

3 RESULTS AND DISCUSSION

3.1 Structural Analysis

The crystal structure and phase formation of the deposited ZnS thin films are analyzed using XRD pattern. Fig. 1 presents the XRD pattern of ZnS thin films deposited at 400˚C. From the pattern it is clear that deposited films are having intense peaks at 2θ =28.42˚, 48.26˚ 56.39˚ that are attributed to the planes of (111), (220) and (311) respectively. These XRD pattern can be perfectly indexed as ZnS having cubic structure with space group of F-43m[216] (JCPDS card 80-0020). The average crystallite size of the deposited film is calculated using the Debye Scherrer formula,

$$D = K\lambda/(\beta\cos\theta) \qquad (1)$$

Where K is the Scherrer constant (K = 0.89), λ denotes the wavelength of used radiation Cu-Kα (λ = 1.5406 Å), β is the full width at half maximum of the diffraction peaks and θ is the Bragg's angle. The average crystallite size of the obtained ZnS film is calculated 3.84 nm.

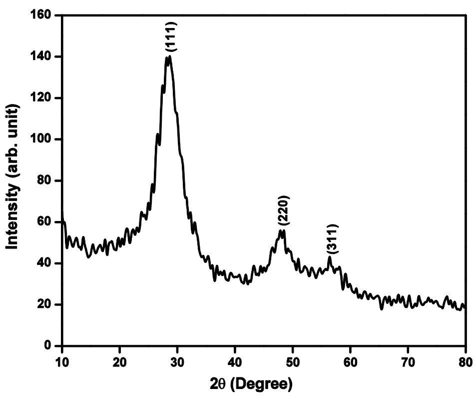

Fig-1: XRD pattern of ZnS thin film

3.2 Morphological Analysis

The surface morphology of the sample prepared at 400˚C temperature is studied using field emission scanning electron microscope (FESEM) are shown in Fig. 2. From the images it is clear that the film is coated uniformly and there are no apparent cracks on the surface of the deposited film. The surface morphology of the deposited ZnS nanostructured thin films is composed of a large number of uniform spheres like particles.

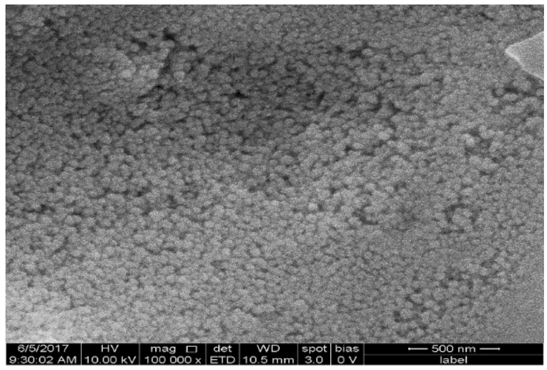

Fig-2: FESEM images of ZnS thin films

3.3 Compositional Analysis

Elemental composition of the deposited ZnS nano structured thin film is studied using EDS analysis and the equivalent pattern is shown in Fig. 3. EDS pattern clearly indicate that ZnS thin film consists of Zn, S and a small amount of the O atom. The presence of O element in the deposited film is due to the open aperture deposition and high temperature.

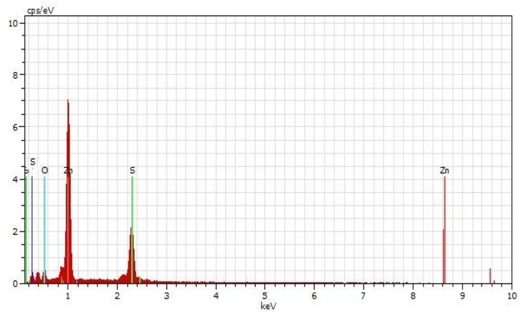

Fig-3: EDS pattern of ZnS thin films

3.4 Optical Properties

The optical properties of the deposited ZnS nanostructured thin films are studied by UV-Visible spectroscopy and Photoluminescence. Optical transmittance and absorption spectrum for the ZnS thin film on the glass substrate are measured in the range of 300-1100 nm. Fig.4 gives the transmittance spectrum of the deposited film. From the transmittance spectrum it is evident that the deposited film is having 50-60% transmittance in visible and near IR region. Absorption spectrum of ZnS thin films that are shown in Fig.5 clearly indicate that the material is having low absorption in the entire visible and near IR region.

The optical band gap is calculated using the formula,

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

where α is the absorption coefficient, A is a constant, Eg is the band gap energy and n = ½ for direct allowed transitions. The band gap energy can be determined by extrapolating straight of the plot $(\alpha h\nu)^2$ verses $h\nu$ that are shown in Fig.6. The band gap of the deposited nanostructured ZnS thin film is found to be 3.5 eV, having the wide direct band gap energy is suitable for optoelectronic device applications.

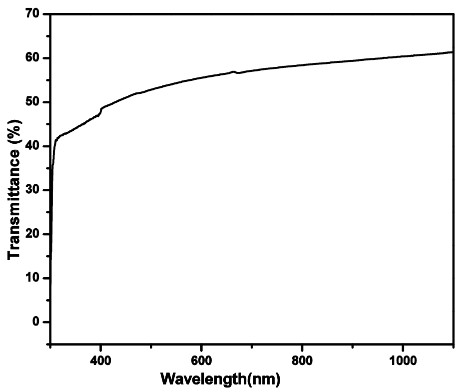

Fig-4: Transmittance spectrum

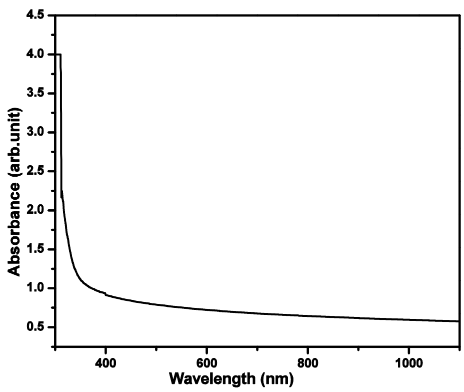

Fig-5: Absorbance spectrum

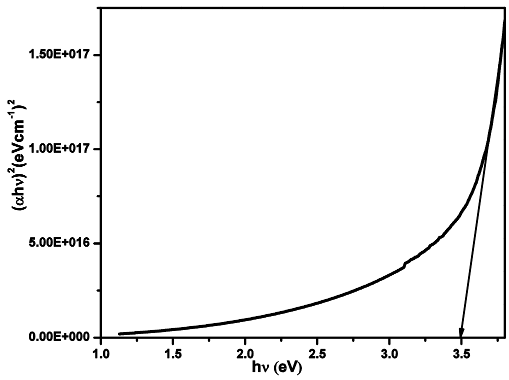

Fig-6: Tauc plot of the ZnS thin film

Fig.7 shows the photoluminescence (PL) emission spectrum of the ZnS thin films. Xenon lamp was used as a source with optical filters to filter the specified wavelength light. The emission was obtained at an excitation wavelength of 350 nm. The spectrum shows that there are two emission peaks at 475 nm and 530 nm respectively.

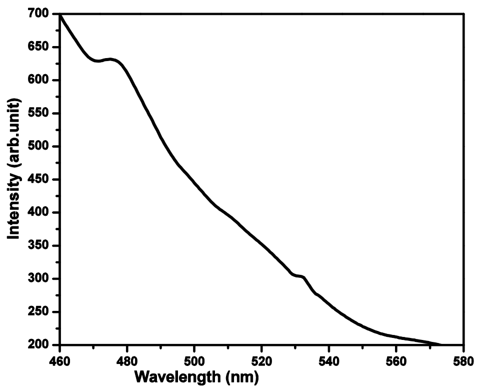

Fig-7: Photoluminescence spectrum

4 CONCLUSIONS

ZnS nanostructured thin films were deposited using the simple chemical spray pyrolysis method. In this work, the reaction temperature was 400°C. XRD pattern confirmed the polycrystalline nature of the ZnS nanostructured thin films. Average crystallite size of the deposited film was calculated to be 3.84 nm. The FESEM images showed that the deposited film formed as sphere like particles. The EDS analysis confirmed the chemical presence of the material. The optical direct band gap energy of the deposited film was found to be 3.5 eV and the material was having wide band gap energy. Photoluminescence spectrum showed two emission peaks in 475 nm and 530 nm respectively. The above mentioned results exhibits that the material is suitable for optoelectronic applications.

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