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Study of the Structural and Optical Properties of Thin Films Copper Sulfide (Cus) Prepared by Chemical Spray Pyrolysis

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Abstract: *In this research we deposited CuS thin films by chemical spray pyrolysis at substrates temperature equal to (190- 200 ^oC) . The composition of the prepared films consist of from solution of Thiouria $(NH_2)_2CS$ (TU) with four molar concentration (0.03,0.04,0.05 and 0.08 M) and Copper Chloride $CuCl_2.2H_2O$ with molar ratio (0.01 M) were deposited on glass substrates, the rate of spraying approximately (10 ml/s.). As deposition and annealed films were studied, the results of X-ray diffraction showed that the films were polycrystalline with Hexagonal structure . The optical properties of CuS thin films recording by the transmittance and absorbance spectrum for wave length range (300-1100) nm, the results showed that the transmittance increases with increasing molar concentration of Sulfide source (TU) for as deposited and annealed films. It is noticed that the electronic transitions is directly allowed transition and the values of energy gap ranging between (1.6 – 2.5) eV corresponding to increasing of molar concentration of Thiouria.*

Keywords: *Copper Sulfide, Chemical Spray Pyrolysis, Thiouria , Structural and optical properties.*
Subject Classification: *Physics Subject Classification : Library of congress Classification QC170-197.*

I. Introduction

Copper Sulfide (CuS) Chemical Compound complex consisting of sulfur S and Copper Cu . It occurs in nature as black or lumps [1], belongs copper sulfide to the important class of Semiconducting compounds called (chalcogenides) which comprise the interaction of transition elements with elements of a clique sixth in the league ,such as sulfur or selenium, or tellurium .At room temperature CuS in the bulk form is known to exist in five stable phases: chalcocite (orthorhombic Cu_2S),djurleite ($Cu_{1.95}S$),digenite ($Cu_{1.8}S$),anilite ($Cu_{1.75}S$) and Covellite (CuS) rich in sulfur have a hexagonal system [2,3,4] . Thin films (CuS) importance in field of industrial application where they are used in photovoltaic applications in solar cells ,which is an important source of new sources of energy industry , Photothermal , photo cells ,architectural windows , selective radiation filters ,solar control coating ,heat mirrors, Gas Sensors[5][5].

In this paper ,CuS thin films were deposited on substrate of glass by chemical spray pyrolysis deposition, Then these thin films were annealed at 150 ^oC for 1h . X-Ray Diffraction (XRD) ,Atomic Force Microscopy (AFM) , Scaning Electron Microscopy (SEM), Hall effect measurements, I–V characteristics measurement and optical properties were studied for thin films before and after annealing.

II. Experimental Procedure And Measurement

Copper chloride and Thiourea were used to prepare the solution for depositing CuS thin film by spray pyrolysis deposition . The deposition by this method is simple ,cover a large area ,low cost and widely used .The solution was sprayed on glass substrates at (190-200 ^oC), the best results of CuS thin films were obtained at (190-200 ^oC), this rang of temperature was chosen because CuS is reported to decompose at ~220 ^oC[6] .The distance between the nozzle and the substrates was 30 cm ,which is the best spray distance because more than this will cause spray flight out of the substrate . The spray solution were prepared by dissolving appropriate amounts of copper chloride ($CuCl_2.2H_2O$) (99% purity) and Thiourea $(NH_2)_2CS$(99% purity) into distilled water . The molar ratio of Copper chloride to Thiourea was varied from 1:3,1:4,1:5,1:8, these molar ratio corresponding to concentrations of Copper chloride in the solution equal to (0.01M) and the molar ratio of Thiourea were ((0.03,0.04,0.05,0.08)M) . The glass substrates were cleaned using alcohol) Methyl ethyl ketone C_4H_8O) (99.9 % purity) and distilled water in an ultrasonic bath for 15 min and then dried in a air. Phase formation of the films was studied by X-ray diffraction (XRD) System using Cu-k_α radiation (λ =1.5404 A^o) and the optical characterization of the samples was performed by Using a (UV-Visible) Spectrophotometer-1800 is equipped with the company (Shimmdzu) Japanese ,to the extent wavelengths (300-1100nm) to conduct optical measurements for all thin films prepared in this study. Surface morphology was studied using Scaning Electron Microscopy (SEM Manufacture model :FEL,Quanta450,Czech). Surface Texture Analysis)Nanosulrf Flex AFM) .

III. Results And Discussion

3.1. Structural and morphological analysis

The structural analysis of copper sulfide thin films was carried out by using x-ray diffractometer that the diffraction angle 2 varied from 20^o to 80^o . The X-ray diffraction patterns of these thin films on glass substrates are shown Fig.1. The data analysis show the single covellite phase with hexagonal crystal structure ,with (102) as the preferential crystallite direction in Fig.1-a1,b1 As deposition (before annealing-(B.A)) and Fig.1-a2, b2 after annealing(A.A) ,this result is consistent with the published result of the researchers described in previous studies [7,8,9,10,11,12, 13,14,15,16] . To find the predominant average crystallite size (D_{ave}) in polycrystalline samples we used scherrer`s formula[17] .

$$D_{ave} = \frac{0.9\lambda}{\beta cos\theta} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

Where λ is the x-ray wavelength , $\beta$is (FWHM) (Full Width at Half Maximum) and Ө is the Bragg angle corresponding to the main diffraction line. It has been found that the values of the measured particle size within the range (36-104) nm)) and through the results listed in Table (1), we note that the average crystallite size of the films prepared tends to decrease with increasing molar ratios of sulfide source (Thiouria) CuS.

Table 1. The Crystallite size of the studied films .

Crystallize size D_{ave}(nm)	CuS – with different molar ratio ($CuCl_2$:Thiouria)	Sample CuS
102.5444	1:3	(B.A)
94.3331	1:4	As deposition
77.1240	1:5	
36.938	1:8	
104.322	1:3	(A.A)
69.85	1:4	After annealing
86.23	1:5	
68.497	1:8	

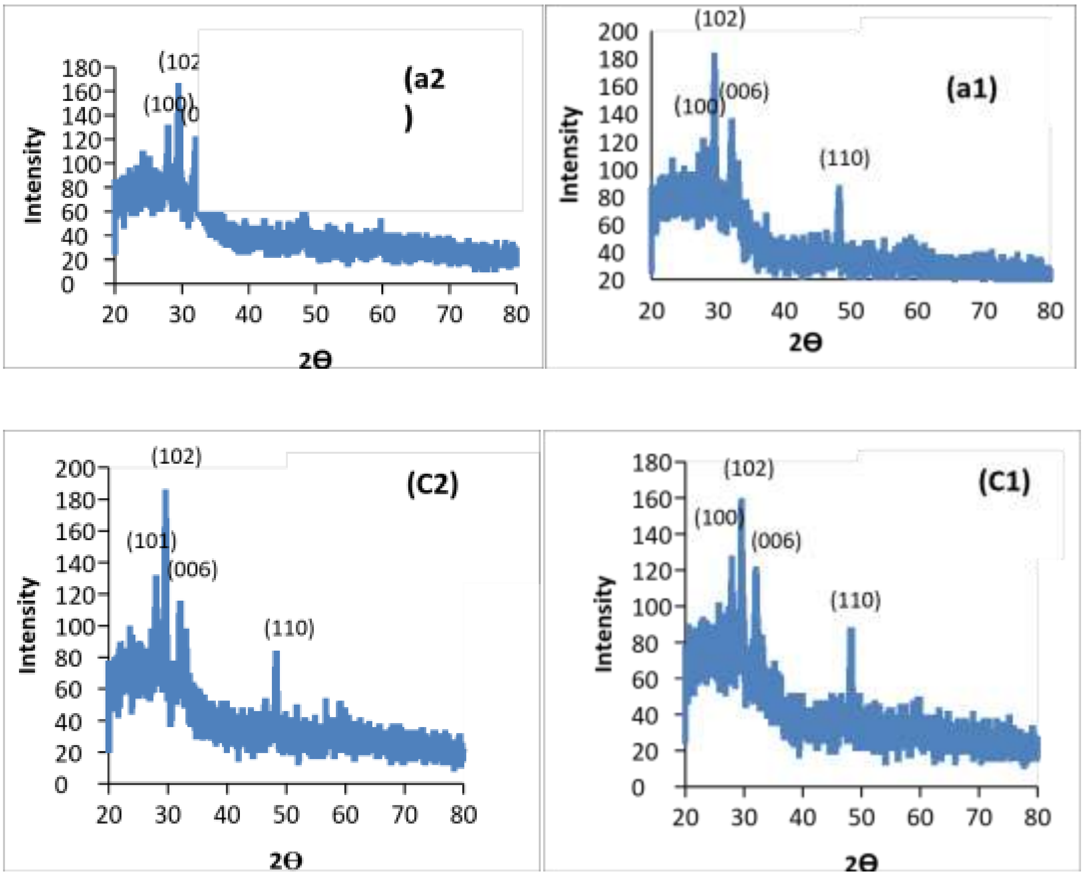

Fig (1). XRD pattern of CuS thin films ($CuCl_2.2H_2O$ + TU) for different molar concentration, a1, b1 for as deposited films and a2, ,b2for annealed films (T= 150 ^{o}c for 1 h.).

In order to study the surface morphology ,the produced films were examined by SEM as shown in Fig.2. It was found from the figure that the prepared thin films have homogeneous distribution, dense and free of voids or distinctive islands, in comparation with the results of tests crystallite size, we find that the granular size of the thin films prepared became any lower when annealing and therefore the images scanning electron microscope examination showed homogeneous in films prepared and these results are consistent with previous studies [7,9,10] .

B.A (1:3) A.A (1:3)

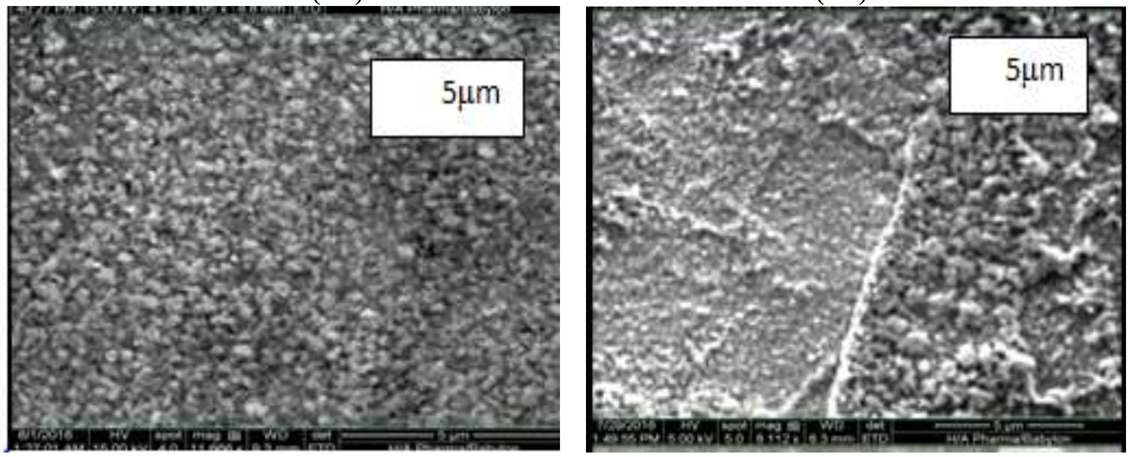

Fig .2. Shows images of (SEM) for CuS thin films; as deposited and annealed films with molar concentration ratio (1:3).

According to the AFM images of CuS thin films that shown in (Fig. 3) ,we can show that the surface roughness and the values of the square root of the average surface roughness (RMS) decreases with increasing the molar ratio of the concentration of sulfide source (Thiouria) , and this result can be attributed to the decrease in the values of crystallite size of the prepared films of CuS as shown in table (1).

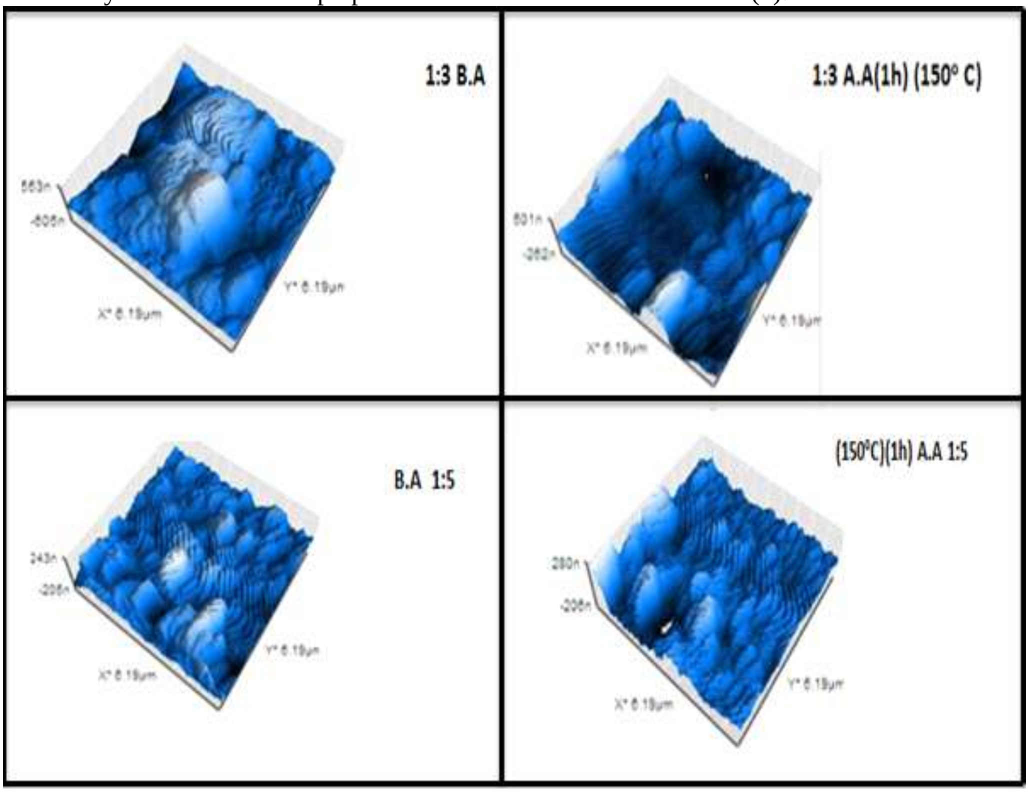

Fig . 3. Results of (AFM) for CuS thin films; as deposited and annealed films for molar concentration ratio (1:3 and 1:5)

3.2 Optical properties

The optical transmission spectra of CuS films obtained by spray pyrolysis are presented in fig.4. It can be seen that the films transmittance increase somewhat in general with an increased in molar sulfide source (Thiouria) for the prepared thin films (CuS) for as deposited and annealed films. Fig.5. shows The absorbance spectra of these films with different molar ratio for as deposited and annealed films. The spectra shows that the absorption of the films decreases with increasing of molar ratio**.**

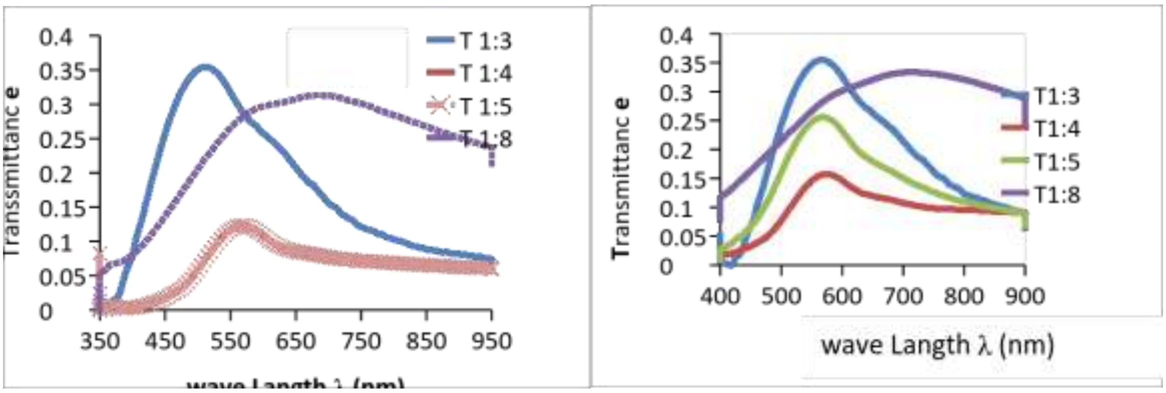

Fig.4.shows transmission spectra of the CuS thin films; as deposited and(A.A) annealed films with different molar ratio.

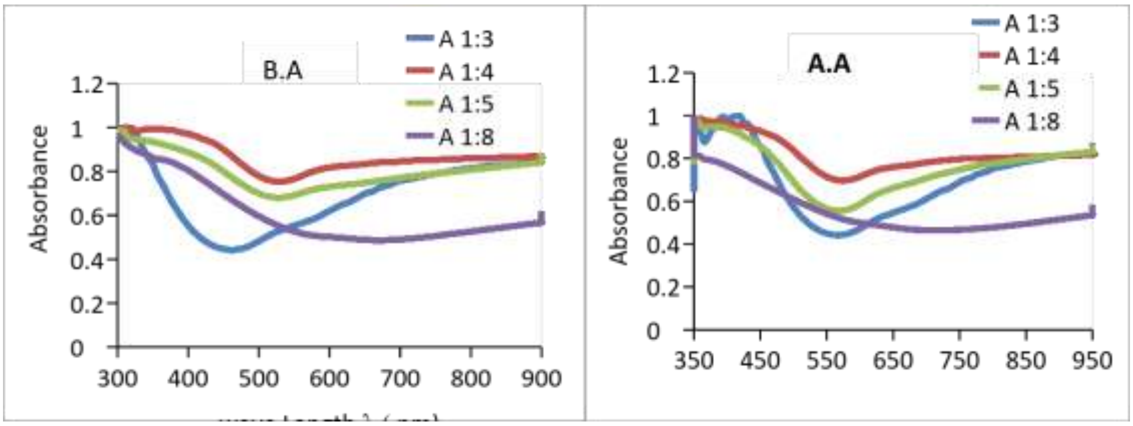

Fig.5.shows Absorbance transmission spectra of the CuS films; as deposited and(A.A) annealed films with different molar ratio.

Fig .6. shows the variations of the calculated absorption coefficient in the samples, Evidenced a decrease in the values of absorption coefficient with increasing ratio of molar concentrations of sulfur source (TU) and the values of absorption coefficient for all the films and all concentrations in both cases as deposited and annealed films are ($\alpha > 10^4$ cm^{-1})

The band gap energy of the film can be estimated from the absorption spectrum using the relation between the absorption coefficient (α) and the energy of incident light h [18].

$$\alpha h\nu = P(h\nu - E_g)^r \quad \text{..............} \quad (2)$$

Where h is the photon energy , P is constant ,and r represents the transition type (r=2 for direct transition ,r=1/2 for indirect transition) Having been to make sure that the type of transfer is of direct allowable type any that fixed value (r = 2) and draw a relationship between $(\alpha h\upsilon)^2$ and photon energy falling (hυ), and through the extension of the straight part of the curve to determine the intersection with the axis point (X) Special photon card where $(\alpha h\upsilon)^2 = 0$) (which represents the value of the optical energy gap, and as shown in the fig((6)-a,c), this figure represents the case of the as deposited and annealed thin films and for four molar concentrations of sulfide source (TU). Table (2) shows us clearly that the optical energy gap for Four molar concentration is increased with annealing of the films. It has been found that the values of energy gap for as deposited CuS thin films is within the range ((1.85-2.1) eV) and for annealed thin films within the range ((2.2-2.35) eV) These results are consistent with previous studies [6,16].

Table 2. The direct optical band gaps in the CuS

Molar ratio	(Optical band gap.)E_g(ev)	
	As deposited films	After annealing Films(150^{o}C - 1h.)
	1.85	2.35
	1.9	2
	1.92	2.1
1:8	1.2	2.2

Fig.(6-a, c,) shows the optical energy gap E_g for allowed direct transitions CuS thin films; (a1,b1) as deposited film (B.A.) and (a2,c2annealed films (A.A) at 150^{o}C for 1h, for different molar concentration ratio.

IV. Conclusion

Copper sulphide (CuS) thin films with different Cu to S molar concentration ratios (0.03,0.04,0.05,0.08) have been deposited on glass substrates by spray pyrolysis method using an aqueous solutions of copper chloride and Thiourea at substrate temperature of 190-200^{o}C . x-ray analysis showed the formation of the CuS single phase covellite structure With the installation of a multi-crystallization of all molar concentrations and type hexagonal . It was Found that the optical energy gap increases with molar concentrations of sulfide source (TU). It was found that the values of optical band gap for as deposited CuS thin films is within the range (1.85-2.1) eV and for annealed CuS thin films within the range (2.2 -2.5) eV

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