Annealing Effect on The Structural and Optical Properties of CuS Thin Film Prepared By Chemical Bath Deposition (CBD)

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Abstract

Thin films of copper sulfide (CuS) with various molarities values of Cu concentrations (0.2,0.3,0.4)M have been prepared by Chemical Bath Deposition Technique on glass slides substrate at room temperature . The prepared films with different ion concentrations were annealed in air at constant temperature 400 ºC and constant time (180) min .Structural and optical properties of CuS thin films were investigated and analyzed extensively before and after annealing . The structure of the prepared films has been found with amorphous structure at different Cu ion concentrations , annealed CuS films also showed amorphous structure. The optical properties of CuS thin films has been studied by transmittance and absorbance spectral in the range of wave length (190-1100)nm by using UV- Vis. spectrophotometer. Transmittance decreased with increasing the Cu ion concentrations of CuS films, also the transmittance increased with annealing process for (CuS) thin films. The fundamental absorption edge of (CuS) thin films shifted to word the lowest photon energies with increasing the Cu ions concentrations before and after annealing. From the absorption coefficient values which calculated from the absorbance spectrum which is larger than $10^{-4}cm^{-1}$ gives an indicate that CuS films were direct semiconductors and the electronic transition was a direct transition. The optical energy gap values of CuS thin films for allowed direct transition found vary in the range between (2.433-2.526) eV with (0.2- 0.4 M) Cu ions concentration and in the range of (2.416-2.349) eV for the same concentrations after annealing. The optical constant such as reflectance (R), absorption coefficient (α), refractive index (n) and extinction coefficient (K) were evaluated and analyzed .

الخلاصة

في هذا البحث تم تحضير أغشية كبريتات النحاس CuS بتراكيز مختلفة لأيونات النحاس Cu (0.2,0.3,0.4 M) بتقنية الحمام الكيميائي على أرضيات زجاجية بدرجة حرارة الغرفة لأغشية CuS .تم أجراء عملية التلدين للأغشية المحضرة في الهواء بدرجة حرارة ثابتة 400 ºC عند زمن ثابت 180)min) ولجميع التراكيز . وتضمن هذا البحث دراسة وتحليل الخصائص التركيبية والبصرية لأغشية CuS قبل وبعد التلدين . إن الخصائص التركيبية للأغشية المحضرة قد دُرست وحللت بإستخدام تقنية حيود الأشعة السينية و تبين أن جميع الأغشية المحضرة بمختلف تراكيز الأيونات كانت عشوائية التركيب ، و أظهرت أغشية CuS الملدنة تركيب عشوائي . وإن الخصائص البصرية لأغشية CuS الرقيقة تتضمن دراسة أطياف النفاذية والإمتصاصية في مدى الأطوال الموجية 190-1100)nm) بإستخدام مطياف الأشعة المرئية-فوق البنفسجية UV-visible spectrophotometre. وإن النفاذية تتناقص بزيادة تركيز أيونات النحاس Cu ، وإن عملية التلدين أدت الى زيادة النفاذية بالنسبة لأغشية CuS . وحافة الامتصاص الأساسية لأغشية CuS الرقيقة أزيحت بإتجاه الطاقات الفوتونية الواطئة بزيادة تركيز الأيونات وبعد عملية التلدين .من خلال قيم معامل الأمتصاص المحسوبة من طيف الإمتصاصية للأغشية المحضرة والتي كانت أكبر من $10^{-4}cm^{-1}$ والتي تشير الى أن أغشية CuS هي أشباه موصلات مباشرة وأن الإنتقالات الألكترونية هي أنتقالات مباشرة. ووجدت قيم فجوة الطاقة البصرية للإنتقال الألكتروني المباشر المسموح لأغشية CuS الرقيقة أنها تتغير في المدى مابين eV (2.433-2.526) مع تراكيز أيونات النحاس 0.2-0.4)M) وأنها في المدى eV (2.416-2.349) لنفس التراكيز بعد عملية التلدين . كما تم دراسة وحساب يعض الثوابت البصرية مثل الإنعكاسية (R) و معامل الإمتصاص (α) و معامل الإنكسار(n) ومعامل الخمود (K) .

Keywords :CuS thin film , chemical bath deposition (CBD) , TCMs, Structure and optical properties .

Introduction:

Copper sulfide is an important semiconductor material and has received a great deal of attention due to its unique physical and chemical properties .Transparent conducting materials TCMs are widely used as electrodes in solar cells, flat-panel displays, light emitting diodes, defrosting windows, and other optoelectronics. Commercialized TCMs, such as In_2O_3:Sn ITO_, SnO_2:F _FTO_, ZnO:Al, etc., behave *n*-type conduction. In contrary, the overall transparent conducting properties of *p*-type TCMs are still unsatisfactory The room-temperature conductivities of these compounds are in the order of 10^{-1} S cm^{-1}, far below the *n*-type ITO __10^3 S cm^{-1}. In order to obtain a high optical transmittance in the visible-light range, the main effort was to explore new wideband gap compounds with *Eg* 3.1 eV. Zinc oxides doped with univalent metal or nitrogen/phosphor have a good transmittance, but the major drawback is the unstable *p*-type conduction. However, a wide band gap may not be a necessary requirement for TCMs in certain applications. Human eyes are most sensitive to the wavelength of 560 nm 2.21 eV, and most of dye-sensitized solar cells DSSCs have highest quantum efficiencies at 500–600 nm. Therefore, by reducing the film thickness and accordingly the total absorption, semiconductors with narrow band gaps could also be candidates for TCMs[1].

The properties of CuS thin films are affected by accurate stoichometry, which depends on preparative conditions used for the thin film deposition. CuS thin films have recently received considerable attention due to numerous technological applications. It has been used in photovoltaic application, such as Cu_2S/ CdS solar cell which demonstrated an efficiency of around 10% [2].The active layer in these cells is the chalcocite (Cu_2S) film such as $Cd_{1-y}Zn_y$ S/ Cu_2S cell [3]. In the photothermal conversion of solar energy (as solar absorber coating) as in selective radiation filters on architectural windows (for solar control in Warm climates in electro conductive coatings), deposited on organic polymers .The most striking benefit obtained by utilizing Cu_xS as sensor material is the low operating temperature for sensor application [4] .

2. Experimental:

Microscope glass slides were used as the substrate during the deposition process. The substrates were first cleaned in HCL solution and distilled water. Substrates were then dried in air. Aqueous solutions of copper sulfate, thiourea , Triethanolamine TEA, ammonia and distilled water separately prepared before experiment. To obtain 0.2,0.3and 0.4 molarities concentrations of $CuSO_4$ solutions dissolve (1.997,2.996 and 3.994)gm were dissolved respectively in 40 ml of distilled water for each one with continues stirrer for 10 minutes, to obtain 60% concentration of TEA solution mixed 120 ml of TEA with 80 ml of distilled water to make up 200 ml of 60% TEA solution. By dissolving 7.612 gm of $SC(NH_2)_2$ with 200 ml of distilled water to obtain 0.5 M concentration of TU solution were mixed in a beaker. Substrates were immersed vertically in the beaker. The beaker was not stirred during the thin films deposition. In order to determine the best conditions for the deposition process, the films were deposited at constant temperatures (room temperature). After completion of films deposition (120 min), the deposited films were then washed with distilled water and dried in air at room temperature. The copper sulfate and thiourea were a powder white color and fabricated by [Thomas Baker (chemicals) PVT. Limited], but TEA and NH_3 were a solution . The pH (10) was monitoring with pH meter type (HANNA Company). Deposition time was two hours in each experiment.

The crystal structure of the prepared films has been examined by X-ray diffractometer (XRD-6000 Shimadzu). The source of X– ray radiation was Cukα radiation, the scanning angle varied in the range (20-60)º with wavelength 1.5405Å, speed 5deg/min, current 30 mA, and voltage 40 KV.

The optical measurements were included transmittance and absorbance spectra in the wavelength range (190-1100) nm using UV-1650 PC UV- VIS spectrophotometer SHIMADZU .The value of absorption coefficient (α) has been calculated by using eq. A: Absorbance , d: thickness of films [5]

$$\alpha = \frac{2.303A}{d} \quad \text{.........(1)}$$

The extinction coefficient (K) was calculated using the eq. α: absorption coefficient [6]

$$K = \frac{\alpha\lambda}{4\pi} \quad \text{..........(2)}$$

The refractive index was determined by the relationship, R: reflectance [6]

$$n = \frac{\sqrt{1+R}}{\sqrt{1-R}} \quad \text{.........(3)}$$

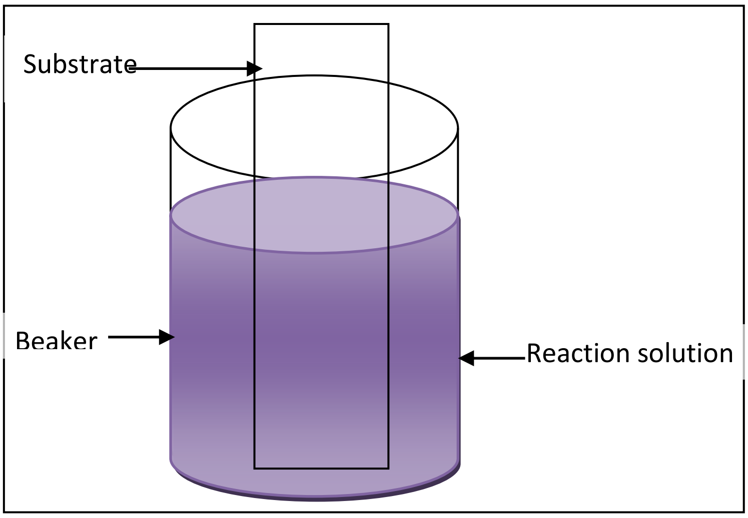

Fig. (1.1): The substrate immersed in reaction solution of prepared films by CBD.

Annealing can be defined as heat treatment of materials at elevated temperatures aimed at investigating or improving their properties. Material annealing can lead to phase transitions, recrystallization, polygonization, homogenization, relaxation of internal stresses, removal of aftereffects of cold plastic deformation (strain hardening), annihilation and rearrangement of defects and so on. The results of annealing depend significantly on its kinetics. the rate of heating and cooling and the time of exposure at a given temperature[1].

All deposited CuS thin films of (0.2,0.3 and 0.4M) were annealed in furnace in air at 400^0c temperature for three hours .

3. Results and discussion:

X-Ray Diffraction:

Fig. (1-2),(1-3) and (1-4) show the nature of the deposited and annealing of (0.2,0.3and 0.4 M) of CuS thin films. The main features were that all films before and after annealing in air at 400^oC were amorphous such results a history mentioned by others [7,8,9,10] . The non crystalline structure in the films could be attributed to many parameters among those the wide band gap, low temperature used during deposition and glass substrate [11,12].

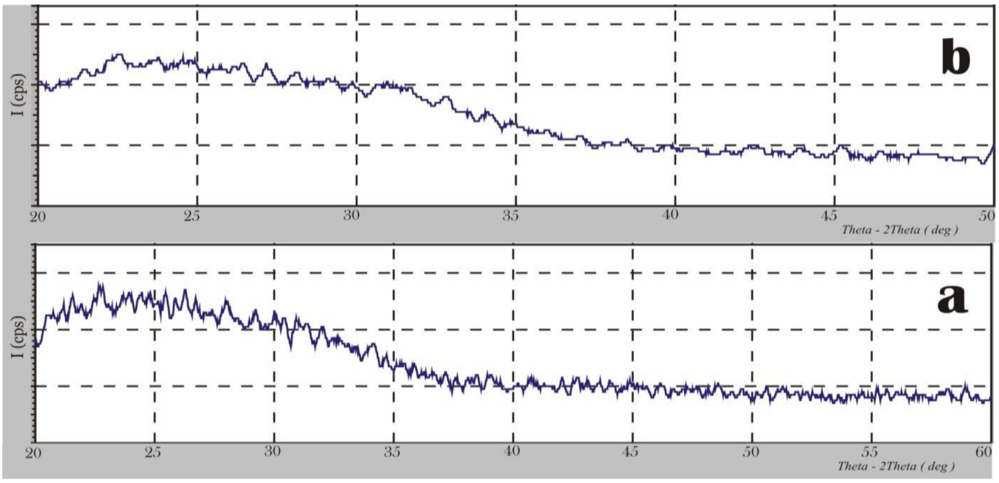

Fig. (1-2): X-ray diffraction patterns for 0.2M of CuS thin films .
(a) before annealing , (b) after annealing .

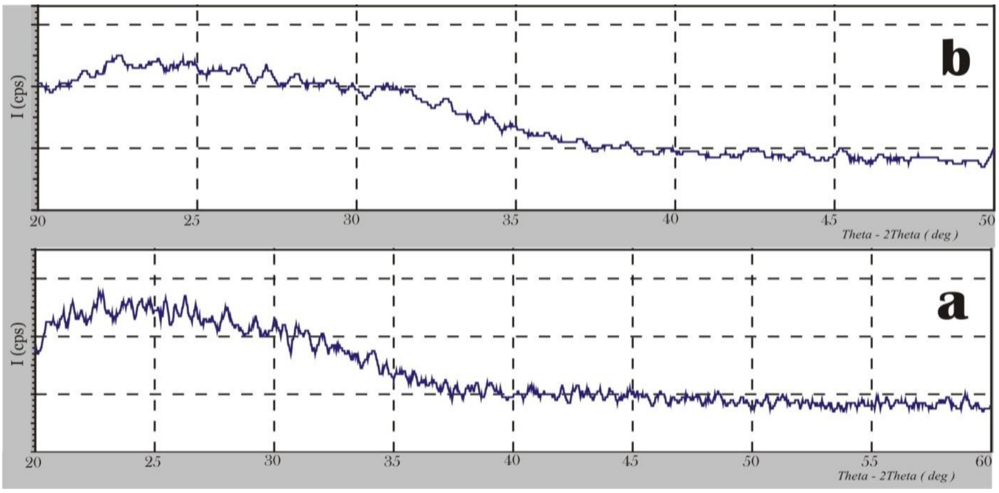

Fig. (1-3): X-ray diffraction patterns for 0.3M of CuS thin films .
(a) before annealing , (b) after annealing .

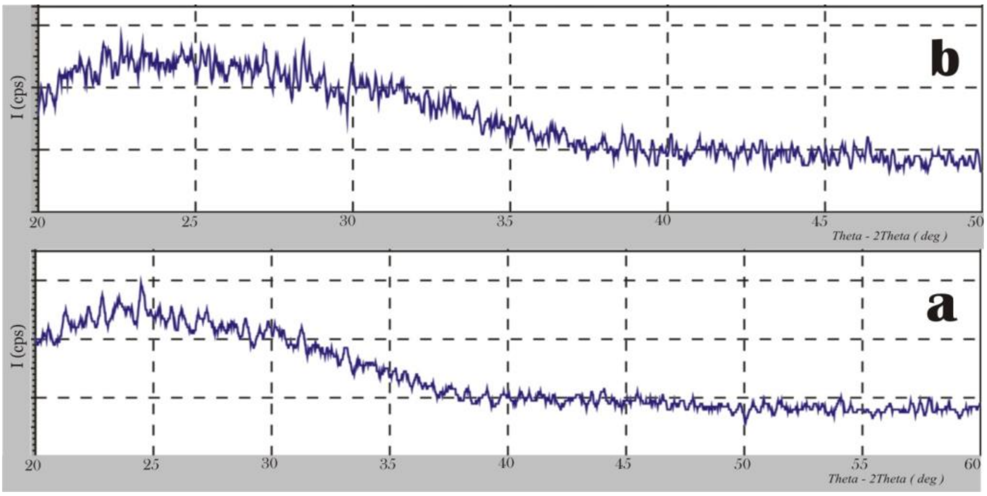

Fig. (1-4): X-ray diffraction patterns for 0.4M of CuS thin films.
(a) before annealing , (b) after annealing .

4. Optical Properties

Transmittance:

Studying the optical transmittance of the prepared film is of great interest due to its valuable scientific significance. The optical transmittance spectra depends on the chemical composition, crystal structure, energy of incident photon, film thickness ,and films surface morphology. Fig. (1-5) shows the effect of as-deposition and annealing on the transmittance spectra. It is clear that the transmittance decreases with increasing the Cu ion concentration for before and after annealing. Increasing the Cu ion concentration means increasing in film thickness, hence increasing absorption. Fig. (1-4) shows also the optical transmittance of annealed films. Annealing process of the as-deposited films increase the optical transmittance, this increasing could be attributed to the decreasing and rearrangement the defects of the films. In addition the annealing leads to improvement the crystallinity of the films structure [11,13,14].Therefore, CuS thin films can be used as transparent conducting materials (TCMs) which is widely used as electrodes in solar cells, flat-panel displays, light emitting diodes, defrosting windows, and other optoelectronics[1].

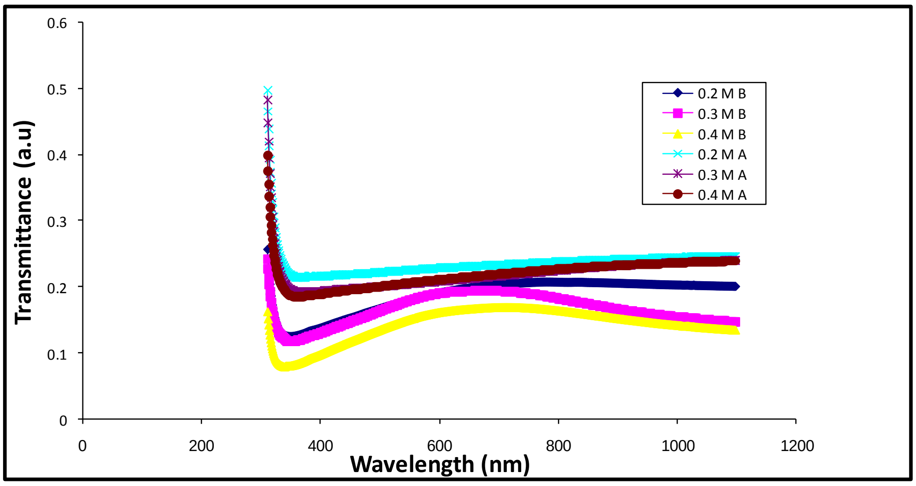

Fig. (1-5): Shows the transmittance of the cus for 0.2,0.3,0.4 M . before and after annealing .

Absorbance:

Fig. (1-6) shows the spectral variation of absorbance for as-deposited and annealed films . The absorbance increased with the increasing of the Cu ion concentration of the films before and after annealing , which lead to increasing in the thickness of deposited films. It's clear from fig. (1-6) the annealing process leads to decreasing in the absorbance spectra. The previous behavior of transmission inversely reflected in the spectral absorption as shown in Fig. (1-6) where the value of absorption exponentially decreased. Here it can be explained the increase in the absorption with thickness by another way, where in this case of a thicker films, more atoms are present in the films so more states will be available for the photons to be absorbed[11,15].

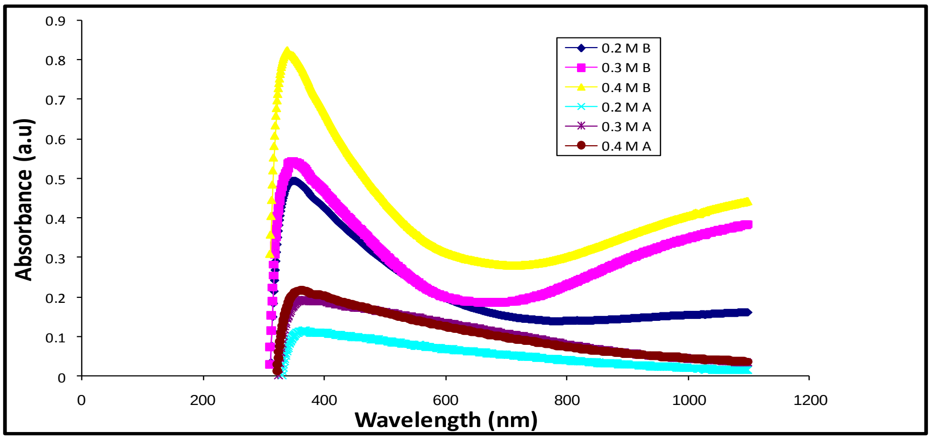

Fig. (1-6): Shows the absorbance of the cus for 0.2,0.3,0.4 M . before and after annealing .

Absorption Coefficient:

The graph of optical absorption coefficient, α vs photon energy, hν is shown in fig. (1-7) for CuS thin films of different ion concentration .The data from absorption spectrum are used to calculate the absorption coefficient by using equation (1). It is clear that the films have a high absorption coefficient ($\alpha > 10^5$ cm^{-1})that means all films have direct band gap. This curve shows that α is not linearly related with hν. It can as well be seen that the thermally treated CuS has lower value than the as-deposited sample. Maximum values of absorption coefficient are observed at shorter wavelengths. The spectral behavior of the absorption coefficient for as-deposited and annealed CuS thin films is shown in Fig. (1-7). CuS thin films clearly showed high absorption coefficient value. Annealing decreases the value of the absorption coefficient in the whole spectra and shifts the fundamental absorption edge towards the higher values of the photon energy. The fundamental absorption can be used to determine the nature and the value of the optical band gap of crystalline and non-crystalline materials[16,17].

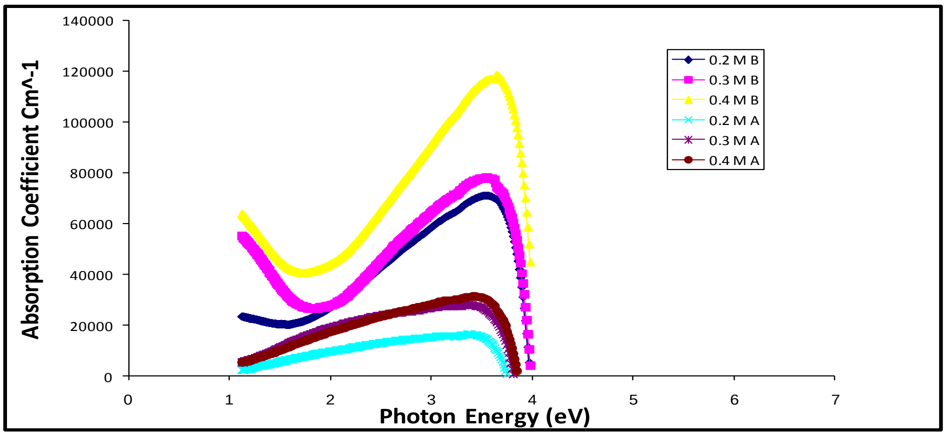

Fig. (1-7): Shows the absorption coefficient of the CuS for 0.2,0.3,0.4 M . before and after annealing .

Optical Energy Gap :

The direct energy gap values were calculated by extrapolation of the straight line of the plot of $(\alpha h\nu)^2$ versus photon energy. Fig. (1-8),(1-9),(1-10),(1-11), (1-12) and (1-13) shows that the films have direct band gap and it is clear from fig. (1-8),(1-9) and (1-10)that the energy gap value of the films before annealing were greater than that after annealing. From fig. (1-8),(1-9) and (1-10) it can be seen that the energy band gab decreasing with increasing the Cu ion concentration of films that's means increasing in films thickness. It is found that the band gap energy decreases from 2.526 to 2.433 eV as the concentration of films increased from 0.2 to 0.4 M [13,15,18] . Fig. (1-11),(1-12) and (1-13) shows the annealed films with different ion concentration. The annealing process normally decrease in the energy gap values, This could be attributed to improvement in the crystal and change in grain size of the film [16,19]. It is found that the band gap energy decreases from 2.423 to 2.349 eV as the ion concentration of films increased from 0.2 ,0.4 M and for o.3 M decrease from 2.484 to 2.423 eV . Table (1) show the results of the optical energy gap of CuS thin films before and after annealing .

Table (1): The result of energy gap of CuS thin films before and after annealing .

Concentration Of CuS thin film (M)	Direct energy band gap Eg^{opt} (eV) Before annealing	Direct energy band gap Eg^{opt} (eV) after annealing
0.2	2.526	2.416
0.3	2.482	2.359
0.4	2.433	2.349

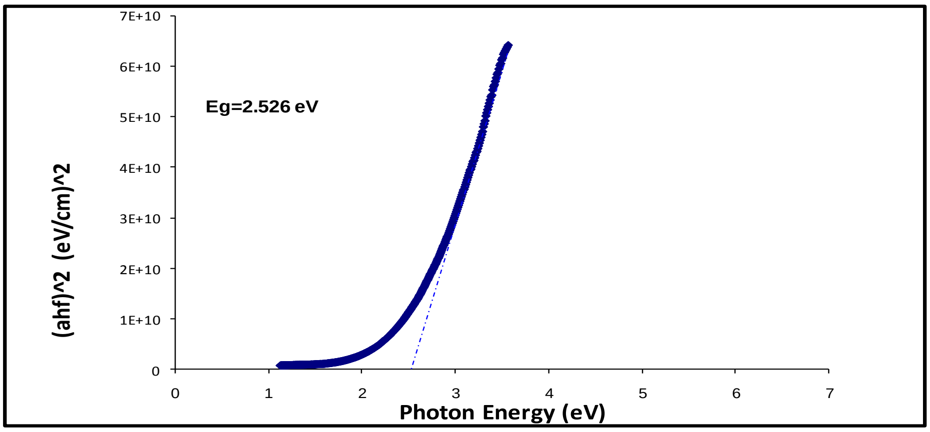

Fig. (1-8): The direct optical energy gap for CuS 0.2M before annealing .

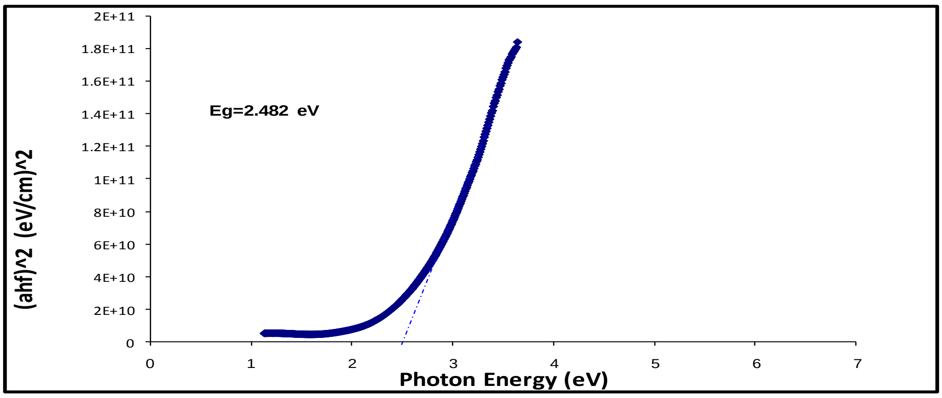

Fig. (1-9): The direct optical energy gap for CuS 0.3M before annealing .

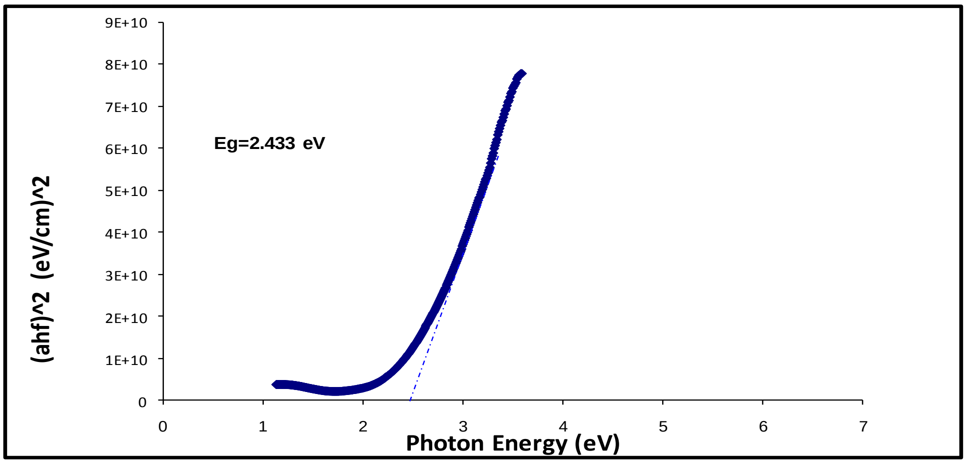

Fig. (1-10): The direct optical energy gap for CuS 0.4M before annealing .

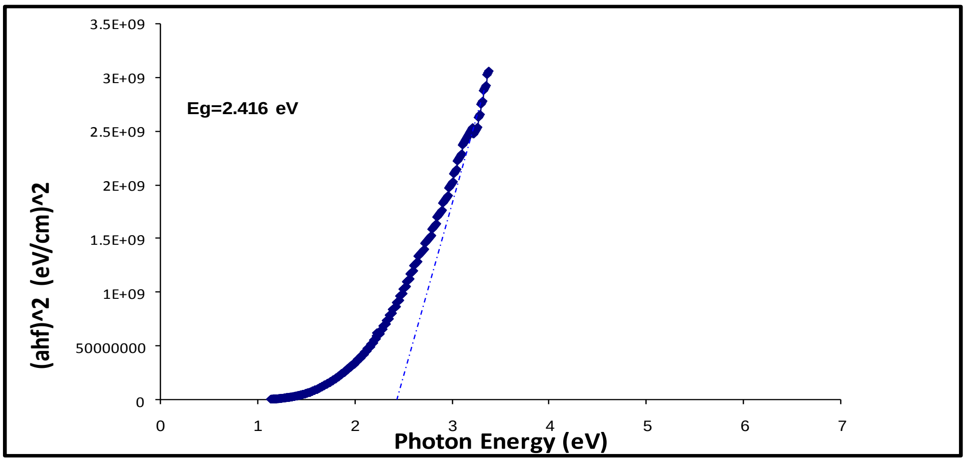

Fig. (1-11): The direct optical energy gap for CuS 0.2M after annealing .

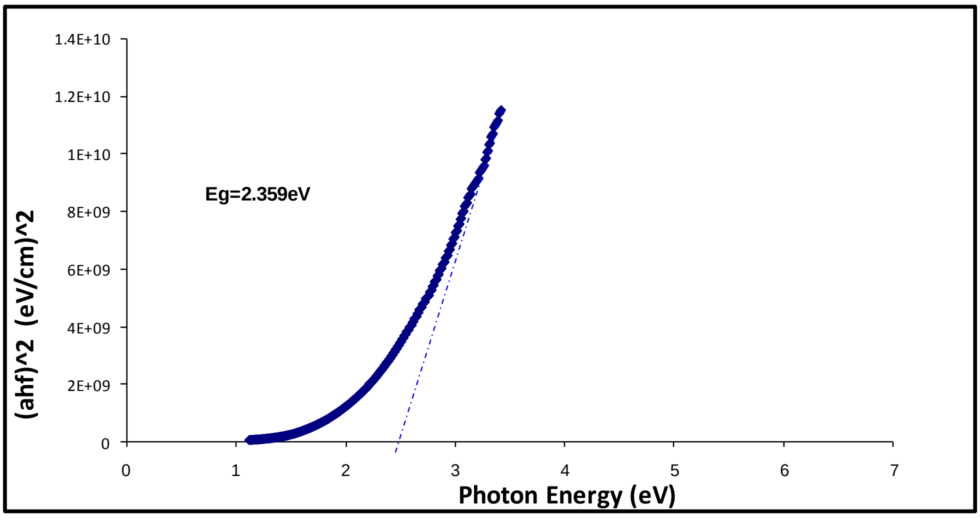

Fig. (1-12): The direct optical energy gap for CuS 0.3M after annealing .

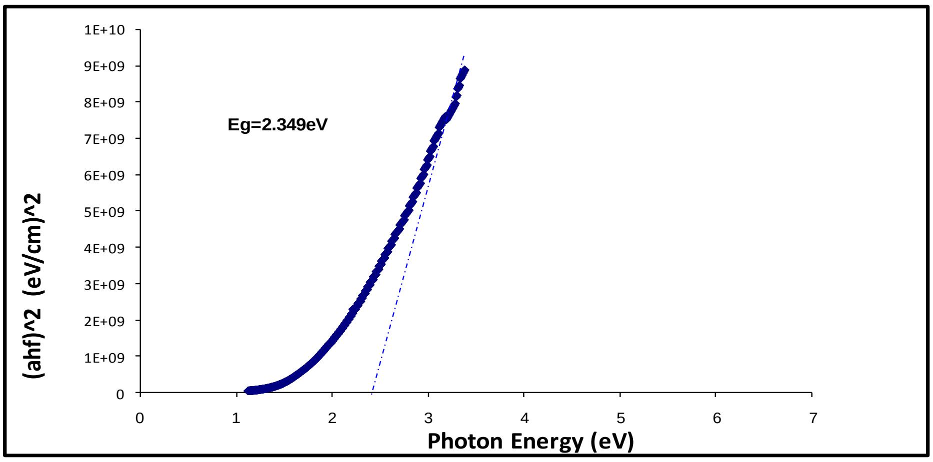

Fig. (1-13): The direct optical energy gap for CuS 0.4M after annealing .

Reflectance :

The reflectance (R) is the ratio between the intensity of reflected photon to the intensity of incident photon .The reflectance (R) of CuS and thin films is calculated from the absorption and the transmittance spectrum using the relation; R+T+A = 1. Fig. (1-14) shows the variation of reflectance spectra for three ions concentrations of as-deposited and annealed CuS thin films . The reflectivity of the films before and after annealing decreased with increasing the ion concentration of films because the increased of ion concentration leads to absorption of more electromagnetic radiation in the samples. It's clear from the figure that the annealing process leads to increasing in the reflectivity of the films which refers to the decreasing in the absorption of electromagnetic radiation as explained later in fig.(1-6), This result confirmed some earlier studies [11,20].

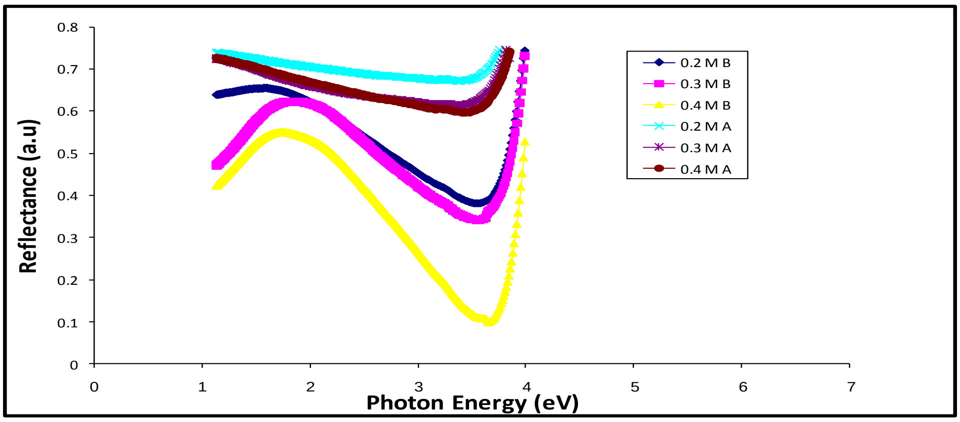

Fig. (1-14): Shows the reflectance of the CuS for 0.2,0.3,0.4 M . before and after annealing .

Refractive Index :

The refractive index is the ratio between speed of light in vacuum to its speed in material which doesn't absorb this light. The values of refractive index (n) were calculated using equation (3) depending on the reflectance values. Studying the refractive index will complete the fundamental study of the optical properties and optical behavior of the material. For all deposition conditions in addition to the annealing , the refractive index increases to a maximum value at energies corresponding to the optical energy gap and then decreases because of the increasing in the electronic transports . Fig. (1-15) shows the variation of the refractive index with different ions concentrations for as-deposited and annealed of CuS thin films. The values of refractive index decreases with increasing the copper ion concentration for as-deposited and annealed films, this trend can be attributed to the increase of optical absorption in the UV-visible region. The fig. also shows the effect of annealing process on the refractive index behavior which lead to increase in its values in the UV-visible region, which can be attributed to the decrease of optical absorption and to the influence of the annealing process on the morphology of the films and hence caused change in the refractive index[11,21]. The behavior of the refractive index is similar to the behavior of many CuS films which prepared by different techniques especially chemically deposited such as CuS films prepared by CBD technique [16] and Cu_2S films prepared by dip-coating technique[22].

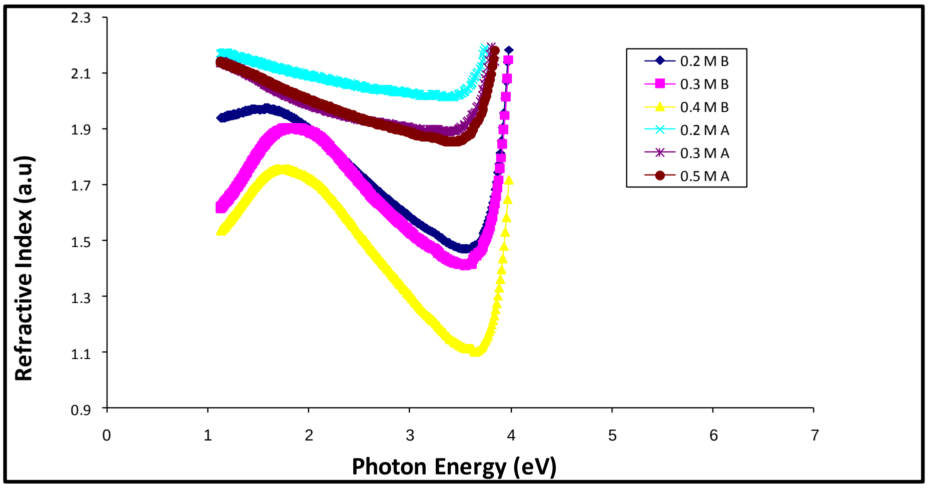

Fig. (1-15): Shows the refractive index of the CuS for 0.2,0.3,0.4 M . Before and after annealing .

Extinction Coefficient :

The extinction coefficient (K) represents the amount of absorption energy in the thin film material, which means the attenuation of an electromagnetic wave that is traveling in a material. The values of (K) depends on the density of free electrons in the material and also on the structure defects . The extinction coefficient was evaluated using the relation (3), and through the relation the extinction coefficient is directly related to the absorption coefficient . Fig. (1-16) shows the extinction coefficient of the samples as-deposition and annealing with different concentrations. The values of extinction coefficient are directly related to the absorption of light. The rise and fall in the extinction coefficient is due to the variation in the absorbance . From the figure the values of extinction coefficient before and after annealing increases with the increasing of Cu ions concentration [22,23]. The annealing process leads to decrease in the extinction coefficient values for each Cu ion concentration because the annealing process leads to decreases the defects or the tails deep (that's means decreases in the absorbance of the films) [18] .

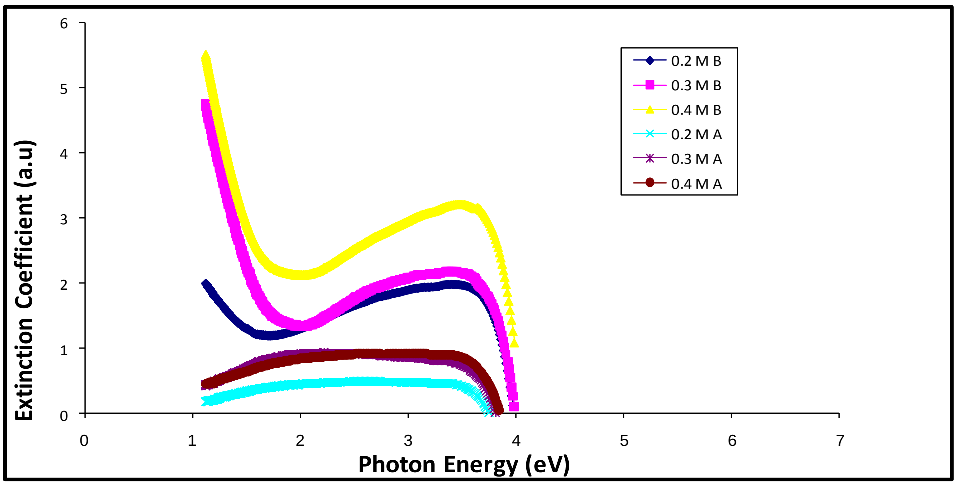

Fig. (1-16): Shows the extinction coefficient of the CuS for 0.2,0.3,0.4 M . before and after annealing .

5. Conclusion:

1- The structural nature of the CuS thin films was amorphous structure before and after annealing.

2- The optical transmittance of CuS thin film decreases with increasing the concentration of Cu in the Bath solutions.

3- The transmittance for CuS thin film increases after annealing process, therefore it can be used as transparent conducting materials (TCMs) which is widely used as electrodes in solar cells, flat-panel displays.

4- The optical energy gap values of CuS thin films for allowed direct transition decreased with the increases of the Cu ion concentration before and after annealing.

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