

# Structure and optical properties of $\text{CuAlS}_2$ thin films prepared via chemical bath deposition

Tariq J. ALWAN and Mushtak A. JABBAR

*Al-Mustansiriyah University, College of Education, Department of Physics-IRAQ  
e-mail: tariqjaffer2000@yahoo.com*

Received 18.07.2010

## Abstract

$\text{CuAlS}_2$  thin films of thicknesses  $118 \pm 5$  nm were deposited on glass substrates using chemical bath deposition technique. 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  $\text{CuAlS}_2$  films were investigated. The structures of the films were studied by X-ray diffraction and FTIR spectrophotometer. The optical properties of the films were ascertained by UV-VIS 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.

**Key Words:**  $\text{CuAlS}_2$  , optical properties, 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  $\text{CuAlS}_2$  (CAS), which has a direct gap of 3.49 eV at room temperature, the widest value among other chalcopyrite compounds [12–14]. The  $\text{CuAlS}_2$  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  $\text{CuAlS}_2$  thin films that deposited by chemical bath method on glass slides substrate. [5] While A. F. Sabbar studied the  $\text{CuS}_x$  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]

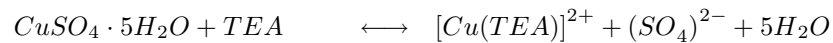
In the present paper, we report the preparation of  $\text{CuAlS}_2$  thin films by chemical bath deposition and physical characterization of the thin films. The effects of heat treatment on structural, optical properties of these films are investigated with the aim of finding the best conditions for the deposition process. The high variation of Absorption of the  $\text{CuAlS}_2$  films with wavelength, special when approach from near ultra-violet region of electromagnetic spectrum. Hence,  $\text{CuAlS}_2$  could serve as good material for opto-electronic and photo-thermal applications.

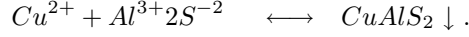
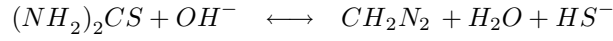
## 2. Experimental

In this work,  $\text{CuAlS}_2$  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 cleaned with alcohol in an ultrasonic bath for 30 min and dried. Finally, the samples were washed repeatedly in distilled water.

Aqueous solutions of 0.12 M  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ , 1.0 M thiourea  $[(\text{NH}_2)_2\text{SC}]$ , 0.08 M  $\text{Al}_2(\text{SO}_4)_3 \cdot 14\text{H}_2\text{O}$ , 7.4 M of triethanolamine (TEA) and pH adjuster ammonia ( $\text{NH}_3$ ) were used to prepare  $\text{CuAlS}_2$  thin films. First, 5ml of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  was put in a 50 ml beaker and this was followed with the addition of 5 ml of TEA. The resulting solution was stirred for few minutes until the solution becomes bluish and homogenous. 5 ml of  $\text{Al}_2(\text{SO}_4)_3$  was later added and the solution was also stirred before addition of 5ml of ammonia and 5ml of thiourea respectively. A dark orange black solution was formed and distilled water was finally added making up the volume to a total of 50 ml.

Several baths were prepared in this way and left to stand for 24 hours, after which the slides were removed, rinsed in distilled water, and dried in open air at room temperature (300 K). During preparation the following chemical processes were expected to have occurred:





Sulphide ions are released by the hydrolysis of thiourea and  $Cu^{2+}$  and  $Al^{3+}$  ions form cuprous tri-ethanolamine and tri-ammonium aluminate complex ions respectively by combining with TEA and  $NH_3$  in the pH range of 8 and 9. The  $[Cu(TEA)]^{2+}$  and  $[Al(NH_3)_3]^{3+}$  complexes which combine with  $S^{2-}$  ions to form dark green or black  $CuAlS_2$  thin film on the glass slide, same as was used in [5].

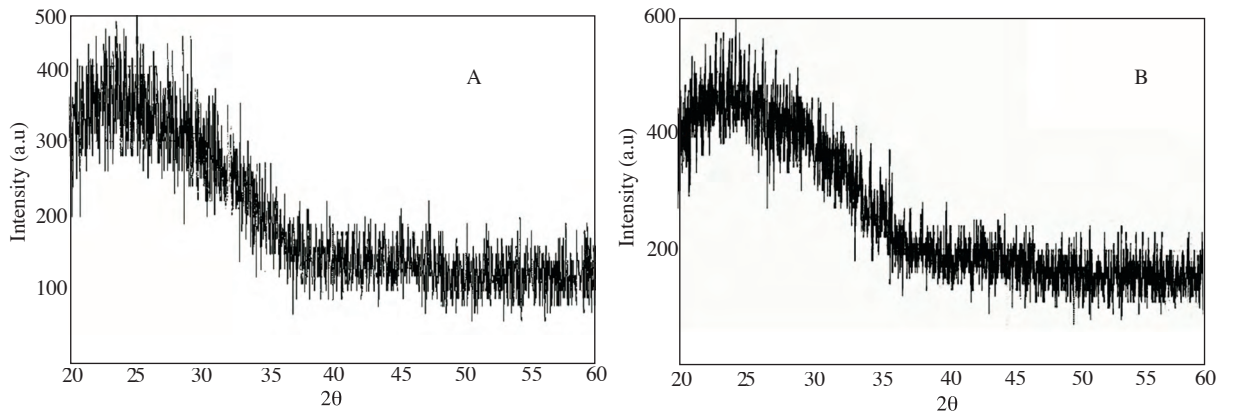
The films thicknesses were measured by using an optical interferometer method, and found it  $118 \pm 5$  nm. Post annealing was carried out in air for 3 hours at 473 K and 573 K.

X-ray diffraction (XRD) patterns of films were recorded using a Philips PW1830 X-ray diffract meter. The FTIR analyses of CBD  $CuAlS_2$  films were studied via Shimadzu FTIR-8400S Fourier Transform infrared spectrophotometer with range  $400-4000\text{ cm}^{-1}$ . The measurements of transmission and absorption spectra were carried out using a Shimadzu UV-160A UV-VIS Recording Spectrophotometer with wavelength range 300–900 nm. The optical absorption and reflectance spectra were analyzed to determine the optical constants such as refractive index  $n$ , extinction coefficient  $k$ , and absorption coefficient  $\alpha$ . Analysis of the absorption coefficient was also carried out to determine the optical band gap and nature of transitions.

### 3. Results and discussion

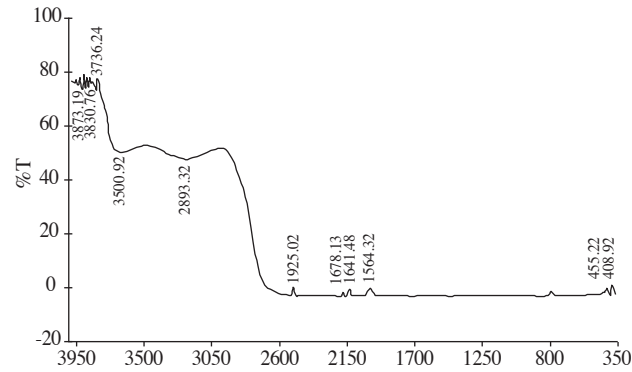
#### 3.1. XRD and FTIR analysis

The X-ray diffraction patterns of annealed, as-deposited CBD  $CuAlS_2$  thin films are shown in Figure 1. The thin films exhibit no  $CuAlS_2$  peaks, meaning that all films were amorphous, and has been observed by others [17, 18]. In addition, the level intensity of the X-ray patterns increased with annealing temperature  $T_a$ , indicating the annealing increased the amorphous nature of the  $CuAlS_2$  thin films, which further consolidates the suggestion that  $T_a$  does not enhance the crystallinity [19].



**Figure 1.** The X-ray diffraction patterns of  $CuAlS_2$  thin films A) for as deposit film and B) for annealing film at 573 K.

Figure 2 shows the FTIR spectrum of CuAlS<sub>2</sub> thin films. The spectrum has been recorded in the region 400–4000 cm<sup>-1</sup>. The vibrational frequencies of the various chemical bonds in the films can be assigned from FTIR spectra in terms of the peak positions. By the assignments of stretching and bonding modes of vibrations to the observed frequencies we can identify the associated molecule.



**Figure 2.** FTIR Spectrum of annealed CuAlS<sub>2</sub> thin film at 573 K.

The CuAlS<sub>2</sub> stretching vibration is at 290 cm<sup>-1</sup>. Since the FTIR spectrum has been acquired in the range 400–4000 cm<sup>-1</sup>, the presence of chemical constituents cannot be identified using the FTIR spectrum. If the range had been widened, metal sulfide, for example, might have been identified as its stretching bonds occur within 200–400 cm<sup>-1</sup>.

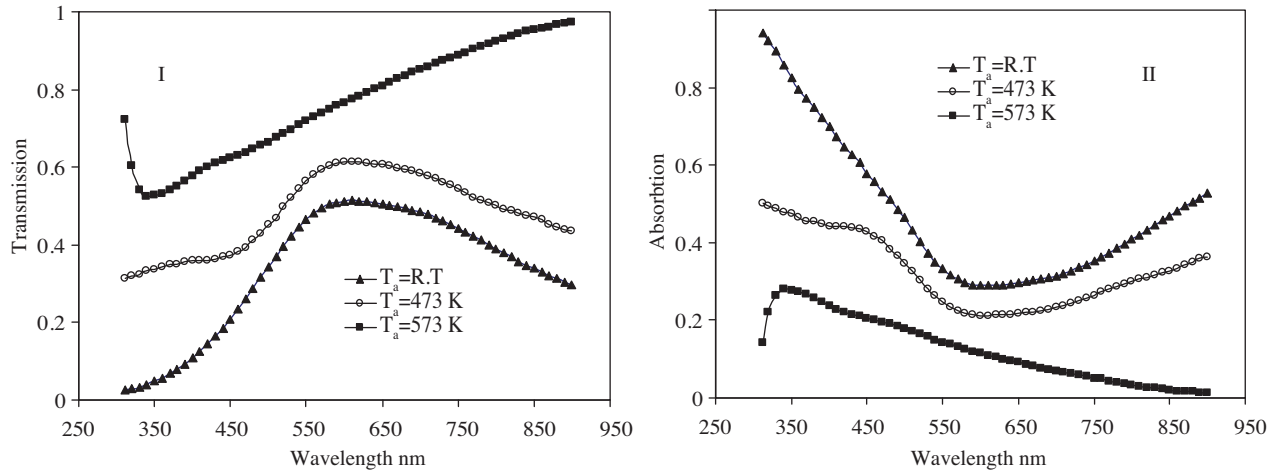
Stretching vibrations of the water O-H bond at 3873 cm<sup>-1</sup> and 3736 cm<sup>-1</sup> has been observed in CuAlS<sub>2</sub> thin films, confirms that oxygen appears as water in CuAlS<sub>2</sub> thin films. Absorption bands at 3500 cm<sup>-1</sup> and 2893 cm<sup>-1</sup> are due to hydroxyl groups. The absorption band at 1678 cm<sup>-1</sup> and 1564 cm<sup>-1</sup> is due to Cu-O (HCO<sub>2</sub>) or Al-O (HCO<sub>2</sub>). The less intense peaks at 455 cm<sup>-1</sup> and 408 cm<sup>-1</sup> enable indicate that small amounts of CuO or AlO are also present in CuAlS<sub>2</sub> thin films. Thus FTIR spectrum has been employed to conclude the form of the occurrence of oxygen in CBD grown CuAlS<sub>2</sub> thin films as water, carbonate, copper hydroxide, aluminum hydroxide, aluminum oxide and copper oxide [20, 21].

### 3.2. Optical properties

The transmission spectra of CuAlS<sub>2</sub> thin films are shown in Figure 3 (I) 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 573 K. It is noticed that the CuAlS<sub>2</sub> 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 575 K, while the other films exhibit nonlinear but degreasing transmission after this point.



**Figure 3.** The variation of Transmission (I) and Absorption (II) spectra with (Wavelength). of CuAlS<sub>2</sub> films.

The Absorptions spectra of CuAlS<sub>2</sub> films are illustrated in Figure 3 (II). 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 473 K and 573 K.

The energy optical gap  $E_g$  was calculated from the equation

$$\alpha h\nu = B(h\nu - E_g)^r, \quad (1)$$

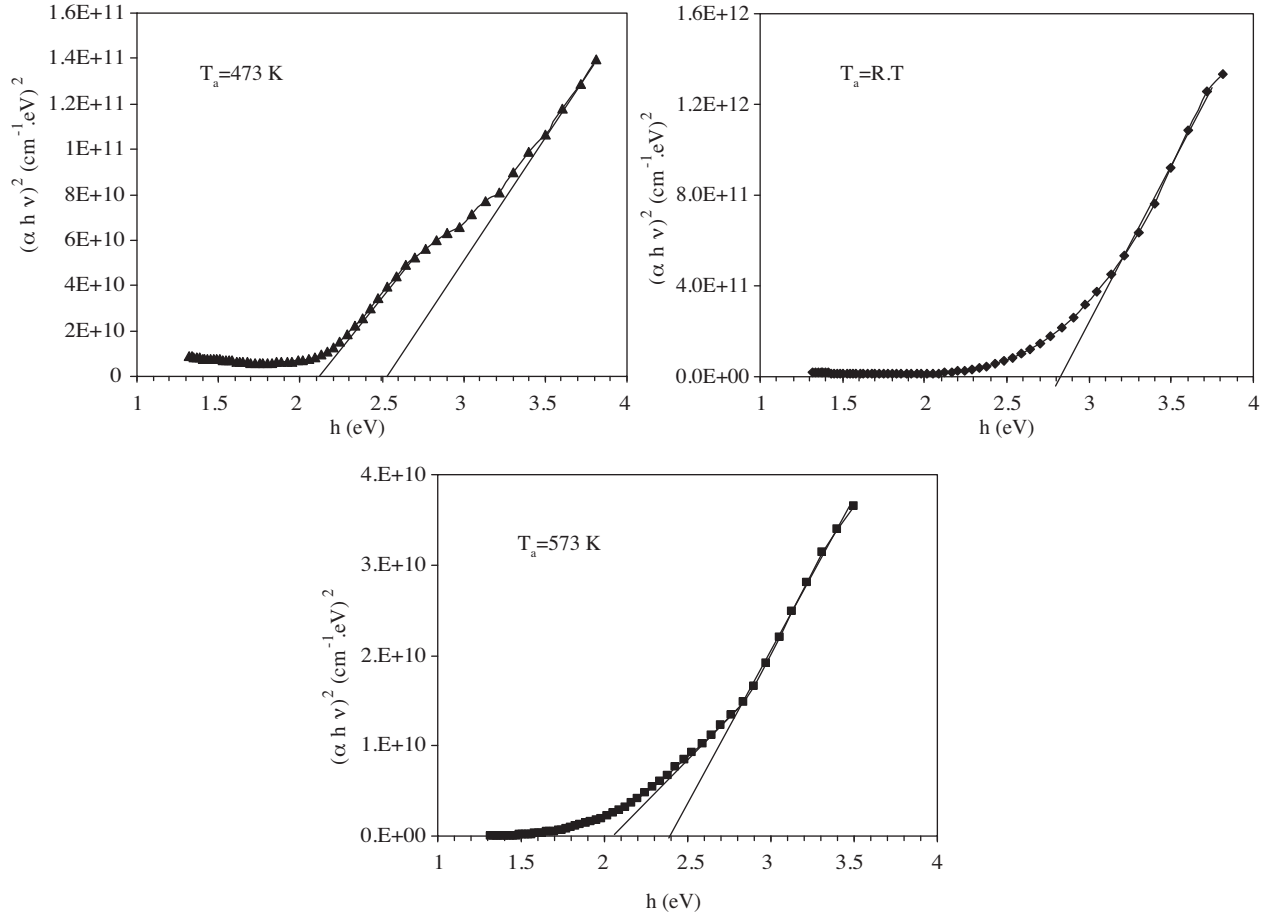
where  $\alpha$  is the absorption coefficient,  $B$  is a constant and  $r$  is an index which can be assumed to have values of 1/2, 3/2, 2 and 3, depending on the nature of the electronic transition responsible for the absorption. Exponent  $r = 1/2$  for allowed direct transition,  $r = 3/2$  for 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  $\alpha > 10^4 \text{ cm}^{-1}$ , this means the direct transitions takes place in material, while indirect transitions occur for  $\alpha < 10^4 \text{ cm}^{-1}$  [25].

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

In Figure 4 are the plots of  $(\alpha h\nu)^2$  against  $h\nu$  for films annealed at three different annealing temperatures. Those annealed at 473 and 573 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<sub>2</sub> films decreased slightly from 2.81 eV, for as-deposited films, to 2.4 eV, for films annealed at 573 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<sub>2</sub> films.



**Figure 4.** The variation of  $(\alpha h\nu)^2$  with  $h\nu$  for CuAlS<sub>2</sub> thin films at different annealing temperatures.

**Table 1.** The optical parameters of CuAlS<sub>2</sub> films at different annealing temperatures.

Annealing Temp. K	$E_{g1}$ (eV)	$E_{g2}$ (eV)	$B$ (eV/cm <sup>2</sup> )	$\Delta E$ (eV)
R.T	2.81	—	$1 \times 10^{12}$	0.98
473	2.52	2.12	$7 \times 10^{10}$	1.07
573	2.4	2.05	$3 \times 10^{10}$	1.93

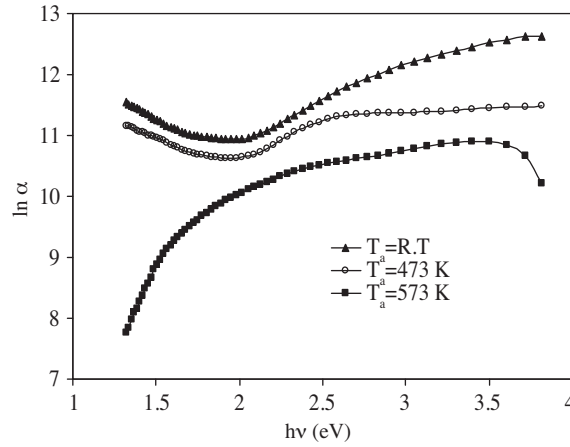
The coefficient  $B$  (slope in the Tauc equation) has been obtained from the root square of the straight line slope, as shown in Figure 4. From this figure, one can observe that  $B$  decreased with increasing  $T_a$ , as seen in Table 1.  $B$  is inversely proportional to amorphousness and the width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

A smaller  $B$  value means a larger amorphousness and the decreased of  $B$  with increasing  $T_a$  for CuAlS<sub>2</sub> films suggests a decrease of film crystallinity.

The density of the localized states in the band can be evaluated from the Urbach energy ( $\Delta E$ ). 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

$$\alpha = \alpha_o \exp(h\nu/\Delta E) \quad (2)$$

by plotting  $\ln \alpha$  as a function of  $h\nu$ , as shown in Figure 5 for CuAlS<sub>2</sub> films. The reciprocal slope of the linear part gives the value of  $\Delta E$ . The variation of  $\Delta E$  for CuAlS<sub>2</sub> films at different annealing temperature (room temperature, 473, 573 K) is shown in Figure 5 and tabulated in Table 1. We can observe that  $\Delta E$  increased with  $T_a$  from 0.98 for the as-deposited film to 1.93 eV for the annealed film at 573 K. This may be attributed to structure change and increasing the degree of amorphous character, leading to increase in the localized states [30].



**Figure 5.** Variation of  $\ln(\alpha)$  versus  $h\nu$  for CuAlS<sub>2</sub> thin films at different annealing temperatures.

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]

$$n = \sqrt{\frac{4R}{(R-1)^2 - k^2} - \frac{(R-1)}{(R-1)}}, \quad (3)$$

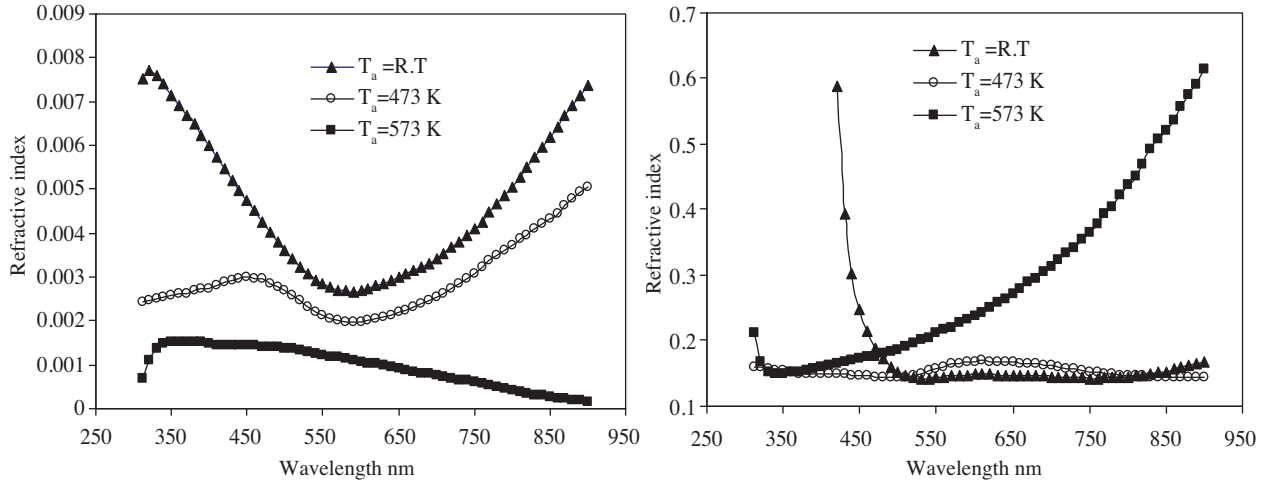
where  $R$  the reflectance and  $k$  the extinction coefficient defined as

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

and where  $\lambda$  is the wavelength and  $\alpha$  is the absorption coefficient.

Variation of the refractive index with annealing temperature for CuAlS<sub>2</sub> films is shown in Figure 6. Observe that the behavior of refractive index for CuAlS<sub>2</sub> 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<sub>2</sub> films at different annealing temperatures. From Figure 5 we can observe that the extinction coefficient for CuAlS<sub>2</sub> films decreases with increasing the annealing temperature, and attributed to the same reasons as previously mentioned.



**Figure 6.** The variation of refraction index  $n$  and extinction coefficient  $k$  with wavelength of  $\text{CuAlS}_2$  films at different annealing temperatures.

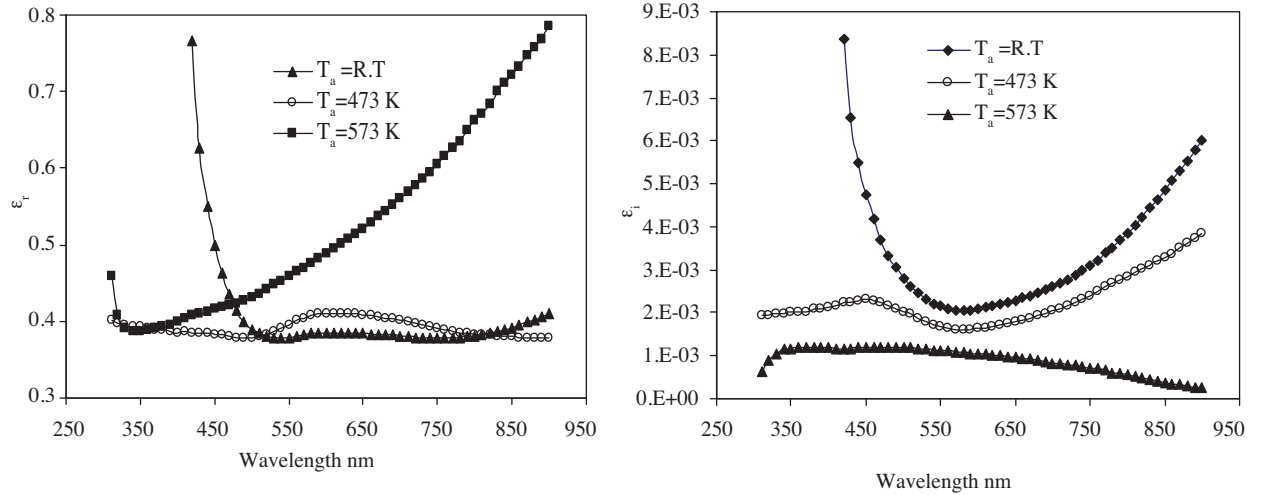
We also calculated the imaginary and real parts of the dielectric constant, as it is directly related to the density of states within the energy gap of the films. The real  $\varepsilon_r$  and imaginary  $\varepsilon_i$  parts of the dielectric constant of the films were determined by the relations [32]

$$\varepsilon_r = n^2 - k^2 \quad (5)$$

and

$$\varepsilon_i = 2nk. \quad (6)$$

The imaginary and real parts of dielectric constant are shown in Figure 7. The behavior of  $\varepsilon_r$  is similar to refractive index because of the smaller value of  $k^2$  comparison to  $n^2$ , while  $\varepsilon_i$  depends mainly on the  $k$  values,



**Figure 7.** The variation of the real and imaginary part of the dielectric constants,  $\varepsilon_r$  and  $\varepsilon_i$ , respectively, with wavelength for  $\text{CuAlS}_2$  films at different annealing temperatures.



which is related to the variation of absorption coefficient. For CuAlS<sub>2</sub> films,  $\varepsilon_r$  decreased with increasing  $T_a$ , while  $\varepsilon_i$  decrease with increasing annealing temperature.

## 4. Conclusions

Structural and optical characteristics of CuAlS<sub>2</sub> thin films prepared by chemical bath deposition technique have been studied. The X-ray diffraction reveal that the films prepared at 300 K possess an amorphous structure and the amorphous character increases with annealing temperature, while  $T_a$  does not enhance the crystallinity. FTIR spectra enabled resolving the occurrence of oxygen in the prepared CuAlS<sub>2</sub> thin films. The optical constants (optical energy gap, refractive index  $n$ , absorption coefficient  $\alpha$ , and extinction coefficient  $k$ ) of CuAlS<sub>2</sub> 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 573 K. We consider that amorphous of structure play a major role effect on optical constants.

## References

- [1] F. C. Eze, and C. E. Okeke, *Mater. Chem. Phys.*, **47**, (1997), 31.
- [2] F. I. Ezema, and C. E. Okeke, *Greenwich J. Sci. Tech.*, **3**, (2003), 90.
- [3] K. L. Chopra and S. R. Das, *Thin Film Solar Cells.*, (Plenum Press: New York, 1983).
- [4] B. A. Ezekoye, and C. E. Okeke, *Pacific J. Sci. Tech.*, **6**, (2005), 23.
- [5] D. N. Okoli, A. J. Ekpunobi and C. E. Okeke, *Pacific J. Sci. Tech.*, **7**, (2006), 59.
- [6] S. N. Agbo and F. I. Ezema, *Pacific J. Sci. Tech.*, **8**, (2007), 1.
- [7] M. I. Alonso, M. Garriga, C. A. Durante Rinco'n, M. Leo'n, *J. Appl. Phys.*, **88**, (2000), 5796.
- [8] I. V. Bodnar, I. N. Tsyrelchuk, I. A. Victorov, *J. Mater. Sci. Lett.*, **13**, (1994), 762.
- [9] S. Shirakata, H. Miyake, *Jpn. J. Appl. Phys.*, **41**, (2002), 77.
- [10] W. Gebicki, M. Igalson, W. Zajac, R. Trykozko, *J. Phys. D: Appl. Phys.*, **23**, (1990), 964.
- [11] G. Harichandran, N. P. Lalla, *Mater. Lett.*, **62**, (2008), 1627.
- [12] F. Hergert, S. Jost, R. Hock, M. Purwins, *Phys. Status Solidi (a)*, **203**, (2006), 2598.
- [13] S. Chichibu, Y. Harada, M. Sugiyama, H. Nakanishi, *J. Phys. Chem. Solids*, **64**, (2003), 1481.
- [14] M. Caglar, S. Ilican, Y. Caglar, *Opt. Commun.*, **281**, (2008), 1615.
- [15] R. Brini, G. Schmerber, M. Kanzari, J. Werckmann, B. Rezig, *Thin Solid Films*, **517**, (2009), 2191.
- [16] A. F. Sabbar, M.Sc. Thesis, University of Technology, Department of Applied Physics, Baghdad, Iraq, 2008.
- [17] M. T. S. Nair and P. K. Nair, *Journal of Semicond. Sci. Technol.*, **4**, (1989), 191.

- [18] I. Grozdanov, C. K. Barlingay, S. K. Dey, M. Ristov and M. Najdoski, *Journal of Thin Solid Film*, **250**, (1994), 67.
- [19] S. V. Bagul, S. D. Chavhan and Ramphal Sharma, *Journal of Physics and Chemistry of Solid.*, **68**, (2007), 1623.
- [20] L. M. N. Salim, *The Spectrum*, (Al-Mawsil Univ. Press, Al-Mawsil. Iraq, 1985)
- [21] V. P. Tolstoy, I. V. Chernyshova and V. A. Skryshevsky, *Handbook of Infrared Spectroscopy of Ultra Thin Films*, (By John Wiley & Sons, Inc. 2003).
- [22] Tariq J. Alwan, K. A. Jassim, *The Proceeding of Materials Science & Technology Conference (MS&T'10)*, (Houston, Texas, U.S.A, 2010).
- [23] J. Tauc, *Amorphous and Liquid Semiconductors*, (Plenum Press, New York, 1979).
- [24] S. M. Sze, *Semiconductor Devices physics and Technology*, (John Wiley & Sons, Inc., 3Edition, Canada, 2007).
- [25] B. Thangaraju, P. kalianna, *Cryst. Res. Techon.*, **35**, (2000), 71.
- [26] H. Ar.zpe- Ch.vez, R. Ram.rez-Bon, F. J. Epinoza-Beltr.n and O. Zelaya-Angel, *Superficies Vacio*, **8**, (1999), 120.
- [27] N. Mott and E. Davis, *Electronic Process in Non-Crystalline Materials*, (2nd ed. Oxford University Press, 1980).
- [28] T. S. Moss, *Semiconductor Opto-electronics*, (Butter Worths Sci.publishing, London, 1973).
- [29] R. A. Greiner, *Semiconductor Device Electronic Energy Series*, (McGraw-Hill Book Co. Inc., 1961).
- [30] M. N. Eman. Al Fawade, Ph.D. Thesis, Baghdad University, Iraq, 2005.
- [31] J. Pankov, *Optical Processes in Semiconductors*, (London, 1971).
- [32] M. A. Omar, *Elementary Solid State Physics*, (Addison-Wesley Publishing Company, 1993).