Optimizing Zinc Sulphide Thin Films for Solar Cells: Effects of Annealing and Substrate Temperature on Structural and Optical Properties

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Abstract

Using the spray pyrolysis method, Zinc sulphide (ZnS) thin films were deposited on microscope glass slides at different substrate temperatures. Zinc acetate and thiourea were used as the precursor to prepare the ZnS films. The substrate temperature were respectively set at 300 °C and 350 °C for the samples under investigation. The annealing temperature for the prepared film is 400 ^{0}C. The films range in thickness from 4.42 to 29.7 µm. The impacts of both substrate and annealing temperature on the optical and structural properties of ZnS were investigated via the UV-visible spectroscopy and x-ray diffraction (XRD) analyses respectively. The results revealed that the grain size of ZnS films varied from 20.74 nm to 28.70 nm as substrate temperature increased from 300 °C to 350 °C. The films also possessed a polycrystalline cubic structure with (111) preferential orientation. The ZnS films showed more than 20 to 25 % transparency in the near-infrared and visible spectrums. The refractive index falls between 3.04 and 3.07. The energy band gaps of prepared films decreases from 3.35 eV to 2.80 eV with increasing substrate temperature, as estimated from the optical analysis for the ZnS. The obtained properties show a suitably fit material as window layer in a thin film solar cell and some other optoelectronic applications.

Keywords: Annealing, spray pyrolysis, Zinc sulphide, solar cell, substrate temperature

1. Introduction

Several researches have been done on silicon as an indirect band gap semiconductor material (Nguyen et al., 2021), especially in solar cell application. The long-term radiation exposure of silicon wafers in space can cause instability (Tu et al., 2021) and their failure to keep up with the fast operation of optical systems (Bera et al., 2021) have piqued scientists' interest in finding new materials that can make up for this shortfall. Chalcogenide, chalcopyrite, rare earth doped metal oxides, and transition metals are a few of the ones that have been found. These resources are all very helpful in various fields, including photovoltaic technology, optoelectronics, spin tonics, and phonics. Due to the significance of the physical and chemical characteristics, the synthesis of binary metal chalcogenides in crystalline form has been a quickly expanding field of study.Furthermore, due to the optical and electrical characteristics of ternary chalcogenide semi-conductive materials of II-VI type, which have significant applications in linear and non-linear optical devices as well as photovoltaic solar panels (Schoir & colleagues, 2006), the materials experience vast study in recent times. Zinc sulfide (ZnS) thin film is a widely used chalcogenide binary semiconductor (Ajayi *et al.,* 2021) that can range in thickness from a monolayer to several micrometers. It has garnered significant attention in the field of device fabrication and has the potential to be an excellent window layer for heterojunction photovoltaic solar cells because of its wide band gap, which enhances the cell's short-circuit current (Pham *et al.,* 2021). Additionally, it is appropriate for use in photocatalysis, phosphors in flat panel displays, and UV light-emitting diodes. Numerous methods, including elemental chemical vapor deposition, metallic precursor sulfurization, co-evaporation, electrodeposition, spray pyrolysis etc. Every deposition method is different, and the settings of the experiment have a major impact on the final product.

Contrary to what obtains in many other film deposition techniques, spray pyrolysis is a simple and relatively cost-effective method. It is an extremely easy technique for preparing films of any composition. According to Akinsola *et al.,* (2021), spray pyrolysis does not need high-quality substrates or chemicals. Researchers have long faced difficulties with the deposition of very transparent ZnS because of the techniques used, such as variances in the surface area to volume ratio and other property values. This constraint is addressed by the research methodology, which allows for the modification of all deposition parameters, including substrate types, temperatures, dopant concentrations, spray rates, and deposition times (Abejide *et al.,* 2022). Despite being the only variable in this research, the literature reports that the substrate temperature is one of the most important factors in spray pyrolysis technique of thin film deposition (Akinsola, *et al.,* 2019). Hence this work focuses on the simple spray pyrolytic deposition method of ZnS and its properties for suitability as a component of thin film solar cell.

2. Methodology

Zinc sulphide (ZnS) was synthesized using spray pyrolysis technique. 0.1M of Zinc acetate dihydrate (Sigma-Aldrich product) and 0.1M of thiourea [NH_2CSNH_2] (Sigma-Aldrich) were used as source of Zinc and Sulphur, respectively. The precursors, having been mixed with distilled water of required volume, were stirred by the magnetic stirrer (ARGO LAB M2- A). Micro-slide glasses were used as substrate for the thin films. The substrates were cleaned with detergent and distilled water as well as with methanol in an ultrasonic cleaner (VWR ultrasonic cleaner). The substrate temperatures were varied between 300°C and 350°C using the Proportional Integral Derivative (PID) temperature controller, in the interval of 50°C. The air pressure used was 30 psi and the distance between the nozzle and substrate was kept at 30 cm. The solution was sprayed at a rate of 10 mlmin^{-1}, and temperature controlling hot plate with a power range of 1500W–3000W was used. The thickness of the films was calculated using weight difference method. The films were annealed in an electric furnace at 400°C for 1hour. The structural and optical properties of the prepared film were obtained from the X-ray diffractometer (Model: EMPYREAN) and a UV-vis spectrophotometer.

3. Results and Discussion

3.1 Structural properties

The X-ray diffraction pattern of ZnS film is reported in this work with the help of an EMPYREAN X-ray diffractometer by using CuKα radiation (= 1.540598 Å). Figures 1 and 2 represent the XRD patterns of the ZnS deposited at 300 ^{0}C and 350 ^{0}C respectively. The grain size was calculated from the Debye Scherrer formula expressed in equation 1, which involves the width of the X-ray diffraction line:

$$D = \frac{K\lambda}{\beta \cos\theta} \qquad (1)$$

Where θ is the diffraction angle, λ is the wavelength of the X-ray source, and β is measured in radian as full-width at half maximum of the diffraction line. The grain size of ZnS thin films were found to be about 20.74nm and 28.70nm for 300 ^{0}C and 350 ^{0}C substrate temperature respectively. Both are annealed at the same temperature of 400 ˚C. A significant increase in the garin size was observed as the temperature increases.

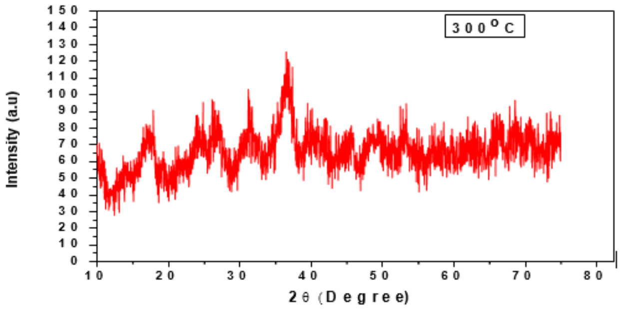


Figure 1:The XRD Pattern of ZnS at 300 ˚C

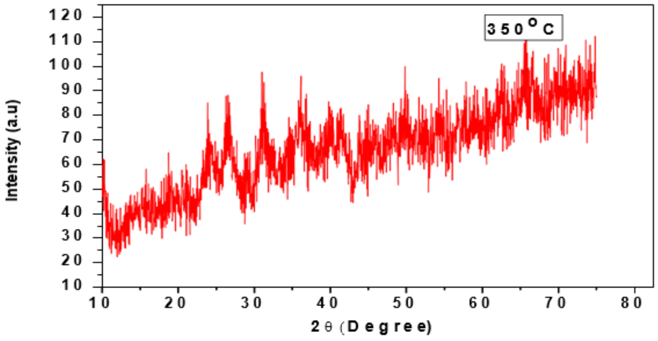


Figure 2: The XRD Pattern of ZnS at 350 ˚C

Figure 1 shows a progressive emergence of the diffraction peak located at $2\boldsymbol{\theta} = 28^0$ underlining a strong preferential orientation growth perpendicular to the crystallographic plane (111), which corresponds to the ZnS cubic structure (Gitashri *et al.,* 2020). The intensity of the peak is enhanced with increased substrate temperature, as shown in Figure 2.

3.2 Optical Properties

The study of optical properties is crucial to understanding the behavior of optical semiconductor materials. It is evident that the crystal structure and energy level installation of the material have a direct bearing on the practical implementation of the material. The optical features of ZnS films prepared using the chemical spray pyrolysis method on glass substrates at substrate temperatures of 300°C and 350°C were reported in this work. The thicknesses of 4.42 µm and 29.70 µm were obtained for film at 300°C and 350°C respectively.

UV-vis spectrophotometer was used to investigate the transmittance tendency of ZnS thin films; covering the wavelength range of 300 nm to 850 nm. Figure 3 illustrate the transmittance spectra of the prepared films. As the temperature rises, the transmittance falls in the visible region of electromagnetic radiation. With peaks in the visible and infrared region, the rise in the transmision of light occurs between 300 and 850 nm. These demonstrate that the excellent transmittance of the ZnS thin films makes them suitable for use as a window layer in solar cells, reflectors, and dielectric filters; this is consistent with the finding of Osanyinlusi (2020).

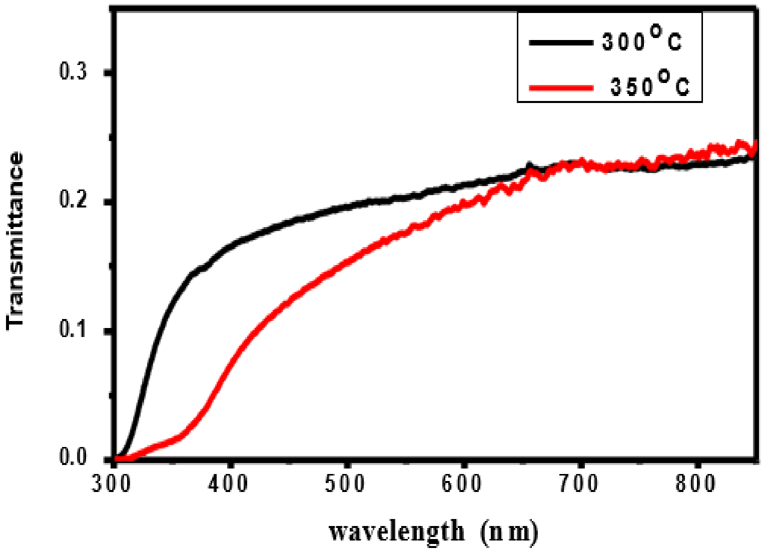


Figure 3: Transimttance spectra of ZnS prepared films at 300 ^{0}C and 350 ^{0}C substrate temperature

Spectral absorbance and transmittance can be computed using reflectivity, which is defined as the ratio of the reflected beam's reflecting intensity to the amount of incident radiation. As a function of wavelength, Figure 4 displays the ZnS film's reflectance. If the red shift is nearly constant between 600 and 850 nm, then there will be a sharp decline between 490 and 590 nm. This indicates that the film will absorb relatively little at the photon energy level, less than the energy gap value (hω< Eg). According to Oluyamo and Abdulsalam (2015), ZnS thin films exhibit a minor reflectance in the visible and near-infrared spectrums, but their overall reflectance increases with temperature.

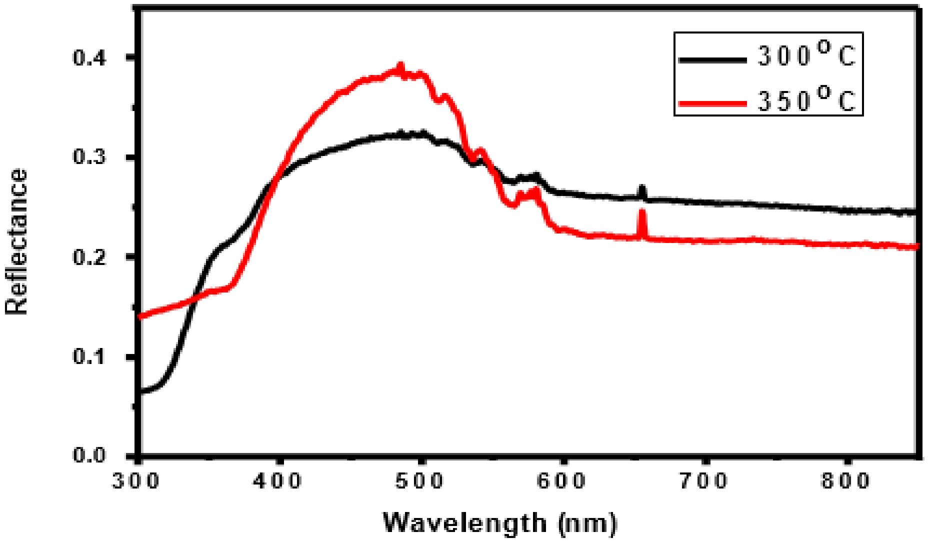


Figure 4: Reflectance spectra of ZnS thin film prepared with substrate temperature 300 °C and 350 °C.

The absorbance spectra of ZnS thin films at various temperatures were computed using this formula expressed in (2). Absorptance, transmittance and reflectance are denoted by A, T and R respectively.

$$A = 1 - T - R \tag{2}$$

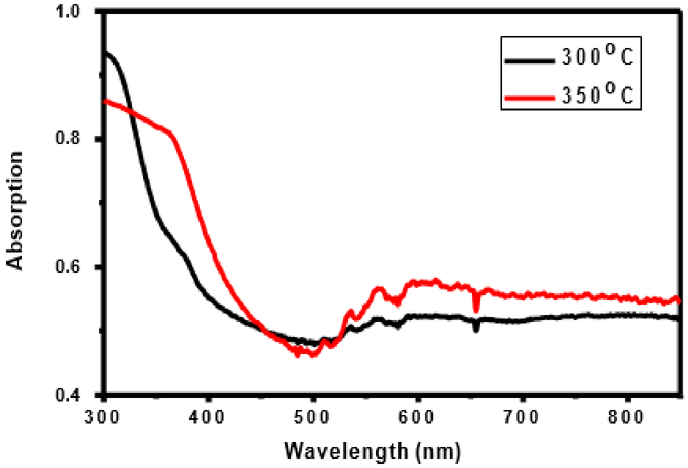
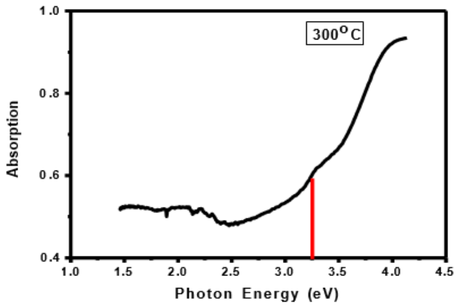


Figure 5 : Absorption spectra of ZnS thin film prepared with substrate temperature 300 ^{0}C and 350 ^{0}C

ZnS films have good absorption in the short-wavelength region of the electromagnetic radiation; as demonstrated in Figure 5. The absorption decreased with increasing wavelength. Electronic transfers between the valance band and the conduction band start when the photon energy equals the energy gap, which causes an increase in absorption, as shown in Figures 6 and 7, which is a plot of absorption vs photon energy (Akinsola *et al.,* 2021). This observation is in tandem with the report of Agbo *et al.,* 2017.



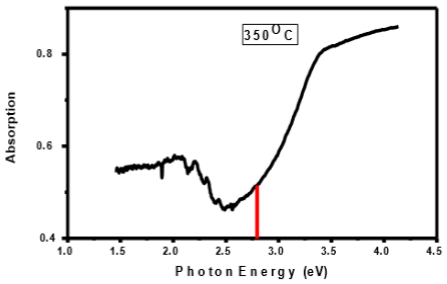


Figure 6 : Absorption of ZnS at 300 ˚C

Figure 7: Absorption of ZnS at 350 ^{0}C

In order to have proper nucleation and growth of ZnS crystals, the prepared film was subjected to annealing process, so as to lessen or completely remove the possible impurities present. Nonetheless, annealing is frequently done to increase a material's crystallinity, as seen in Figures

1 and 2. A shift in a material's optical band gap is also suggested by changes in its crystallinity. According to several research, the band gap shrinks as the substrates temperatures rises (Alwany *et al.*, 2023). This is confirmed in Figures 8 and 9, with optical band gaps of 3.35 eV and 2.80 eV for 300 and 350 degree celcius films respectively.

(a) The Optical Energy Gap

The optical energy gap for the direct allowed transition between valence bands and conduction bands of ZnS thin films was calculated from the expression in equation (3) :

$$ahf = A\,(hf - \;)^{r} \qquad (3)$$

using r = ½ . The values of the band gap of ZnS thin film for the direct transition can be determined by extrapolating the straight-line portion of the $(ahf)^2$ versus hf, as shown in Figure 8. The energy band gap of ZnS films is 3.35 eV and 2.8 eV at temperatures of 300 ℃ and 350 ℃ respectively. Additionally, the energy band gap shrinks with increasing temperature, indicating that ZnS thin film energy band gap is temperature dependent. Because it reduces window absorption loss and increases the cell's short circuit current, the energy band gap for ZnS thin films deposited at 300 °C makes them suitable materials for potential uses in optoelectronic devices like multilayer dielectric filters and solar cells (Agbo *et al.,* 2017; Oluyamo and Abdulsalam, 2015).

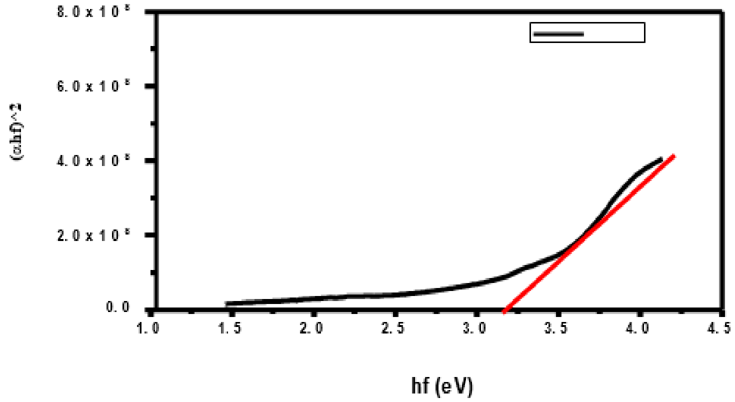


Figure 8: The energy band gap of ZnS at 300 ˚C.

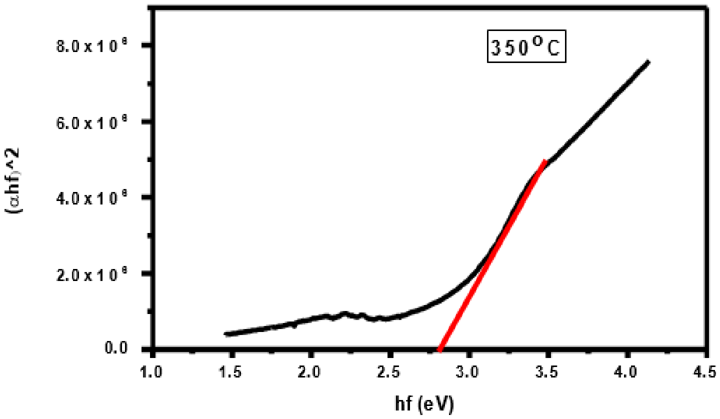


Figure 9: The energy band gap of ZnS at 350 ^{0}C

(b) Refractive index

A reflectance spectrum was used to calculate the refractive index, **n** as a function of photon energy in the 300–850 nm wavelength range. The formula in (4) was used to get the refractive index from the reflectance spectrum. The refractive index decreases in the visible range.

$$n = \frac{1+R^{1/2}}{1-R^{1/2}} \qquad (4)$$

Figure 10 illustrates this and it was determined to be 3.65 and 4.2 at 500 nm for substrate temperatures of 300 °C and 350 °C, respectively. Between 500 nm and 850 nm, there is a modest and consistent variation in the refractive index. Moreover, as temperature rises, refractive index also rise.

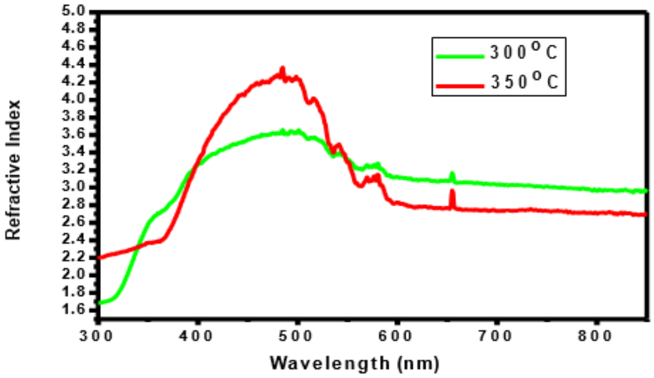


Figure 10: The variation of refractive indices of ZnS with wavelength at 300 ℃ and 350 ℃

4. Conclusion

ZnS thin films were successfully synthesized and deposited at substrate temperatures of 300 ^{0}C and 350 ^{0}C using the chemical spray pyrolysis method. X-ray diffraction (XRD) and UV spectrophotometers (UVS) were used to study the samples' structural and optical characteristics. It was observed that the deposition temperature has a significant impact on the optical characteristics, composition, and structure of the film The films exhibit a stoichiometric ZnS content and (111) preferred orientation when they become polycrystalline at higher temperature. There is an increase in grain size from 20.74 nm to 28.70 nm. The prepared ZnS films show transparency of around 25 % in the visible and near infrared region of electromagnetic radiation. The refractive index is between 2.8 and 3.0. The ZnS films with varying temperatures are found to have band gap energies ranging from 2.80 eV and 3.35 eV. Additionally, band gap dependence on substrate temperatures was found in the optical studies. ZnS film is a good fit for thin film solar cell fabrication and optoelectronic applications due to its high transmittance and wide energy band gap .

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