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Characteristics $CuAlS_2$ thin films grown by Vacuum Thermal Evaporation Technique for Solar cell devices

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Abstract— $CuAlS_2$ thin films of thicknesses 118 ± 5 nm were deposited on glass substrates using chemical bath deposition technique (CBD). The details of the preparation method are well described. The method is relatively simple and is easily controlled and sufficient to produce large area and good adherence to the substrate films. Effect of annealing temperature T_a on the structure, and optical properties of $CuAlS_2$ films were investigated. $CuAlS_2$ thin films of thicknesses 118 ± 5 nm were deposited on glass substrates using chemical bath deposition technique (CBD). The details of the preparation method are well described. The method is relatively simple and is easily controlled and sufficient to produce large area and good adherence to the substrate films. Effect of annealing temperature T_a on the structure, and optical properties of $CuAlS_2$ films were investigated. The analysis of its optical characteristics indicated the ability of these films to absorb the visible light due to its graded energy gap. As the annealing temperature increases of the film, the optical band gap decreases. The optical properties of the films were ascertained by model UV-1650PC spectrophotometer (wavelengths ranging between 300 and 900 nm). The optical transmittance and absorption were utilized to compute the absorption coefficient, band gap energy and optical constant of the films. Nature of the optical transition of the films has been observed in direct allowed with band gap energies between 2.81 eV and 2.4 eV depending on annealing temperatures. The refractive index and extinction coefficient behavior were found to very affect by annealing temperature. Therefore this property indicated that these films are considered as good absorber for solar cell devices.

Index Terms— $CuAlS_2$, optical properties, materials physics, chemical bath, thin films..

1 INTRODUCTION

Chemical bath deposition technique (CBD) has been used extensively for the deposition of the thin films of sulfides and selenides [1] oxides [2–3] and ternary compounds [4–5]. The choice of this method arises from its low cost, ease of handling, and possibility of application on a large surface; hence it is most suitable for adaptation in developing countries where facilities for other highly expensive and technically advanced techniques such as Chemical Vapor Deposition, Molecular Beam Epitaxy, RF Sputtering, etc. are not easy to come by. [6] I–III–VI ternary semiconductors have recently received considerable attention due to their potential applications such as solar cells, non-linear optical crystals, parametric oscillators and detectors. These compounds are structurally correlated to zinc blende semiconductors. These semiconductors are used in photovoltaic optical detectors, solar cells, and light emitting diodes [7–11] or in nonlinear optics. One of the promising chalcopyrite type semiconductors for non linear optical applications is copper aluminum disulfide $CuAlS_2$ (CAS), which has a direct gap of 3.49 eV at room temperature, the widest value among other chalcopyrite compounds [12–14].

The $CuAlS_2$ semiconductor has good luminescent properties making it suitable for the use as material for light-emitting devices in the blue region of the spectrum. [15]

D. N. Okoli Studied the effect of Ph adjuster of chemical bath on the optical properties of $CuAlS_2$ thin films that deposited by chemical bath method on glass slides substrate. [5] While A. F. Sabbar studied the CuSx films that prepared by C.B. and the effect of doped by (Al) on the structure films and found the doped films has good homogeneous with increasing the doping weight. [16]

In the present paper, we report the preparation of $CuAlS_2$ thin films by chemical bath deposition and physical characterization of the thin films. The effects of heat treatment on structural, optical properties of these films are investigated with the aim of finding the best conditions for the deposition process. The high variation of Absorption of the $CuAlS_2$ films with wavelength, special when approach from near ultra-violet region of electromagnetic spectrum. Hence, $CuAlS_2$ could serve as good material for optoelectronic and photo-thermal applications. Vacuum thermal evaporation has become a popular technique among different techniques available for the deposition of thin films. Vacuum thermal evaporation method yields high-quality thin films with smooth surfaces. Aim of this research is to prepare $CuAlS_2$ films by thermal evaporation at room temperature at different thicknesses and study the optical films were annealed at 348 K and 373 K temperatures.

2 MATERIAL AND METHODS

In this work, $CuAlS_2$ thin films were deposited on to glass substrates using CBD technique. In this method, it is important that substrates are cleaned well prior to deposition. The glass slides substrates were cleaned by soap, followed by washing rinsing with distilled water, and subsequently the substrates were

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cleaned with alcohol in an ultrasonic bath for 30 min and dried. Finally, the samples were washed repeatedly in distilled water.

$CuAlS_2$ compound was synthesized in a quartz tube by taking cooper, aluminum, and sulfur metal in their respective stoichiometric ratios as 0.4, 0.6 and 1.0, respectively. The tube was evacuated then sealed. It was slowly heated in an electrical furnace at 1200 K and kept it at this temperature for 18 hours. The furnace was then left to cool at room temperature.

Vacuum thermal evaporation was used to deposit $CuAlS_2$ thin films at room temperature at 400 nm thickness using an Edward E306A coating unit onto glass substrates, which were cleaned by distilled water, pure alcohol, and then by ultrasonic vessel in order to deposit thin films for structural and optical measurements. Thickness measurement was made by Thickness monitor. A molybdenum boat was used as the source holder and the pressure inside the chamber was better than 10^{-6} mbar the substrate was held at a distance of 12 cm exactly above the boat. The rate of deposition was 0.9 nm/s. Annealing of the thin films was conducted under vacuum, in oven at 300, 400, 500, 600, and 700 K, which are the available temperatures in our laboratory.

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2.1 The structural properties for XRD revealed of the films:

Figure (1a) shows XRD patterns for as deposited samples, it is clear that no meaningful diffraction peaks were observed, this implies that the films show no evidence of molecular crystallization, the grain size of the film was so small suggesting that the disorder within these grains is so high leading to amorphous nature. Thus in this case films grown at a low substrate temperature such as room temperature and did not undergo post thermal treatments are usually randomly oriented and amorphous. Similar observation was reported by [17] on thermally evaporated Cu-In precursors and has accounted that the formation of amorphous Cu-In thin films by evaporation when deposition was carried out at a temperature between room temperature and 700K was attributable to incomplete reaction at such low temperatures.

Figure (1b, 1c, 1d, and 1e) depict samples sulfurised at 400K, 500K, 600K and 700K respectively. It is observed that films sulfurised at 400K (fig 1b) were characterized by two main crystalline peaks; the first peak appeared at $2\theta \sim 28^0$ while the second peak appeared at $2\theta \sim 48^0$. On comparing with ICDD (card no. 01-074-7042) and reported values of [18] and [19], the first peak observed at $2\theta \sim 28^0$ was identified to be belonging to $CuAlS_2$ chalcopyrite structure with the (112) preferred orientation, the second peak observed at $2\theta \sim 48^0$ is designated to (220) orientation also belongs to $CuAlS_2$ chalcopyrite structure.

Figure (1c) depicts XRD patterns for samples sulfurised at 500K. It is observed that in addition to first and second peaks exhibited by thin films grown at room temperature, a third peak appeared at $2\theta \sim 55^0$ and is designated to (312) orientation and belongs to crystalline $CuAlS_2$ chalcopyrite structure as confirmed by ICDD (card no. 01-074-7053) and previous work of [20] and [21].

Figure (1d) depicts XRD patterns for samples sulfurised at 600K. It is observed that in addition to first and second peaks exhibited by thin films grown at room temperature, a third peak appeared at $2\theta \sim 55^0$ and is designated to (312) orientation and belongs to crystalline $CuAlS_2$ chalcopyrite structure.

Figure (1e) illustrates the diffraction patterns for samples sulfurised at 700K. As seen from the figure fourth peak emerged and is assigned to (400) reflections of $CuAlS_2$ in accordance with ICDD (card no. 01-075-6862). The emergence of reflection peaks with increase in sulfurisation temperature is a clear improvement in crystallinity of the films attributed this to interdiffusion of sulfur and restructuring of particles at a sulfurisation temperature itself during sulfurisation process. For films grown at very low substrate temperature, sulfurisation temperature augment particle's gain in thermal energy which enhances their restructuring, enlarge grain size and reduce defects thus leading to crystalline film, the grain sizes were calculated through the Scherer's formula:

$$\mathbf{D = 0.9\lambda / \beta \cos \theta} \qquad [1]$$

Where D is the grain size, β experimentally observed diffraction peak width at Full wave half maximum intensity (FWHM), and θ is Bragg angle. The Dislocation density of thin films were calculated by employing the relation [10]

$$\delta = \mathbf{n / D^2} \qquad [2]$$

The micro strain (ε) developed in thin films was calculated from the relation [15].

$$\varepsilon = \beta \mathbf{\cos \theta / 4} \qquad [3]$$

Where β = FWHM (Full width at half maximum intensity.

The lattice parameters a and c value for tetragonal crystallographic system can be calculated from the following equation using *hkl* parameter and the inter planer spacing d:

$$\frac{1}{d^2} = \frac{h^2 + K^2}{a^2} + \frac{l^2}{C^2} \qquad [4]$$

2.2 Optical properties

The transmission spectra of $CuAlS_2$ thin films are shown in Figure 2 (a) for as-deposited and annealed films, it is very clear the transparency of the films increase with annealing temperature from 50% at wavelength 575 nm for the as-deposited films, to 79% for films annealed at 700 K. It is noticed that the $CuAlS_2$ thin film has higher transmission values in the visible range of spectrum. The increase in transmission may be due to the increase in the amorphous nature that occurs with increasing T_a. On the other hand, an increase in localize states in the energy gap leads to decreasing E_g and absorption, and thus increasing transmission [22].

Note also the positive liner relationship between the wavelength and transmission for the film annealed at 700 K, while the other films exhibit nonlinear but degreasing transmission after this point. The Absorptions spectra of $CuAlS_2$ films are illustrated in Figure 3. They exhibit opposite behavior in spectra transmittance. These absorption spectra, which are the most direct and perhaps simplest method for probing the band structure of semiconductors, are employed in the determination of the energy gap E_g. The films show a decrease in absorbance after annealing the films at 300, 400, 500, 600, and 700 K. The energy optical gap E_g was calculated from the equation:

$$\mathbf{\alpha h\upsilon = B (h\upsilon - E_g)^r} \qquad [5]$$

where α is the absorption coefficient, B is a constant and r is an index which can be assumed to have values of 1/2, 3/2, 2 and 3, depending on the nature of the electronic transition responsible for the absorption. Exponent r = 1/2 for allowed direct transition, r = 3/2 for forbidden direct transition and r = 3 for forbidden indirect transition, with r = 2 refers to indirect allowed transitions [23, 24].

Type of the electron transitions can be known by dependence on the values of the absorption coefficient; if the values of $\alpha > 10^4$ cm^{-1} , this means the direct transitions takes place in material, while indirect transitions occur for $\alpha < 10^4$ cm^{-1} [25].

The present $CuAlS_2$ films exhibit direct allowed transition and the optical energy gap of as deposited and annealing films were determined from straight line plot of $(\alpha h\upsilon)^2$ as function of photon energy, as shown in Figure 4.

In Figure 4 the plots of $(\alpha h\upsilon)^2$ against hυ for films annealed at three different annealing temperatures. Those annealed at 300, 400, 500, 600 and 700 K exhibit two linear-like regions. One region lies in the low energy range, and the other in the high energy range; this may have resulted from degradation in films associated with annealing at high temperature.

The direct optical energy gaps of the $CuAlS_2$ films decreased slightly from 2.63 eV, for as-deposited films, to 1.55 eV, for films annealed at 700 K. Variation of E_g with T_a is tabulated in Table 1. The decrease in E_g is in agreement with the observed increase in the amorphous films as T_a increases, which further consolidates the suggestion that T_a does not enhance the crystallinity [26]. This result is reinforced by XRD results from $CuAlS_2$ films.

The coefficient B (slope in the Tauc equation) has been obtained from the root square of the straight line slope, as shown in Figure 4. From this figure, one can observe that B decreased with increasing T_a, as see in Table 1. B is inversely proportional to amorphously and the width of the band tails [27].

A smaller B value means a larger amorphously and the decreased of B with increasing T_a for $CuAlS_2$ films suggests a decrease of film crystallinity.

The density of the localized states in the band can be evaluated from the Urbach energy (E). There are absorption tails at energies smaller than E_g, and the absorption coefficient can exhibit exponential behavior [28, 29]. The Urbach energy can be calculated from the equation

$$\alpha = \alpha_0 \exp(h\upsilon / \Delta E) \qquad [6]$$

By plotting ln α as a function of hν, as shown in Figure 5 for $CuAlS_2$ films. The reciprocal slope of the linear part gives the value of E. The variation of E for $CuAlS_2$ films at different annealing temperature (room temperature, 400, 500, 600, 700 K) is shown in Figure 5 and tabulated in Table 1. We can observe that E increased with Ta from 0.97 for the as-deposited film to 1.92 eV for the annealed film at 700 K. This may be attributed to structure change and increasing the degree of amorphic character, leading to increase in the localized states [30].

It is necessary to give attention to the refractive index in order to complete the fundamental study of the optical properties and the optical behavior of the material. The refractive index of the films was calculated using the equation [31]

$$n = \sqrt{\frac{4R}{(R-1)^2 - K^2} - \frac{(R-1)}{(R-1)}} \qquad [7]$$

Where R the reflectance and k the extinction coefficient defined as:

$$K = \alpha \lambda / 4\pi \qquad [8]$$

And where λ is the wavelength and α is the absorption coefficient. Variation of the refractive index with annealing temperature for $CuAlS_2$ films is shown in Figure 6. Observe that the behavior of refractive index for $CuAlS_2$ films is very affected by annealing temperature. Refractive index for wavelengths below 460 nm decreased with increasing T_a, while for wavelengths above 460 nm it is observed to increase with T_a .

The behavior of the extinction coefficient is very similar to the corresponding absorptions spectra, as shown in Figure 5 for $CuAlS_2$ films at different annealing temperatures. From Figure 5 we can observe that the extinction coefficient for $CuAlS_2$ films decreases with increasing the annealing temperature, and attributed to the same reasons as previously mentioned.

The results of dependence of extinction coefficient k on wavelength for $CuAlS_2$ thin films deposited at three different annealing temperatures and sulfurised at 700K temperatures is illustrated in Figure 7. It is observed in each case that the extinction coefficient k decreases with increasing annealing temperature, and wavelength. This behavior is a clear indication that films are becoming highly transparent at long wavelengths. Thus, this suggests that the increase in transparency is likely to be originating from the observed decrease in k with increasing substrate temperature in the same wavelength range.

The observed k in respect of the film prepared at room temperature is 0.40. As substrate temperature increases from room temperature to 700K a further decrease in k was exhibited by the films, in which k slashed to 0.30. By further elevating the substrate temperature to 500 K, extinction coefficients as low as 0.35 was observed. These values of k are in good agreement with those obtained by [32, 33]. The decrease of k with increasing substrate temperature may be due to the improvement in the crystallinity which leads to minimum imperfection.

3 Conclusions

The deposition of $CuAlS_2$ film was successfully carried out on a glass substrate (glass slide) at room temperature using two stage vacuum thermal evaporation techniques. XRD characterizations reveal that sulfurisation temperature has a great influence on the structure of films. It was discovered that the crystallinity of the grown films increase with increasing sulfurisation temperature.

Structural and optical characteristics of $CuAlS_2$ thin films prepared by chemical bath deposition technique have been studied. The optical constants (optical energy gap, refractive index n, absorption coefficient α, and extinction coefficient k) of $CuAlS_2$ thin films were determined by simple straight forward calculations using the transmission and absorption spectra. A high change in optical constants is observed when the annealing temperature increases from room temperature to 700 K.

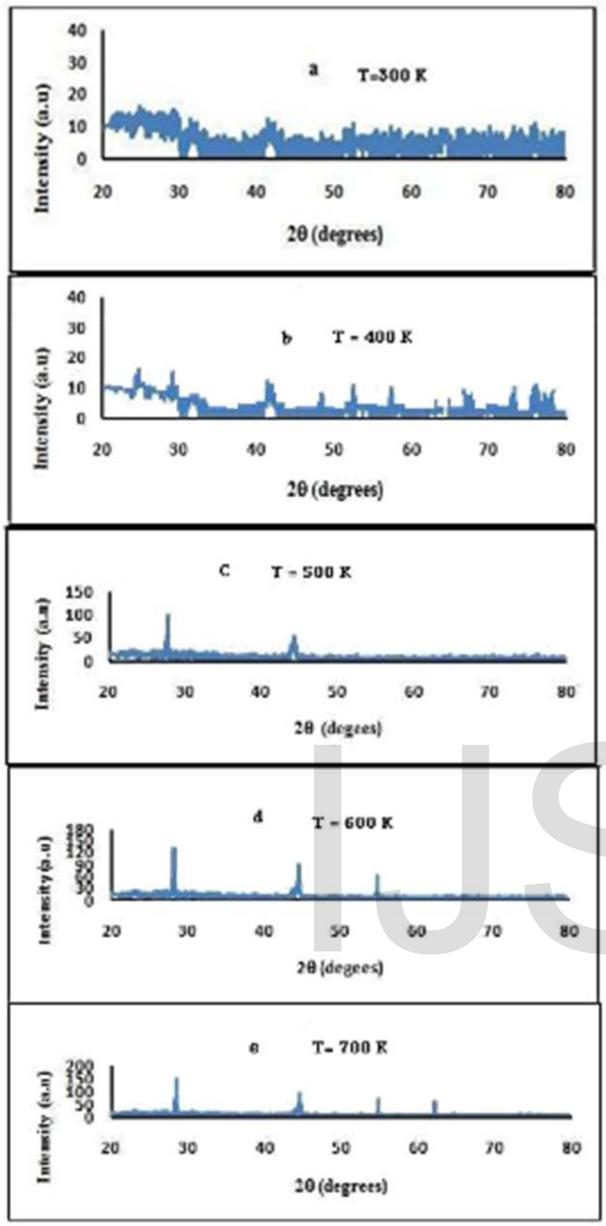

Fig. 1. XRD patterns for (a) deposited at 300K (b) sulfurised at 400K (c) sulfurised at 500K (d) sulfurised at 600K (e) sulfurised at 700K

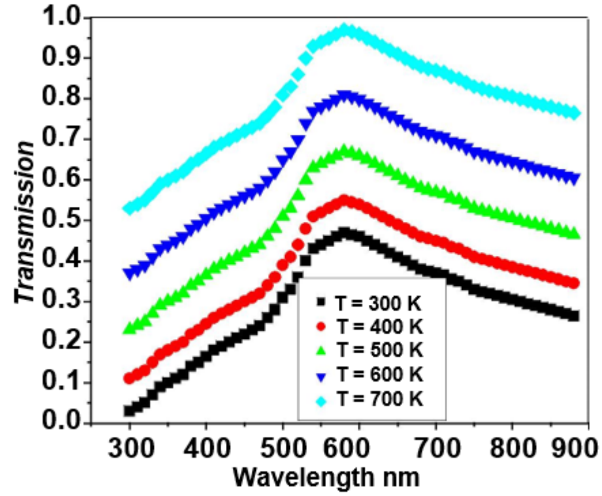

Fig. 2. Variation of transmission spectra with wavelengths of $CuAlS_2$ films

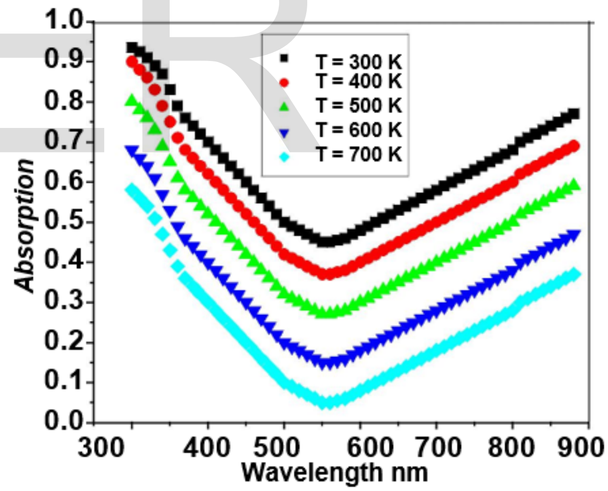

Fig. 3. Variation of absorption spectra with wavelengths of $CuAlS_2$ films

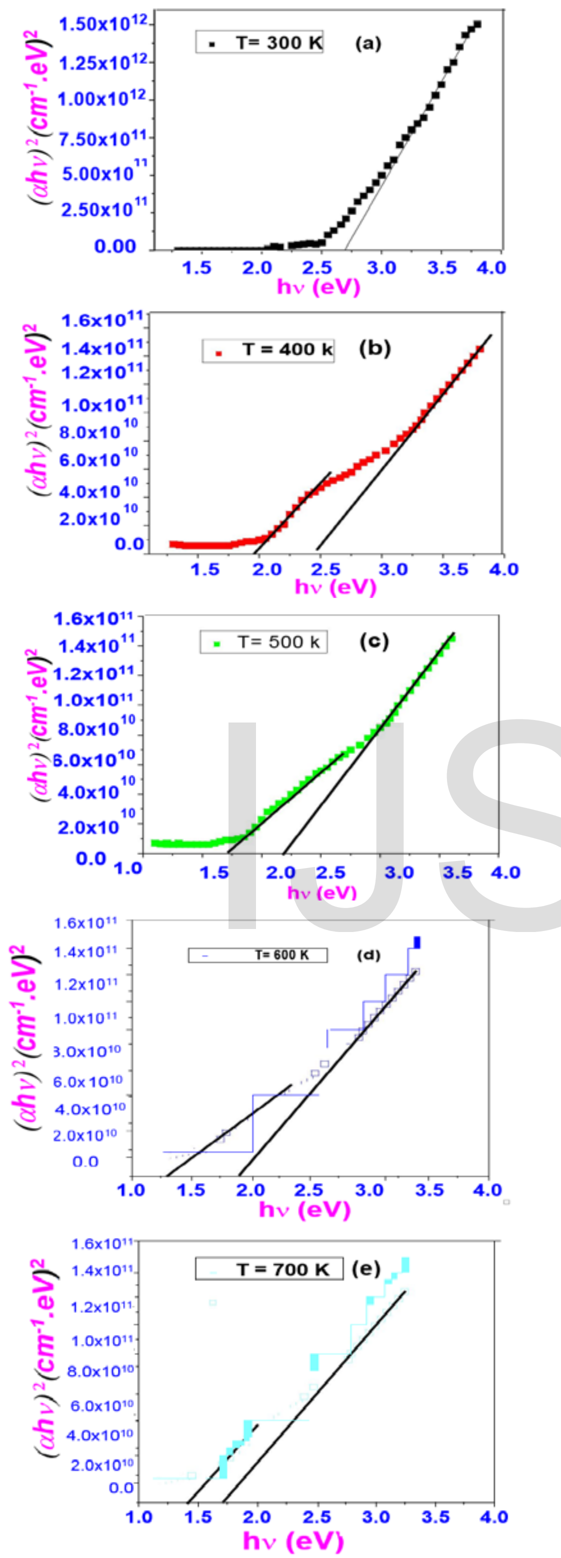

Fig. 4. **The variation of $(\alpha h\upsilon)^2$ with *hν* for $CuAlS_2$ thin films at different annealing temperatures.**

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