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Effects of Annealing on the Optical and Structural Characterization of Spray-Pyrolysed Semiconductor NiXZn1-XS Nanostructure Thin Films for Optoelectronic Applications

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Abstract

Nickel-doped Zinc Sulfide (NixZn1-xS) semiconductor materials are widely used in optoelectronic devices; however, the effects of post-annealing temperature on their properties have not been previously reported. This study investigates the impact of annealing temperature on the structural and optical properties of NixZn1-xS nanostructured thin films, synthesized using a cost-effective Chemical Spray Pyrolysis (CSP) technique. NixZn1-xS films with a thickness of 320 nm and a mole ratio of x = 0.08 were deposited on hot glass substrates at 250 °C. The precursor solutions consisted of nickel acetate, zinc acetate, and thiourea. We examined the influence of annealing temperatures of 300 °C, 400 °C, and 500 °C on the films, employing X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM), and Ultraviolet-visible spectroscopy (UV-Vis) for characterization. XRD analysis confirmed that all samples exhibited a cubic structure with a unit cell parameter of a = 5.4090 Å and a density of 4.082 g/cm³. The calculated grain sizes for films annealed at 300 °C,

400 °C, and 500 °C were approximately 4.23 nm, 6.40 nm, and 9.54 nm, respectively. SEM images indicated improved surface homogeneity and crystallinity with increased annealing temperature. Optical characterization revealed direct band gaps of 3.82 eV, 3.6 eV, and 3.04 eV for the respective annealing temperatures, with enhanced optical transmittance and reflectance at 500 °C. The decrease in band gap with increased temperature is attributed to improved crystallinity, indicating that annealing enhances the transmittance and overall quality of the semiconductor thin films, making them suitable for optoelectronic applications.

Keywords: Annealing; Thin films; Chemical spray pyrolysis; Nickel-doped Zinc Sulfide; Optoelectronic devices.

Introduction

Thin-film semiconductors, especially those synthesized through low-cost, scalable methods, are gaining interest in optoelectronic applications, including photodetectors, solar cells, and LEDs. Among the various synthesis methods, spray pyrolysis offers advantages due to its simplicity, cost-effectiveness, and compatibility with large-area deposition. $Ni_xZn_{1-x}S$ is a versatile compound semiconductor, tunable through nickel (Ni) and zinc (Zn) composition adjustments, allowing for bandgap engineering suited to specific optoelectronic applications [1,2,3]. However, optimization of these films post-deposition is crucial to enhancing their electronic and optical performance, making annealing a key process step. Here, we report the impact of annealing on the structural and optical properties of $Ni_xZn_{1-x}S$ nanostructure thin films prepared by spray pyrolysis [4].

Theoretical Consideration

The weight measurement method called gravimetric technique was employed to calculate the thin films thickness. Knowing the film mass *m*, the deposit area *A*, and the film density ϱ, the thickness t, is given as

$$t = \frac{m}{pA} \quad (1)$$

the crystallite size which can be characterized by the position and width of the diffraction peaks can be calculated from the FWHM using the Scherrer's formula [5]

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

Where λ = X- Ray wavelength, β = Full width of half maximum, θ = Diffraction angle, D = Particle size and K = Wave vector.

The optical absorption is described by an absorption coefficient (α) which can be derived from transmittance measurement and is expressed by the equation

$$\alpha = \frac{1}{t}\ln\left(\frac{1}{T}\right) \quad (3)$$

The absorption coefficient is therefore related to the extinction coefficient (k) as

$$k = \frac{\alpha\lambda}{4\pi} \quad (4)$$

The refractive index (n) is therefore given by equation 5

$$n = \frac{1+\sqrt{R}}{1-\sqrt{R}} \quad (5)$$

where, reflectance (R) is obtained from the equation 6

$$T = \frac{(1-R)^2 e^{-\alpha d}}{1-R^2 e^{-2\alpha d}} \quad (6)$$

The optical conductivity of the film was calculated from the following relation [6,7,8,9]:

$$\sigma = \frac{\alpha n c}{4\pi} \quad (7)$$

where σ is the optical conductivity of the nanostructure film, α is absorption coefficient of the film, n is the refractive index and c is the speed of light.

The absorbance (A), transmittance (T) and reflectance (R) satisfy the law of conservation of energy by the equation [10]:

$$A + R + T = 1 \quad (8)$$

Experimental Details

Materials and Thin Film Preparation

Thin films of $Ni_xZn_{1-x}S$ were synthesized on glass substrates using an aqueous precursor solution containing nickel nitrate, zinc nitrate, and thiourea as the sulfur source. The molar ratio of Ni and Zn was varied to prepare different compositions of $Ni_xZn_{1-x}S$. The precursor solution was atomized and sprayed onto a preheated substrate at 300°C to initiate thermal decomposition and form nanostructured thin films [11,12,13.14].

Annealing Process

After deposition, three samples of $Ni_xZn_{1-x}S$ (x = 0.08) ware annealed at different temperatures of 300^0C, 400^0C and 500^0C for 1hour with annealing furnace to determine the best among the samples in a nitrogen atmosphere to prevent oxidation. The samples were held at each temperature for 1 hour, then allowed to cool to room temperature. This annealing treatment aimed to improve film crystallinity, modify grain boundaries, and reduce defect densities. the films were subjected to post thermal treatment characterization were also done [15].

Characterization Techniques

Structural Characterization

The crystal structure and phase composition were analyzed using XRD. The diffraction patterns were examined to calculate the average crystallite size using the Scherrer equation. XRD gives whole range of information about crystal structure, orientation, crystalline size, phase content and stresses in films. G B C EMMA X-ray diffractometer using CuK_α radiation (λ = 1.5418 Å) was used to analyze the various thin films prepared. Experimentally result was compared with the Joint Council Powder diffraction (JCPDS) data to obtain inferences about different crystallographic phases, orientations and relative abundance. Average grain size was also calculated using Debye Scherrer's formula. Interplanar spacing *d* was determined from the X-ray diffraction profiles using Bragg's law [17].

Scanning Electron Microscopy (SEM)

SEM provided information on surface morphology and grain size distribution. The microstructural/morphological features of the various thin films were investigated with a Carl Zeiss Scanning Electron Microscope (SEM). The optical transmittance, T, and reflectance, R, of the films were measured by a UV-Vis (Lambda 950) spectrophotometer, equipped with an integrating sphere, in the wavelength range 300 - 750 nm. Absorbance, A, optical conductivity, refractive index and extinction coefficient were calculated from the data obtained.

Optical Characterization

UV-Visible Spectroscopy: Absorbance and transmittance spectra were recorded in the 300–900 nm range[18]. The optical bandgap was calculated using Tauc plots derived from UV-Vis data.

Results and Discussion

Structural Changes with Annealing

XRD analysis showed a marked increase in crystallinity with increasing annealing temperature. The as-deposited films exhibited broad XRD peaks, indicating a high degree of amorphous character [19,.20]. However, annealing at 400°C and above resulted in sharper peaks, suggesting enhanced crystallinity and larger grain sizes. The diffraction peaks corresponding to the $Ni_xZn_{1-x}S$ phase were more defined, and the calculated crystallite size increased from approximately 10 nm (as-deposited) to 25 nm at 600°C. This improvement in crystallinity is expected to reduce grain boundary scattering, thus enhancing carrier mobility.

SEM images revealed a transformation in surface morphology due to annealing, with the grain size increasing and surface roughness decreasing.

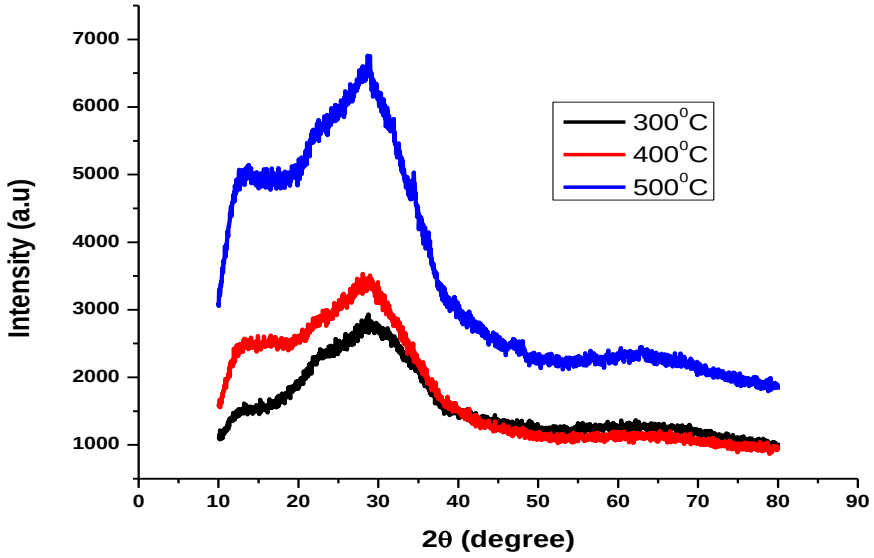

Figure1: X-ray diffraction pattern of $Ni_{0.08}Zn_{0.92}S$ at different annealing temperature

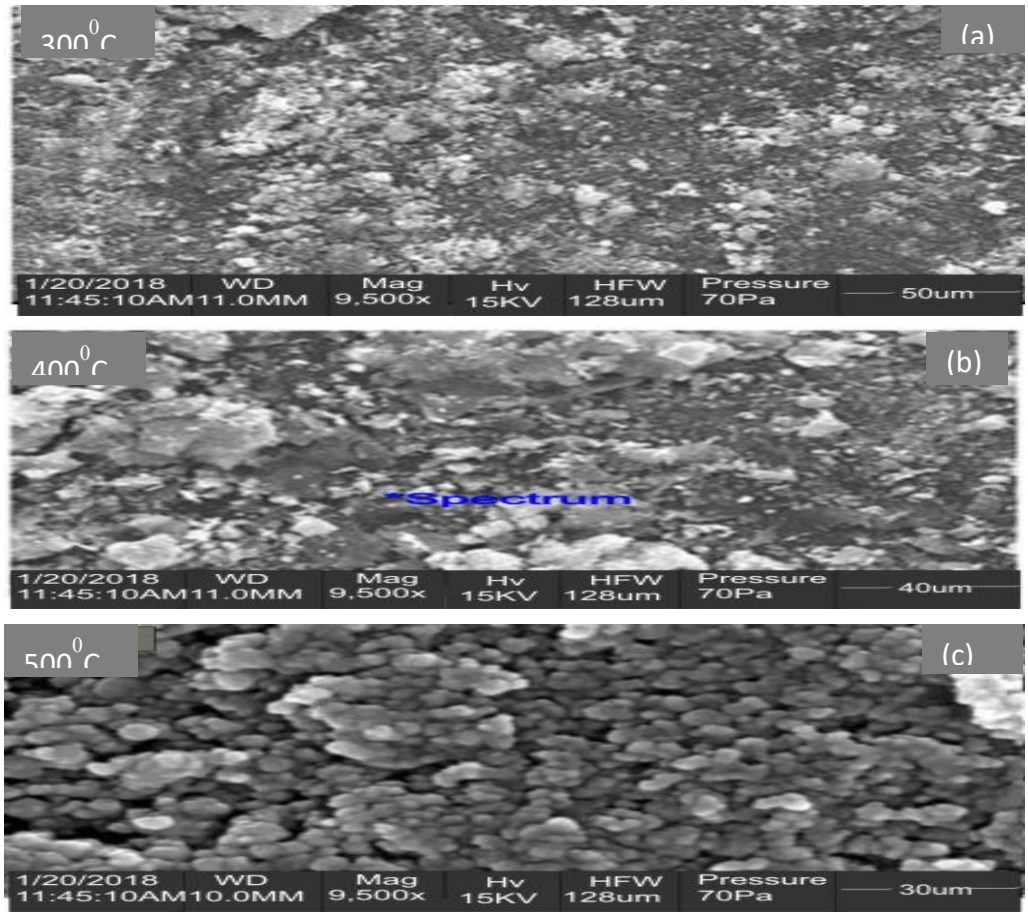

Figure 2: Micrograph of $Ni_{0.08}Zn_{0.92}S$ with different annealing temperature: (a) 300°C (b) 400°C (c) 500°C

Optical Results

The Transmission Spectra of the Samples

UV-Vis measurements indicated an increase in transparency across the visible spectrum with annealing. The as-deposited films had a bandgap of approximately 3.2 eV, which decreased slightly with annealing, reaching around 3.0 eV at 600°C. This reduction in bandgap may be attributed to improved crystallinity and reduced defect density. Annealing at 400°C was found to optimize the transparency and absorption characteristics of the films, making them suitable for applications requiring high optical clarity and tailored bandgap values.

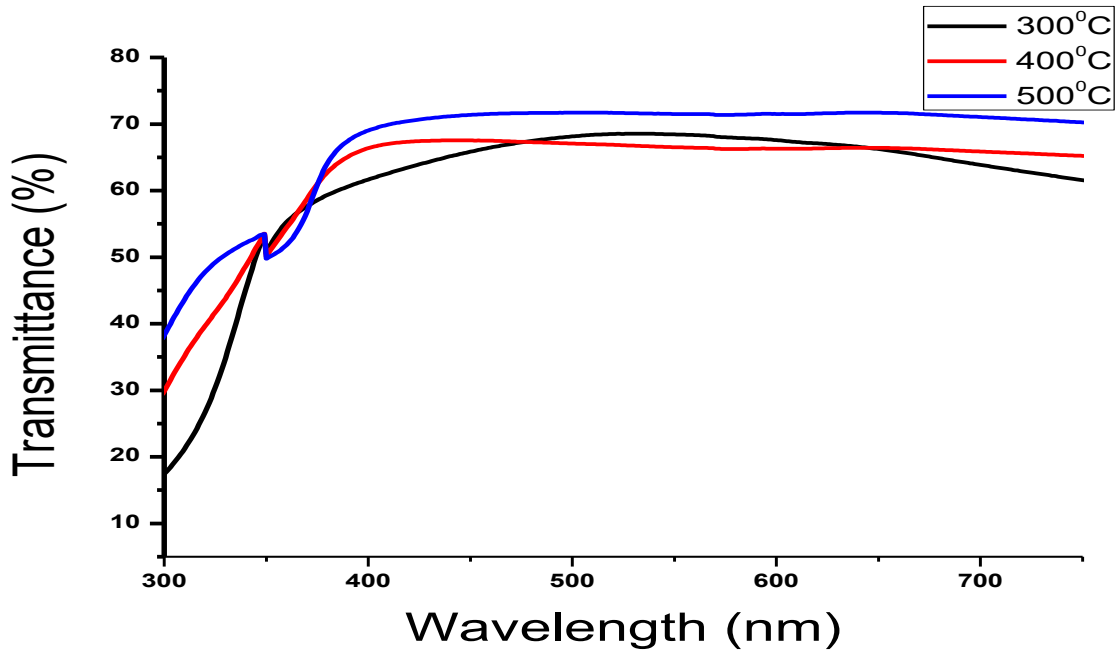

Figure 3: Transmittance against Wavelength for $Ni_{0.08}Zn_{0.92}S$ at different annealing temperature

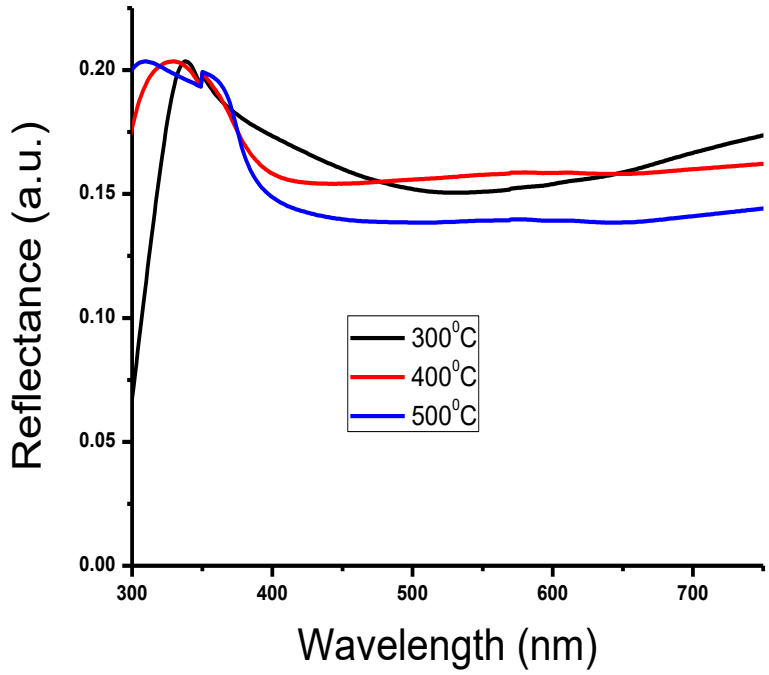

Figure 4: Reflectance Spectra of $Ni_{0.08}Zn_{0.92}S$ at different annealing temperature

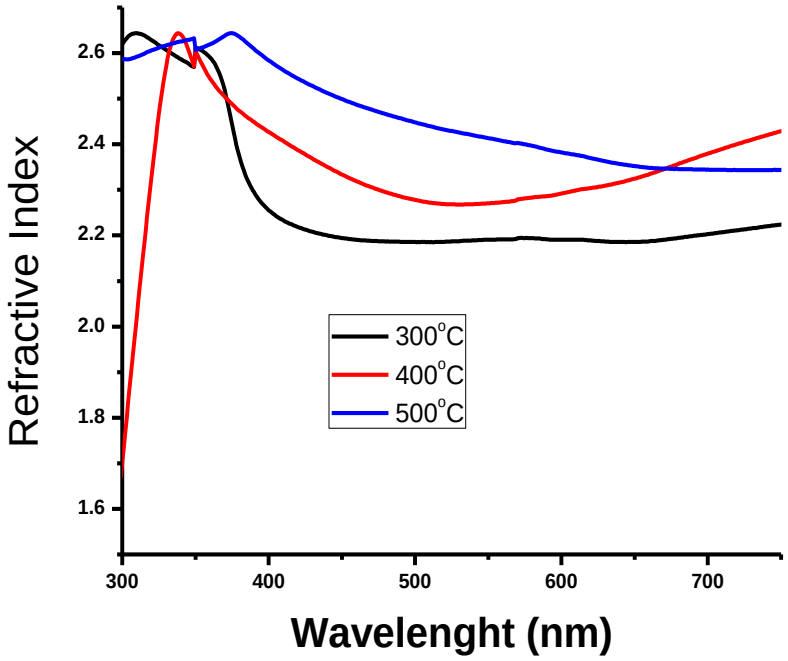

Figure5: Refractive index of $Ni_{0.08}Zn_{0.92}S$ at different annealing temperature

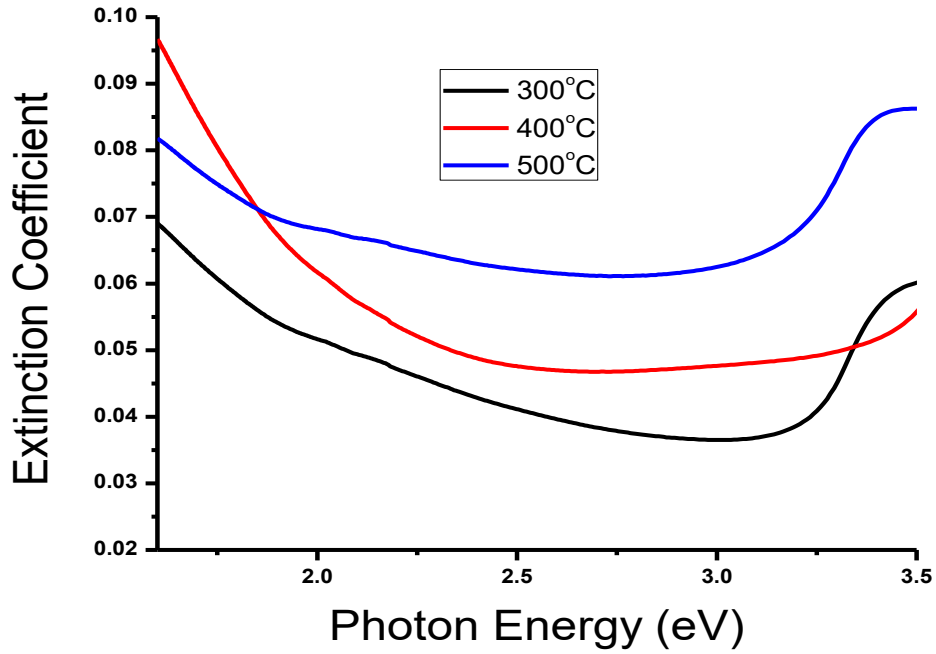

Figure 6: Extinction Coefficient of $Ni_{0.08}Zn_{0.92}S$ with incident photon energy at different annealing temperature

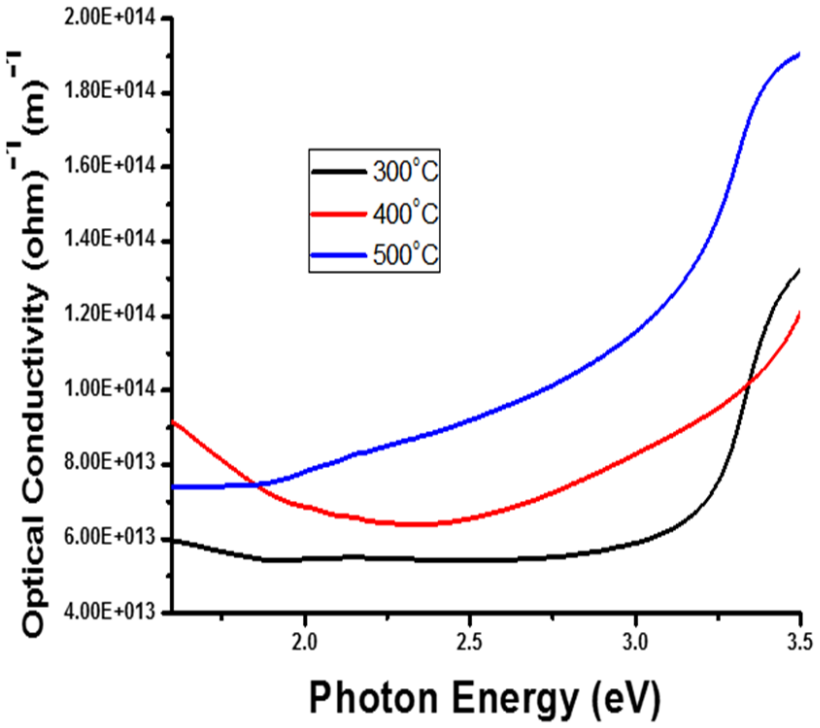

Figure 7: Optical Conductivity of $Ni_{0.08}Zn_{0.92}S$ with incident photon energy at different annealing temperature

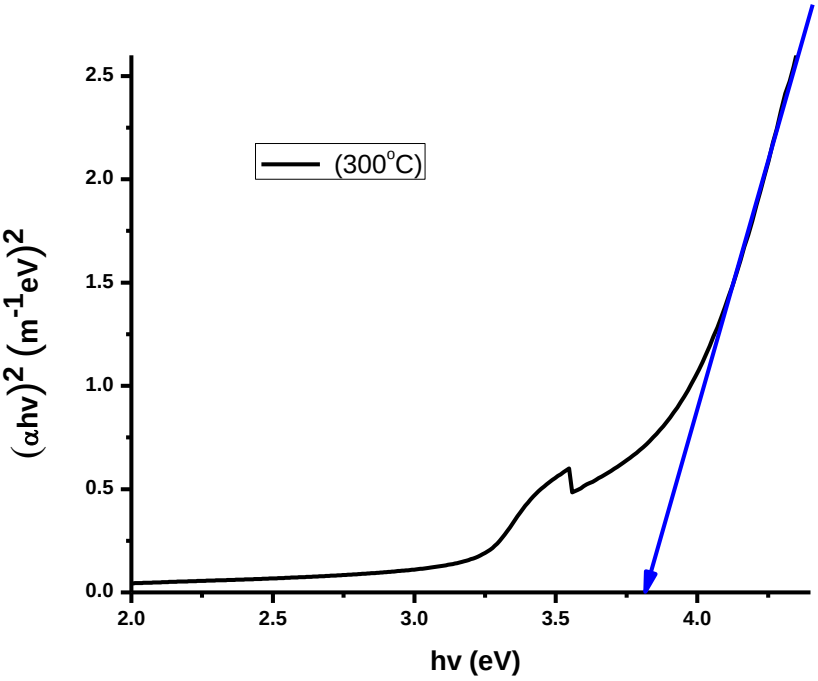

Figure 8(a): Band gap of $Ni_{0.08}Zn_{0.92}S$ at annealing of temperature 300°C

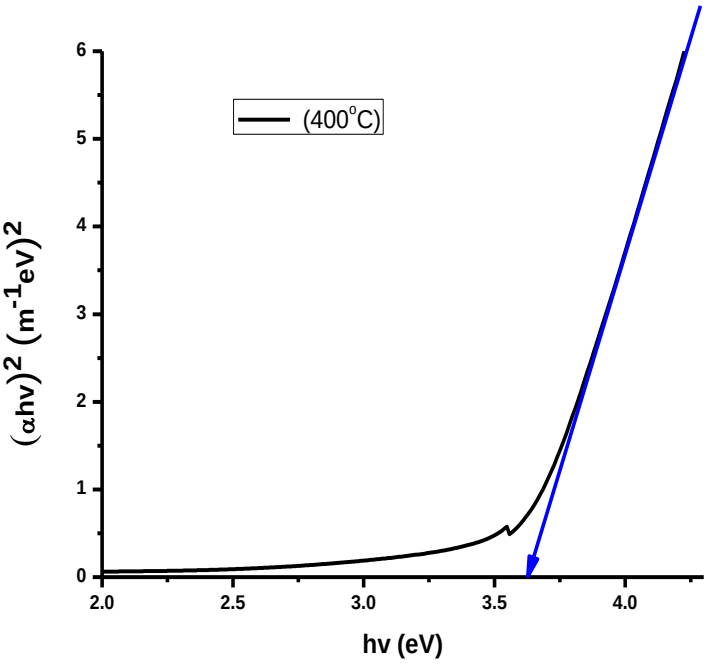

Figure 8(b): Band gap of $Ni_{0.08}Zn_{0.92}S$ at annealing temperature of 400°C

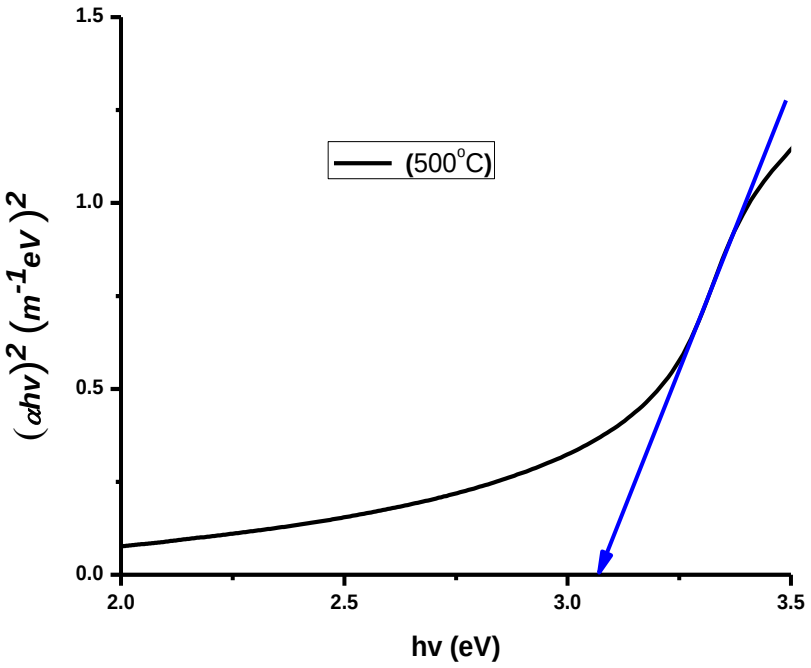

Figure 8(c): Band gap of $Ni_{0.08}Zn_{0.92}S$ at annealing temperature of 500°C

Table 1: Variation of crystalline size, energy gap with different temperature

Temp (^{0}C)	Crystalline size (nm)	Band gap (eV)
300	4.23	3.82
400	6.40	3.63
500	9.64	3.07

Conclusion

Annealing has a profound effect on the structural and optical characteristics of $Ni_xZn_{1-x}S$ thin films. This study demonstrates that annealing enhances crystallinity, reduces defects, and improves optical transparency and photoluminescence properties. Optimal annealing conditions (e.g., 400°C) balance structural improvements with favorable optical characteristics, making these films promising candidates for optoelectronic devices such as photodetectors, solar cells, and LEDs. Future work will involve fine-tuning the annealing process and exploring additional dopants to further optimize $Ni_xZn_{1-x}S$ thin films for specialized applications.

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