# Effect of precursor on the efficient formation of ZnS thin films for buffer layer

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**Abstract -** *ZnS thin films were found to be a promising replacement for the toxic CdS buffer layers in thin film photovoltaic cells in the recent years. The ZnS thin films were prepared using chemical spray pyrolysis technique with an equimolar ratio of Zn-S precursors. The effect of different precursors Zinc (II) chloride dihydrate, Zinc acetate dihydrate, Zinc Nitrate hexahydrate and Zinc sulphate heptahydrate were taken as precursors for Zinc and thiourea was taken as sulfur source in the preparation of ZnS thin films. The films were deposited at a temperature of 400°C and with a flow rate of 1.5ml/min. The deposited films were characterized using X-ray diffraction (XRD), Field Emission Scanning Electron Microscopy (FESEM), UV-Visible spectroscopy and photoluminescence. The XRD pattern confirmed the polycrystalline film formation with the intensed (111) phase. The morphological images showed sphere like shapes of the particles. The UV-Visible spectrum showed maximum transmittance value for a buffer layer and a wide bandgap for the photons to pass through. The optical emission spectrum and purity of the material was analyzed from the photoluminescence study.*

***Key Words***: **ZnS, thin films, precursors, spray pyrolysis, buffer layer.**

## 1. INTRODUCTION

ZnS thin films are promising replacements for CdS buffer layers in thin film solar cells. Though CdS layers are suitable and available in application level in efficient photovoltaic cells a requirement for replacement is CdS buffer layers is due to its toxic nature and less transparency [1]. Replacement of 'Zn' in the place of 'Cd' makes it as a toxic free material which is useful for the eco-friendly fabrication of thin film solar cells. ZnS has high transmittance in the Visible and IR region and has an optimum bandgap of ~3.7 eV [2].

Various deposition techniques are followed to deposit buffer layers in thin film solar cells. The most common methods among them is spray pyrolysis [3-5] and chemical bath deposition [6] because it is large scale applicable economically and convenient for ambient conditions. Other deposition techniques such as sputtering [7], thermal evaporation [8], pulsed lased deposition [9] and sol-gel [10]. Wide range of investigations is being done on this material such as pH variation, temperature variation and variation in molar ratio, etc.

In the present study ZnS thin films are deposited onto glass substrates with four different Zinc precursor materials and their structural, morphological and optical properties are studied. This work helps in identifying the suitable starting material to deposit ZnS thin films using chemical spray pyrolysis technique.

## 2. EXPERIMENTAL

ZnS thin films were prepared using aqueous solutions of four precursor materials Zinc Nitrate hexahydrate ($Zn(NO_3)_2.6H_2O$), Zinc (II) chloride dihydrate ($ZnCl_2.2H_2O$), Zinc acetate dihydrate ($Zn(CH_3COO)_2.2H_2O$) and Zinc sulphate heptahydrate ($ZnSO_4.7H_2O$) for Zinc source and Thiourea ($CH_4N_2S$) for Sulphur source. The films were deposited using spray pyrolysis technique at a temperature of 400°C, pressure of 1.2 kg/cm$^2$ and a solution flow rate of 1.5 ml/min. The concentrations were constantly taken at 1:1 molar ratios for Zn and S materials in 40 ml of aqueous solution. The solutions were sprayed continuously onto the cleaned and preheated glass substrates. Four types of films were prepared named as ZnS-1, ZnS-2, ZnS-3 and ZnS-4 in the above precursor order respectively.

The prepared films were characterized using X-ray diffractometer (XPERT-PRO) with a scan range of 10° to 80° with CuKα radiation to study the structural formation. The surface morphology was studied using FESEM (Carl Zeiss) at 10kV source voltage. The optical properties were studied using UV-Visible spectroscopy (Perkin Elmer Lambda 576) for a wavelength region of 300-1100 nm and Photoluminescence spectrometer (Fluorimeter LS45) with an excitation wavelength of 270 nm.

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## 3. RESLTS AND DISCUSSIONS

### 3.1 Structural Analysis

The crystalline structure of the films is analyzed using XRD which is shown in Fig-1. The deposited films possess polycrystalline nature with cubic crystal structure (JCPDS: 80-0020) and the lattice parameters are of a=b=c=5.345Å [11]. The peak at 28.6˚ corresponds to (111) plane and the peak at 48.1˚ corresponds to (220) plane and a minor peak at

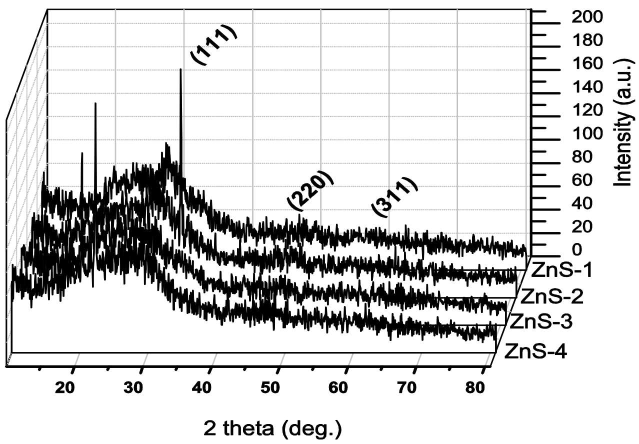


**Fig -1**: XRD pattern of ZnS-1, ZnS-2, ZnS-3 and Zn-4

56.3˚ (311) is identified [12]. The intensed peak at 28.6˚ is identified in all the films. The minor peak presence is there in ZnS-1 and trace presence are seen in remaining samples.

### 3.2 Morphological Analysis

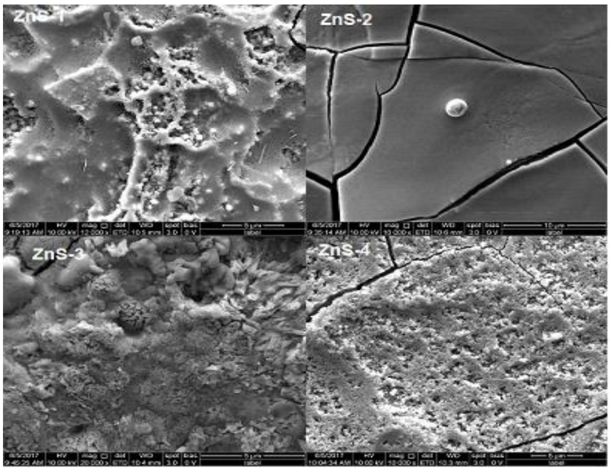


**Fig-2:** SEM images of ZnS-1, ZnS-2, ZnS-3 and ZnS-4.

The morphological images show sphere like shape of the particles which is seen in Fig -2. The films ZnS-2 and ZnS-4 films contain micro cracks on the surface. The films are having smother and uniform deposition. The films show larger grain growth on the upper surface.

### 3.2 Optical Analyses

The optical transmittance of the films is shown in Fig -3a. All the films exhibit considerable optical transmittance value with the maximum transmittance value obtained for ZnS-1 film. The ZnS-1 film exhibits high transmittance value of 80% whereas a low transmittance is obtained for ZnS-2 with 50%. The ZnS-3 and ZnS-4 shows 60 and 70% of transmittance values respectively.

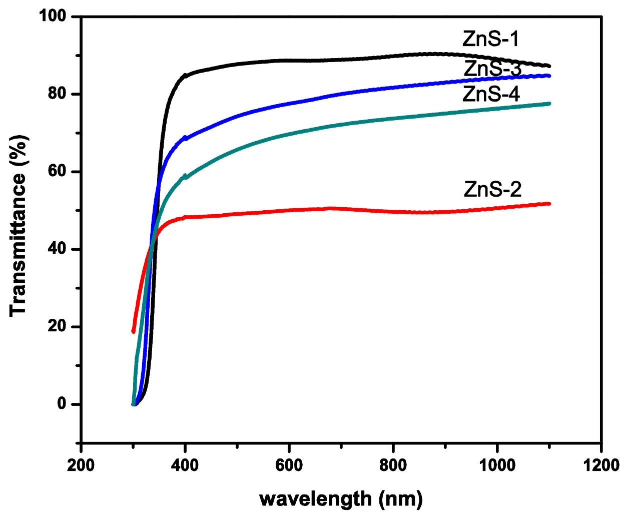


**Fig -3a:** Optical transmittance of ZnS-1, ZnS-2, ZnS-3 and Zn-4

The optical bandgap value is calculated from Tauc plot as shown in Fig-3b by plotting hν vs. $(\alpha h\nu)^2$ and is found to be 3.54, 3.44, 3.6, 3.36 eV for ZnS-1, ZnS-2, ZnS-3 and ZnS-4 respectively. The optimum bandgap value is obtained for ZnS-3 film of 3.6 eV is useful for buffer layer. [13]

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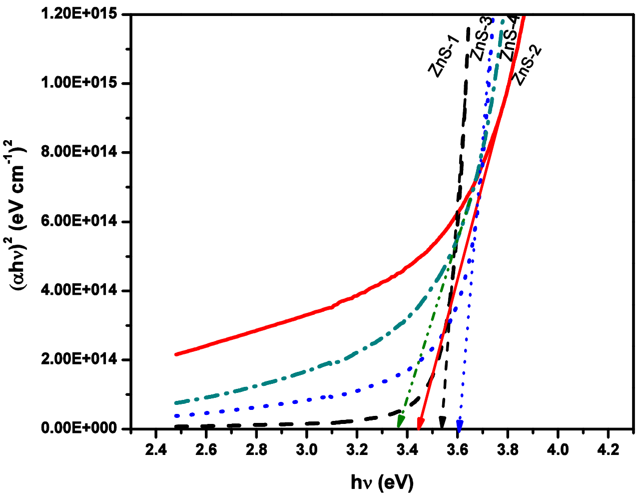


**Fig -3b:** Optical bandgap of the films

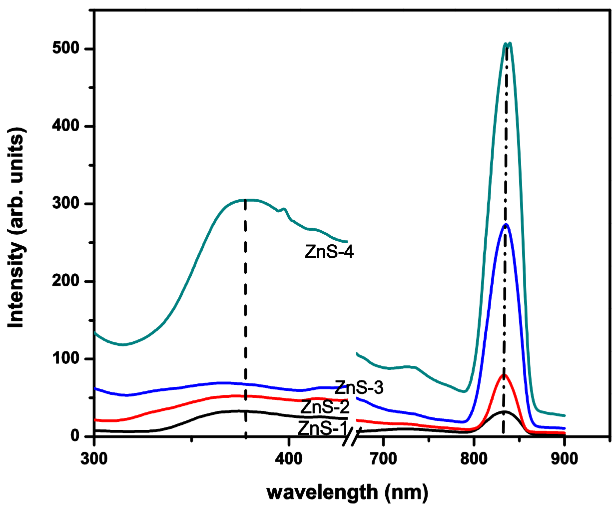


**Fig -4**: Photoluminescence spectra of the films

The photoluminescence analysis in Fig -4 shows the emission spectrum of the films. It has emission in both smaller and longer wavelength regions. The emission at 377 nm corresponding to 3.3 eV green bands [14-16] corresponds to ZnS phase whereas the higher wavelength emission shows the phosphorescence property. This material possesses both fluorescence and phosphorescence characteristics which emits in both lower and higher wavelength regions.

## 4. CONCLUSIONS

ZnS thin films were deposited using spray pyrolysis technique with four different precursor sources and their structural, morphological and optical properties were studied. Among those samples ZnS-3 exhibits good crystalline nature and morphological property. It has a wide bandgap of 3.6 eV which is optimum for buffer layer in photovoltaic cell.

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