Comparative Studies for Determining the Optical Band-gap Energy of the Novel Polycrystalline Thin ZnGa_2S_4 Films Sprayed at Different Film Thicknesses

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Comparative studies for determining the optical band-gap energy of the Novel polycrystalline thin ZnGa₂S₄ films sprayed at different film thicknesses

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ABSTRACT

This article has dedicated to studying some structural features and optical characteristics of the Novel polycrystalline ZnGa₂S₄ (ZGS) thin films utilizing spray pyrolysis process at different thicknesses (293, 375, 452, and 517nm). The microstructural properties and crystal defects of these films have been studied in previous work. While in this work, the crystallinity degree and crystalline volume fraction have been studied using X-ray diffractograms. The stoichiometry of these ZnGa₂S₄ films has been checked using the energy dispersive x-ray analysis. The field-emission-scanning-electron microscope has been utilized to investigate the morphology of ZGS films' surfaces. Optical properties have been studied via transmittance and reflectance spectra in the range 300nm - 2500nm. Some important optical parameters such as absorption coefficient, skin depth, Urbach's energy, steepness parameters, and electron-phonon interactions have been extensively studied. The direct and indirect gap energy were determined by different four models and compared with Tauc's model. Optical data analysis revealed that; all studied properties are strongly dependent on the film thickness. The optical band gap values were slightly decreased from 3.7eV to 4.1eV with increment of the film thickness owing to improving the crystallization process. These obtained results confirm that these films are wide band gap semiconductors, which makes them recommended for use in many solar cell applications as a window layer.

Keywords: Polycrystalline thin films; Crystalline volume fraction; Optical absorption coefficient; Urbach energy; Tauc plot; Optical band-gap energy.

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1. Introduction

In the last few decades, scientists, researchers and engineers have focused their efforts on studying manufactured novel materials that are used to convert photovoltaic energy into reliable electrical energy. So, there is an increased recall to use abundant, inexpensive, and environmentally friendly materials in thin-film solar cells. CuInGaSe₂ (CIGS) has been used as an absorbent in thin-film solar cells since it achieved the highest efficiency, which may reach about 20 % [1-3]. The search for toxic elements, scarcity, and the need to reduce the cost of mass production are driving chalcogenide-based solar cells as one of the next generations of thin-film solar cells [3]. Recently, the chalcogenides (ChG) thin films have received much attention in the past years owing to their diverse and numerous applications in electronic devices and memory switching, as well as in the nonlinear optical devices [4-8]. These ChG materials are characterized by their low phonon energy and their transparency in visible and infrared regions [9-12]. Also be doped by some rare earth elements, like Pr, Er, Nd, ... etc. Moreover, these ChG-glasses are highly optical nonlinear materials and hence can be used for the optical-switching devices, OS. These glasses are also sensitive to the absorption of electromagnetic radiation and show a variety of photoinduced effects because of illumination.

The ChG materials are varied and found in abundance in the earth and have distinct and unique characteristics such as good optical and electrical properties, as well as their cheap prices, ease of production, and chemical stability. Hence, and owing to these wonderful properties, they are very suitable for producing window layers and economical absorbers for the solar cells [13]. It is worth noting that, the fabrication of the window layers require a semiconducting material that has a wide band gap (3.5 eV - 3.8 eV) and of higher transmittance [14]. These unique conditions have been exhibited in the metal oxides, such as ZnO, SnO₂, and In₂O₃, which have good efficiency to make as window layers of solar cells [15]. Moreover, the production of the absorbing layer of electromagnetic waves requires a semiconducting material that has a narrower energy gap (1.0 eV-1.5 eV), and a distinguished absorption of light of a wavelength arranged between 350 nm and 1000 nm, i.e., more than 10⁴ cm⁻¹ [16].

Thin Cu-ChG films like either Cu-Zn-Sn-S, or Cu-Zn-Sn-Se, CZTS(Se) exhibited better efficiency in solar cells. The scientists and researchers deposited thin CZTS films utilizing the sputtering technique and then they have measured their p-type conductivity. The electronic transition was found to be direct band gap about 1.45 eV, and their absorption coefficient was more than 10⁴ cm⁻¹ in the visible region [17]. The CZTS compositions and their films can be crystallized as a bland-zinc crystalline structure similar to other semiconducting materials such as Cu-In-Ga-Se, CIGSe, and Si. Generally,

CZTS compositions can have two other forms; the first one is the stannite crystal structure, which has the same tetragonal coordination, but with unlike symmetry owing to the alternate situation of cations in the main crystal lattice. While the second is the wurtzite-derived crystal structure, which is a hexagonal close-packed array [18]. The three crystal structures have a formal $\text{Cu}_2\text{ZnSnS}_4$ stoichiometric, although the kesterite structure is the most often used in solar cells. The experimental procedures of manufacturing CZTS(Se) solar absorber layers could be classified into two different categories, they are: The vacuum-based techniques include flash evaporation, thermal evaporation, sputtering, and atomic layer deposition techniques. While the non-vacuum-based techniques (or the solution-based) processes include all chemical deposition processes, such as spray pyrolysis, sol-gel, electro-deposition, molecular precursors, and nano-crystal techniques [17-21].

The II-III₂-VI₄ compounds like ZnIn_2S_4 , CdIn_2S_4 , ZnGa_2S_4 , and CdAl_2S_4 are also considered as significant ChG materials as they showed the n-type conductivity, higher transparency, and a wide gap ranged between 3.4 eV and 3.8 eV [19]. The importance of these ChG materials encourages the researchers to look for synthesizing of new compositions from this group, for the possibility of their using in solar cells as new optical windows [20]. The present work has focused on the novel thin ZnGa_2S_4 films owing to their non-toxic, low economical price, earth-abundant, and stability, along with their wide band gap and higher thermal stability.

The aim of the present work is to continue the previous study that presented a thorough study of the synthesis of the Novel nanocrystalline thin ZnGa_2S_4 films of various thicknesses by an inexpensive spray pyrolysis technique. In addition, the authors have studied the effect of film thickness on the surface morphology, crystal structure, crystal defects, and microstructure properties of these novel films [21]. The X-ray diffractions, XRD, Field emission-scanning electron microscope, FESEM, and the energy dispersive X-ray spectroscopy, EDX techniques have been employed to inspect the structural characteristics of the ZnGa_2S_4 thin films. Consequently, the authors of the current article will focus on studying the optical properties of these film samples. The optical characteristics of the films have been studied via studying the transmission, reflection, and absorption spectra and determining the parameters that describe the electronic transitions, such as: absorption coefficient, absorbance or optical density, the skin depth, band gap energy, Urbach energy, and valence band tails. Along with some important optical parameters of the ZnGa_2S_4 thin films that related to the principal optical transitions in the UV, Vis, and IR regions have been investigated and discussed. Moreover, the optical band-gap

energy values will be determined by various methods, such as Tauc's plots, the absorption-spectra fitting curves, ASF, Cody representations, and Davis-Mott model.

2. Experimental details

2.1. ZnGa₂S₄ film formation

In this research work, an inexpensive spray pyrolysis method has employed to obtain the ZnGa₂S₄ thin films. At first, we make substrate cleaning process to get the ZnGa₂S₄ thin films of better quality. The used substrates are ordinary micro slides of soda lime glass of dimension 26×76×2 mm³ which have good optical characterizations. The cleaning process was carried out as follows; first, the glass sheets have been dipped in freshly equipped chromic acid, which has been heated up to 60°C. The glass sheets have been removed from the acid and washed with a distilled water. Subsequently they were placed in the solution of an alkaline soap for at least ten minutes. Thereafter, they have been washing with running water, where the process of washing was repeated. Next, the substrates have been washed using double-distilled water then using the ultrasonic waves. Finally, the glass sheets have been dried in a furnace of hot air. This removes any dust particles that may be sticking to a surface, ensuring maximum hygiene and making the film stickier to the substrate.

Chemicals in the powder form have been used to synthesize the ZnGa₂S₄ solution. This solution was used to precipitate thin films using the spray pyrolysis process. These chemicals are (GaCl₃), (Zn(CH₃COO)₂·2H₂O) and (Na₂S₂O₃·5H₂O) of molecular weights 281.26, 219.51 and 248.18, respectively. These chemical powders have high purity degrees (99.99%) and were purchased from the company Sigma-Aldrich. These chemicals were utilized without any further purification.

The precursor solutions for fabricating the novel ZnGa₂S₄ films were synthesized using: (i) 0.1 M from Zn (CH₃COO)₂·2H₂O, the zinc acetate dihydrate, (ii) 0.2 M from GaCl₃, gallium trichloride, which is used as a gallium source and (iii) 0.4 M from Na₂S₂O₃, sodium thiosulfate, as a sulfur source. The ZnGa₂S₄ solution was stirred well for one hour to produce a yellow solution. These molarity values were chosen to ensure that thin film having the stoichiometric ratio 1: 2: 4 were obtained. The ZnGa₂S₄ solution was sprayed from a nozzle on the pre-cleaned glass substrates via the spray pyrolysis technique, where the substrate temperature was fixed at 300 °C, the rate of flow was adjusted at 10 ml/min, and the airflow pressure from the compressor was fixed invariant at 3 bar. While the distance between the spray nozzle and the substrate was fixed at 30 cm, for all films. Furthermore, the deposition time during the spray process was 5, 10, 15, and 20 min to get thin films having these thicknesses: 293 nm, 375 nm, 452 nm, 517 nm, respectively, as measured by the alpha step D-500 stylus profilometer. It is worthy to

mention that the thickness of each film was measured multiple times, and mean values were taken into account. For more specifics on the used spray pyrolysis method and the experimental procedures that have been exercised during the preparation of film samples, refer to the authors' previous work [22-25].

2.2. Materials characterization

The polycrystalline nature of ZnGa_2S_4 thin films was examined using a Philips-X'Pert X-ray diffractometer, with $\text{CuK}\alpha$ radiation. The X-ray diffractograms were published elsewhere [21]. The crystallographic studies showed that the samples the tetragonal crystal nanostructure of the lattice constants equal $a = 0.5272$ nm and $c = 1.0451$ nm that consistent with the following XRD Cards: JCPDS 89-4207, 80-1707, and 40-1462. Moreover, the average crystallite size of films increased from 14 nm to 40 nm as the thickness of the film increased [21]. The compositional element percentages and the surface morphological features of the ZnGa_2S_4 thin films were characterized via using the Quanta-FeG-250 USA field-emission-scanning-electron microscope, *FE-SEM*. The energy-dispersive X-ray spectroscopy technique, *EDAX* was also employed to investigate the elemental compositions and the finding confirmed that all thin-films have a good stoichiometry, along with in a good match with the theoretical computations. For more details about these *EDAX* characteristics and *FE-SEM* micrographs, anyone can refer to the previous work [21]. Optical properties of the ZnGa_2S_4 films were carried out via measuring the reflectance, R and transmittance, T of films in the spectral range 400 nm - 2500 nm. A double beam UV-Vis-NIR-Shimadzu spectrophotometer of the model UV-310-PC was used to record the R - and T -spectra of the film samples. All optical measurements are performed at room temperature.

3. Results and discussions

3.1. Sample identification and structural studies

3.1.1. FE-SEM and EDS investigations

Optical microscopes are effective tools used to specify the morphology, microscopic structural imperfections, and macro- surface defects that may manifest in the crystalline films, especially the optically transparent microscopes. Where the electron beam interacts with the atoms of the film sample, to produce various signals. These signals provide good information about the morphology, topography, and compositional elements of the surface. The electron beam is generally scanned using raster scanning and the location of the beam is combined with the signal to produce an image [21]. By scanning the

sample and collecting the secondary emitted electrons with a special detector, an image showing the surface morphology is created.

The morphological features of ZnGa_2S_4 film surface have been scanned by the field-emission-scanning-electron microscope, FE-SEM of the type Quanta-FeG-250 USA. Figures (1-a) and (1-b) depict the obtained FE-SEM micrographs of nano-dimensions ZnGa_2S_4 films for the smallest thickness (293 nm) and largest thickness (517 nm) samples, respectively, as typical samples of ZnGa_2S_4 films. These FE-SEM micrographs show that the polycrystalline ZnGa_2S_4 thin films have a good surface shape and that the particle sizes are almost homogeneous and uniform. These FE-SEM-micrographs also illustrate that the particle size of the film sample is almost increasing as the film thickness increases. This affirms the improvement of the crystallization of film and crystallinity degree of ZnGa_2S_4 film samples. These results are also in good matching with those obtained from the study of the X-ray diffraction.

On the other hand, the apparatus of FE-SEM has been equipped with interface equipment for the energy-dispersive x-ray spectroscopy investigations, EDS to check and analyze the percentage of the compositional elements of the studied thin films. The EDS spectra have been shown in Fig. (1-c) and Fig. (1-d) for these two films (of thicknesses 293 nm and the thickness 517 nm, respectively), as representative film samples. The elemental percentages of the present thin ZnGa_2S_4 film samples have been recorded in Table 1. The analysis of the EDS data and their chart spectra of the polycrystalline ZnGa_2S_4 thin films confirmed that all synthesized films are consisting of Zn, Ga, and S elements, only, and no others detected. It is worthy to mention that the atomic fractional percentages of the three constituent elements (Zn, Ga, and S) are almost stoichiometry, where their percentages were close to the ratio (1: 2: 4) for all films. Furthermore, it is observed that the percentage of the S-element is slightly increasing with the increment of the film thickness. This increase is occurring on the account of the Si-percentage.

The thicker the film, the greater the distance traveled by the incident beam of electrons through the film compared to thinner films. Therefore, the higher the thickness of the film, the more accurate the percentages of the thin-film elements obtained for the film itself. At the same time as the thickness of the sample increases, it is found that the silicon percentage is decreasing. On the other hand, when excluding the percentage of Si originated from the glass substrate used, it turns out that the percentages of the three elements are almost invariant unaffected as the film thickness increases (maybe varied very slightly). This is because the solution used to prepare all samples has not changed, but what has changed is the deposition time that increases the film thickness.

Fig. (1): FE-SEM micrographs (a and b) and EDS-spectra (c and d) of the present thinner and thicker film samples (of thicknesses 293 nm and 517 nm), as typical samples of the ZnGa_2S_4 thin films.

Table 1: The FE-SEM compositional element percentages of the polycrystalline ZnGa_2S_4 films.

Thickness of film (nm)	Elements percentage included the Si of glass substrates (at. %)				Percentage of elements without that of Si (at. %)		
	Zn (%)	Ga (%)	S (%)	Si (%)	Zn (%)	Ga (%)	S (%)
293	8.192	17.231	34.423	40.154	13.686	28.796	57.518
375	8.530	17.954	35.281	38.235	13.683	28.797	57.520
452	8.739	18.378	35.925	36.958	13.687	28.796	57.517
517	9.381	19.122	36.311	35.186	13.684	28.801	57.515

3.1.2. Crystal structural studies

X-ray diffractograms, XRD of the current novel prepared thin ZnGa_2S_4 films with different thicknesses have depicted that all films have the same polycrystalline nature, as shown in Fig. (2). The diffraction patterns are almost similar but with different intensities of the diffraction lines, as well as the positions of these lines are slightly shifted towards higher degrees of Bragg's diffraction angles (2θ). Moreover, the obtained diffraction lines are detected at the following diffraction angles 29.09° , 31.61° , 36.98° , 54.14° and 65.15° for the first film of thickness 293 nm. These angles are in accordance with the following crystals' diffraction planes: (112), (103), (202), (310) and (206), respectively, as depicted in Fig. (2).

Fig. (2): X-ray diffraction pattern of the ZnGa_2S_4 thin films of different thickness; The Red line represents the experimental curve (it is a mixture of the amorphous and crystalline phases), while Blue line is the amorphous phase.

Further, these diffraction lines are also found to have strong intensity, which confirm that the film samples are well crystallized. These detected diffraction peaks are in good consistency with the following XRD cards: JCPDS card No. 40-1462, JCPDS card No. 80-1707 and JCPDS card No. 89-4207. It is worthy to mention that there are no other diffraction peaks except these observed five peaks, which confirm that the formed phase is the ZnGa_2S_4 tetragonal polycrystalline phase. The details and explanations about the crystallography and crystal microstructure of these films were published elsewhere [21].

3.1.3. Evaluation of the degree of crystallinity

The physical, mechanical, and morphological properties of thin films depend on the degree of crystallinity and the direction of the preferred orientation growth during the preparation of materials and the deposition of film samples. Usually, these two factors have changed according to the used preparation route and the followed preparative parameters (such as the temperature of the substrate, the rate of the deposition, time of deposition, and the solution molarity). This is because of the growing crystallites of the films are exposed to thermal and kinetic energy during the deposition process. This increases the microscopic stress, lattice strains, and internal pressures that prevent the molecules from naturally arranging to form a certain crystal structure or to stacking in the form of crystals. This means that the degree of crystallinity of the thin films depends primarily on the preparation properties of those materials. Therefore, thin films are usually a mixture of crystalline and amorphous phases.

The XRD-charts of ZnGa_2S_4 thin film shows that the crystallization process of films improves with increasing film thickness, where the diffraction Bragg's peaks become sharper and more intense with respect to the diffraction line of the crystalline phase of the largest thickness. The XRD-data can be employed to compute the crystallinity degree of the partially crystalline or polycrystalline films [26-30]. For the currently studied ZnGa_2S_4 thin films, this procedure succeeded in integrating all diffraction peaks corresponding to the observed lines: (112), (103), (202), (310) and (206), where the intensity of the X-ray diffraction lines is as depicted in Fig. (2). Subsequently, by summing these intensities into one intensity that represents the integration of the crystallized part. For the subsequent analysis, we adopted a two-phase concept typically applied to thin films in which the amorphous contribution to the spectrum, which occurs as a broad diffraction band has been approximated by the background curve separating the amorphous part from the crystalline portion. Then the degree of crystallinity of each sample was obtained as a ratio between the area under the crystalline peaks and the total area under the diffraction curve.

In this work, a typical fitting procedure was used to separate the crystalline peaks from the amorphous halo of the ZnGa_2S_4 thin films of different thicknesses, as shown in Fig. (2). The crystal fraction was detached from the non-crystalline one using a computer program (EVA program) using the Hermans-Weidinger method [31]. Subsequently the degree of crystallinity, X_{Cryst} of each sample has been determined from the ratio between the area under the crystalline peaks, A_{Cryst} and the whole area under the *XRD* curve, $(A_{Cryst} + A_{Amorph})$ according to a simple formula:

$$X_{Cryst} = \frac{A_{Cryst}}{(A_{Cryst} + A_{Amorph})} \times 100 \quad (1)$$

It is clear from the tabulated results of Table 2 that the degree of crystallinity and the total area under the curves increase gradually with increasing the film thickness. This is evidence of an improvement in crystallinity of films and an increase in x-ray scattering. This in turn leads to a decrease in the amorphous ratio of the ZnGa_2S_4 thin films. The crystalline percentage, X_{Cryst} of thin ZnGa_2S_4 films increases with the increment of the thickness of films from 9.204 to 16.921. This means that an increment in crystallinity of ZnGa_2S_4 films has been observed for all samples of different thicknesses due to improvement in the crystallization. Consequently, it can be concluded that the film thickness increasing has a pronounced effect on the degree of crystallinity of ZnGa_2S_4 thin films [32].

3.1.4. Crystalline volume fraction

The determination of the crystalline volume fraction, V_{Cryst} of a substance can simply be considered as a quantitative phase analysis of two-phase materials (crystalline and amorphous phases). To work on such a hypothesis, a common XRD-based procedure as hypothesized by B.D. Cullity (1978) [33,34]. Thereby, to determine the volume fraction of the crystalline phase of partially crystalline materials from the structural measurements using XRD and by comparing the integrated intensities of the peaks derived from the amorphous and crystalline phases according to Huang's proposal [35]. In this case, the volume fraction of crystalline phase, V_{Cryst} can be estimated from the following Eq. [35]:

$$V_{Cryst} = \frac{I_{Cryst}}{(I_{Cryst} + \alpha I_{Am})} \quad (2)$$

Where I_{Cryst} and I_{Am} are the integral intensities of the diffraction lines from the crystalline and amorphous phases, respectively. However, the parameter (α) is unknown, and it is called the Huang parameter. Indeed, for $\text{Fe}_{73.5}\text{Cu}_1\text{Nb}_3\text{Si}_{13.5}\text{B}$ alloy, $\alpha = 1.05$ [36], and for $\text{Al}_{88}\text{Ni}_4\text{Sm}_8$, $\alpha = 0.37$ [37]. To determine the value of this α -parameter, a series of diffraction patterns were measured which could be different for different systems. When subtracting the background of the diffraction pattern, the diffractograms could

be decomposed into two components owing to the amorphous and crystalline phases and subsequently the integrated reflection intensities from each phase could be estimated.

Table 2: Analysis of X-ray diffraction data, degree of crystallinity, crystalline volume fraction and some optical factors of the Novel thin ZnGa₂S₄ films with various thicknesses.

<i>Inferred parameters</i>	<i>Film thickness (nm)</i>			
	<i>293</i>	<i>375</i>	<i>452</i>	<i>517</i>
<i>Area of amorphous; A_{Am}</i>	<i>1388.061</i>	<i>1408.047</i>	<i>1416.278</i>	<i>1528.428</i>
<i>Total Area; A_T = (A_{Cryst}+A_{Am})</i>	<i>1528.647</i>	<i>1614.848</i>	<i>1649.756</i>	<i>1839.811</i>
<i>Area of crystalline; A_{Cryst}</i>	<i>140.594</i>	<i>206.813</i>	<i>233.478</i>	<i>311.378</i>
<i>Degree of crystallinity; X_{Cryst}%</i>	<i>9.204</i>	<i>12.813</i>	<i>14.154</i>	<i>16.921</i>
<i>Amorphous ratio; A_{Am} %</i>	<i>90.803</i>	<i>87.192</i>	<i>85.853</i>	<i>83.081</i>
<i>Intensity of crystalline & amorphous; I_{Total}</i>	<i>70</i>	<i>219</i>	<i>221</i>	<i>241</i>
<i>Intensity of amorphous; I_{Am}</i>	<i>36.503</i>	<i>35.439</i>	<i>33.148</i>	<i>30.267</i>
<i>Intensity of crystalline phase; I_{Cryst}</i>	<i>33.503</i>	<i>183.561</i>	<i>187.848</i>	<i>210.728</i>
<i>Corrected amorphous phase intensity; αI_{Am}</i>	<i>33.001</i>	<i>32.052</i>	<i>29.978</i>	<i>27.367</i>
<i>Crystalline phase; C₁</i>	<i>0.478</i>	<i>0.827</i>	<i>0.849</i>	<i>0.868</i>
<i>C₂= I_{Cryst}/(I_{Cryst}+I_{Am})</i>	<i>0.311</i>	<i>0.722</i>	<i>0.741</i>	<i>0.779</i>
<i>Huang parameter; α</i>	<i>0.904</i>	<i>0.904</i>	<i>0.904</i>	<i>0.904</i>
<i>Crystalline volume fraction; V_{Cryst}</i>	<i>0.325</i>	<i>0.851</i>	<i>0.862</i>	<i>0.885</i>
<i>Urbach energy, E_U (eV)</i>	<i>0.431</i>	<i>0.531</i>	<i>0.617</i>	<i>0.699</i>
<i>Absorption coefficient; α_o ×10⁴ (cm⁻¹)</i>	<i>2.664</i>	<i>3.242</i>	<i>3.681</i>	<i>3.378</i>
<i>Steepness parameter (σ) ×10³</i>	<i>60.051</i>	<i>48.704</i>	<i>41.927</i>	<i>37.005</i>
<i>The resistivity, ρ_{opt} (Ω/m)</i>	<i>12.509</i>	<i>19.758</i>	<i>45.658</i>	<i>94.338</i>
<i>The optical conductivity, σ_{op} ×10⁻² (s⁻¹)</i>	<i>7.989</i>	<i>5.059</i>	<i>2.189</i>	<i>1.063</i>
<i>Electron -phonon interaction (E_{e-ph})</i>	<i>11.103</i>	<i>13.689</i>	<i>15.902</i>	<i>18.021</i>
<i>The wavelength of absorption edge (direct transition) (λ_g),(nm) by ASF method</i>	<i>302</i>	<i>307</i>	<i>323</i>	<i>330</i>
<i>The wavelength of absorption edge (indirect transition) (λ_g),(nm) by ASF method</i>	<i>345</i>	<i>360</i>	<i>370</i>	<i>385</i>

Fig. (3) illustrates the dependence of the integrated intensity ratios of the real (*C₁*) concentration of the crystalline phase in the sample *I_{Am}* and *I_{Cryst}* are integral intensities of the amorphous and crystalline phase, respectively, derived from the experimental data, and (*C₁*) is the true concentration of the crystalline phase [38,39]. To find integrated intensities, the diffractions obtained in this way by Gaussians

were approximated with the least squares fit. In this work the graphical relationship between I_{cryst} and $(I_{Cryst}+I_{Am})$ was plotted versus the crystalline phase (C_1) as a linear relationship and the slope was calculated so the value of (α) was equal to 0.9043. It has been shown that the volumetric fractions of the crystal phase derived from different techniques can vary significantly [40].

Fig. (3): Dependence of intensity's ratios for the integrated intensities on the true C_1 concentration of the crystalline phase, the slope of the straight line represents the α -coefficient (Huang parameter).

The crystalline volume fraction, V_{Cryst} of the investigated samples were calculated by the change of film thickness and recorded in Table 2. It is clear that, this fraction, V_{Cryst} , was found to be in the range from 0.325 to 0.885 for crystalline $ZnGa_2S_4$ films as the increment of thickness from 293 nm to 517 nm, respectively. It can be observed that the increase in the film thickness induces a change in the amorphous-crystalline transition, showing an increase in V_{Cryst} for the investigated samples. As the film thickness increases, the growth of the repeated layers of ions increases, leading to the construction of a crystal agglomerations. Thus, complete grain growth does not occur, which reduces the formation of crystallite of $ZnGa_2S_4$. This fact is related to a crystallization of the material for higher film thickness [41].

3.2. Optical characteristics

3.2.1. Transmittance and reflectance spectra

The optical parameters of the examined thin ZnGa_2S_4 films have been determined from the transmission and reflection data. The spectral variation of the normal transmittance $T_{\text{exp}}(\lambda)$ and reflectance $R_{\text{exp}}(\lambda)$ due to the effect of the used substrate is given as follows [42,43]:

$$T_f(\lambda) = \frac{T_{\text{exp}} T_{\text{sub}} (1 - R_{\text{exp}} R_{\text{sub}})}{T_{\text{sub}}^2 - T_{\text{exp}}^2 R_{\text{sub}}^2} \quad (3)$$

$$R_f(\lambda) = \frac{R_{\text{exp}} T_{\text{sub}}^2 - T_{\text{exp}}^2 R_{\text{sub}}}{T_{\text{sub}}^2 - T_{\text{exp}}^2 R_{\text{sub}}^2} \quad (4)$$

Where T_{sub} is the transmittance and R_{sub} is the reflectance of the glass substrate. Figs. (4-a) and (4-b) show the corrected optical transmittance $T_f(\lambda)$ and reflectance $R_f(\lambda)$ of the current ZnGa_2S_4 thin films measured in the wavelength range from 300 nm to 2500 nm. The transmittance and absorbance of thin films of various thicknesses increase without the presence of a shift in the absorbing edge, while the reflectance exhibits the opposite behavior with the change in the film thickness. These variations can be attributed to the crystallinity improvement of films and enhancing of the crystallization process and the film morphology, along with the minimizing of the crystal defects [23].

Fig. (4): The spectral variations of (a) transmittance and reflectance, and (b) absorbance as functions of the wavelength incident on thin ZnGa_2S_4 films.

It can also be observed that the transmittance and absorption spectra of all thin films can be divided into three main special regions: (1) the strong absorption region, which extends to wavelengths

smaller than 750 nm, (2) the transparent region, which is after the wavelength of 1750 nm; (3) The absorption region between these two regions (750 nm – 1750 nm). Also, the spectral distribution of both transmittance $T(\lambda)$ is decreasing while that of the reflectance $R(\lambda)$ is gradually increasing as increasing the film thickness. This is due to improving the film crystallinity and minimizing the crystal defects [23], which in turn leads to the increase in absorption of the ZnGa₂S₄ thin films of different thicknesses. Moreover, the absorption edge remains unchanged with increasing film thickness while the summation of T and R is less than the unity after the absorption edge due to the scattering of light produced by the roughness of the surface of the studied films [43-46].

3.2.2. Absorption coefficients

The absorption coefficient of materials plays a substantial role in choosing a specified material to be used in the possible applications, especially semiconductor materials. Along with, the study of the absorption nature of this material supplies basic information about the forbidden optical band gap and the electronic transitions type of materials. Therefore, it was indispensable to study the absorption coefficient (α) of the thin ZnGa₂S₄ films. The values of the absorption coefficient can be inferred through the spectra of both transmittance, $T(\lambda)$, and reflectance, $R(\lambda)$. This coefficient, α , can be computed from this Eq. [47-49]:

$$\alpha(\lambda) = \frac{1}{t} \ln \left[\frac{(1-R)^2}{2T} + \sqrt{\frac{(1-R)^4}{4T^2} + R^2} \right] \quad (5)$$

Where T , R and t are the transmittance, reflectance, and the thickness of ZnGa₂S₄ thin films in centimeters. High absorption coefficient values after the bandgap range are among the most important and critical characterizations of thin films. The extremely high α -values, in the order of 10^4 cm^{-1} and more than this, increase the importance of ternary compositions and their suitability in optoelectronic applications, which is the case for ZnGa₂S₄ thin films. The variation of the absorption coefficient versus the incident wavelength at and near the absorption edge of the ZnGa₂S₄ thin films is shown in Fig. (5-a) and Fig. (5-b). These figures depict that the absorption coefficient increases significantly to the highest value at about 300 nm wavelengths at the edge to reach values of approximately $2.5 \times 10^4 \text{ cm}^{-1}$. Subsequently its value suddenly decreases at a wavelength ranging from 500 nm to 600 nm and thereafter reaches an invariant value after a wavelength of more than 600 nm, for all film samples. It is also clear that films of smaller thickness have higher absorption coefficient values in the visible region, but after 750 nm, all films have almost the same absorption values. The published literature has shown that these results are well consistent with many similar semiconductor films [49-51].

Fig. (5): The variation of the absorption coefficient versus the wavelength of thin ZnGa₂S₄ films (a) along the studied range and (b) at the absorption edge.

3.2.3. Skin effects and skin depth

The absorption of electromagnetic waves in thin semiconductor films relies on many parameters, the most important of which are (1) the type of film material itself, (2) the thickness of the film, (3) the morphology of the film surface, and (4) the absorption index of the film material (k), as well as the optical conductivity of the film. When a ray of light passes through thin films, the photon intensity decreases dramatically for many reasons, like the density of the material, refractive index, morphology of the surface, and the film microstructure. When the optical intensity of the photon becomes $(1/e)$ below the surface of the thin film, subsequently the thickness of the film that causes this is called skin depth (δ_d). This depth also depends on the photon frequency and the film's optical conductivity, which depends extremely on the width of the forbidden bandgap. So, the two parameters (α) and (δ_d) for any film could be linked by these forms [52-54]:

$$\delta_d = \frac{1}{\alpha} = \frac{\lambda}{4\pi k} = \sqrt{\frac{\rho_{opt}}{\pi \cdot \mu_o \mu_r \cdot f}} \quad (6)$$

$$\delta_d = \sqrt{\frac{\lambda}{\pi \cdot c \cdot \mu_o \mu_r \sigma_{opt}}} = \frac{1}{\sqrt{\pi \cdot c \cdot \mu_o \mu_r \cdot \sigma_{opt}}} \cdot \sqrt{\lambda} \quad (7)$$

Where ρ_{opt} and σ_{opt} are the optical resistivity and conductivity, respectively of the thin ZnGa₂S₄ film, f is the frequency. While μ_r and μ_o are the relative permeability which is usually considered to be the unity and the absolute permeability constant, respectively ($\mu_r = 1$ and $\mu_o = 4\pi \times 10^{-7}$ H/m). Using the spectra of

(a) the depth, δd can be computed for ZnGa₂S₄ thin films. Figure (6-A) exhibits the variation of (δd) versus the photon energy ($h\nu$) for the thin ZnGa₂S₄ films of different thicknesses.

Fig. (6): Variation of the skin depth as a function of (a) the photon energy and (b) $\sqrt{\lambda}$, for ZnGa₂S₄ films of different thicknesses.

The figure illustrates that the spectral values of δd decrease as the increment of the photon energy and the influence of absorption will be vanished at a certain point, which is the cut-off of the wavelength. It is observed also that at energy values larger than or equal to the optical gap energy, the δd -value decreases gradually till it reaches/approaches zero value. The energy value at which the depth δd reaches the zero value is called the cut-off energy, $E_{cut-off}$ and the corresponding wavelength is called the cut-off wavelength, $\lambda_{cut-off}$. The $E_{cut-off}$ value = 4.490 eV, and $\lambda_{cut-off}$ = 275 nm, for the current thin ZnGa₂S₄ films (See the figure). Hence, the absorption of the present films completely vanished at wavelengths less than 275 nm, and the wave amplitude is decreasing after traveling a long distance, where δd depends on the transmittance, $T(\lambda)$ of films. Similar results have been obtained for some previous work on semiconductor films [55-59].

On the other hand, and according to Eq. (6), σ_{opt} of thin ZnGa₂S₄ films can be deduced from (δd) and ($\sqrt{\lambda}$). Fig. (7-b) illustrates the dependence of (δd) on ($\sqrt{\lambda}$) of the thin ZnGa₂S₄ films of different thicknesses. It can observe that the relationship between (δd) and ($\sqrt{\lambda}$) is a linear relationship for all thicknesses and almost increases with the thickness. The values of the optical conductivity, σ_{opt} and the resistivity, ρ_{opt} at different film thicknesses of the ZnGa₂S₄ were estimated from the straight-line's slope that was fitted, as illustrated in the Fig. (7-b) and subsequently recorded in Table 2. It can also observe here that the (σ_{opt})-values decrease as the film thickness increases. This is owing to several reasons, like the activated thermal transfer of electrons from VB to CB in the semiconducting materials, and the charge

carriers short-range hopping at the grain boundaries, as well as the localized hopping of the charge carriers within the grains, too [59]. Additionally, the strong coupling between an electron and a phonon is formed by the vibrations of the ions of the crystal lattice at a limited temperature known as a polaron [59,60].

3.2.4. Urbach energy

The absorption coefficients of the thin ZnGa₂S₄ films are shown as the exponential rise, called the tail of Urbach which exists down the excitonic peaks. This tail, which has an exponential nature, appears in polycrystalline, partially crystalline, and non-crystalline materials, because of the existence of these localized states, which extended in the forbidden gap between **VB** and **CB** [61-63]. Where this band tail's energy can be estimated from the spectral variations of the logarithmic value of the coefficient of absorption (**ln α**) and the energy of the photon (**hν**) according to the Urbach's experimental Eq., which has the following form [47]:

$$\alpha = \alpha_o \exp\left(\frac{h\nu}{E_U}\right) \quad (8)$$

Where α_o is constant and E_U refers to the energy of the band- tail width (Urbach energy). This energy, E_U depends slightly on temperature and is often interpreted as the band-tail width owing to the localized states in the forbidden band gap and associated with the perturbation of the non-crystalline and low crystalline materials [47,64-66]. Taking the logarithmic value of the two sides of Eq. (8), thus, it could obtain an equation of a straight line:

$$\ln \alpha = \ln \alpha_o + \frac{h\nu}{E_U} \quad (9)$$

Consequently, the energy (E_U) can be evaluated from the reciprocal of the slope of the line when **ln (α)** versus (**hν**) is plotted. Fig. (7-a) depicts this representation, where it illustrates the low absorption range (Urbach energy) and high absorption range (Tauc regions). Moreover, Fig. (7-b) exhibits the straight part of the Urbach exponential region if **ln (α)**-values are represented versus (**hν**)-values for the thin ZnGa₂S₄ films of variable thicknesses, so that the **slope** = (**1/E_U**) and cut-crossed value from the ordinate gives **ln (α_o)**. The determined values of (E_U) and (α_o) are recorded in Table 2. Apparently, the values of **both** (E_U) and α_o increase with the increment of the thickness of the films. This points out that a significant improvement in the crystallinity degree of the thin ZnGa₂S₄ films. The literature of similar works shows that the obtained results have the same trend [66-68]. Further, these results have already been affirmed from XRD findings.

Fig. (7): Plotting of $\ln(\alpha)$ versus $(h\nu)$ of the polycrystalline ZnGa_2S_4 thin films. (A) shows the low and high absorption range (Urbach and Tauc regions, respectively) and (B) shows linear relationship.

According to Urbach assumption, there is another formula that correlates the two parameters (α) and (E_g) according to his suggestion [67-69]:

$$\alpha = \beta \exp \left[\frac{\sigma(h\nu - E_o)}{K_B T} \right] \quad (10)$$

Where σ is a new optical constant called the steepness parameter, β is another pre-exponential parameter, E_o is the energy of the electronic transitions, its value depends upon the electronic transition, where: For direct transitions: $E_o = E_g$; While for the indirect transitions: $E_o = E_g \pm E_{ph}$. Where the energy parameter, E_{ph} represents the energy that bounds the phonon. Hence, $E_{ph} = 0$ for the current study. Hence, if the direct transition case is considered, then $E_o = E_g$. Thus, it can substitute and reformulate Eq. (10) to get the following form:

$$\ln \alpha = \ln \beta + \frac{\sigma h\nu}{K_B T} - \frac{\sigma E_g}{K_B T} \quad (11)$$

$$\ln \alpha = \left(\ln \beta - \frac{\sigma E_g}{K_B T} \right) + \frac{\sigma h\nu}{K_B T} \quad (12)$$

From Eqns. (9) and (12), it can conclude that:

$$\ln \alpha_o = \ln \beta - \frac{\sigma E_g}{K_B} \quad (13)$$

And

$$\frac{h\nu}{E_U} = \frac{\sigma h\nu}{K_B T} \quad (14)$$

Therefore, the estimation of the sharpness or steepness of the absorption edge, which is called the regression parameter (σ), and is calculated as follows:

$$\sigma = K_B \times \frac{T}{E_U} \quad (15)$$

Where K_B is the Boltzmann's constant, and T is the room temperature (300 K), $K_B = 8.6173 \times 10^{-5} \text{ eV/K}$. Hence, the steepness parameter, σ of the ternary compound ZnGa_2S_4 thin films has been computed for all films of varying thicknesses and recorded in Table 2. It is clear that, the steepness parameter decreases with the increment of the film thickness, which is acceptable results due to the increased value of the Urbach band-tail energy. On the other hand, the strength of the interaction between the electron and the phonon (E_{e-ph}) is linked with the parameters (σ) by this simple form [63,69]:

$$E_{e-ph} = \frac{2}{3\sigma} \quad (16)$$

Consequently, the value of the strength of interactions (E_{e-ph}) could be determined for the present films and subsequently recorded in Table 2. It can be seen that there is a gradual increase in the steepness parameter values with the values of electron-phonon interaction decrease as the increase in the film thickness. The decrease in the strength of the interaction between the electron and phonons can be attributed to the increase in the vibrational motion of atoms, unit cells, and crystal lattices, along with the improvement in the degree of crystallinity. It is worthy to note that the resultant greatest values of the atomic vibrational motion do not match with the free-electron frequencies of the ternary ZnGa_2S_4 thin films. Thus, there is no coupling between the free-electrons' frequency and that of the phonons. [70].

3.2.5. Optical band-gap energy

As a result of the extreme importance of the optical band gap of the semiconducting materials and the energy value of this gap, there were many attempts to study this optical band gap and deducing the amount of energy required for the electronic transition from the level of the valence band to that of the conduction band. Thus, several models are used to evaluate the energy of the band gap, such as the absorption spectra fitting (ASF) procedure, Tauc's plots, Cody representations, and Davis-Mott model. These assumptions and models are based on the value of the absorption coefficient, α which appears near the edge of the band in semiconductors as an exponential function of the photon energy according to the following empirical relationship [47]:

$$\alpha h\nu = B(h\nu - E_{gap})^y \quad (17)$$

Where B is a parameter associated with the structural order of the semiconductors, E_{gap} is the band-gap energy of the studied material, $h\nu$ is the energy of the incident electromagnetic waves and the exponent (y) is a parameter determines the nature of the electronic transitions. Since the value of (y) is what determines the type of transition; if it is allowed or forbidden; direct or indirect. If y is equal to $1/2$ then the transition is allowed direct, but if it is equal to 2 then the transition is allowed indirect transition [47,57,69].

In this study, the authors will infer the optical bandgap energy values using different models, and subsequently compare these results to judge which models give the best and most accurate result.

3.2.5.1. Absorption spectrum fitting (ASF) procedure

The absorption spectrum fitting (ASF) procedure gives relatively good results, where this method depends also on Eq. (17). This equation can be rewritten as a function of the wavelength ($c = \nu\lambda$), as follows [71]:

$$\frac{\alpha hc}{\lambda} = B \cdot \left(\frac{hc}{\lambda} - \frac{hc}{\lambda_{gap}} \right)^y \quad (18)$$

Where λ_{gap} , h , and c are the wavelength corresponding to the optical bandgap value, Planck's constant, and the velocity of light, respectively. In the case of the allowed direct transition ($y = 1/2$); so, Eq. (18) can be reformulated to become as follows:

$$\left(\frac{\alpha}{\lambda} \right)^2 = (B^2(hc)^{-1}) \times \left(\frac{1}{\lambda} - \frac{1}{\lambda_{gap}} \right) \quad (19)$$

Subsequently, squaring this equation and let $(B^2(hc)^{-1}) = K$, thereby,

$$\left(\frac{\alpha}{\lambda} \right)^2 = K \left(\frac{1}{\lambda} - \frac{1}{\lambda_{gap}} \right) \quad (20)$$

Thus, by representing a graphical relationship between $\left(\frac{1}{\lambda} \right)$ on the abscissa versus $\left(\frac{\alpha}{\lambda} \right)^2$ on the ordinate as illustrated in Fig. (8-a), by the linear extrapolation at $\frac{1}{\lambda} = 0$, we can obtain the value of λ_{gap} , which expresses the wavelength corresponding to the direct band-gap energy of thin ZnGa₂S₄ films of different thicknesses and thereafter recorded in Table 2. On the other hand, for the case of indirect allowed transition, let $y = 2$, thus Eq. (18) becomes as follows:

$$\frac{\alpha}{\lambda} = B/hc \cdot \left(\frac{1}{\lambda} - \frac{1}{\lambda_{gap}} \right)^2 \quad (21)$$

By taking the square root of both sides and let $\sqrt{B/hc} = C$, thus:

$$\sqrt{\alpha/\lambda} = C\left(\frac{1}{\lambda} - \frac{1}{\lambda_{gap}}\right) \quad (22)$$

Consequently, by graphical representation of the relationship between the value $(1/\lambda)$ on the horizontal axis versus $\sqrt{\alpha/\lambda}$ on the vertical axis, as shown in Fig. (8-b). The linear extension of the straight line intersects the abscissa at a wavelength value that gives λ_{gap} of the indirect band-gap energy of the ZnGa₂S₄ thin films of different thicknesses and then the values have been recorded in Table 2.

Fig. (8-a): Plotting of $(\alpha/\lambda)^2$ versus $(1/\lambda)$ for thin ZnGa₂S₄ films of different thicknesses to obtain the direct band-gap energy.

Table 3: The optical bandgap using different models and Urbach energies for the Novel ZnGa₂S₄ thin films.

Film thickness (nm)	Absorption spectrum fitting E_g (eV)		Tauc's Plots E_g (eV)		Cody Representations E_g (eV)		Davis-Mott model E_g (eV)		Urbach's energy (eV)
	Direct	Indirect	Direct	Indirect	Direct	Indirect	Direct	Indirect	
293	4.106	3.594	4.001	3.153	4.003	3.033	3.902	3.521	0.431
375	4.018	3.447	3.979	3.122	3.972	2.951	3.853	3.403	0.531
452	3.841	3.348	3.949	3.104	3.901	2.910	3.701	3.222	0.617
517	3.754	3.221	3.902	3.051	3.854	2.901	3.682	3.103	0.699

Fig. (8-b): Plots of $(\alpha/\lambda)^{1/2}$ versus $(1/\lambda)$ of thin ZnGa_2S_4 films with different thicknesses to get their indirect band-gap energy values.

It is clear that the wavelength value corresponding to the bandgap energy (λ_{gap}) increases gradually from 280 nm to 313 nm for the direct transition and from 345 nm to 385 nm for the indirect one (Table 2). with the increase in the film thickness of the ternary compound ZnGa_2S_4 . While the direct and indirect gap energy values decrease gradually as the thickness increases, where the direct energy gap decreases from 4.106 eV to 3.754 eV and the indirect one decreases from 3.594 eV to 3.221 eV, as recorded in Table 3. Moreover, the dependence of the direct energy gap upon the film thickness (t) measured in (nm) by using this method of the film samples of the ternary composition ZnGa_2S_4 is illustrated in Fig. (12-a). The figure is linearly fitted to get the following experimental Eq.:

$$E_g \text{ (eV)} = 4.603 - 1.65 \times 10^{-3} t \text{ (nm)}.$$

3.2.5.2. Tauc's Plots

This most popular model allows us to derive the band gap energy E_g as a function of the incident photon energy ($E = h\nu$) according to Eq. (17) [71]. The Tauc's optical band-gap associated with the thin films can be determined by extrapolating the linear trend observed in the spectral dependence of $(ah\nu)^2$ and $(ah\nu)^{1/2}$ over a finite range of photon energies ($h\nu$) [72]. The bandgap energy value of Tauc is obtained from the intersection of the linear portion of the curve with the abscissa [73]. Figs. (9-a) and (9-

b) represent the plot of $(ah\nu)^2$ and $(ah\nu)^{1/2}$ versus photon energy ($h\nu$), respectively, to find the value of the allowed direct and allowed indirect band gap energies of the ZnGa_2S_4 films of different thicknesses, which are prepared of different thicknesses. The extension of the straight-line segment of Figs. (9-a) and (9-b) with the abscissa (x-coordinate) gives the value of the direct and indirect gap energies, respectively for the studied ZnGa_2S_4 samples.

Fig. (9-a): The graphical relationship between $(ah\nu)^2$ and $(h\nu)$ according to Tauc's plots for the ternary ZnGa_2S_4 thin film with different thicknesses.

The obtained values of the band gap energies of the present samples of different thicknesses are recorded in Table 3. It is noticeable that there is a slight change in the value of the two gap energies with the increase in thickness of the films. Where the direct band gap energy decreases from 4.001 eV to become 3.902 eV, while decreases from 3.153 eV to 3.051 eV. This decreasing in the energy gap values is due to the improvement in crystallization with the greater the thickness of the film. Moreover, the direct band gap energies are represented against the film thickness of ZnGa_2S_4 composition, as depicted in Fig. (12-b), and the resultant was fitted linearly to get an empirical equation of a straight line that is given as:

$$E_g \text{ (eV)} = 4.134 - 4.31 \times 10^{-4} t \text{ (nm)}.$$

Fig. (9-b): The graphical relationship between $(\alpha h\nu)^{1/2}$ and $(h\nu)$ according to Tauc's method for the ternary ZnGa_2S_4 thin film with different thicknesses.

3.2.5.3. Cody representations

Cody assumed that the increasing value of Tauc's optical gap that is associated with the decrease in the thickness of films takes place owing to the curvature of the dependence of the spectra of the function $(\alpha h\nu)^{1/2}$ upon the energy of the incident photon, $f(h\nu)$ [74]. According to the model presented by Cody [75], the optical gap energy of the polycrystalline ZnGa_2S_4 thin films of different thicknesses can be evaluated from the cut-cross of the extension of the linear part observed in the figure of representation of the spectra of $(\alpha/h\nu)^2$ or/and $(\alpha/h\nu)^{1/2}$ against $(h\nu)$, along a limited range of the energy of the incident photons (the studied range). The intersection of this linear extension for the abscissa in accordance with the Cody model of the optical-band gap and to inferring the optical gap energy gives the band energy as shown in Figs. (10-a) and (10-b) for the allowed direct and indirect energy gap, respectively. Cody representations show a moderate curvature than those of Tauc's matches and a milder reliance in the optical gap associated with the thickness of thin ZnGa_2S_4 films compared to the optical gap case of Tauc [72]. Tauc assumed that the component of the matrix of the momentum does not depend on the photon energy, and Cody proposes, while that the dipole matrix element does not actually depend on the energy of photons. Table 3 illustrates the estimated optical gap values using the Cody's model.

Fig. (10-a): Plots of the graphical relationship between $(\alpha/h\nu)^2$ versus $(h\nu)$ according to Cody model for the ternary compound ZnGa_2S_4 thin film with different thicknesses.

The obtained results from these graphs showed that the energy of the allowed direct band gap decreases from 4.003 eV to 3.854 eV, while for the indirect one, it decreases from 3.033 to become 2.901 eV. Moreover, the direct gap energy is represented against the film thickness in Fig. (12-c), which is linearly fitted to get this linear Eq. between E_g values and the thickness of films (t) in nm:

$$E_g \text{ (eV)} = 4.221 - 6.88 \times 10^{-4} t \text{ (nm)}.$$

Although slight differences in the band gap energy values can be noticed when making a comparison between the results obtained from applying Tauc 'plots and Cody's representations, it can neglect these differences if we take the measurement error range into account. Thus, it can conclude that these differences are not really important, so that use it. Generally, either model aims to compute the energy band gap for inorganic and organic semiconductors.

Fig. (10-b): Plot the graphical relationship between $(\alpha/h\nu)^{1/2}$ versus $h\nu$ according to Code model for the ternary compound ZnGa₂S₄ thin film with different thicknesses.

3.2.5.4. Davis-Mott model

In the amorphous materials the density of hypothetical states is an unexpected equivalent, although it may be valid for states beyond E_c and E_v according to Davis and Mott model [76]. The density of state distributions may contribute to explaining the existence of three types of possible optical transitions according to the Mott-CFO model [77], which may contribute to the inter-band absorption. The matrix elements for these transitions are related to the spatial overlap between initial and final state wavefunctions. Davis and Mott showed that the matrix elements for transitions between extended states and those between weakly localized states. Accordingly, the absorption coefficient (α) is defined by the following relationship [77,78]:

$$\alpha h\nu = \frac{4\pi\sigma_{min}}{3nc(\Delta E)^2} (h\nu - E_2)^3 \quad (23)$$

Here (n) is the index of the refraction of the investigated material, and $\sigma_{min} = \left(\frac{2\pi^3 c^2 h^3 a}{m^2}\right) [N(E_c)]^2$ is the minimum metallic conductivity. Thus, plotting $(\alpha h\nu)^{1/3}$ versus $(h\nu)$ will give a straight line, subsequently, E_2 , which was produced from the cut-cross of the line to the abscissa, $(h\nu)$ -axis, i.e., when

$ah\nu=0$ equals $E_2 = E_c - E_v$. Figs. (11-a) and (11-b) represent the relationship between $(ah\nu)^{1/3}$ versus $h\nu$ for the allowed direct electronic transition and $(ah\nu)^{2/3}$ vs $(h\nu)$ for the indirect one of thin ZnGa_2S_4 films. The estimated values that deduced from these figures have been recorded in Table 3 for the direct and indirect gap energies.

Fig. (11-a): The graphical relationship between $(ah\nu)^{1/3}$ and $(h\nu)$, in accordance with the Davis–Mott model of the ternary ZnGa_2S_4 thin film.

It can see that this model gives also results in the line with those obtained from the previous methods. The band gap energy values of the direct electronic transition decrease from 3.902 eV to 3.682 eV, while the indirect band gap energy values decrease from 3.521 eV to 3,103 eV. Moreover, the direct band gap energy value has been also plotted graphically versus the film thickness, t of the ZnGa_2S_4 samples, as depicted in Fig. (12-d) for this case, and the graph was fitted to obtain an experimental linear Eq., gives as:

$$E_g \text{ (eV)} = 4.230 - 1.09 \times 10^{-3} t \text{ (nm)}$$

Fig. (11-b): The graphical relationship between $(\alpha h\nu)^{2/3}$ and $(h\nu)$ in accordance with Davis–Mott model for the ternary ZnGa₂S₄ thin film.

Fig. (12): The dependence of the direct optical energy gap upon the film thickness as computed by different methods for the ternary ZnGa₂S₄ thin films.

Consequently, by comparing the results of the determined energy gap values of the direct and indirect transitions measured by the different models with that of the Tauc's model, it is found that the ASF procedure ranges from (-3.74) % to (+2.65) %. This difference is considered permissible in experimental measurements. Furthermore, the results of the Cody's model are completely identical to the results of the Tauc's model without a difference. While the Davis-Mott model has a ratio of differences in measurements ranging from (-2.5) % to (-6.41) % and this error percentage did not affect the results, absolutely. Therefore, it can be concluded that these four methods used in determining the energy gap of semiconductors are all considered accurate and reliable and the differences between them are practically acceptable.

4. Conclusions

Novel nanocrystalline ZnGa_2S_4 thin films were fabricated with good quality using an inexpensive spray pyrolysis technique at different film thickness. XRD analysis showed that all samples are single-phase and have the polycrystalline quadrangular crystal structure. The degree of crystallinity and the volume fraction have been studied via x-ray diffractograms and the findings were that these parameters directly dependent on the thickness of the films.

The energy-dispersive x-ray spectroscopy, EDAX is employed to investigate the elemental compositions of films and the result confirmed that all films have a good stoichiometry, along with in a good match with the theoretical computations. The field-emission-scanning electron microscope, FE-SEM was used to examine the morphology of the films' surfaces.

The optical transmittance and reflectance have been employed to investigate some important optical parameters such as absorption coefficient, Urbach energy, steepness parameters, and electron-phonon interaction have been extensively studied and discussed.

The direct and indirect gap energy were also determined by different four models and compared with Tauc's model. The optical band gap values were slightly decreased if the film thickness increased, this is owing to the improvement of the crystallization process of films. The optical band gap energy of these films ranges from 4.106 eV to 3.754 eV. This means than that these film samples are wide band gap semiconductors, which makes them strongly recommended for use in many optical applications as in thin-film solar cells and as a window layer.

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Figures

Figure 1

FE-SEM micrographs (a and b) and EDS-spectra (c and d) of the present thinner and thicker film samples (of thicknesses 293 nm and 517 nm), as typical samples of the ZnGa₂S₄ thin films.

Figure 2

X-ray diffraction pattern of the ZnGa₂S₄ thin films of different thickness; The Red line represents the experimental curve (it is a mixture of the amorphous and crystalline phases), while Blue line is the amorphous phase.

Figure 3

Dependence of intensity's ratios for the integrated intensities on the true C_1 concentration of the crystalline phase, the slope of the straight line represents the α -coefficient (Huang parameter).

Figure 4

The spectral variations of (a) transmittance and reflectance, and (b) absorbance as functions of the wavelength incident on thin ZnGa₂S₄ films.

Figure 5

The variation of the absorption coefficient versus the wavelength of thin ZnGa₂S₄ films (a) along the studied range and (b) at the absorption edge.

Figure 6

Variation of the skin depth as a function of (a) the photon energy and $\sqrt{\lambda}$, for ZnGa₂S₄ films of different thicknesses.

Figure 7

Plotting of $\ln(\alpha)$ versus $(h\nu)$ of the polycrystalline ZnGa_2S_4 thin films. (A) shows the low and high absorption range (Urbach and Tauc regions, respectively) and (B) shows linear relationship.

Figure 8

a. Plotting of $(\alpha/\lambda)^2$ versus $(1/\lambda)$ for thin ZnGa₂S₄ films of different thicknesses to obtain the direct band-gap energy. b. Plots of $(\alpha/\lambda)^{1/2}$ versus $(1/\lambda)$ of thin ZnGa₂S₄ films with different thicknesses to get their indirect band-gap energy values.

Figure 9

a. The graphical relationship between $(\alpha h\nu)^2$ and $h\nu$ according to Tauc's plots for the ternary ZnGa₂S₄ thin film with different thicknesses. b. The graphical relationship between $(\alpha h\nu)^{1/2}$ and $h\nu$ according to Tauc's method for the ternary ZnGa₂S₄ thin film with different thicknesses.

Figure 10

a. Plots of the graphical relationship between $(\alpha/h\nu)^2$ versus $h\nu$ according to Cody model for the ternary compound ZnGa₂S₄ thin film with different thicknesses. b. Plot the graphical relationship between $(\alpha/h\nu)^{1/2}$ versus $h\nu$ according to Code model for the ternary compound ZnGa₂S₄ thin film with different thicknesses.

Figure 11

a. The graphical relationship between $(\alpha h\nu)^{1/3}$ and $h\nu$, in accordance with the Davis–Mott model of the ternary ZnGa_2S_4 thin film. b. The graphical relationship between $(\alpha h\nu)^{2/3}$ and $h\nu$ in accordance with Davis–Mott model for the ternary ZnGa_2S_4 thin film.

Figure 12

The dependence of the direct optical energy gap upon the film thickness as computed by different methods for the ternary ZnGa₂S₄ thin films.