Effects of copper doping and annealing on the structure and optical properties of $Zn_xCd_{x-1}S$ thin films

Anmar Dhrar, Faisal H. Antar, Salam K. Mousa

Department of Physics, College of Education for Pure Science, Al-Anbar University, Iraq

Abstract

Effect of copper doping and thermal annealing on the structural and optical properties of $Zn_{0.5}Cd_{0.5}S$ thin films prepared by chemical spray pyrolysis have been studied. Depositions were done at 250°C on glass substrate. The structural properties and surface morphology of deposited films were studied using X-ray diffraction (XRD) and photomicroscope (PHM) techniques. XRD studies reveal that all films are crystalline tetragonal structure. The film crystallinity are increased with 1% Cu-doping concentration and also increased for the films annealed at 300°C than the other studied cases. The lattice constant 'a' and 'c' varies with doping concentrations from 5.487Å to 5.427Å and 10.871Å to 10.757Å respectively. The grain size attained maximum value of 24 nm. Films thicknesses results were between 1 and 2 µm. The optical characteristics of the prepared thin films have been investigated by UV-VIS spectrophotometer in a wavelength ranging (300-1100) nm. The energy band gap of the films decreased linearly with increase of Cu-doping concentration and annealing temperature which varied from 2.4 eV to 2.48 eV.

Key words
$Zn_xCd_{x-1}S$ thin films, copper doping, thermal annealing, spray pyrolysis.

Article info
Received: Apr. 2012
Accepted: May. 2012
Published: Oct. 2012

تأثير التطعيم بالنحاس والتلدين على الخواص التركيبية والبصرية للأغشية الرقيقة $Zn_xCd_{x-1}S$

أنمار ضرار كوسج ، فيصل حماد عنتر، سلام خلف موسى

قسم الفيزياء ، كلية التربية للعلوم الصرفة، جامعة الأنبار

الخلاصة

إن دراسة التركيب البلوري والخواص البصرية للأغشية الرقيقة $Zn_xCd_{x-1}S$ المحضَرة بطريقة الرش الكيميائي الحراري تمت لبيان تأثير التطعيم بالنحاس والتلدين عليها. إذ أُثبت ومن خلال دراسة حيود الأشعة السينية أن الأغشية المحضَرة تمتلك تركيب الجالكوبارايت متعدد التبلور ذو الترتيب الرباعي والإتجاه المفضل على طول المستوى (112) ، وأن التبلور يزداد نقاءً عند التطعيم بتركيز 1% من النحاس وعند التلدين بحرارة 300°C ، كما ان ثوابت الشبيكة "a" و "c" تتغير مع التلدين من 5.487Å الى 5.427Å ومن 10.781Å الى 10.757Å على التوالي. وأُثبت من خلال دراسة طيف الإمتصاصية لمدى الأطوال الموجية (300-1100) nm أن الإنتقالات الألكترونية من النوع المباشر وأن فجوة الطاقة للأغشية تتناقص خطيا مع إزدياد تراكيز التطعيم وزيادة حرارة التلدين وتتغير من 2.48eV الى 2.40eV.

Introduction

The information available on ternary $Zn_xCd_{x-1}S$ system is very limited especially in the presence of Cu as dopant [1,2]. It is well established that $Zn_xCd_{x-1}S$ films possess properties between those of ZnS and CdS [3]. Metal sulfides usually have a narrow band gap and show good photo responses under visible light irradiation. CdS is a well-known photo catalyst for producing hydrogen from aqueous solution containing sacrificial reagents [4,5]. In fact, $Zn_xCd_{x-1}S$ films have variable band gap energy of 2.4–3.7 eV, primarily dependent on a relative Cd:Zn Ratios[6]. Also, $Zn_xCd_{x-1}S$ is widely used as a wide-band-gap window material in heterojunction solar cells, low-voltage cathode luminescence, high-density optical recording and blue, and ultraviolet laser diodes [7, 8].

The main object of such mixing is to facilitate the substitution of Cu in their presence because ionic radii of Zn^{+2}, Cd^{+2} and Cu^{+2} are 0.74, 0.97 and 0.72 ˚A, respectively. Therefore, Cu can easily be substituted in place of Cd^{+2}/Zn^{+2} either in substitutional or interstitial positions [9].

$Zn_xCd_{x-1}S$ films have been prepared by photochemical deposition (PCD), chemical bath deposition (CBD) and co-evaporation deposition [10].

The spray pyrolysis technique is particularly attractive because of its simplicity in comparison with methods requiring vacuum conditions or complex equipment's. It is fast, inexpensive, vacuum less and is suitable for mass production. The spray pyrolysis technique is basically a chemical deposition technique, in which Solutions of the desired material are sprayed onto a preheated substrate. Continuous films are formed onto hot substrate by thermal decomposition of the reactants. Films prepared by this technique are generally polycrystalline in structure and their properties are extremely influenced by the deposition process. In particular, spray pyrolysis has proved well suited for producing semiconductor films of the desired stoichiometry on large and non-planar areas [11]. Although the spray deposition technique was employed earlier for the preparation of $Zn_xCd_{x-1}S$ thin films, zinc chloride and cadmium chloride were used as source for the zinc and cadmium in the deposits [12].

Experimental details

The $CdCl_2$, $ZnCl_2$ and NH_2–CS–NH_2 were used as the source materials for Cd^{+2}, Zn^{+2} and S^{-2} ions respectively, in addition of $CuCl_2.2H_2O$ as a doping source material for Cu^{+2} ions. All the chemicals used in this work were of analytical reagent grade and used without further purification.

1. Film preparation

$Zn_xCd_{x-1}S$ thin films were prepared by dissolving the appropriate amount of $ZnCl_2$ and $CdCl_2$ in distilled water. The ZnCdS ternary thin film was co-precipitated by slowly adding aqueous solution of $(CS(NH_2))_2$ to the mixture of $ZnCl_2$ and $CdCl_2$ aqueous solution, with stirring at constant 60 rpm throughout the reaction. For the preparation of good quality films, the concentration of (0.10M) $ZnCl_2$, (0.10M) $CdCl_2$ and (0.10M) NH_2–CS–NH_2 were optimized and used as deposited solution. The appropriate amount of $ZnCl_2$, $CdCl_2$ and NH_2–CS–NH_2 solutions were mixed.

Chemical spray pyrolysis technique was used to deposit $Zn_xCd_{x-1}S$ thin films on micro glass substrates having area of 2×2 cm^2 which were cleaned using distilled water and dipped in ethyl alcohol for 5 min at room temperature. In each run, 100 ml of solution was sprayed at a rate of 2 ml/min on the substrates maintained at an optimized temperature of 250°C. To avoid excessive cooling of substrate, spraying was achieved in periods was about 10 sec followed by 15 sec wait [13]. To deposit films of uniform thickness the distance between the substrate and spray nozzle was kept at 50 cm.

$Zn_xCd_{x-1}S$ thin films were doped with different Cu concentrations (for 1, 3, 5 %) and annealed at 200°C and 300°C for 2 hours.

2. Surface morphology and structure.

The films were characterized by X-ray diffraction (XRD) with Cu Kα radiation (model: Philips pw. 1840) in the 2θ range from 20° to 60° and the thickness of the films was measured by optical method (pezos fringes).

The surface features of the deposited and annealed samples were characterized using (Nikon-73346) photomicroscope (PHM) analysis under magnification of 108 X.

3. Absorbance measurement

Absorbance spectra of the films were measured as a function of incident photon wavelength at normal incidence and at room temperature using double beam Junwa-6800 spectrophotometer equipment. The optical data were obtained within the spectral rang 350-750 nm and a blank substrate was on the reference beam for all measurements.

Results and Discussion

1.Structural study

II-VI Chalcogenide semiconductor materials show the structural duality, and can be formed as either sphalerite (cubic) or wurtzite (hexagonal) type [14]. The X-ray diffraction patterns were studied to determine the crystal structure of the $Zn_{0.5}Cd_{0.5}S$:Cu thin films.

In Figs.1 and 2 three diffraction peak are seen corresponding to diffraction angle (2-theta) in all studied cases, the major peak for the doping concentrations and annealing temperatures located at 27.27°, 27.37° and 27.57° are attributed to 112 diffractive peak of tetragonal structure. The annealed filmed show -0.3° shift in 2-theta while the doped films showed +0.3° shift. They are also showed that the intensity of diffraction peak is inversely proportional to doped concentrations while it is increased after annealed.

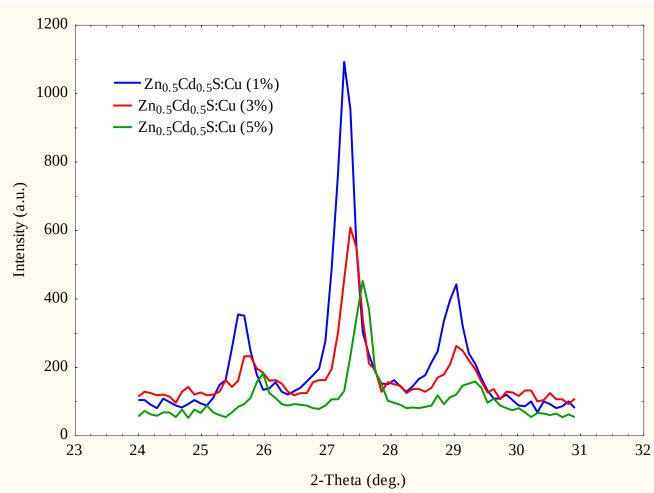


Fig.1: X-ray diffractograms of $Zn_{0.5}Cd_{0.5}S$:Cu films at varied doping concentration and annealing by 300°C.

The lattice constant a and c for tetragonal phase of $Zn_{0.5}Cd_{0.5}S$:Cu thin films were calculated using the following equation [14].

$$\frac{1}{a^2} = \frac{4}{3}\left(\frac{h^2 + hk + k^2}{a^2}\right) + \frac{l^2}{c^2}$$

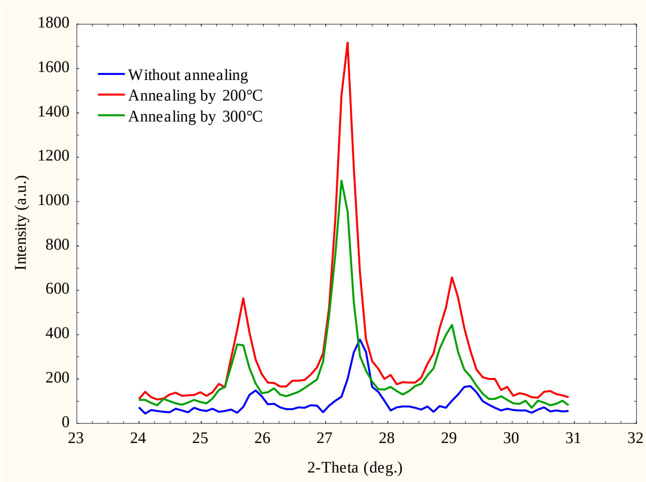


Fig.2: X-ray diffractograms of $Zn_{0.5}Cd_{0.5}S$:Cu films at varied annealing temperatures and doping by (1%).

And the grain size 'D' of the samples was estimated by using 'Scherrer's formula [14].

$$D = \frac{0.94\,\lambda}{\beta \cos\theta}$$

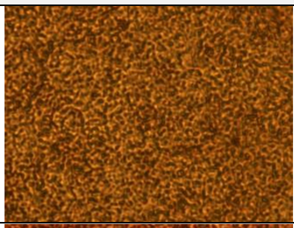
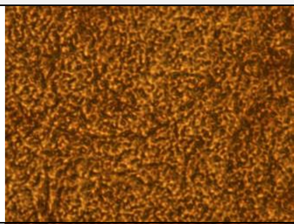
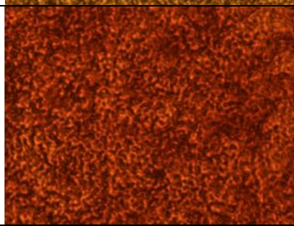
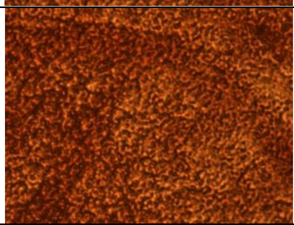
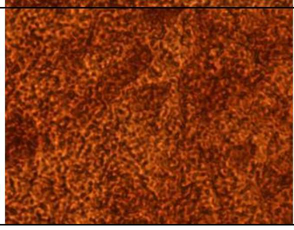
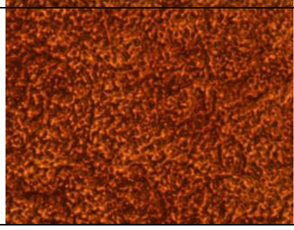
where λ is the wavelength of the X-ray used, β is the broadening of the diffraction line measured at half of its maximum intensity (FWHM) and h is the Braggs' angle. The value of the lattice constant 'a' and 'c' varies with doping concentrations from 5.487Å to 5.427Å and 10.871Å to 10.757Å respectively as shown in Table1, also from this table it is observed that the grain size attains maximum value of about 24 nm.

Surface morphological study has been carried out on $Zn_{0.5}Cd_{0.5}S$:Cu films as shown in table 2. Spherically shaped grains are seen in the form of clusters in undoped sample, which are not distributed uniformly. A Cu-doped and annealed samples shows compact distribution over the surface and good connectivity between grains. The thicknesses of the films are found to be between 1 and 2 μm.

Table 1: the structural parameters of $Zn_{0.5}Cd_{0.5}S$:Cu films.

Thin films pattern		2-theta	Average grain size (nm.)	Crystal system	Cell parameters	
					a (°A)	c (°A)
Doping concentrations (ml.)	1.0	27.27	24	Tetragonal	5.487	10.848
	3.0	27.37	22		5.427	10.871
	5.0	27.57	24		5.449	10757
Annealing temperature (°C)	Without	27.57	23	Tetragonal	5.487	10.848
	200	27.37	24		5.487	10.848
	300	27.27	24		5.487	10.848

Table 2: The surface features of the deposited and annealed samples were characterized through (Nikon) photomicroscope (PHM) analysis.

Cu Doping concentrations	Annealing	
	without	300°C
without		
1%		
3%		
5%		

2. Optical study

The optical absorption spectra for $Zn_{0.5}Cd_{0.5}S$:Cu films at varied doping concentration of Cu:[1%, 3%, 5%] before And after annealing by 200°C and 300°C are presented in Figure (3), the band gap of materials can be determined from the Tauc's plots.

The materials employed in the study are of direct band gap nature. The band gap was found to decrease with Cu-doping before annealing. While it is more decrease after annealing by 200°C. Although, this annealing temperature is less than the temperature of preparation, but it lasted for a longer time which helped to complete the interaction between the metals to make a more homogeneous films. The annealing by 300°C has led to invariant broadness in energy gap with and without doping that broadening of band gap may be due to filling up of conduction band edge by the excessive carriers donated by the impurity atoms [3]. This leads to blue shift in optical band to band transitions by blocking the low energy transitions. These values are compared in Fig.4.

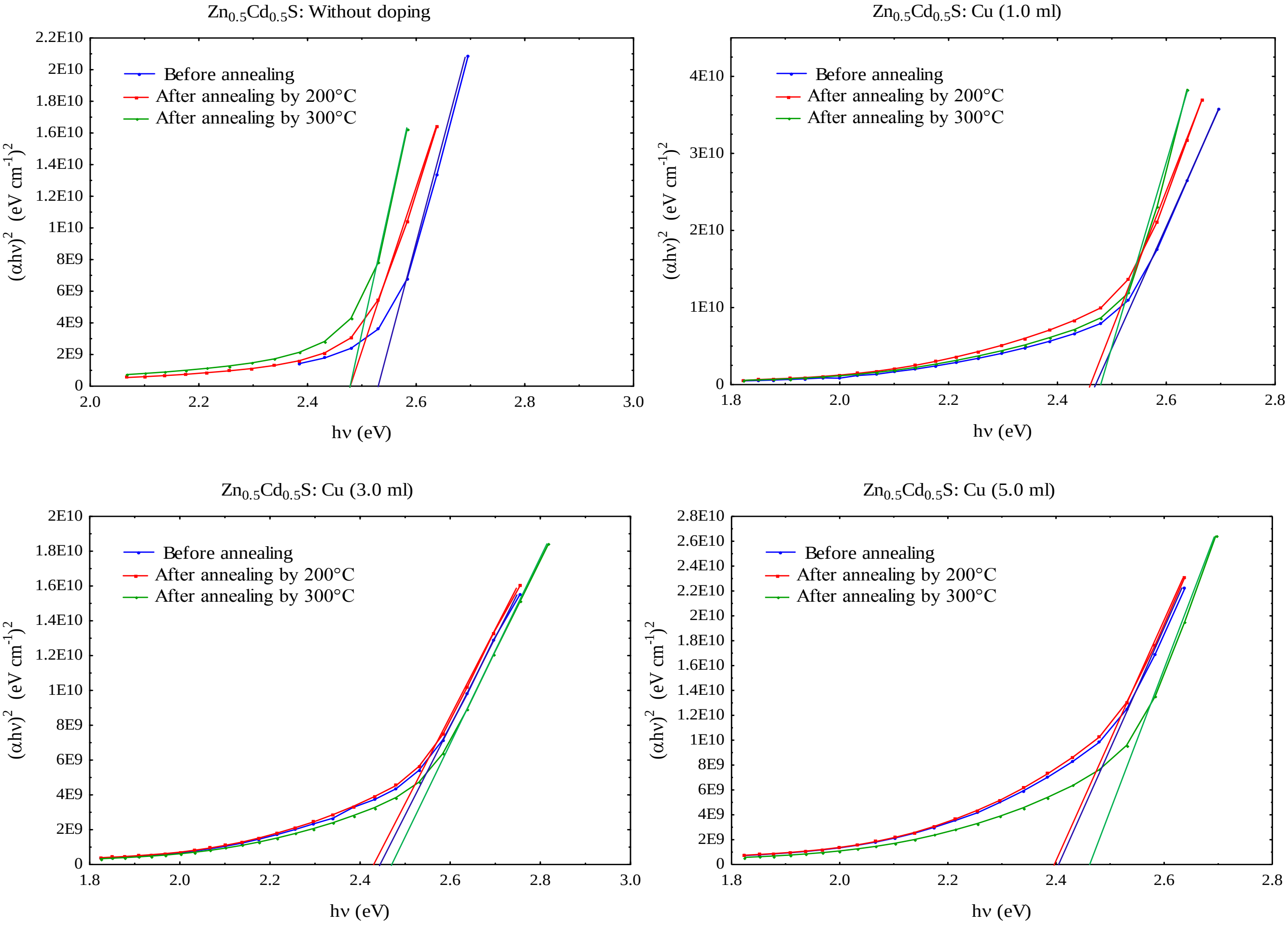


Fig. 3: Tauc's plots of different $Zn_{0.5}Cd_{0.5}S$:Cu films at varied concentration of Cu:[0.0 ml, 1.0 ml, 3.0 ml, 5.0 ml].

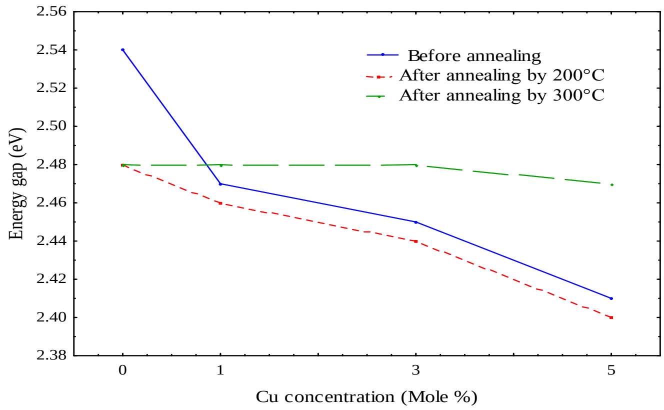


Fig. 4: The optical energy gap as a function of Cu concentration in $Zn_{0.5}Cd_{0.5}S$:Cu films before And after annealing by 200°C and 300°C.

The absorption coefficient (α) of the prepared $Zn_{0.5}Cd_{0.5}S$:Cu thin films were found from the following relation [15].

$\alpha = 2.303\ A/t$

Where (A) is the absorbance and (t) is the film thickness.

Figs.5 and 6 shows the plot of absorption coefficient with wavelength, which obtained that the value of $\alpha > 10^4\ Cm^{-1}$ for all films in the visible region, this means that the transition must corresponding to a direct electronic transition, and the properties of this state are important, since they are responsible for electrical conduction. These figures also show that the absorption coefficient increases linearly with doping concentration and annealing temperature. Except for the behavior observed in the form of (1%) doping concentration, that may be due to the increases in grain size and decreases in the number of defects [13] .

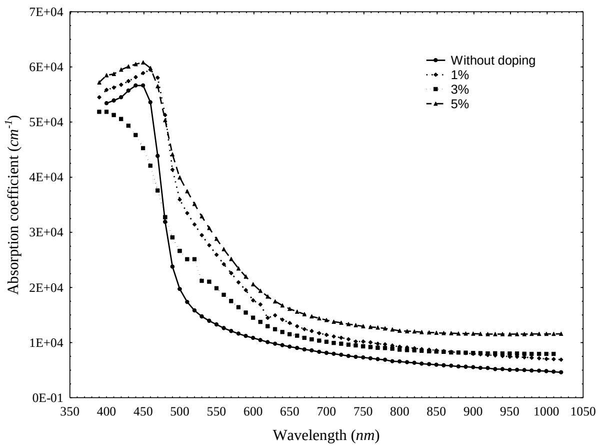


Fig.5: The variation of absorption coefficient for $Zn_{0.5}Cd_{0.5}S$:Cu films without and with (1%, 3%, 5%) doping concentration.

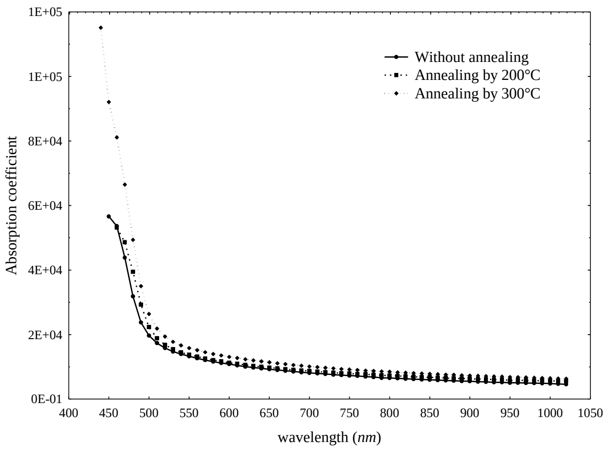


Fig.6: The variation of absorption coefficient for $Zn_{0.5}Cd_{0.5}S$:Cu films without and with (200°C,300°C) annealing temperatures.

The extinction coefficient (K) was calculated using the related [15]:

$K = \lambda\alpha/4\pi$

where λ is the wavelength.

The variations at the extinction coefficient values are a function of wavelength are shown in Figs.7 and 8. It is observed that the spectrum shape of the extinction coefficient as the same shape of the absorption coefficient. The value of (K) as the visible region was depend on the film treatment method, where the value of (K) at $\sim 500\ nm$ was varied from 17 to 41 and that variation values become smaller at NIR region.

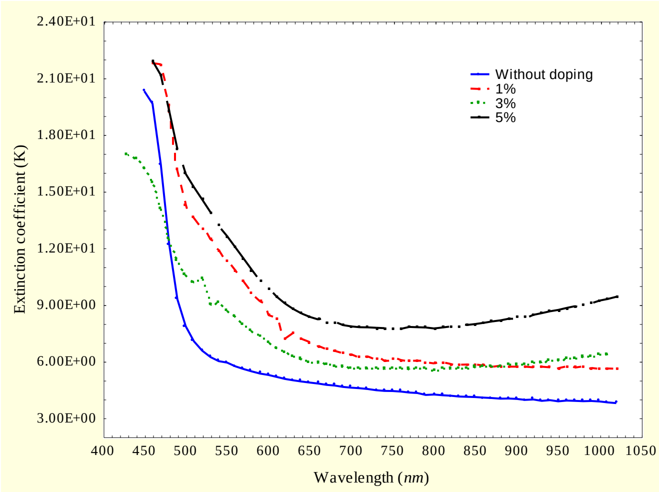


Fig.7: The variation of extinction coefficient for $Zn_{0.5}Cd_{0.5}S$:Cu films without and with (1%, 3%, 5%) doping concentration.

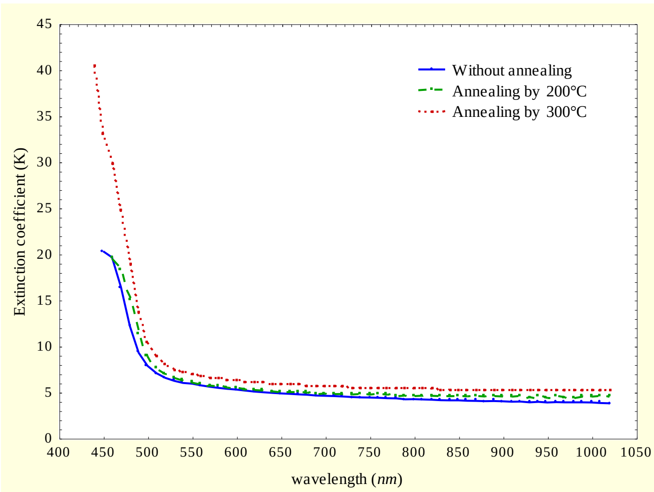


Fig.8: The variation of extinction coefficient for $Zn_{0.5}Cd_{0.5}S$:Cu films without and with (200°C,300°C) annealing temperatures.

The refractive index (n) is the refractive between speeds of light in vacuum to its speed in material which does not absorb this light. The value of refractive index was calculated from the equation [15]:

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

where (R) is the reflectivity.
The variation of refractive index vas wavelength is shown in Figs.9 and 10, which shows that the maximum value of (n) is (2.6) for all films at the same wavelength. Also shows that the films become more transparent in the visible region.

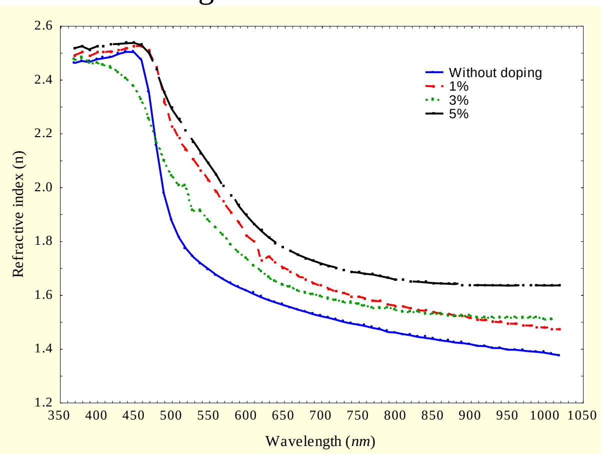


Fig.9: The variation of refractive index for $Zn_{0.5}Cd_{0.5}S$:Cu films without and with (1%, 3%, 5%) doping concentration.

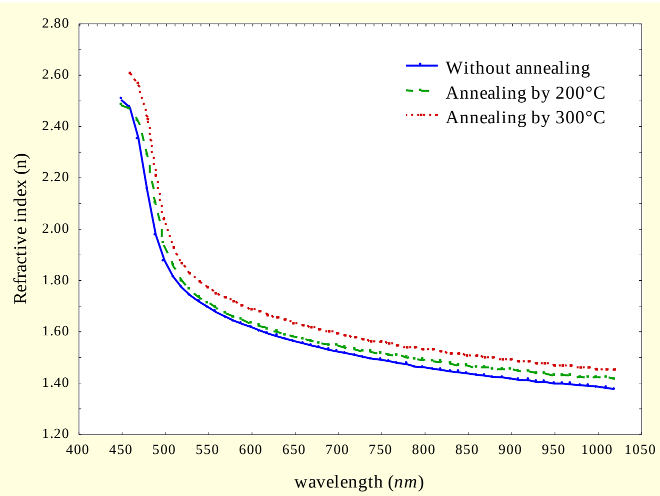


Fig.10: The variation of refractive index for $Zn_{0.5}Cd_{0.5}S$:Cu films without and with (200°C,300°C) annealing temperatures.

Conclusions

$Zn_{0.5}Cd_{0.5}S$:Cu thin films have been synthesized by the chemical spray pyrolysis technique using aqueous solutions of $CdCl_2$, $ZnCl_2$ and NH_2–CS–NH_2 were used as the source materials for Cd^{+2}, Zn^{+2} and S^{-2} ions respectively, In addition of $CuCl_2.2H_2O$ as a doping source materials for Cu^{+2} ions. The XRD study showed the compounds to have tetragonal phase and its preferred orientation is in the 112 direction. It was observed that crystallinity of film increased with doped at (1%) and annealed at high temperatures (300°C) than the other samples. The lattice constant 'a' and 'c' varies with doping concentrations from 5.487Å to 5.427Å and 10.871Å to 10.757Å respectively, also the grain size attains at maximum value about 24 nm. Surface morphological study of Cu doped and annealed samples showed compact distribution over the surface and good connectivity between grains. The thicknesses of the films are found to be between 1 and 2 μm. It is concluded from the structural analysis that the Cu-doping and the $Zn_{0.5}Cd_{0.5}S$:Cu annealing has a strong effect on the structural properties. The energy band gap of the $Zn_{0.5}Cd_{0.5}S$:Cu thin films decreases linearly with increases Cu-doping concentration and annealing temperature. In conclusion, it can be stated that the influence of Cu content and thermal annealing on the optical properties of $Zn_{0.5}Cd_{0.5}S$:a Cu film is noticeable.

Acknowledgements

The authors owe special gratefully acknowledge to the technical and advisership support by *Asst. Proff. Dr. Hamid S. Al-Jumaili.*

References

[1] Ayush Khare: journal of luminescence, 130, (2010) 1268-1274.
[2] V. C. Chaudhari, R. H. Patil, M. G. Patil, C. S. Shalgonkar: Materials Chemistry and Physics, 59, 2 (1999) 162-167.

[3] Y. Raviprakash, Kasturi V. Bangera, G.K. Shivakumar: Current applied physics, 10, (2010) 193-198.
[4] Mingtao Li, Jiangang Jiang, Liejin Guo: International journal of hydrogen energy, 35, (2010) 7036-7042.
[5] T. Prem Kumar, S. Saravanakumar: Applied surface science, 169 (2010)1259-1265.
[6] S. K. Kulkarni, U.Winkler, N. Deshmukh: Applied surface science, 170, (2010) 438-446.
[7] Bhaskar Kumar, Parag Vasekar, Shirish A. Pethe: Thin Solid Films, 517(2009) 2295-2299.
[8] Sonal Singhal, Amit Kumar Chawla, Hari Om Gupta: Thin Solid Films, 518 (2009) 1402-1406.
[9] C. Unni, Daizy Philip, S.L. Smitha, K.M. Nissamudeen, K.G. Gopchandran: Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 72, 4 (2009) 827-832.
[10] Joy George: Preparation of thin films, (1992), CRC Press.
[11] Idris Akyuz, Salih Kose, Ferhunde Atay: Materials Science Semiconductor, 10(2007) 103.
[12] S.Ilican, M. Caglar, Y. Caglar: journal of optoelectronics and advanced materials, 9 (2007) 1414.
[13] Hamid S. Al-Jumaili, Journal of Al-Anbar University for pure science, 1. 3 (2003) 70-79.
[14] E. D. Williams: Thin Films - Structure and Morphology, (1997), MRS Proceedings, Vol. 441.
[15] Saliha Ilican, Muhsin Zor, Yasemin Caglar, Mujdat Caglar: Optica Applicata, 36, 1 (2006) 29-37.