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Synthesis and Characterization of Pulsed Laser Deposited $\text{Cu}_x\text{Zn}_{1-x}\text{S}$ Thin Films Nanocomposite for Photosensor Application

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ABSTRACT: Thin films of $\text{Cu}_x\text{Zn}_{1-x}\text{S}$ nanocomposite with varying copper content ($x = 0.3, 0.5, \text{ and } 0.7$) were successfully synthesized by the pulsed laser deposition (PLD) technique from their fabricated powders by the precipitation method for optoelectronic applications. The impact of Cu content on the film's structural, morphological, optical, and electrical characteristics was investigated. Elemental composition analyses indicated that thin CZS films consisted only of their constituent elements and were free of any noted impurities. XRD patterns demonstrated that all as-grown thin films were polycrystalline in nature and adopted various planes and phases of CuS and ZnS binary compounds. Increasing the Cu content caused a more pronounced CuS phase while, at the same time, suppressing the ZnS phase. This alteration also resulted in an increase in crystallite size and a decrease in crystal defects. AFM images showed that Cu content had a significant effect on the surface topography of the films. Optical results pointed to a red shift at the film absorption edge, indicating a drop in the direct energy band gap with the rise in Cu content. The optical constants, such as the extinction coefficient, dielectric constant, and refractive index, were also determined. Hall effect measurements suggested that increasing the Cu content in the as-deposited thin films resulted in enhanced electrical conductivity and hole concentration. The electrical characteristics of fabricated Al/p-CZS/n-Si/Al heterostructures (HSs) showed photosensing properties. The photosensing parameters, such as photosensitivity, photoresponsivity, and resistance-based sensitivity, were calculated as a function of Cu content under an illumination of 40 mW/cm^2 . CZS-based photosensor with heterojunction (HJ) interface exhibited a maximum photosensitivity of 6.6 at a reverse bias of 0.75 V.

KEYWORDS: CZS thin films; structural properties; electrical conductivity; CZS/Si junction; photosensitive properties

1 Introduction

In the field of solid-state technology, ternary semiconductor thin films play a vital role in advanced photonic and electronic devices because of their unparalleled elemental and structural characteristics [1]. Ternary semiconductor compounds can be synthesized by tuning the stoichiometry or by mixing of binary systems, providing the ability to tailor the properties of semiconductors between those of the original binary compounds. This, in turn, affects their photoelectric properties [2]. The CuZnS (copper zinc sulfide) is a ternary compound material consist of the binary compounds CuS and ZnS [3], combining the transparent properties of ZnS with the metallic conductive properties of covellite CuS [4,5]. The optical and electrical properties of this compound can be adjusted by varying the atomic ratio of Cu_x and Zn_{1-x} [6], making it appropriate for photovoltaic and optoelectronic applications. $\text{Cu}_x\text{Zn}_{1-x}\text{S}$ is a non-oxide ternary chalcogenide composed

of low-toxicity, eco-friendly, earth-abundant, inexpensive elements and can be fabricated economically at low temperatures for utilization in transparent and flexible electronic applications [4,7]. The CZS compound is a promising semiconductor for many optical device applications like photovoltaic solar cells, sensors, lasers, light-emitting diodes, and plasma displays [8–10]. At room temperature, copper sulfide has five stable stoichiometric phases: analite ($\text{Cu}_{1.75}\text{S}$), chalcocite (Cu_2S), djurleite ($\text{Cu}_{1.95}\text{S}$), digenite ($\text{Cu}_{1.8}\text{S}$), and covellite (CuS) [11–13], as seen in Fig. 1a [14]. The transition metal chalcogenide (CuS) is a semiconductor with a p-type conductivity [15], a direct energy band gap (1.2–2.73 eV) [16], and an absorption coefficient of the order 10^{-4} cm^{-1} [11]. At 1.6 K, the metallic conductivity of covellite CuS transforms to superconductivity [17,18]. ZnS , a metal chalcogenide semiconductor, has two natural phases: the cubic phase (sphalerite, zinc blende) at RT and the hexagonal phase (wurtzite) at higher temperatures [19] (see Fig. 1b,c [14]). The zinc sulfide (ZnS) compound exhibits n-type conductivity [20] and wide direct band gaps of 3.54 eV and 3.91 eV for the sphalerite and wurtzite phases, respectively. Based on the previous research, this compound tends to either (1) phase segregate into a nanocomposite material (ZnS and Cu_yS), usually by employing chemical synthesis methods; (2) form a heterostructural, heterovalent alloy to varying degrees, usually by using physical deposition methods; or (3) form some combination of the first two behaviors. However, the exact reason behind high electrical conductivity of this compound stills not fully understood. It may be due to the formation of a conducting network of semimetallic Cu_yS or metallic Cu phases, doping of Cu^+ cations into ZnS , realization of a unique heterovalent ternary alloy, or some combination of these effects [21–24]. $\text{Cu}_x\text{Zn}_{1-x}\text{S}$ thin films were successfully synthesized by different chemical and physical methods such as chemical bath deposition (CBD) [2], sol-gel [25], electrochemical atomic layer deposition (ECALD) [26], ultrasonic spray pyrolysis (USP) [27], metal organic chemical vapor deposition (MOCVD) [28], vacuum thermal evaporation (VTE) [29], and pulsed laser deposition (PLD) [30].

This paper aims to study the effect of Cu content on the structural, optical, and electrical properties of CZS films PLD-synthesized to evaluate their prospective utilization as active layers in photonic technologies. $\text{Cu}_x\text{Zn}_{1-x}\text{S}$ thin films were examined within a p-CZS/n-Si-based photosensor using silicon as the substrate to assess their photosensing performance.

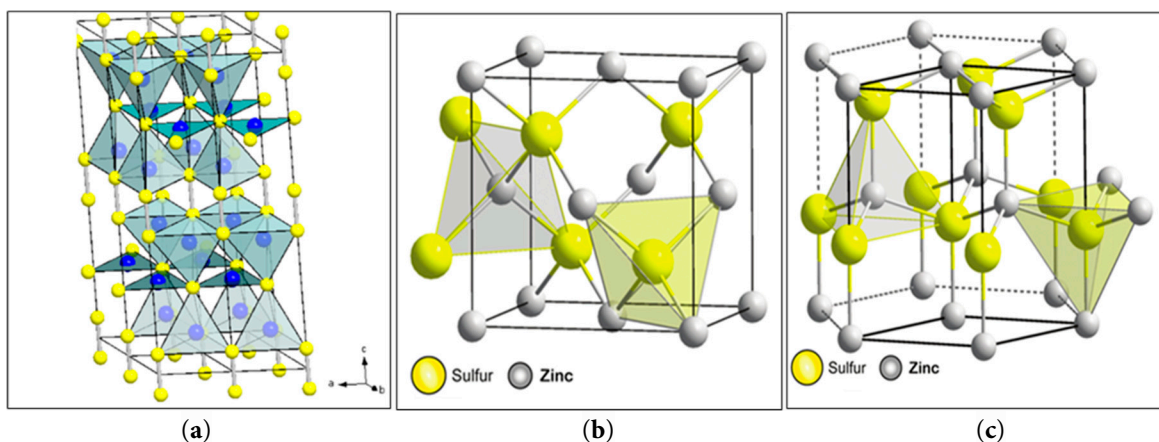


Figure 1: Crystal structure for (a) covellite CuS [13], (b) cubic ZnS , and (c) hexagonal ZnS [14].

2 Experimental

Thin CZS nanocomposite films with a thickness of 450 nm were deposited on pre-cleaned Corning glass and silicon wafer substrates at room temperature (RT) by employing the pulsed laser deposition (PLD) method from their synthesized powders. $\text{Cu}_x\text{Zn}_{1-x}\text{S}$ powders were prepared by using the precipitation

method. By the homogeneous nucleation mechanism, powders were synthesized, where metal-[complexing agent]^{x+} ions react with S²⁻ ions in the solution [31] to form molecular clusters. These clusters grow into particles, which finally accumulate as powder within the solution. The chemical precursors utilized as a source of Cu²⁺, Zn²⁺, and S²⁻ ions are cupric chloride (CuCl₂, 99.6% purity) used at molar ratios of 0.3, 0.5, and 0.7; zinc chloride dihydrate (ZnCl₂·2H₂O, 99.8% purity) at a molar ratios of 0.7, 0.5, and 0.3; and thiourea (CH₄N₂S, 99.6%) at molar ratio of 2, respectively. All chemicals were provided by BDH Chemical Ltd. of Poole, England. The reagents used to adjust pH, control ion precipitation, and provide the reaction medium are 25% aqueous ammonium (NH₃(aq)), triethanolamine (TEA) (C₆H₁₅NO₃), ethylenediaminetetraacetic acid (EDTA) solution, and deionized water (DI) (+H₂O). The EDTA solution was synthesised by dissolving 2 mol of Na₄ (C₁₀H₁₆N₂O₈) in 20 mL of +H₂O. The Cu_{0.3}Zn_{0.7}S powder was obtained as follows: three separate glass beakers were used to produce solutions of [0.3 mol CuCl₂ + 5 mL + H₂O (for dissolution)], [0.7 mol ZnCl₂·2H₂O + 5 mL (+H₂O) (for dissolution)], and [2 mol CH₄N₂S + 5 mL (+H₂O) (for dissolution)] and then put on a magnetic stirrer device to stir the liquids with intermediate speed for some time (10–15 min) at RT to ensure their homogeneity. After that, twelve and four sequential drops of EDTA and TEA were added into the Cu-Zn solutions, respectively, with constant stirring. Then NH₃(aq) was added to the Zn source to tune the pH of the solution to approximately 11, which was measured by employing a pH meter. CuCl₂, ZnCl₂, and CH₄N₂S solutions were mixed together under stirring, and DI water was added until the volume reached 50 mL. The temperature of the bath was gradually raised at a constant rate to 80°C. During this, the color of the solution changed from blue to dark brown as the reaction advanced. The solutions were then left to cool to room temperature and filtered using suitable filter paper. The change in the solution color may indicate partial reduction of Cu²⁺ to Cu⁺ under experimental conditions [32]. The prepared powder was washed adequately with deionized water and then placed in an electric oven to dry completely. The powder was collected and finely ground. The same steps were followed to prepare CZS powders with 0.5 and 0.7 molar copper ratios. Subsequently, using a 5-t hydraulic press, the Cu_xZn_{1-x}S powders were pressed into pellets to be the targets with diameters and thicknesses of 1.2 and 0.6 cm, respectively. The pellets were heated in a thermal oven at 773 K for 1 h. The oven was turned off, and the samples were allowed to gradually cool to RT. The deposition process was carried out at a 10⁻² Torr, using a 1064 nm Nd:YAG laser (400 pulses, 800 mJ pulse energy, 10 ns pulse duration, and 2 Hz repetition rate). The substrate was placed at a constant distance of 2 cm from the CZS target.

Energy Dispersive X-ray Spectroscopy (EDS) of the AIS 2300C type (1–2 μm spatial resolution) was used to verify the elemental composition of all prepared CZS thin films/glass substrates. The crystalline structure of Cu_xZn_{1-x}S powders and thin films was examined using a Shimadzu XRD-6000 diffractometer (Japan) with Cu Kα radiation at a wavelength of 1.5406 Å and 2θ scan angle in the range of 10°–80°, with typical resolution ~0.01°. The interplanar spacing (d_{hkl}) for various planes was calculated using Bragg's law [33]:

$$2d\sin\theta = n\lambda \quad (1)$$

where n is the order of reflection. The average size of crystallite (D) of the CZS thin films was obtained by the Debye-Scherrer equation [34]:

$$D = (K\cdot\lambda)/B\cos\theta \quad (2)$$

where K is the shape factor, and B is the FWHM of predominate peak.

The lattice defects which including dislocation density (δ) and micro-strain (ε) were calculated using the two equations below [35,36]:

$$\delta = 1/D^2 \quad (3)$$

$$\varepsilon = B\cos\theta/4 \quad (4)$$

SPM-AA3000 atomic force microscopy (typical resolution 1–10 nm) (AFM) was used to analyze the morphological characteristics of thin CZS films grown on glass substrates. The absorbance (A) and transmittance (T) of prepared films/glass substrates were recorded using a UV-Visible 2601 double-beam spectrophotometer in the wavelength range of 400–1100 nm (1–2 nm spectral resolution). The absorption coefficient (α) was calculated from the Beer-Lambert law [34,37]:

$$\alpha = 2.303A/d \quad (5)$$

where d is the thickness of CZS thin films, which is 450 nm, as measured by the gravimetric method. The absorption coefficient and energy of the incident photons ($h\nu$) are related by the following formula below [38]:

$$\alpha h\nu = \beta (h\nu - E_g^{\text{opt}})^r \quad (6)$$

where β is a constant oppositely proportional to the non-crystallinity and is a measure of the disorder in the material. It reflects the extent of band tail states (localized states) in the gap. E_g^{opt} is the optical energy band gap, and r is the exponential variable dependent on the kind of transition.

In general, optical constants, such as the extinction coefficient, refractive index, and dielectric constant are determined dependent on the optical behavior of the substance.

The extinction coefficient (k) is related to the wavelength (λ) and α as follows [39]:

$$k = \alpha\lambda/4\pi \quad (7)$$

The refractive index (n) of semiconductor materials is of significant interest for both applied and fundamental considerations. Furthermore, devices such as waveguides, photonic crystals, detectors, and solar cells need prior knowledge of the refractive index for optimal design and performance [40].

In this paper, the refractive index of CZS thin films was estimated using the two different equations below:

i. The Moss equation [41,42]:

$$n^4 E_g = K \quad (8)$$

where K is a constant equal to 108 eV.

ii. The Herve and Vandamme equation [43,44]:

$$n = \sqrt{1 + \left(\frac{B}{E_g + C} \right)^2} \quad (9)$$

where B and C are constants with values 13.6 and 3.4 eV, respectively.

The dielectric behavior of solid materials is essential for several electronic device characteristics. Both static and high-frequency dielectric constants (ϵ_s & ϵ_∞) were calculated for all prepared CZS thin films. The static dielectric constant (ϵ_s) was estimated using the following relation [42]:

$$\epsilon_s = 18.52 - 3.08E_g \quad (10)$$

Based on the calculated values of n , the high-frequency dielectric constant (ϵ_∞) has been calculated for different Cu contents by applying the relation below [42]:

$$\epsilon_\infty = n^2 \quad (11)$$

The Hall effect measurement system was employed to estimate the electrical characteristics of thermally evaporated Al electrodes/CZS thin films/glass substrates, which included carrier concentration (P), Hall coefficient (R_H), Hall mobility (μ_H), Hall resistivity (ρ_H), and Hall conductivity (σ_H). These characteristics were calculated using the equations shown below [45]:

$$P_H = 1/e \cdot R_H \quad (12)$$

where e is the electron charge.

$$R_H = \text{slope} * \frac{t}{B_Z} = \frac{V_H}{I_x} * \frac{t}{B_Z} \quad (13)$$

where B_Z is the applied magnetic field, V_H is the electric potential difference across the sample, and I_x is the current passing through the sample.

The photosensing characteristics of all the fabricated Al/p-CZS/n-Si/Al heterostructures, with a 1 cm^2 effective area (s), were tested through I-V measurements under both dark and illuminated conditions by a Keithley 2450 Source Meter, employing white light of an intensity of 40 mW/cm^2 . The sensor outputs, such as responsivity (R), photosensitivity (P.S.), and resistance-based sensitivity percentage (S%), were estimated under a constant reverse bias voltage using the relations below [46,47]:

$$R = \frac{I_L - I_D}{P_{in}} = \frac{I_{ph}}{P_{in}} \quad (14)$$

$$P.S. = \frac{I_{ph}}{I_D} \quad (15)$$

$$S\% = \frac{100 * (R_D - R_L)}{R_D} \quad (16)$$

where I_L & I_D are the values of dark and light currents, respectively, I_{ph} is the photocurrent, P_{in} is the light power in the sensor's effective area, and R_D & R_L are the resistances of heterostructure in the dark and light, respectively.

3 Results and Discussions

The structural analysis of the synthesized $\text{Cu}_x\text{Zn}_{1-x}\text{S}$ powders and their corresponding thin films was carried out using XRD measurements. Fig. 2 displays the XRD spectra as a function of Cu contents ($x = 0.3$,

0.5, and 0.7). It is seen from the obtained XRD patterns that all samples exhibit a polycrystalline structure along various planes and phases. $\text{Cu}_x\text{Zn}_{1-x}\text{S}$ alloy can be considered a mixture of CuS and ZnS phases [48]. CZS structural analysis was done by comparing the obtained XRD patterns with those of CuS and ZnS and Cu_2S phases. The $\text{Cu}_x\text{Zn}_{1-x}\text{S}$ samples showed reflection planes that belong to the ZnS cubic phase (β -ZnS), the ZnS hexagonal phase (α -ZnS), and the CuS hexagonal phase (Table 1a,b), and no peak corresponding to the Cu_2S phase was seen in XRD patterns. This result is consistent with results obtained by previous studies [27,29,41]. With an increasing copper ratio (x), the intensity of the (103) peak, corresponding to the hexagonal CuS phase, increased, and conversely, the intensity of the (111) peak, associated with the cubic ZnS phase, decreased. Moreover, new peaks belonging to the copper sulfide (CuS) phase appeared, while other crystalline peaks associated with the zinc sulfide (ZnS) phases disappeared. The intensity of the new peaks gradually increased with increasing copper concentration, indicating a transformation in the crystal structure of the material in which the copper sulfide phase became dominant. This result is consistent with the previous study [41]. Therefore, CuS can be considered the main crystal phase, where copper (Cu^{2+}) can occupy the host sites in the ZnS crystal lattice due to the close similarity in ionic radii between Cu^{2+} (0.72 Å) and Zn^{2+} (0.74 Å), which improves the possibility of substituting zinc ions for copper ions within the crystal lattice [49]. The amorphous glass substrates on which the thin CZS films were deposited are the cause of the broad hump in the XRD patterns between $2\theta = 20^\circ$ and 35° [50]. The structural parameters of the (103) peak for CZS alloys and their corresponding thin films are presented in Table 2a,b, respectively. As can be noticed from these tables, the CZS specimens have a nanocrystal size that grows as the Cu content increases, while the crystal defects, such as dislocation density (δ) and microstrain (ϵ), decrease. Fig. 3 summarizes the relationship between Cu concentration and calculated crystal defects. These alterations show that the crystalline quality of the material has improved [33,51]. Nanostructures with large crystallite sizes are suitable for light-sensing applications. This is because reducing structural crystal defects leads to longer lifetimes of photo-excited carriers and thus increased photocurrent [52,53]. In a polycrystalline $\text{Cu}_x\text{Zn}_{1-x}\text{S}$ structure with mixed phases of CuS and ZnS (cubic and hexagonal), increasing the Cu content enhances the CuS phase, suppresses the ZnS phase, increases crystallite size, and reduces defects (dislocation density δ and microstrain ϵ). This means that the incorporation of Cu into the ZnS lattice leads to improved crystallinity, which positively reflects the employment of thin CZS films in photosensing applications where the recombination centers are decreased and carrier lifetimes rise.

Table 1: (a) Lattice parameters of $\text{Cu}_x\text{Zn}_{1-x}\text{S}$ powders. (b) Lattice parameters of $\text{Cu}_x\text{Zn}_{1-x}\text{S}$ thin films.

(a)						
x	$d_{\text{exp.}}$	$d_{\text{stand.}}$	$2\theta_{\text{exp.}}$ (deg.)	hkl	Phase	Card No.
0.3	3.1181	3.1200	28.5938	111	ZnS Cubic	00-001-0792
	2.8244	2.8100	31.6413	103	CuS Hexagonal	00-001-1281
	2.3127	2.2709	38.8947	1010	ZnS Hexagonal	01-072-0162
	2.2099	2.1542	40.7833	1011	ZnS Hexagonal	01-072-0162
	1.9727	1.9925	45.9502	1010	ZnS Hexagonal	01-072-0163
	1.8939	1.8900	47.9792	110	CuS Hexagonal	00-001-1281
	1.6569	1.6558	55.3860	200	ZnS Hexagonal	01-072-0162
	1.5827	1.5778	58.2249	206	ZnS Hexagonal	01-072-0162
	3.0927	3.1200	28.8449	111	ZnS Cubic	00-001-0792
0.5	2.7810	2.8100	32.1608	103	CuS Hexagonal	00-001-1281
	2.3007	2.2709	39.1045	1010	ZnS Hexagonal	01-072-0162
	1.8878	1.8900	48.1641	110	CuS Hexagonal	00-001-1281
	1.5644	1.5695	58.9947	205	ZnS Hexagonal	01-072-0163

Table 1: Cont.

(a)						
x	d _{exp.}	d _{stand.}	2θ _{exp.} (deg.)	hkl	Phase	Card No.
0.7	3.0678	3.1200	29.0845	111	ZnS Cubic	00-001-0792
	2.7971	2.8100	31.9710	103	CuS Hexagonal	00-001-1281
	1.8997	1.8900	47.8435	110	CuS Hexagonal	00-001-1281
	1.7389	1.7300	52.5871	114	CuS Hexagonal	00-001-1281
	1.5599	1.5600	59.1587	116	CuS Hexagonal	00-001-1281
(b)						
x	d _{exp.}	d _{stand.}	2θ _{exp.} (deg.)	hkl	Phase	Card No.
0.3	3.1484	3.1200	28.3239	111	ZnS Cubic	00-001-0792
	2.7948	2.8100	31.9851	103	CuS Hexagonal	00-001-1281
	2.6188	2.6582	34.1987	107	ZnS Hexagonal	01-072-0162
	2.4886	2.5200	36.0470	108	ZnS Hexagonal	00-012-0688
	1.9694	1.9925	46.0302	1010	ZnS Hexagonal	01-072-0163
	1.6395	1.6397	56.0457	202	ZnS Hexagonal	01-072-0163
0.5	3.1613	3.1200	28.2058	111	ZnS Cubic	00-001-0792
	2.7494	2.8100	32.5403	103	CuS Hexagonal	00-001-1281
	1.8961	1.8900	47.9182	110	CuS Hexagonal	00-001-1281
0.7	3.1968	3.1200	27.8862	111	ZnS Cubic	00-001-0792
	2.7851	2.8100	32.0991	103	CuS Hexagonal	00-001-1281
	1.9126	1.8900	47.4798	110	CuS Hexagonal	00-001-1281
	1.5461	1.5600	59.7644	116	CuS Hexagonal	00-001-1281

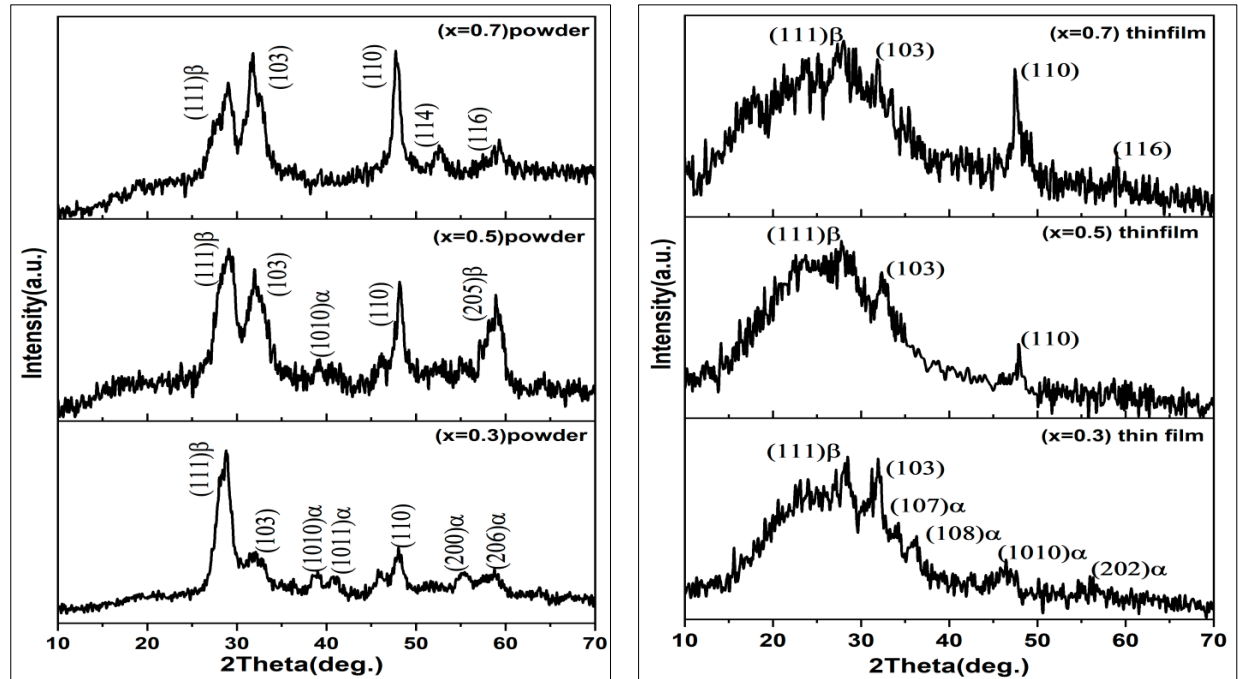
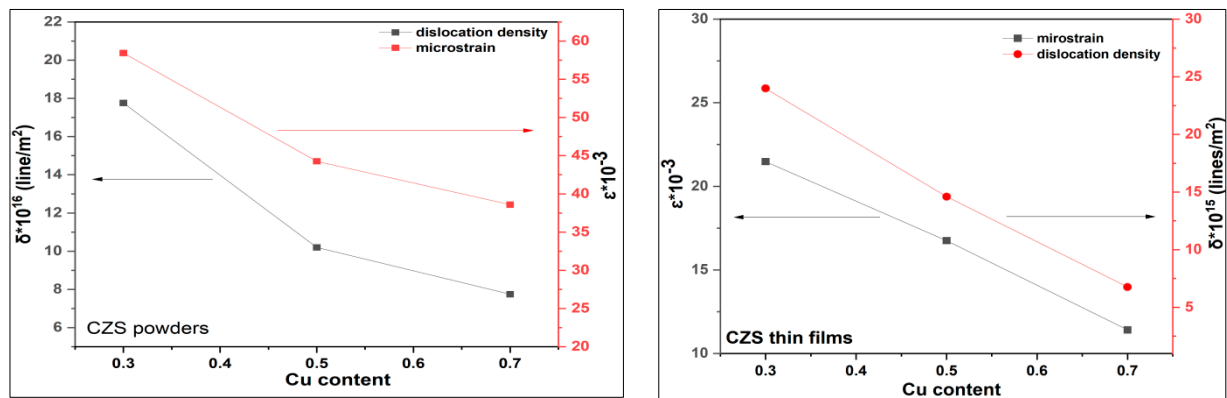
Figure 2: XRD patterns of $\text{Cu}_x\text{Zn}_{1-x}\text{S}$ powders and their thin films.

Table 2: (a) Structural parameters of peak (103) of CZS powders. (b) Structural parameters of peak (103) of thin CZS films.

(a)					
x	$2\theta_{\text{exp.}}$ (deg.)	FWHM (deg.)	C.S (nm)	$\delta \times 10^{16}$ (lines/m ²)	$\epsilon \times 10^{-3}$
0.3	31.6413	3.4800	2.3727	17.7629	14.6092
0.5	32.1608	2.6400	3.1317	10.1962	11.0685
0.7	31.9710	2.3000	3.5930	7.7461	9.6476

(b)					
x	$2\theta_{\text{exp.}}$ (deg.)	FWHM (deg.)	C.S (nm)	$\delta \times 10^{15}$ (lines/m ²)	$\epsilon \times 10^{-3}$
0.3	31.9851	1.3200	6.4563	23.9901	5.5367
0.5	32.5403	1.0000	8.2757	14.6013	4.1886
0.7	32.0991	0.6800	12.1566	6.7667	2.8514

**Figure 3:** The relationship between Cu content and calculated crystal defects.

The elemental composition of the deposited thin CZS (copper zinc sulfide) films was determined using energy dispersive X-ray analysis (EDXA). As reported in a prior study [54], the properties of semiconductor compounds are highly sensitive to changes in their elemental composition. Therefore, accurate control and precise quantification of each individual element are essential for optimal performance and ensure chemical stability during the fabrication of thin films. The EDX spectra demonstrated in Fig. 4 confirm the presence of only the constituent elements (Cu, Zn, and S) in all samples, revealing the purity of the thin-film composition. The results presented in Table 3 show a high degree of consensus between the calculated values and the natural composition, with small deviations that may have resulted from the partial deficiency of zinc or a minor increase in sulfur ratio during the preparation process. The slight decrease in Zn concentration can be explained based on the fact that Zn volatilization is a known phenomenon at very high temperatures. In this work, the pellets were heated at 773 K (500°C), and the deposition process of films was performed at room temperature; significant Zn loss is less common than in higher-temperature processes [53–56], whereas the slight increase in S content could be attributed to doubling the quantity of thiourea (CH₄N₂S) as a source of S during preparation. Additionally, an evident increase in the experimental ratio of Cu/(Cu + Zn) was noted with increasing theoretical Cu content, suggesting successful control of thin film composition during the preparation process.

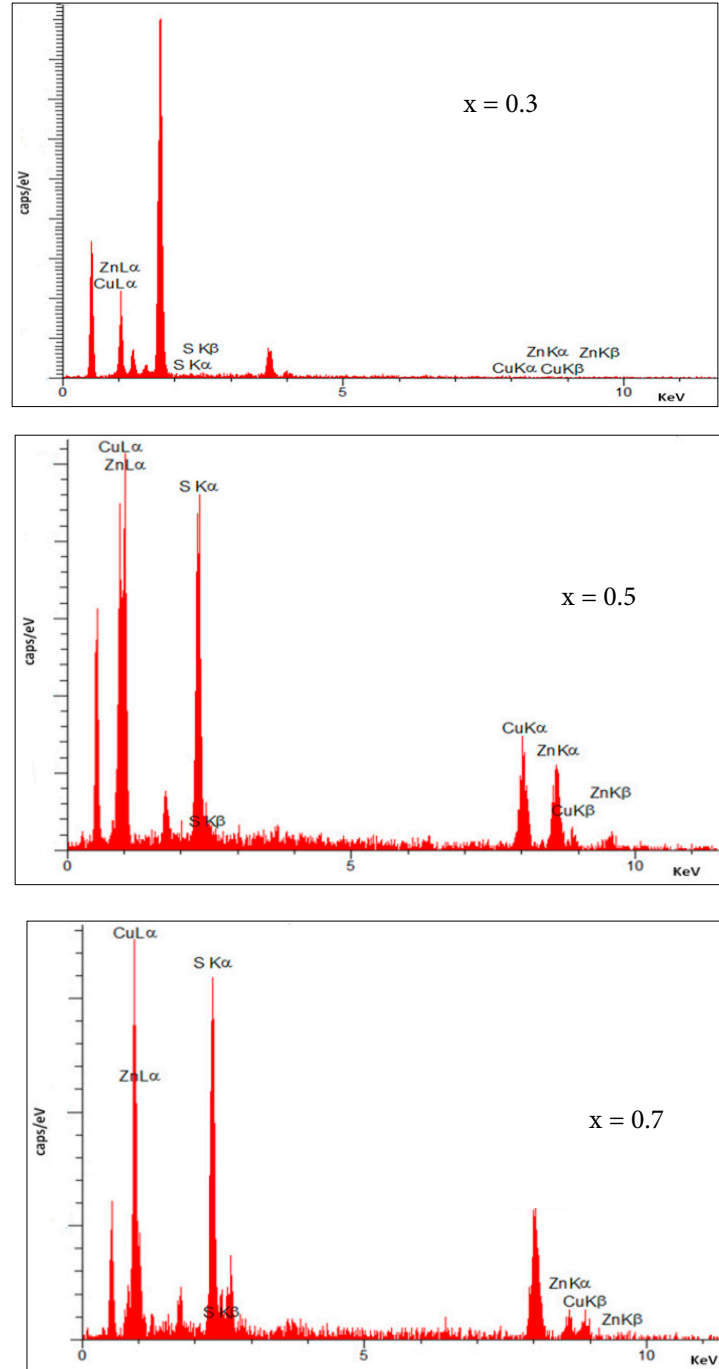


Figure 4: EDXA spectra of $\text{Cu}_x\text{Zn}_{1-x}\text{S}$ thin films.

Table 3: Chemical analysis of thin $\text{Cu}_x\text{Zn}_{1-x}\text{S}$ films based on EDX results.

Composition	Experimental Atomic Ratio %			Normalized Atomic Ratio		
	Cu	Zn	S	Cu/Cu + Zn	Zn/Cu + Zn	S/Cu + Zn
$\text{Cu}_x\text{Zn}_{1-x}\text{S}$						
$\text{Cu}_{0.3}\text{Zn}_{0.7}\text{S}$	13.75	35.30	50.95	0.28	0.72	1.04
$\text{Cu}_{0.5}\text{Zn}_{0.5}\text{S}$	27.24	21.58	51.18	0.56	0.44	1.05
$\text{Cu}_{0.7}\text{Zn}_{0.3}\text{S}$	36.23	12.42	51.35	0.745	0.255	1.055

An AFM machine was employed to obtain 2D and 3D topographical images of thin CZS films, which are represented in Fig. 5. It is clear from Fig. 5 and Table 4 that there are significant alterations occurred in the surface topography of prepared thin $\text{Cu}_x\text{Zn}_{1-x}\text{S}$ films when the Cu content increased. A thin film with a low Cu ratio ($\text{Cu}_{0.3}\text{Zn}_{0.7}\text{S}$) possesses a relatively smooth surface and fine grains with uniform distribution, implying a regular crystal growth and a low root mean square roughness (Rq) magnitude. All AFM parameters (G.S., Ra, and Rq) rise when the Cu reaches the moderate ratio ($x = 0.5$). The film's surface roughness increased and the crystallite growth improved when the grains with smaller size in the surface layer coalesced. An increase in Ra beside a decrease in G.S and Rq was observed when the Cu ratio increased to 0.7 ($x = 0.7$) as in Table 3. This may be attributed to the crystalline structure reorganization process, which leading the formation of smaller grains with a larger number. That means the grown $\text{Cu}_{0.7}\text{Zn}_{0.3}\text{S}$ thin film has a smooth surface with less uniformity. These surface topography changes are required for some applications, like photovoltaic solar cells and photosensors. The rough surface layer causes an increase in the effective area of the thin film's surface, therefore resulting in the enhancement of absorption efficiency [55].

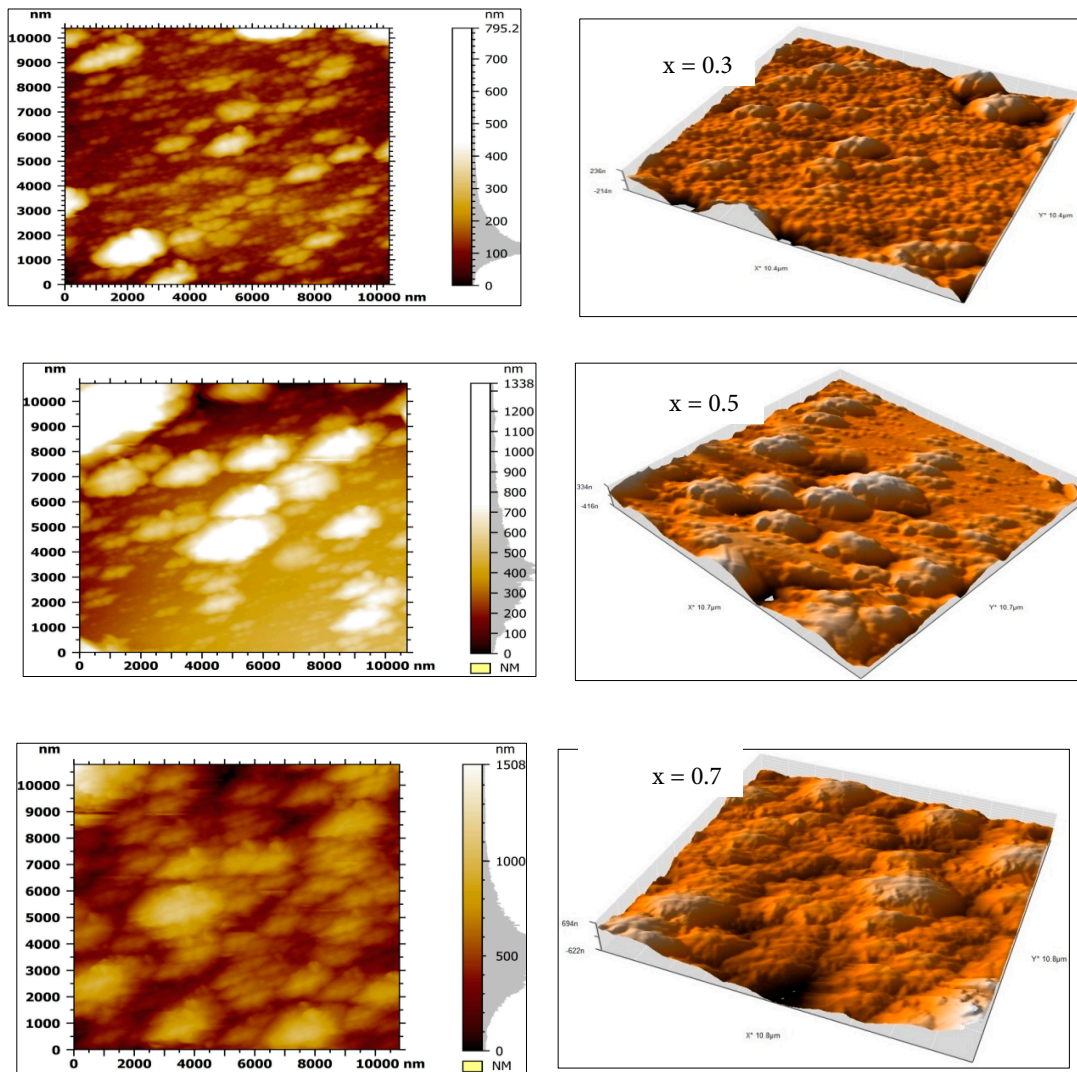


Figure 5: 2D and 3D AFM images for CZS thin films.

Table 4: AFM results.

$\text{Cu}_x\text{Zn}_{1-x}\text{S}$	Grain size (G.S.) nm	Mean roughness (Ra) nm	RMS roughness (Rq) nm
$\text{Cu}_{0.3}\text{Zn}_{0.7}\text{S}$	85.94	45	84.75
$\text{Cu}_{0.5}\text{Zn}_{0.5}\text{S}$	98	75	222.8
$\text{Cu}_{0.7}\text{Zn}_{0.3}\text{S}$	51.52	111.6	193.5

The optical absorption and transmission of thin CuZnS films prepared on Corning glass substrates were measured in the wavelength range (300–1100 nm). Fig. 6 shows the spectral absorbance and transmittance curves of these thin films, which were synthesized with different Cu contents. As can be seen, an increase in the Cu ratio improves the film's optical absorption, resulting in a corresponding decrease in its transmittance. The absorbance improvement can be attributable to improved light trapping, which originates from an increase in the film surface roughness [56,57]. The rough surface acts as an effective mechanism of light trapping, causing incident light to scatter in multiple directions. This scattering increases the probability of light being absorbed on the film surface and has a clear antireflection effect [58]. Goktas [59] attributed the increase in absorbance in the visible region of the spectrum to the improvement in the crystal structure and packing density of the films. The appearance of a distinct absorption peak in the near ultraviolet region (330–370 nm) may be attributed to the electronic transition from deep levels in the valence band to the conduction band. The increase in absorbance can also be attributed to the improved crystallinity of CZS thin films with Cu content, resulting from the reduction of structural defects and grain boundaries [60,61]. As the Cu content increased, the absorption edge of CZS films shifted towards longer wavelengths (i.e., red shift), indicating a decrease in optical energy band gap value as Cu content increases (see Table 5). The optical band gap was evaluated by using plots of $(\alpha h\nu)^2$ against the photon energy ($h\nu$), applying the Tauc's equation. The linearity of the plots indicates that the prepared films exhibit a direct allowed band gap [37]. The band gap value was specified by extrapolating the linear part of the plot to the energy axis where $(\alpha h\nu)^2 = 0$, as expressed in Fig. 7. The fall in the energy band gap with rising Cu ratio can be result from the gradual transition from zinc sulfide to copper sulfide phase [41], as estimated from the XRD results. CuS has a smaller optical energy gap compared to ZnS (3.6 eV), causing it to control optical absorption properties and thus become the main factor dictating the optical absorption edge, resulting in a gradual reduction in the band gap of the CZS system. The shift towards lower energies is consistent with the trend observed in previous studies [1,7,9,29,41,62]. The band gap of ternary compound semiconductors, such as copper zinc sulfide (CZS), typically depends linearly on the band gaps of the constituent materials, namely copper sulfide (CuS) and zinc sulfide (ZnS). However, factors such as lattice mismatches, differences in electronic structures, variations in atomic size, and periodic crystallization discontinuities often cause the deviation from linearity, named as band gap bowing [41,63]. An exponential model was used to depict a non-linear behavior of the CZS energy band gap with Cu content, using the empirical relation below:

$$E_g(x) = A_1 \exp\left(\frac{-x}{t_1}\right) + y_0 \quad (17)$$

where A_1 is variation amplitude, t_1 is decay constant, and y_0 is an asymptotic magnitude.

From Fig. 8, the exponential fitting adopts good agreement with our experimental values. The fitting findings reflect a non-linear dependence of the band gap on dopant contents, where a diminishing trend is noticed with the rise of the Cu concentration. This diminution is more noticeable at low contents and slowly becomes less pronounced at higher contents.

The extinction coefficient (k) is a measure of how strongly a material absorbs light. It's related to the absorption coefficient (α) by Eq. (7) and represents how much light is lost (absorbed/scattered) as it travels through the material. A high k magnitude means strong absorption and low transmission. In CuZnS films, increased Cu content raises k and enhances absorption due to improved light trapping (surface roughness), better crystallinity, and minimized defects.

The refractive index (n) is an essential optical property that can be defined as the ratio between the light speed in a vacuum and the light phase velocity in the material ($n = c/v$). It represents the ability of the material to slow the light propagation. The interaction between the electric field of incident light and the electrons in the matter causes a reduction in the speed of photons. When the oscillating electric field polarizes the substance's electrons, secondary electromagnetic waves are generated and join with the incident wave, causing an effective decrease in light phase velocity through the substance [64]. When the material energy band gap is small, incident photons can more readily excite the electrons in its valence band, increasing the medium's electronic polarizability. The refractive index (n) rises with increasing polarizability. So, generally, the refractive index and the band gap energy have an inverse relationship [65]. Table 5 displays the relationship between the E_g and n . This result is in good agreement with previous study [66]. Fig. 9 illustrates the alteration in the refractive index as estimated by two different models (Moss and Herve-Vandamme) with increasing Cu concentration. As shown in Fig. 9 and Table 5, the refractive index values increased from 2.39 to 2.66 with increasing Cu content from 0.3 to 0.7. It is worth noting that the rate of increase based on the model employed. It can be easily concluded from Eq. (11) that the increase in the refractive index is directly linked to an increase in the high frequency dielectric constant (ϵ_∞), as the square of the refractive index (n^2) nears ϵ_∞ . This relationship indicates that a decrease in the energy band gap leads to an important increase in ϵ_∞ , mainly due to the improvement in electronic polarization resulting from the facilitation of electron movement within the material [67]. On the other side, the static dielectric constant (ϵ_s) encompasses all polarization categories present in the material, particularly electronic, dipole, and ionic polarization [68]. Thus, even without any alterations in the other polarization forms, any enhancement in electronic polarization leads directly to an increase in the value of ϵ_s . In addition, compositional changes in CZS thin films associated with increased Cu content may induce additional internal dipole moments or enhance ionic polarization, leading to a further increase in the value of ϵ_s [69]. This clarifies why ϵ_s continuously exceeds ϵ_∞ in all CZS samples. Fig. 10 and Table 5 illustrate the variation in the dielectric constant values of thin CZS films. The results obtained are consistent with [41,70].

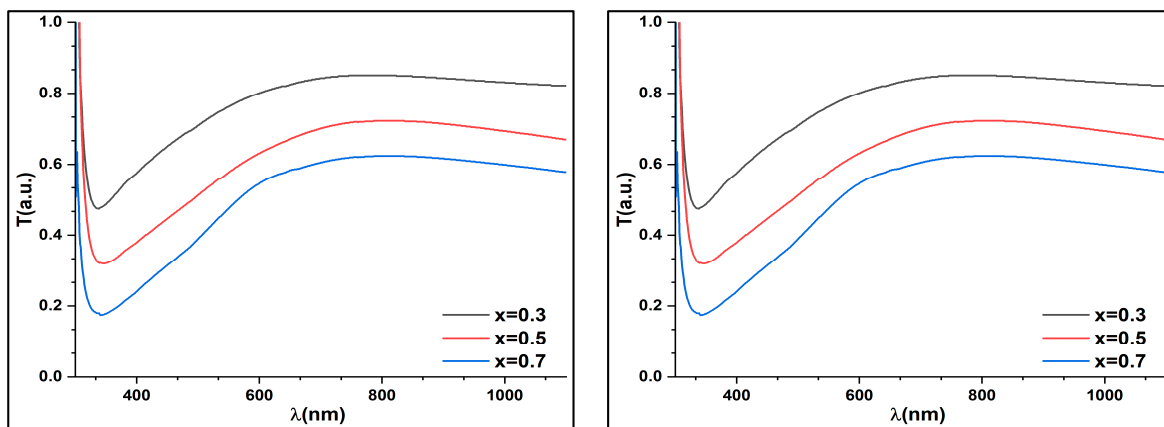
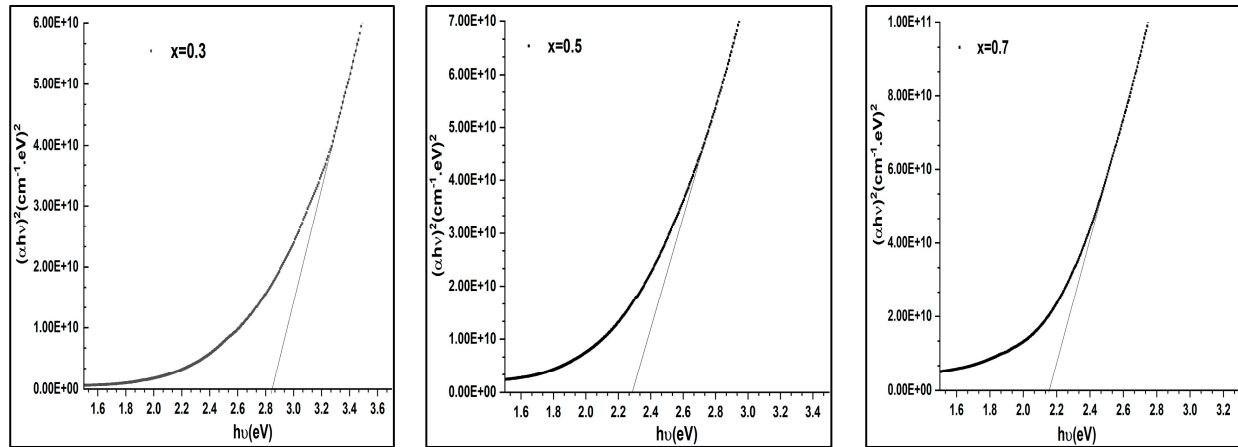
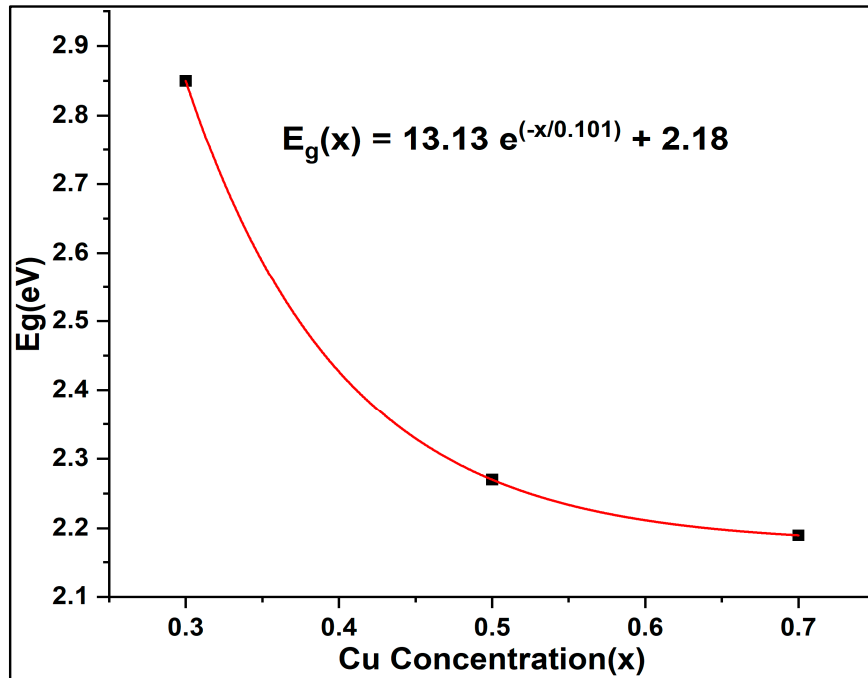


Figure 6: The absorbance and transmittance as a function of wavelength of CZS thin films.

Table 5: Optical parameters values of $\text{Cu}_x\text{Zn}_{1-x}\text{S}$ thin films.

$\text{Cu}_x\text{Zn}_{1-x}\text{S}$	E_g	ε_s	Moss Relation		Herve-Vandamme	
			n	ε_∞	n	ε_∞
$\text{Cu}_{0.3}\text{Zn}_{0.7}\text{S}$	2.85	9.74	2.48	6.15	2.39	5.71
$\text{Cu}_{0.5}\text{Zn}_{0.5}\text{S}$	2.29	11.47	2.62	6.86	2.59	6.71
$\text{Cu}_{0.7}\text{Zn}_{0.3}\text{S}$	2.16	11.87	2.66	7.08	2.64	6.97

**Figure 7:** Optical energy band gap of CZS thin films.**Figure 8:** The variation of CZS optical energy gap with Cu content.

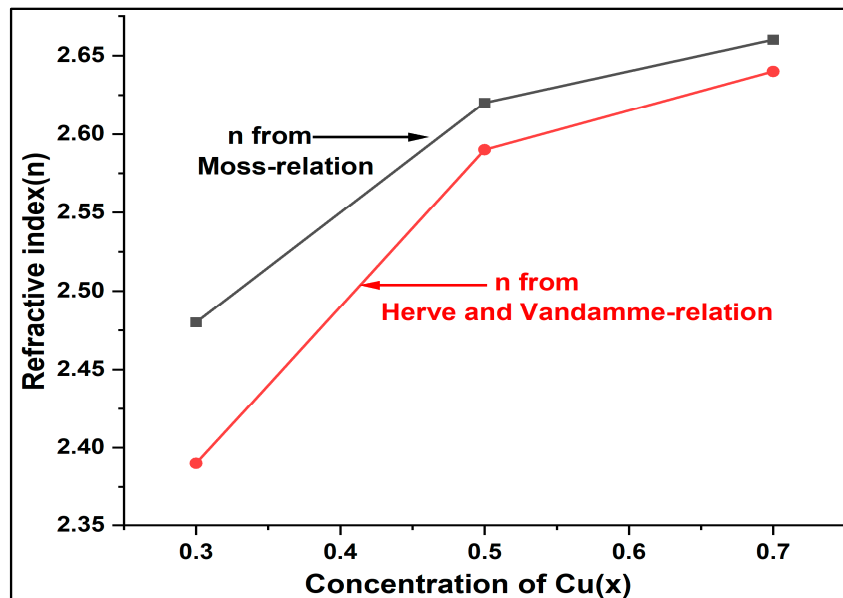


Figure 9: The variation of CZS refractive index with Cu concentration.

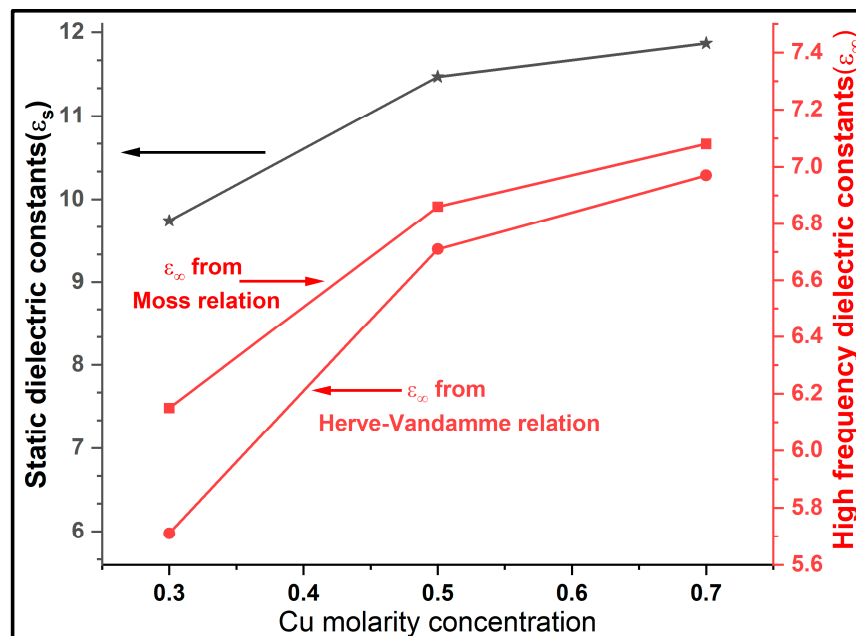


Figure 10: The variation of CZS dielectric constants with Cu content.

The Hall effect measurement results for thin CZS films are displayed in Table 6. The sign of the Hall coefficient (R_H) for all examined CZS thin films is positive, which means that all the prepared thin films exhibit p-type conductivity, i.e., the majority carriers are holes. This result agrees with previous studies [4,7,30,71]. With the replacement of Zn^{2+} ions by Cu^+ ions, Cu_{Zn} antisite defects are formed. These imperfections act as acceptors and produce holes, causing p-type conductivity [30,72]. When thin CZS film is prepared under sulfur-rich and zinc-poor growth conditions, donor imperfection formation energy, like sulfur vacancies (Vs) and zinc interstitials (Zni), increases greatly compared to the Cu_{Zn} point

defects, decreasing the chance of holes recombination [30]. Bogere et al. [60] found that alloying Cu^+ ions in the ZnS structure would create p-type conductivity. As concluded from XRD results, as Cu content increases, the CuS phase, which is characterized by p-type electrical conductivity, becomes the predominant phase. So, CZS thin films show positive electrical conductivity. Increasing holes concentration resulted in higher electrical conductivity (σ), indicating that Cu acts as an effective dopant within the thin CZS film's crystal structure. On the other side, increasing the concentration of holes (N_H) increases the collisions with defects and impurities resulting from copper, causing a reduction in the mobility of holes (μ) [73]. Increasing the holes concentration and electrical conductivity can lead to a great enhancement in the photosensor performance by decreasing response time and increasing detection sensitivity. Table 6 and Fig. 11 display the effect of Cu content on the electrical behavior of CZS samples. The semi-logarithmic plots of current-voltage (I-V) characteristics of the prepared Al/p- $\text{Cu}_x\text{Zn}_{1-x}\text{S}$ /n-Si/Al heterostructures at different Cu contents (0.3, 0.5, and 0.7) under dark and illumination are shown in Fig. 12. All CZS-based devices exhibit clear rectification behavior, confirming the formation of an effective diode. This mechanism can be explained by the predictable energy band diagram of the diode (Fig. 13), where an energy barrier arises at an interface between the p- $\text{Cu}_x\text{Zn}_{1-x}\text{S}$ /n-Si. This barrier forms from energy band offsets between the two semiconductors (CuZnS and Si), specifically the valence band offset (ΔE_v) and the conduction band offset (ΔE_c), in addition to the band bending caused by thermal equilibrium through the p-n junction diode. In reverse bias, the barrier height increases, impeding current flow. In contrast, it decreases with forward bias, facilitating its flow. Furthermore, there is a significant increase in photocurrent compared to the dark current. When the light strikes the device, electrons in the valence band of the active layer (CZS semiconductor) absorb the photons of the suitable energy and are excited to the conduction band, creating electron-hole pairs within the junction's space charge region and diffusion layers. The strong internal electric field of the depletion layer separates the photo-generated carriers within it and drifts them to the suitable electrodes, thereby creating a photocurrent [74]. Photocurrent density greatly depends on the semiconductor's energy band gap and the equilibrium between three fundamental processes: generation, recombination, and transport of charge carriers [75]. The improvement in heterojunction photosensitivity and responsivity can be attributed to enhanced structural and optical properties of thin films with increasing Cu ratio, as previously mentioned. This agrees with increased surface roughness, improved crystallinity, and narrower bandgap that contribute to enhanced optical and photoresponse properties. Reducing structural imperfections, reduction the non-radiative recombination centers. This yields a lower dark current and a higher photocurrent by increasing the lifetime of charge carriers. Copper acts as a sink for defects, reducing recombination centers and increasing available carriers, which suppresses the recombination process and thus minimizes the dark current [76]. Furthermore, discussed earlier, the reduction in the energy band gap, which resulted in an increment in the absorption coefficient, also contributed to the decrease in the dark current [77]. The rise in photo-generated current originates from a significant drop in the sensor's resistance under illumination at constant bias voltage (according to Ohm's law). This lowering reduces the R_L/R_D ratio with increasing Cu content, consequently improving percentage resistance-based sensitivity (see Fig. 14). The calculated parameters of CZS/Si HJ photosensors are tabulated in Table 7.

Table 6: The Hall effect results of CZS thin films.

x	R_H (cm^3/C)	σ ($\text{S}\cdot\text{cm}^{-1}$)	μ ($\text{cm}^2/\text{V}\cdot\text{s}$)	$N_H \times 10^{18}(\text{cm}^{-3})$
0.3	6.0270	0.2041	1.2303	1.0357
0.5	1.1880	0.6434	0.7645	5.2540
0.7	0.8264	0.7240	0.5981	7.5630

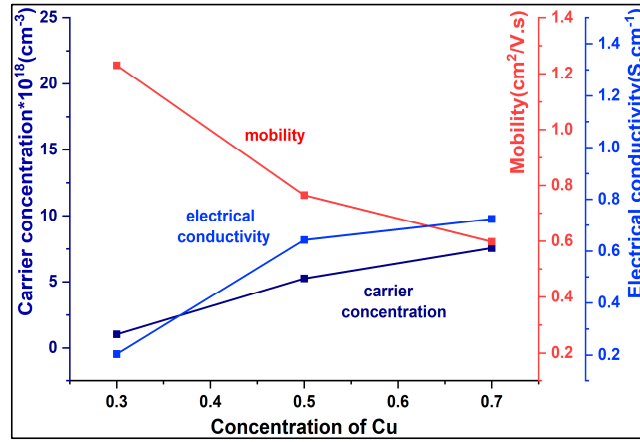


Figure 11: The electrical properties of $\text{Cu}_x\text{Zn}_{1-x}\text{S}$ thin films as a function of Cu content.

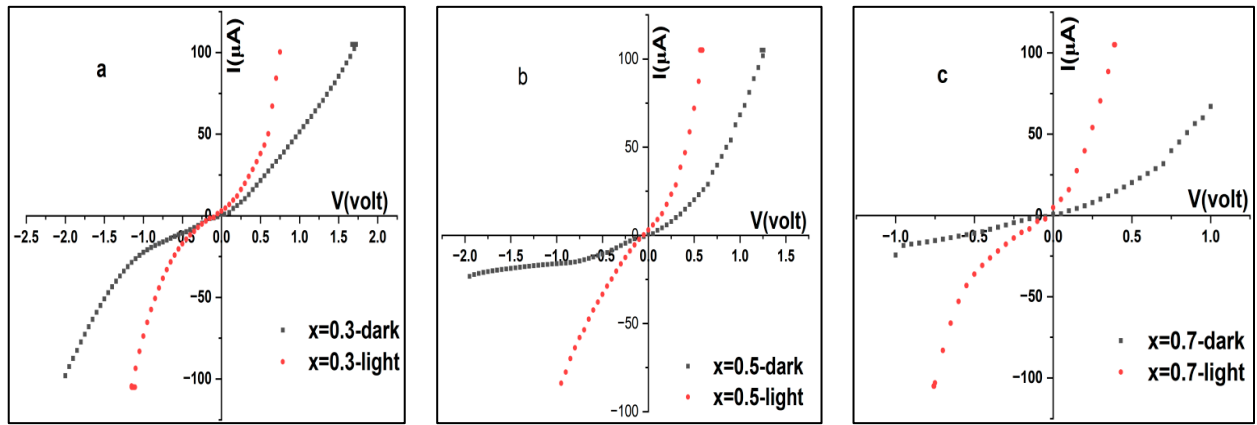


Figure 12: I-V characteristics of Al/CZS/Si/Al HJs at different Cu content: (a) $x = 0.3$, (b) $x = 0.5$, and (c) $x = 0.7$.

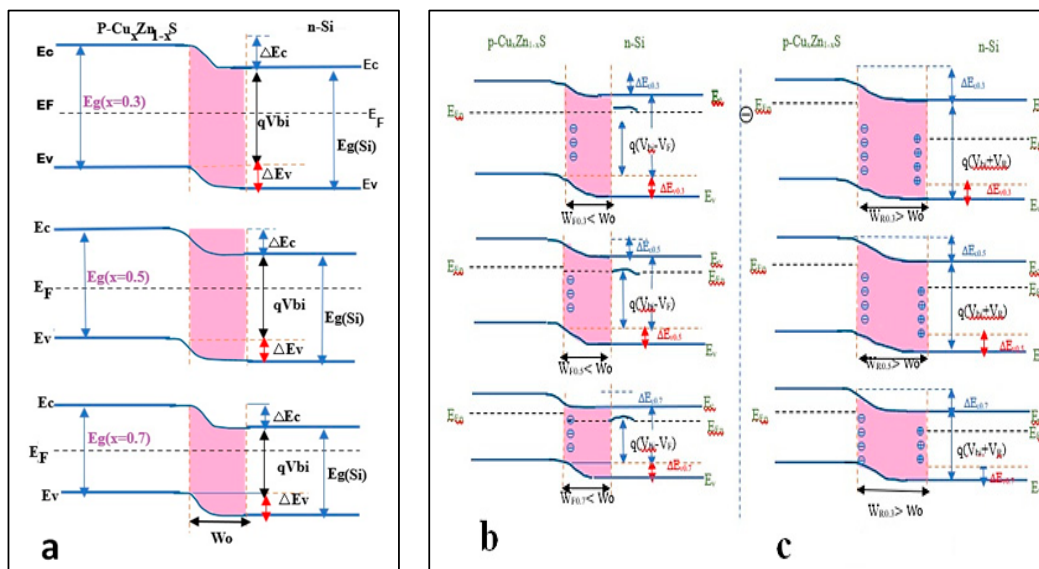


Figure 13: Energy band diagrams of the CZS/Si/Al HJs under: (a) equilibrium, (b) forward bias, and (c) reverse bias.

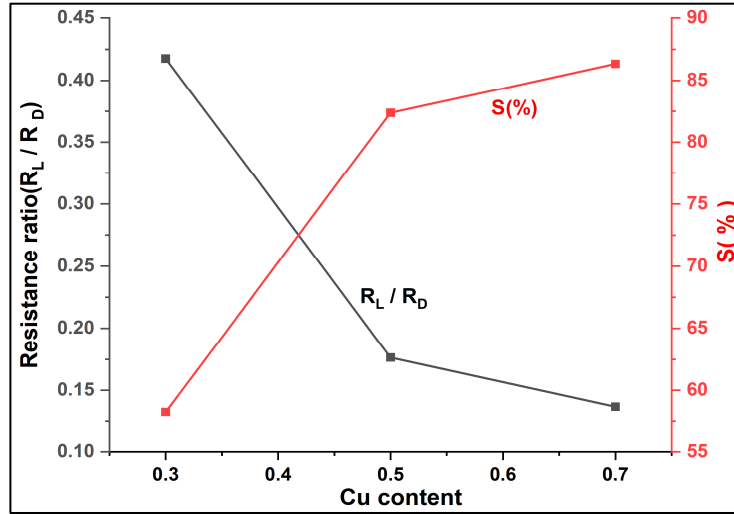


Figure 14: The variation of resistance ratio (R -light/ R -dark) and resistance based sensitivity% (S %) of fabricated sensors with Cu content.

Table 7: Photosensing characteristics of thin $\text{Cu}_x\text{Zn}_{1-x}\text{S}$ films.

Cu Content (x)	Photosensitivity (P.S)	at (-0.75 V)	
		Photoresponsivity (R) mA/W	Resistance Based Sensitivity% (S%)
0.3	2.3949	0.5580	58.2462
0.5	3.9846	1.0859	74.9037
0.7	6.6511	2.1877	84.9652

Table 8 displays the photoresponsivity of different reported thin film heterojunction photosensors based on various materials. The obtained responsivity depends on device structures, material systems, and measurement conditions, like applied bias voltage and wavelength.

Table 8: Photoresponsivity of different reported thin films photosensors.

Heterojunction	R (A/W)	Refs.
WZO/p-Si (Ag NP-coated)	4.83 ($\lambda = 365$ nm)	[78]
W-doped ZnO/p-Si	3.84 ($\lambda = 365$ nm, bias ± 5)	[79]
Graphene/n-Si	0.435 ($\lambda = 400$ – 700 nm)	[80]
n-ZnO/p-CuO	0.4369 ($\lambda = 365$ nm)	[81]
SnO_2 /p-Si	2.16 (≈ 300 nm)	[82]

4 Conclusions

The prepared thin $\text{Cu}_x\text{Zn}_{1-x}\text{S}$ ($x = 0.3, 0.5$, and 0.7) films using PLD technology showed a significant improvement in their structural, optical, and electrical properties with increasing Cu content. This increment contributed to enhancing the film's crystallinity and surface roughness, which in turn led to a decrease in the film's direct band gap from 2.85 to 2.16 eV, with an increase in absorption coefficient. This enhancement was directly reflected in the film's holes concentration and electrical conductivity, which increased from 1.0357×10^{18} to $7.5630 \times 10^{18} \text{ cm}^{-3}$ and from 0.2041 to $0.7240 \text{ S}\cdot\text{cm}^{-1}$, respectively. The obtained results indicated that the increase in the Cu content improved the electrical parameters of Al/p- $\text{Cu}_x\text{Zn}_{1-x}\text{S}$ /n-Si/Al HSs, where photosensitivity, photoresponsivity, and resistance-based sensitivity increased from 2.3949 to 6.6511, 0.5580

to 2.1877 mA/W, and 58.2462 to 84.9652%, respectively. Finally, based on the findings gained, thin CZS films are appropriate for employment as absorber layers in photovoltaic cells and optoelectronic devices.

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Author Contributions: The authors worked together to design and plan the research project. The lead researcher, Hanaa I. Mohammed oversaw the entire process, analyzed the results, and wrote most of the paper. Eman M. Nasir was responsible for conducting the experiments, gathering data, and helping to write up the findings. Iqbal S. Naji contributed to the initial design, carried out lab work, and helped with data analysis and drafting the introduction. All authors reviewed and approved the final version of the manuscript.

Availability of Data and Materials: X-pert software was used for analyzing the XRD data. The authors confirm that the data supporting the findings of this study are available within the article and from the corresponding author upon request.

Ethics Approval: Not applicable. This study did not involve human or animal subjects.

Conflicts of Interest: The authors declare no conflicts of interest.

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