

Influence of Copper Content on Structural and Optical Properties of $\text{Cu}_{2(x)}\text{Zn}_{(1-x)}\text{S}$ Thin Films

Adnan M. Mansoor Al-Saedi

College of Applied Medical Sciences, University of Kerbala

Abstract: $\text{Cu}_{2(x)}\text{Zn}_{(1-x)}\text{S}$ alloy was synthesized by reacting high purity elements Cu, Zn, and S with ratios of Cu $x = (0.0), (0.25), (0.50), (0.75)$ and (1.0) in an evacuated quartz ampoule. $\text{Cu}_{2(x)}\text{Zn}_{(1-x)}\text{S}$ thin films have been prepared by vacuum thermal evaporation method from the $\text{Cu}_{2(x)}\text{Zn}_{(1-x)}\text{S}$ alloy. The thin films were deposited onto glass substrates under vacuum pressure of 10^{-5} torr with thickness of 500 nm. The analysis of structural and optical properties of the $\text{Cu}_{2(x)}\text{Zn}_{(1-x)}\text{S}$ thin films were carried out by X-ray diffraction (XRD) and UV-Vis Spectrophotometer. The X-Ray diffraction method was utilized to test the $\text{Cu}_{2(x)}\text{Zn}_{(1-x)}\text{S}$ film. It was found that the film had a polycrystalline structure with cubic phase and that the average crystal size varied from $(253) \text{ \AA}$ to $(348) \text{ \AA}$. The study of the optical properties were carried out within a range of wavelength between (200nm) and (1100nm) . The average transmission of the films was about $(70-90)\%$. It was decreasing with the increasing of copper concentration (x) . The value of absorbance was very dependent on copper concentration in thin films as the absorbance was proportional with the increase in copper concentration. The absorption coefficient (α) and optical energy gap were measured for direct electronic transitions. And the film energy band gap was in the range of $(3.10-2.08)\text{eV}$, depending on the material of the thin film and the concentration of copper. Finally, the extinction coefficient; refractive index and dielectric constant were measured for all thin films. The refractive index and dielectric constant, at first, increased with the increase of wavelength and reached the largest possible value and then they decreased with the increase of wavelength. The refractive index varied between (1.2) and (2.6) .

Keywords: Structural and Optical Properties, $\text{Cu}_{2(x)}\text{Zn}_{(1-x)}\text{S}$ thin films

1. Introduction

Copper Zinc Sulfides $\text{Cu}_{2(x)}\text{Zn}_{(1-x)}\text{S}$ have an intermediate feature between Cu_2S and ZnS . The increasing of the Copper (Cu) to a greater degree changes the previous compound, Copper Zinc Sulfides ($\text{Cu}_{2(x)}\text{Zn}_{(1-x)}\text{S}$), into Copper Sulfide (Cu_2S) which is used as a buffer window layer material in heterojunction photovoltaic and photoconductive applications. The $\text{Cu}_{2(x)}\text{Zn}_{(1-x)}\text{S}$ thin films band structure has a larger energy band gap than Cu_2S . This makes the thin film much more appealing for the investigation of solar cells, filters and detectors. [1,2].

The $\text{Cu}_{2(x)}\text{Zn}_{(1-x)}\text{S}$ ternary compound is, furthermore, a possible valuable window material for the creation of a p-n junction without a lattice mismatch in the devices [3].

$\text{Cu}_{2(x)}\text{Zn}_{(1-x)}\text{S}$ thin films have been fabricated by several methods such as: RF-sputtering [4], chemical vapor deposition (CVD) [5], chemical bath deposition (CBD) [6], thermal vacuum evaporation [7], thermal spray pyrolysis [8], and atomic layer deposition [9].

Thermal vacuum evaporation is one of the most used techniques [6-8]. This technique has the advantages of many things, such as easiness, low cost and regular crystal size allocation.

The learning of optical and structural properties of thin films is, considerably, of a large importance for the configuration and investigation of thin films to be utilized as a part of photoelectronic devices. The Cu_2S film is a p-type semiconducting material with cubic crystal structure and a band gap value varies within the range 1.2 eV to 2.5 eV [10-11].

ZnS is a transparent white powder which is formed within a two-phase structure: (α Wurtzite) and (β Zincblende) and is an n-type semiconductor with a wide direct band gap of about $(3.2-3.5) \text{ eV}$ in the ultra-violet region [12]. It is utilized as a main material for LED and other photoelectronic applications [13, 14].

The aim of this research it is to examine the influence of copper concentration (x) on the structural and optical properties of $\text{Cu}_{2(x)}\text{Zn}_{(1-x)}\text{S}$ thin films to measure the crystal size, lattice constant and optical constants, such as: absorption coefficient, energy band gap, refractive index, extinction coefficient and dielectric constant.

2. Experiment

$\text{Cu}_{2(x)}\text{Zn}_{(1-x)}\text{S}$ alloy was formed by weighting appropriate atomic weights of Cu, Zn and S with a high purity of about 99.999% in an evacuated quartz ampoules. The elements were mixed in atomic ratios of copper: $(0.0), (0.25), (0.5), (0.75)$ and (1.0) , according to the stoichiometry of $\text{Cu}_{2(x)}\text{Zn}_{(1-x)}\text{S}$. The mixtures were heated firstly, using a furnace from room temperature to (500K) for one hour. Then, the temperature was increased to be about (800 K) for two hours. Sequentially and to ensure homogeneity, the temperature was fixed up to (1100 K) for four hours. The solid ingot was powdered by being grinded to get a $\text{Cu}_{2(x)}\text{Zn}_{(1-x)}\text{S}$ compound.

The $\text{Cu}_{2(x)}\text{Zn}_{(1-x)}\text{S}$ compound, having an accurate weight, was placed inside a boat made of molybdenum (Mo). $\text{Cu}_{2(x)}\text{Zn}_{(1-x)}\text{S}$ thin films were grown on square $(2.5 \times 2.5) \text{ cm}$ soda-lime glass substrates by a vacuum thermal evaporation system model (Edward 306A) with a thickness of (500nm) and vacuum pressure of (10^{-5}) torr. All films were fabricated with a distance between boat and substrate (25 cm) at room temperature.

Volume 5 Issue 11, November 2016

www.ijsr.net

Licensed Under Creative Commons Attribution CC BY

Then, the deposition process leaves the system under low pressure for an appropriate period in order to get rid of the heat caused by the evaporation process and to ensure that there will be no interaction between air and samples.

The next step was to take out the samples and to put them in the petri dishes so as to be kept away from external conditions (such as temperature and humidity) for the sake of examining them. The thickness of the deposited films was measured by using the weighted method.

Structural properties were made by X-ray diffraction device (Philips X-ray Diffractometer), where the specifications of the device are: Target Type (Cu X-ray tube $K\alpha$), the wavelength of X-rays (0.1541 nm); with (40 KV) voltage, (20 mA) current and angles of ($2\theta = 20^\circ - 90^\circ$).

The optical measurement was performed by (UV-Vis) (UV-1800 Spectrophotometer from Shimadzu) within various range of wavelength between (200 nm) and (1100 nm).

3. Results and Discussion

The study of X-ray diffraction pattern for any material can identify the crystal structure of it. The diffraction pattern of the thin film could be done by determining the peak positions. And that appears in the falling of the X-ray on surface material with monochromatic wavelength (λ) at an angle (θ), according to (Bragg's law) [15]:

$$2d \sin \theta = n\lambda$$

where:

n : integer (1, 2, 3, ...).

d : the vertical distance between the two surfaces consecutive.

λ : wavelength of X-rays.

θ : the incident or reflection X-rays angle.

The thin films were examined within the range between (20° and 60°) (2θ) scale angle. To know the value of interplanar spacing (d_{hkl}), Miller indices (hkl) of cards [American Standard for Testing Materials] (ASTM) can be seen, so as to get the lattice constant (a) of the material by using the equation [15]:

$$\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2}$$

Figure (1) shows the XRD patterns of $Cu_{2(x)}Zn_{(1-x)}S$ thin films for different concentrations (x) with a thickness of $t=500$ nm. When $x=0.0$. There are six sharp peaks located at: $2\theta = (29.15^\circ), (31.72^\circ), (33.15^\circ), (47.41^\circ), (56.52^\circ)$ and (57.93°) (which correspond to the reflections from (111), (105), (200), (110), (311) and (201) planes respectively of ZnS thin film with cubic phase), while peaks appeared at $2\theta = (27.77^\circ), (33.56^\circ), (39.02^\circ), (46.74^\circ)$ and (54.57°) for composition $x=0.25$ which correspond to reflections from (111), (107), (102), (110) and (310) planes respectively.

Peaks appeared at $2\theta = (28.64^\circ), (38.52^\circ), (40.16^\circ), (47.85^\circ), (54.11^\circ)$ and (55.95°) for concentration $x=0.50$ which correspond to reflections from (111), (102), (220), (110), (310) and (311) planes respectively. For composition $x=0.75$, the peaks appear at $2\theta = (28.47^\circ), (34.38^\circ), (38.53^\circ), (39.21^\circ), (47.23^\circ), (52.56^\circ)$, and (55.27°) which correspond to reflections from (111), (200), (102), (220), (110), (310) and (311) planes.

Finally, When $x=1.0$, there can be seen six sharp peaks located at $2\theta = (27.31^\circ), (37.22^\circ), (37.84^\circ), (45.42^\circ), (51.25^\circ)$ and (54.26°) which correspond to the reflections from (111), (102), (220), (110), (310) and (311) planes respectively of Cu_2S thin film with cubic phase. These reflections in XRD pattern are, also, in good agreement with the reported values [16, 17].

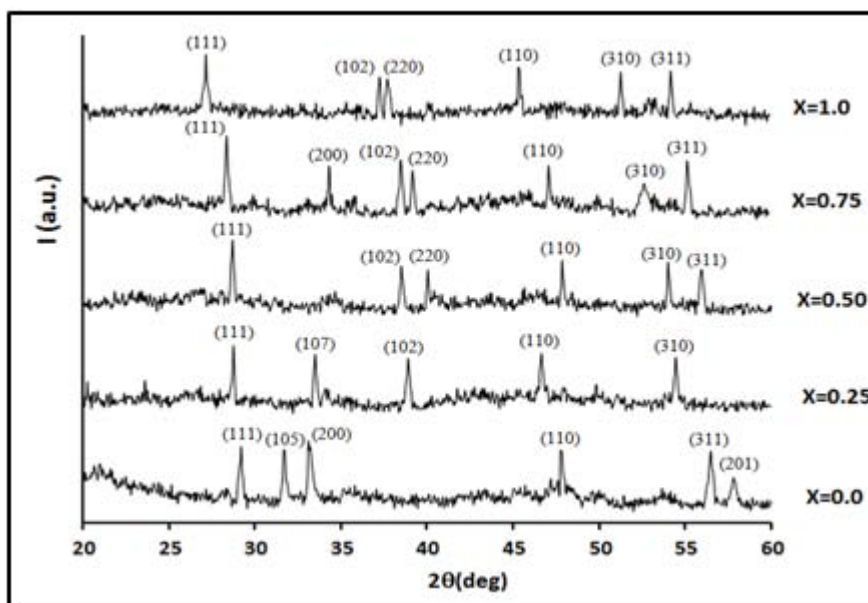


Figure 1: X-ray diffraction pattern for $Cu_{2(x)}Zn_{(1-x)}S$ thin films with different (x)

There is a shift of 2θ location to lower values and an increase of the peaks intensity and crystalline accompanied the increasing of copper content as given in Table (1).

The X-rays diffraction measurements has shown that the thin films were cubic polycrystalline phase because of the presence of X-ray diffraction peaks in most thin films, as

illustrated in figure (1). And this is consistent with [18,19].It also, calculated the size of the crystal grains (crystal size G) for each of the Bragg's peaks of all samples using Scherrer formula [20]:

$$G = \frac{K\lambda}{B \cos \theta_B}$$

$K = 0.89$ is the shape factor

B : Full Width at Half Maximum (FWHM).
 λ : Wavelength of X-rays used ($\lambda = 0.15418 \text{ nm}$).
 θ_B : is the Bragg's angle.

Table 1: X-ray diffraction data for thin $\text{Cu}_{2(x)}\text{Zn}_{(1-x)}\text{S}$ films with different concentrations (x)

X	$d_{(\text{exp.})}$ (Å)	$d_{(\text{stand.})}$ (Å)	$2\theta_{(\text{exp.})}$ (deg.)	$2\theta_{(\text{stand.})}$ (deg.)	hkl	FWHM	Lattice constant (Å^0)	$G_{(\text{ave.})}$ (Å^0)
(0.0) ZnS	3.067	3.130	29.15	28.55	(111)	0.541	5.312	253.26
	2.820	2.759	31.72	32.41	(105)	0.473		
	2.701	2.711	33.15	33.08	(200)	0.522		
	1.915	1.910	47.41	47.54	(110)	0.611		
	1.423	1.634	56.52	56.28	(311)	0.755		
	1.590	1.601	57.93	57.59	(201)	0.874		
$\text{Cu}_{2(0.25)}\text{Zn}_{(0.75)}\text{S}$	3.104	-----	28.77	-----	(111)	0.429	5.376	338.42
	2.673	-----	33.56	-----	(107)	0.433		
	2.312	-----	39.02	-----	(102)	0.565		
	1.944	-----	46.74	-----	(110)	0.259		
	1.681	-----	54.57	-----	(310)	0.282		
0.50 $\text{Cu}_{2(0.50)}\text{Zn}_{(0.50)}\text{S}$	3.117	-----	28.64	-----	(111)	0.342	5.398	348.75
	2.340	-----	38.52	-----	(102)	0.476		
	2.244	-----	40.16	-----	(220)	0.198		
	1.901	-----	47.85	-----	(110)	0.397		
	1.696	-----	54.11	-----	(310)	0.385		
	1.641	-----	55.95	-----	(311)	0.502		
0.75 $\text{Cu}_{2(0.75)}\text{Zn}_{(0.25)}\text{S}$	3.142	-----	28.47	-----	(111)	0.276	5.442	279.35
	2.610	-----	34.38	-----	(200)	0.315		
	2.340	-----	38.53	-----	(102)	0.485		
	2.298	-----	39.21	-----	(220)	0.358		
	1.925	-----	47.23	-----	(110)	0.246		
	1.742	-----	52.56	-----	(310)	1.534		
1.0 Cu_2S	3.274	3.290	27.31	27.17	(111)	1.104	5.670	317.12
	2.414	2.436	37.22	36.95	(102)	0.374		
	2.383	2.406	37.84	37.38	(220)	0.318		
	2.003	2.031	45.42	44.57	(110)	0.229		
	1.782	1.753	51.25	52.18	(310)	0.267		
	1.688	1.703	54.26	53.84	(311)	0.283		

The average crystal size has been shown to be in the range of (253) Å^0 to (348) Å^0 as given in table (1). The increase and decrease in particle size with copper concentration (x) may have been because of the increase in long-range arrangement crystalline or could be subscribed to other factors during the preparation of thin films.

The increase in particle size might be because of the agglomeration that happened between small grains or it might be because of the potential energy difference between the various size of particles. This can, likewise, happen through the diffusion process.

On the other hand, the optical properties have been made by checking the transmittance spectra of thin films prepared by using the type of spectrophotometer (UV-Vis Double Beam Spectrophotometer).

The transmittance of the thin films (T) was measured within a wavelength range between (200nm) and (1100nm). The absorption spectrum of the (ZnS) thin film is within the spectrum UV region and the absorption spectrum of the

(Cu_2S) thin film is within the spectrum visible region, as shown in Fig.(2).

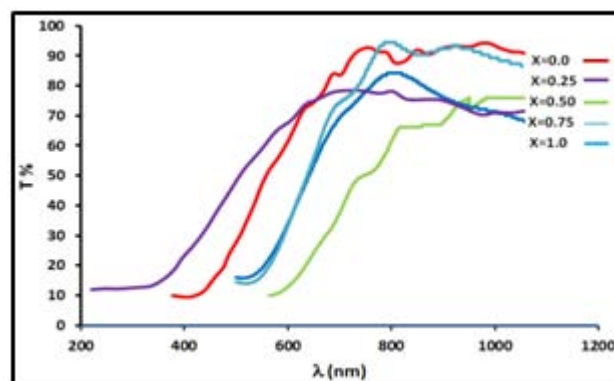


Figure 2: Transmittance (T) versus wavelength (λ) for thin $\text{Cu}_{2(x)}\text{Zn}_{(1-x)}\text{S}$ films with different concentrations (x)

Moreover, the absorbance (A) in terms of transmittance can be calculated by applying the following relationship, as shown in Fig.(2)[21]:

$$A = \log \frac{1}{T}$$

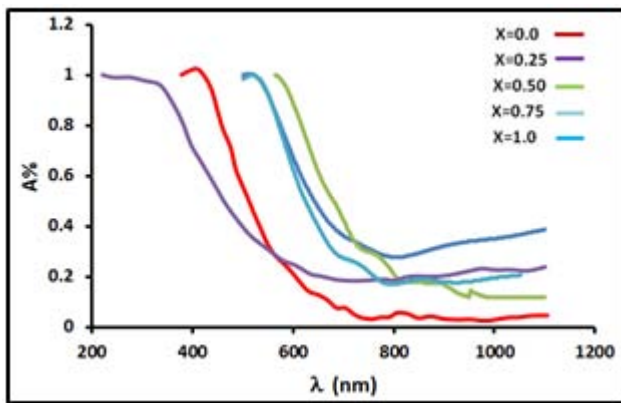


Figure 3: Absorbance (A) versus wavelength (λ) for thin $\text{Cu}_2(x)\text{Zn}_{(1-x)}\text{S}$ films with different concentrations (x)

With respect to the absorption of coefficient (α), it can be calculated by the following relationship [21]:

$$\alpha = 2.303 \frac{A}{t}$$

Where t is the thickness of sample

The value of the absorption coefficient changes with the wavelength (where this change depends on the properties of semiconductor material as well as on energy photons ($h\nu$)), the value of the optical energy gap (E_g) of the thin film can be known by having the value of (α)

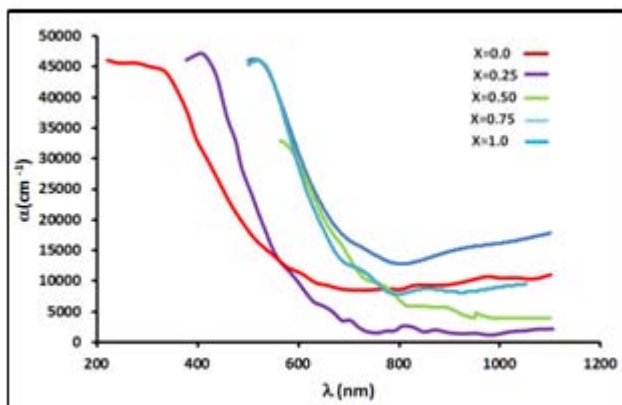


Figure 4: Absorption coefficient (α) versus wavelength (λ) for thin $\text{Cu}_2(x)\text{Zn}_{(1-x)}\text{S}$ films with different concentrations (x)

By plotting the relationship between (α) and (λ), it can be noticed that the absorption coefficient in the absorption region of high values is larger than $(10^4) \text{ cm}^{-1}$, as shown in Fig.(4). And this means that the charge carriers move from the extended levels in the valence band to the extended levels in the conduction band thereby, generating pair electron-hole in a process called as: the fundamental absorption process.

This value of the absorption coefficient shows that the electronic transition of semiconductor is of a direct transition. And this is a general property for compounds Group (II - VI) and especially compound (ZnS) and Cu_2S .

Besides, the possible value of the energy gap calculation is based on the nature of the electronic transitions between energy bands[22]:

$$\alpha (h\nu) = A_i (h\nu - E_g)^n$$

Where A_i is constant and $n= 1/2$ is for allowed direct transition.

Practically, it is possible to calculate the energy value by plotting the relationship between the photon energy ($h\nu$) as a function of $(\alpha h\nu)^2$ and the extrapolation (i.e. E_g) of the portion at $[(\alpha h\nu)^2 = 0]$, as shown in Fig.(5). The value of the optical energy gap decreases with the increasing of copper content (x) for all samples, as shown in Table (2)

The absorption coefficient has small values at low energy of all thin films. But its value increases in the absorption edge, as illustrated in the figure (4) where it is clearly noticed that the increase in the proportion of copper has led to the deviation of the edge of the optical absorption towards the low energies. And that is because of the presence of defects in crystal structure, or the so-called trap states inside the optical energy gap [21]. This deviation has led to a reduction of the optical energy gap.

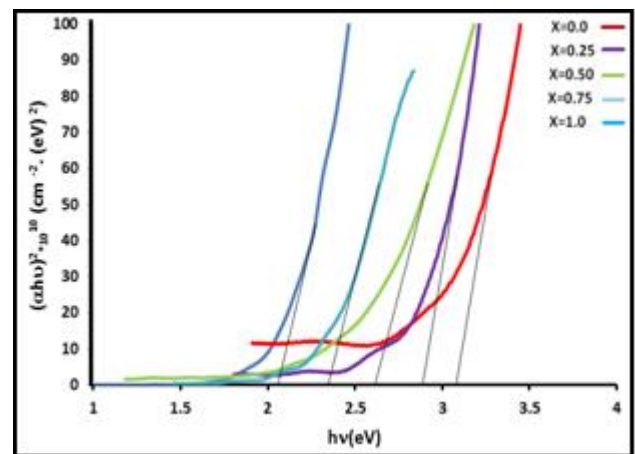


Figure 5: $(\alpha h\nu)^2$ versus $h\nu$ for thin $\text{Cu}_2(x)\text{Zn}_{(1-x)}\text{S}$ films with different concentrations (x)

It can be concluded that the increase in copper ratio has brought about a significant change in the value of the optical energy gap (E_g) which indicates that it may cause a rise to some of the structural defects that appear in tails in the region between the valence and conduction band.

Table 2: Optical energy gap (E_g) for thin $\text{Cu}_2(x)\text{Zn}_{(1-x)}\text{S}$ films with different concentrations (x)

x	E_g (eV)
(0.0) ZnS	3.1
(0.25) $\text{Cu}_{2(0.25)}\text{Zn}_{(0.75)}\text{S}$	2.85
0.50 $\text{Cu}_{2(0.50)}\text{Zn}_{(0.50)}\text{S}$	2.65
0.75 $\text{Cu}_{2(0.75)}\text{Zn}_{(0.25)}\text{S}$	2.35
1.0 Cu_2S	2.08

The extinction coefficient has been calculated from the equation[23]:

$$k = \frac{\alpha \lambda}{4 \pi}$$

Drawing the relationship between the extinction coefficient as a function of wavelength for all thin films, the value of extinction coefficient decreases with increasing wavelength is observed, as shown in Fig.(6).

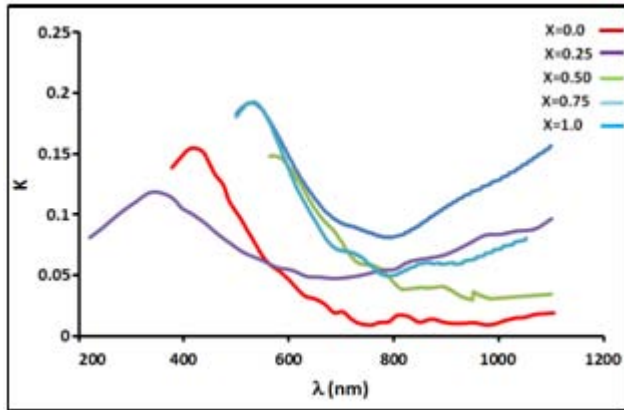


Figure 6: The extinction coefficient (k) versus wavelength (λ) for thin Cu_{2(x)Zn_(1-x)S} films with different concentrations (x)

The values of high extinction coefficient at short wavelengths can be traced back to the loss of photon energy as a result of the fundamental absorption process where the growing influence of extinction coefficient is correlated with the increasing of the copper ratio for all films.

The refractive index (n) can be calculated from the following equation [24].

$$n = \left[\frac{4R}{(R-1)^2} - k^2 \right]^{1/2} - \frac{(R+1)}{(R-1)}$$

where R is a reflectance

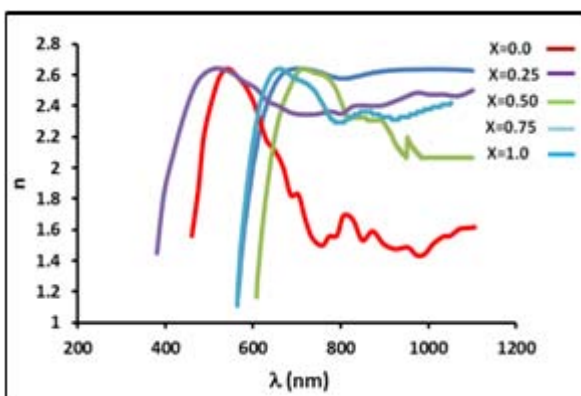


Figure 7: The refractive index (n) versus wavelength (λ) for thin Cu_{2(x)Zn_(1-x)S} films with different concentrations (x)

This figure shows that the refractive index in general increases, then decreases with the increasing of copper content to prepared films, as shown in Fig.(7). The behaviour of the refractive index with various concentrations of the copper impurity is comparatively autonomous.

The real and imaginary part of the dielectric constant (ϵ_r and ϵ_i) can be calculated by using the equations[25]:

$$\epsilon_r = n^2 - k^2$$

$$\epsilon_i = 2nk$$

Variation of dielectric constants (ϵ_r) and (ϵ_i) with wavelength for different concentrations is shown in figures.(8,9). From these figures, it can be shown obviously that the values of dielectric constants initially increases with the increase of wavelength and reaches a maximum value and then decreases with the increase of wavelength as the same fashion of refractive index.

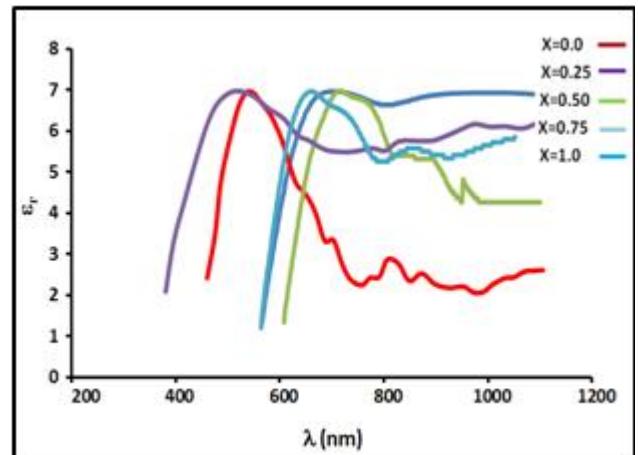


Figure 8: The real part of the dielectric constant (ϵ_r) versus wavelength (λ) for thin Cu_{2(x)Zn_(1-x)S} films with different concentrations (x)

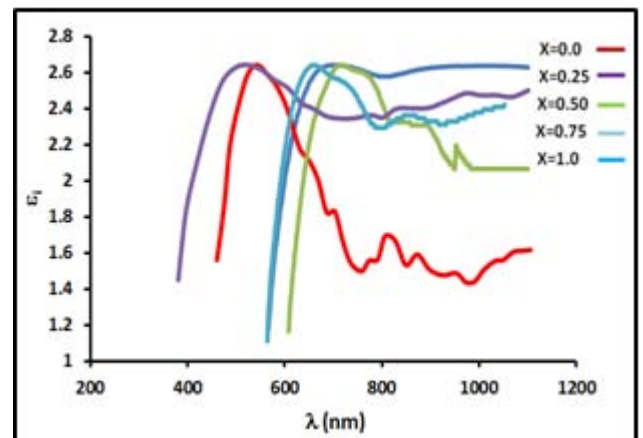


Figure 9: The imaginary part of the dielectric constant (ϵ_i) versus wavelength (λ) for thin Cu_{2(x)Zn_(1-x)S} films with different concentrations (x)

4. Conclusions

The main purpose of this research is to study the effect of copper concentration on the structural and optical properties of Cu_{2(x)Zn_(1-x)S} thin films. So, the thin films have been prepared with ratios of Cu x= (0.0), (0.25), (0.50), (0.75) and (1.0) by heating the mixture of Cu, Zn and S elements in order to prepare the alloys. The thin films have been prepared by vacuum thermal evaporation method with a thickness of (500) nm at room temperature.

X-ray diffraction technique (XRD) results have shown that the thin films of $\text{Cu}_{2(x)}\text{Zn}_{(1-x)}\text{S}$ are polycrystalline structure with cubic phase. The optical measurements have showed that the $\text{Cu}_{2(x)}\text{Zn}_{(1-x)}\text{S}$ thin films have direct energy gap which decreases with the increasing of copper concentration.

As calculating absorption coefficients (α), extinction coefficients (k) and refractive index (n), it has also found that it decreases with the increasing of concentration (x). It was noticed that the edge of the optical absorption shifted towards short wavelength.

For the dielectric constant (ϵ), it is observed that the value of (ϵ) initially increases with the increasing of wavelength and reaches its maximum value and then decreases, as in the same fashion of refractive index.

References

- [1] G. I. Yepifanov, Yu. A. Moma, "Introduction to Solid State Electronics", Publishers, Moscow, (1984).
- [2] C. Kittel, "Introduction to Solid State Physics", 5th edition, John Wiley and Sons, Inc., Canada, (1976).
- [3] D. Gerig, "Electrons in Metals of Semiconductor", McGraw – Hall, Landon, (1969).
- [4] Jacques Vedel, Pierre Cowache and Micheal Soubeyranel *Solar Energy Materials*, 10 ,p.(25-34), (1984).
- [5] S. Schneider, J.R. Ireland, M.C. Hersam, T.J. Marks, *Chem. Mater.* 19 ,p.2780,(2007).
- [6] S.V. Bagul, S.D. Chavhan, R. Sharma, *J. Phys. Chem. Solids* 68,p.1623,(2007).
- [7] Couve, S. , Gousskov, L., Szepessy, L., Vedel, J., and Castel,E, "Resistivity and Optical Transmission of CuXS Layers as a Function of Composition", *Thin Solid Films* ,15,p.(223-231), (1973).
- [8] Wang, S. Y., Wand, W. and Lu, Z. H., "Asynchronous – Pulse Ultrasonic Spray Pyrolysis Deposition of $\text{Cu}_x\text{S}(x=1,2)$ Thin Films", *Mater.Sci.Eng.,B*,103, p.(84-188) ,(2003).
- [9] Elijah Thimsen, Qing Peng, Alex B. F. Martinson, Michael J. Pellin, Jeffrey W. Elam *Chem. Mater.* 23, p.(4411–4413),(2011).
- [10] M.S Shinde, P.B Ahirrao, I.J Patil and RS Patil, *Indian Journal of Pure and Applied Physics*, vol. 50, sep,p. 657-660,(2012).
- [11] S.V. Bagul, S.D. Chavhan and R. Sharma, *J. Phys.Chem, solids*, 68, p.1623-1629,(2007).
- [12] J. Mu and Y. Zhang ,*Appl. Surf. Sci.* 252 . p.7826,(2006).
- [13] K. Skwok and X. Sun, "Thin Solid Films", Vol. 335, p. 229,(1998).
- [14] A. Antony, K.V. Mirali, R. Manoj, M. K.Jayaraj, *Mater.Chem.Phys*, Vol. 90, p. 106,(2005).
- [15] H. P. Klug and L. E. Alexander. *X–ray diffraction procedure*. John Wiley & Sons, New York, USA (1974).
- [16] H. K. Sadekar, N. G. Deshpande, Y. G. Gudage, A. Ghosh, S. D. Chavhan, S. R. Gosavi and R. Sharma, *J. Alloy and Compounds*, 453, 519 (2008).
- [17] M.S Shinde,P.B.Ahirrao,I.J.Patil ,R.S.Patil " thickness dependent electrical and optical properties of nanocrystalline copper sulphide thin films grown by simple chemical route" Vol.50,pp(657-660),(2012).
- [18] M. Oikkonen, M. Blomberg and T. Tuomi, M. Tammenmaa, "X-ray Diffraction Study of Microstructure in ZnS Thin films grown From Zinc Acetate by Atomic Layer Epitaxy", *Thin Solid Films*, Vol. (124), pp. (317-321), (1985).
- [19] A. Yoshikawa, S. Yamaga, K. Tanaka and H. Kasai, "Growth of Low-Resistively High-Quality ZnSe, ZnS films by Low-Pressure Metalorganic Chemical Vapour Deposition", *J. of Cry. Growth*. Vol. (72). pp. (13-16), (1985).
- [20] B.D. Culitty, " Elements of X-ray Diffraction", 2nd edition, (1977).
- [21] David. L. Greenaway and Gunther Harbeke, "Optical Properties and Band Structure of Semiconductors", Pergamon Press, Oxford (1970).
- [22] Steven S. Hegedus and William N. Shafarman. *Thin-film solar cells: Device measurement and analysis. Progress in Photovoltaics: Research and Application*, 12:p.155–176, (2004).
- [23] I. V. Pankove, *Optical Processes in Semiconductors*, Dover Inc.,New York, (1975).
- [24] J.Millman "Microelectronics" Murray – Hill, Book Company Kogakusha, Vol. 642, p.172. (1979).
- [25] I. V. Pankove, *Optical Processes in Semiconductors*, Dover Inc.,New York, (1975).