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Annealing Effect on the Optical Properties of Different Thicknesses of CuS Thin Films Prepared by Growth Solution Method

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ABSTRACT
This work presents the annealing effects on Copper Sulfide (CuS). Different thickness films were prepared from their primary compounds by deposition in a chemical bath at 70°C on a glass substrate. The (pH=9), where copper chloride compounds $CuCl_2$ and sodium sulfide Na2S precipitated and precipitated at 0.1 concentration. According to the deposition duration of; (1, 2, and 3) hours, the growth rate of the films was led to different thicknesses (280 nm, 490 nm, 660 nm). After a heat treatment by annealing at 150°C and 250°C, the optical properties of the absorbance, transmittance, and energy gap were calculated. The results were compared, where a decrease was observed in the absorbance of some samples at 250°C better than 150°C. The energy gap was decreased further by approximately 0.12-0.45 eV,
Keywords:CuS thin film, annealing, growth solution, optical properties.

I. INTRODUCTION

A thin films of semiconducting materials has attracted many researchers in recent years due to its unique advantage, diversity of properties and wide applications. There are many studies and research that have been conducted in the field of thin films and the extent of their development through an interest in studying semiconducting materials and their physical and chemical properties, and among these materials is copper sulfide (CuS). Where the researchers were interested in preparing and studying copper sulfide films by different deposition methods and studying their electrical and optical properties and the importance of using them in electronic applications [1].The chemical structure for CuS belongs to the class of Chalcogenides, which are formed by the interaction of one of the Transition elements with one of the elements of the sixth group in the periodic table, where these compounds enjoy great interest due to the great diversity in their properties and the high possibility of controlling these properties, as is the case with most chalcogenide compounds [2]. The CuS compound has many phases depending on the ratio of copper to sulfur in the compound, [3, 4].CuS thin films are of great importance in the field of industrial applications, as they are used in photovoltaic applications in the manufacture of solar cells, [5, 6].

This study aims to prepare CuS films from their primary compounds by chemical bath precipitation at 70^{o}C. And a study of the effect of annealing by the thermal furnace and a microwave oven on the optical properties of CuS films like the energy gap, absorbance and transmittance.

II. MATERIALS AND METHODS

In our work, CuS films were prepared using a bath deposition technique as follows:

1- Dissolve copper chloride $CuCl_2$ in 40 ml of distilled water using a hot stir plate for 30min at 70°C and 0.1 M, in the Reflux system Figure (1).

2- Dissolve the Na2S sodium sulfide compound in 40 ml of distilled water using a hot plate stirrer for 30 minutes at a concentration of 0.1 M in the Reflux system.

3- Copper chloride ($CuCl_2$) is mixed with sodium sulfide (Na_2S) in 80 ml, mixed and heated in the same apparatus for 30 minutes at a temperature of 70^{o}C

4- After mixing the two solutions, it is filtered with filter paper, and the solution is ready for sedimentation to be placed in the chemical bath. In our work, (ph=9) was taken.

5- The solution was placed in the bath and deposited according to the times (1hr, 2hr, and 3hr) on the glass substrate to complete the deposition process at a temperature of 70°C.

6- After deposition, the samples are removed from the chemical bath and left to dry at room temperature.

7- The thickness was measured using the gravimetric method.The average value of the thickness of the films was as follows:
8- The optical measurements for CuS films were taken using the (721_2000) (UV-Vis-NIR spectrophotometer).

9. The optical absorption coefficient (α) was calculated from the relationship:
α= A/(t 2.303)…., where A, absorbance. t , the thickness of the film.

3 hr	2 hr	1 hr
660 nm	490 nm	280 nm

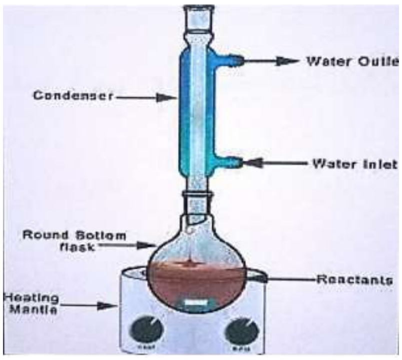
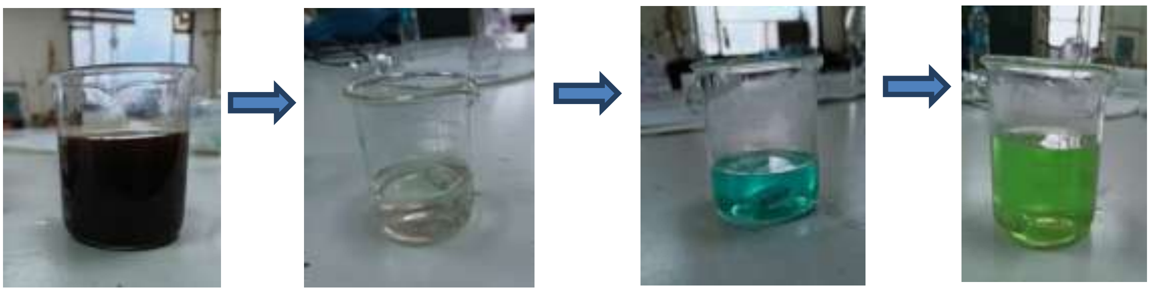


Figure (1): The Reflux system



(a) (b) (c) (d)

(e)

Figure (2):(a) copper chloride compound $CuCl_2$ dissolved in distilled water,(b) sodium sulfide compound Na_2S dissolved in distilled water,(c) mixing copperchloride compound with sodium sulfide,(d) after mixing a solution in a device It is filtered by filter paper,(e) deposited samples.

2.1 Annealing:

In a qualitative way, annealing modifies the surface morphology of materials with temperature and time. Also annealing treatment reduces dislocation emission sources and improves material ductility by strengthening grain boundaries' resistance to cracks,[7]. In this work the samples were divided into three groups according to the deposition time and the annealing times. In Group A the samples which have been deposited for one hour and the annealing process was carried out in a thermal oven at 150°C and 250°C. Group B, that have been deposited for two hours then an annealing process was carried out at 150°C and 250°C. Where group C, an annealing process was carried out at 150oC and 250°C for the samples which were deposited for three hours.

III. RESULTS AND DISCUSSION

The optical properties of CuS films were studied before and after annealing using aspectrophotometer within the wavelength range (340-1000 nm).

3.1 Absorption:

From Figure (3), The blue curve is the absorption before annealing, while the red curve is the absorption after annealing. Here the Figures show that the annealing increased their absorbance clearly, especially those that were below 150°C and for all the wavelengths highlighted. While the absorbance increased in annealing below 250°C, but for wavelengths less than 900 nm.

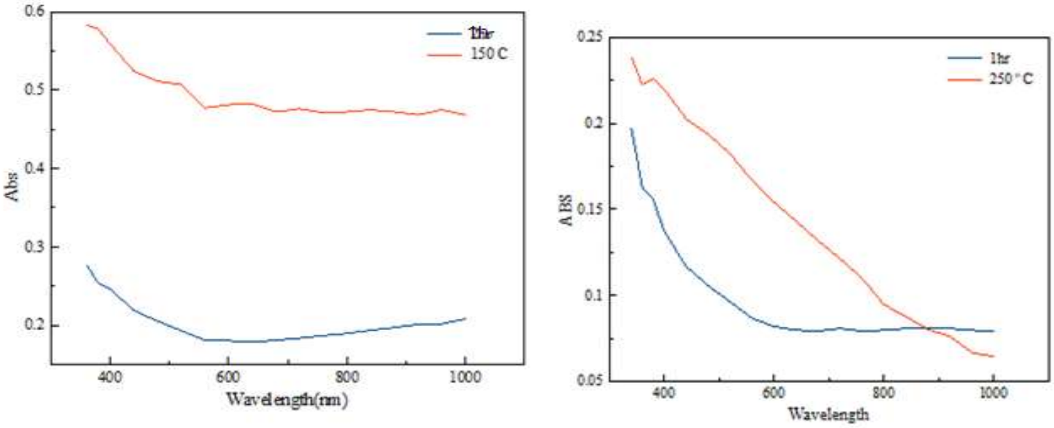


Figure (3) Absorption vs. λ for samples 1, 2, and 3, before (blue) and after (red) annealing for one hour:at 150°C, (b) at 250°C.

Figure (4), shows that the samples prepared in 2 hours of deposition increased the absorbance after annealing. But annealing at 150°C,gives better absorbance behavior than those with annealing at 250°C. For an annealing at 250°C the absorbance decreases above 800nm wavelengths.

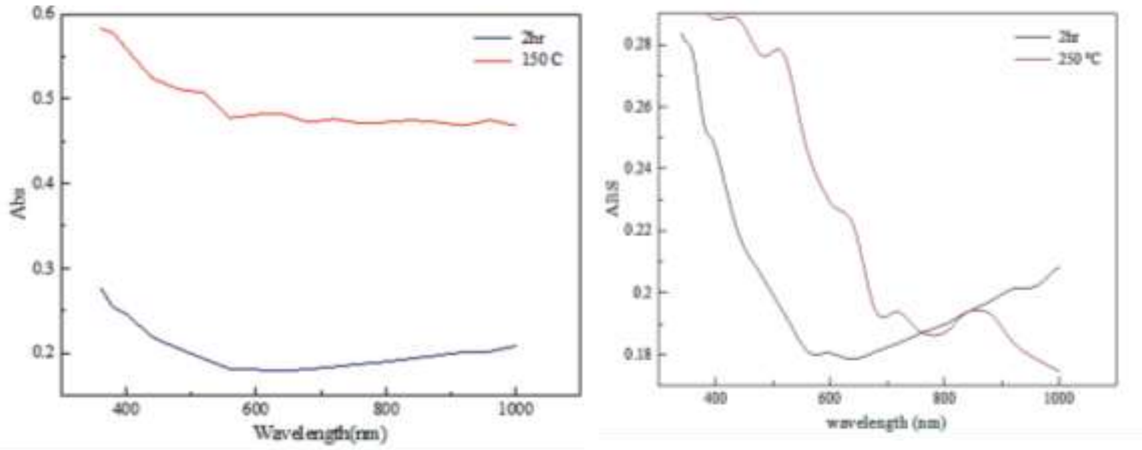


Figure (4) Absorption vs. λ for samples 4, 5, and 6, before and after annealing for two hours: (a) at 150°C, (b) at 250°C.

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Samples 7,8 and 9 were annealed for three hours as in Figure (5). It was observed that the absorbance did not increase at 150°C annealing. Rather, a clear decrease in absorption for all wavelengths. Here also the blue curve is the absorption before annealing, while the red curve is the absorption after annealing. Also at 250°C annealing the absorbance decreases above 800nm wavelengths.

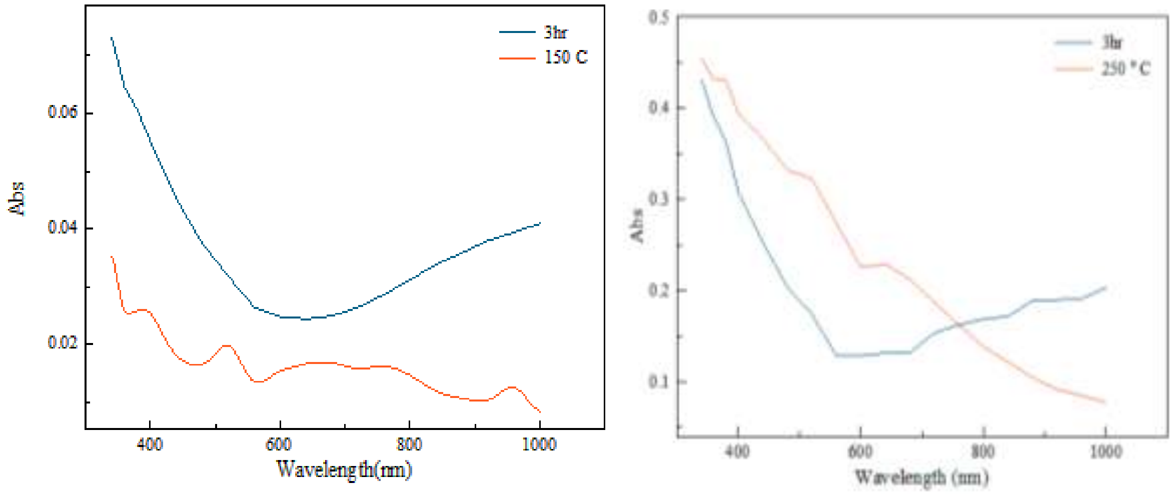

Figure (5): Absorption vs. wavelength λ for samples 7,8, and 9, before (blue) and after(red) annealing for 3 hours:(a) at 150°C, (b) at 250°C.

1.2. Transmittance:

The transmittance values were also calculated as per the following results. In the Figures also the blue curve is the absorption before annealing, while the red curve is the absorption after annealing; Figure (6), for the samples with deposition for one hour, which were annealed at 150°C and 250°C. The effect of annealing indicated a clear decrease in their transmittance, especially those that were below 150 °C and for all wavelengths. The transmittance decreases after annealing below 250oC and at wavelengths of 800nm.

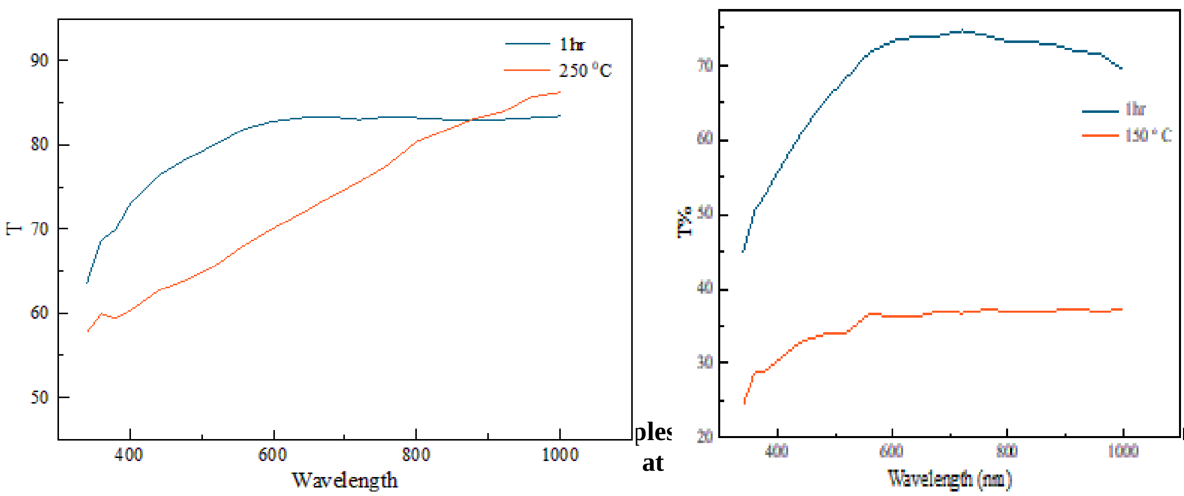

Figure (7) for the two-hour deposition samples notes that the annealing showed an effect clearly, as the transmittance decreased significantly at 150°C, and at 250°C.

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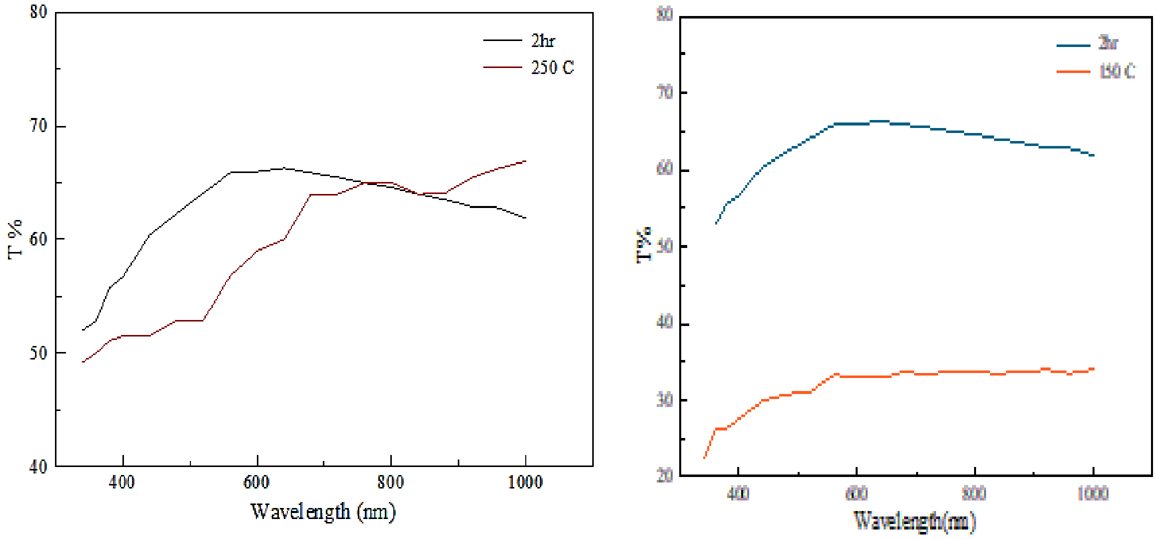

Figure (7):Transmittance vs. the wavelength for samples 4,5 and 6 that have been deposited for 2 hr, before (blue) and after (red) annealing, (a) at 150°C, (b) at 250°C.

Figure (8) shows the transmittance of the samples which deposited for 3 hours, and it is noted that the transmittance increases after annealing at 150°C. While the transmittance decreases when annealing at 250°C. but the transmittance increased above 700nm.

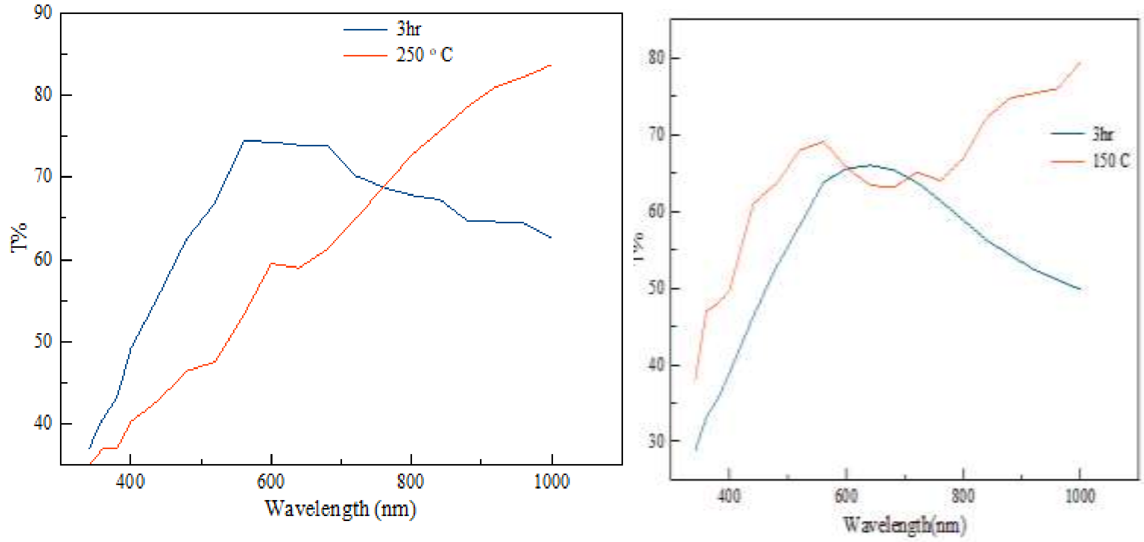

Figure (8):Transmittance vs. the wavelength for samples 7,8 and 9 that have been deposited for 3hr, before (blue) and after (red) annealing, (a) at 150°C, (b) at 250°C.

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1.3. Optical energy gap:

The energy gap of the films prepared before and after annealing was measured. Figure(9) shows that the annealing has reduced the energy gap value for the samples that were prepared with 1hr deposition in both degrees of annealing. It is noted that the average value of the energy gap reduces about (1.5eV) at 150^{o}C and (~1eV) at 250^{o}C.

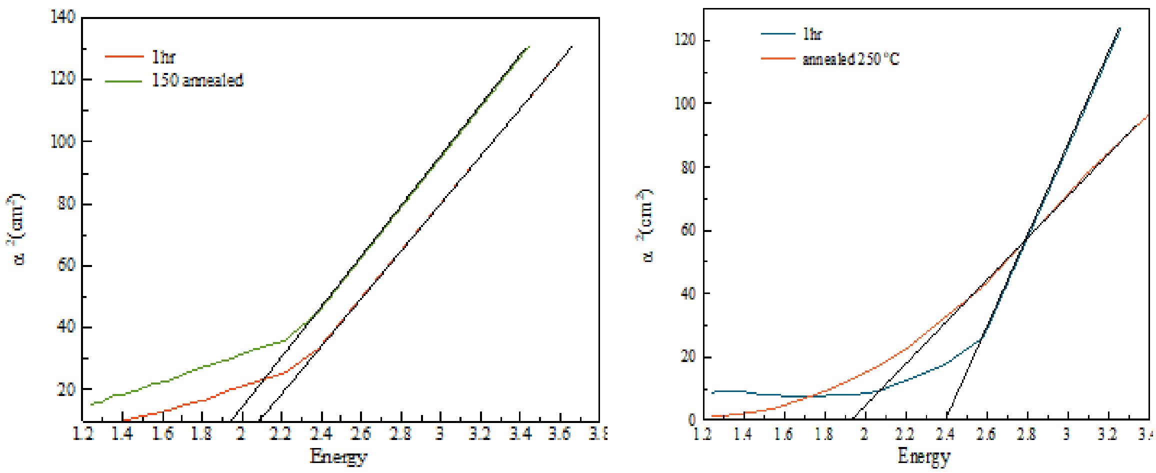
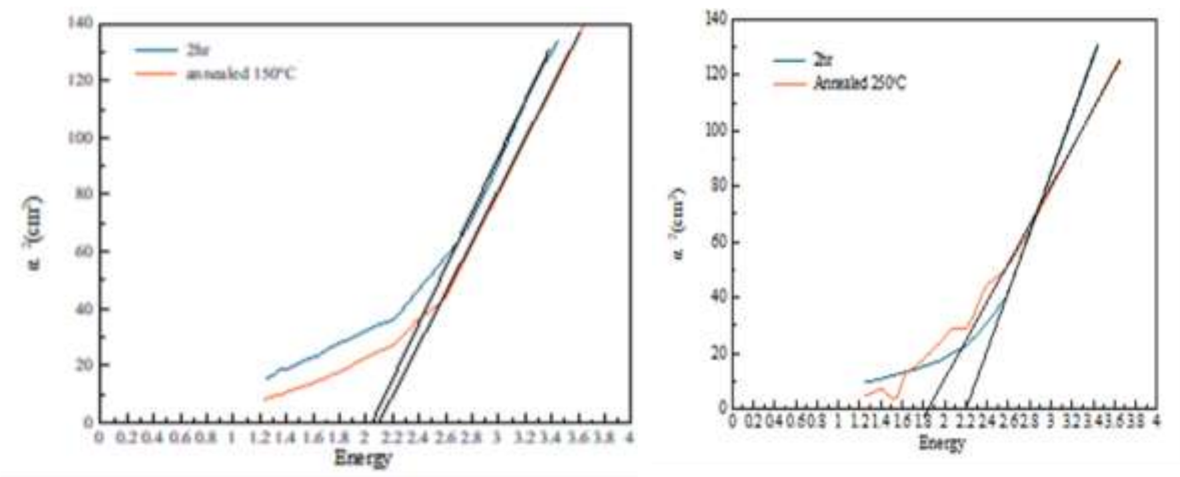


Figure (9): Energy gap for samples prepared with 1hr deposition before (red) and after (blue) annealing, (a) at 150°C: Eg= 2.1eV,then Eg=1.95eV. (b) at 250^{o}CEg=2.4eV, then 1.94eV.

Figure (10) for the samples that were prepared and deposited for two hours, gave different energy gap values after annealing at 150^{o}C, as the value of the gap energy increased after annealing by about(0.02). While the annealing at 250^{o}C, the energy gap decreased by about (0.3eV)



Figure(10): The energy gap of the samples deposited for two hours, before and after annealing:(a)at 150^{o}C: Eg=2.05eV, Eg=2.07eV. (b) at 250^{o}C: Eg=2.2eV, Eg=1.89eV.

Figure (11) for the samples prepared and deposited for 3 hours, the energy gap decreased by (0.14eV) &(0.12eV) when annealing at 150^{o}C and at 250^{o}C, respectively.

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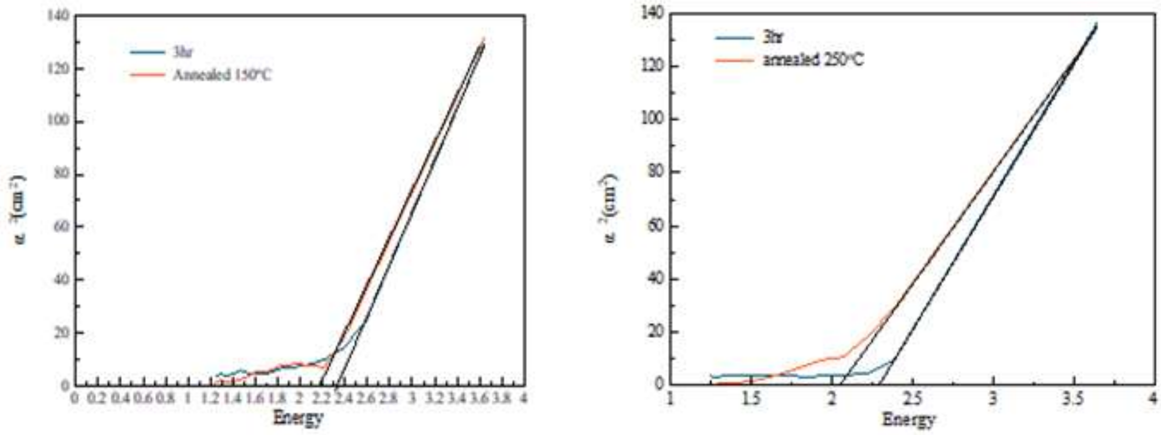

Figure (11): The energy gap for samples deposited for three hours, before and after annealing: (a) at 150°C: Eg=2.33eV, Eg= 2.19eV. (b) at 250 °C: Eg=2.12 eV, Eg=2eV.

Finally the table (1) below includes a summary of the energy gap values (before and after) annealing in (150^{o}C and 250^{o}C) for different deposition times (i.e. different thicknesses).

Table (1): The energy gap (eV) for CuS thin films before and after annealing

Annealing	1 hr 280nm	2 hr 490nm	3 hr 660nm
before	2.09	2.05	2.32
after 150^{o}C	1.94	2.07	2.19
before	2.4	2.2	2.3
after 250^{o}C	1.95	1.89	2.09

In general, from the above table, it is noted that the energy gap values increase with the increase in film thickness. And the annealing reduced the energy gap values at 250^{o}C temperature is more effective than at 150^{o}C. Where the value of the decrease in the energy gap after annealing ranges between (0.15- 0.45)eV for one-hour deposition films (~280nm), and it increases with increasing the temperature of annealing. As for the samples that were deposited for two hours(~490nm), they decreased after annealing by (0.2-0.31). The energy gap for the films with three-hour deposition (~660nm) was decreased after annealing by (0.21-0.13)eV. The differences between the energy gap values are in concordance with the increment of grain size supposed by the annealing.

IV. CONCLUSION

From the results of the optical measurements, The absorption spectrum of the prepared films indicates that the CuS films are direct semiconductors and that the electronic transitions are direct allowed transitions. The annealing process normally decreases the energy gap values, This could be attributed to improvement in the crystal and change in the grain size of the film and this agrees with [8,9]. Also, if the band gap energy decreases it may be the ion concentration of films increased. The absorbance for CuS thin film increases after the annealing process, therefore it can be used in optical applications which are widely used as electrodes in solar cells, and flat-panel displays

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