An Investigation of Structural and Optical Properties of CuS Thin Film Prepared by Chemical Bath Deposition.

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Abstract. Thin film of copper sulfide (CuS) with three molar concentrate of Thiouria (NH₂)₂CS (TU) (0.03, 0.05 and 0.08) M and Copper Chloride CuCl₂.2H₂O with molar ratio (0.01) M have been prepared by Chemical Bath Deposition Technique on glass substrates at (75°C), for one hour. 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 (1.3 – 2.2) eV corresponding to increasing of molar concentration of Thiouria. The purpose of the research is to study the compositional, optical and electrical properties of the prepared films and study the effect of sulfur exporters, On the structural and optical properties.
1. Introduction

Copper sulphide (CuS) is from important semiconductor material and has received a great deal of attention due to its unique physical and chemical properties.[1], different phases as dignity (Cu_{1.8}S), djurleite (Cu_{1.95}S), anilite (Cu_{1.75}S) and the excellent physical and chemical properties of CuS (Covellite), it has become an important candidate for applications in the manufacture of solar cells [2]. Thin films have been prepared by various techniques such as Spray pyrolysis, pulsed laser deposition, vacuum evaporation electrodeposition method, electron beam evaporation 6 and chemical bath deposition .[3], [4], [5]

In this paper, CuS Thin film were deposited on substrate of glass by chemical bath deposition. To enhance the structural properties and to study the possibility of use these films in different applications. Then these thin films were annealed at 120 °C for 2h. X-Ray Diffraction (XRD), Atomic Force Microscopy (AFM).

2. Experimental Work.

Copper chloride and Thiourea were used to prepare the solution for depositing CuS thin film by chemical bath deposition. The deposition by this method is simple, cover a large area, low cost and widely used. The amount of material required can be determined using the equation

\[ M_\text{O} = \frac{W_t}{M_{wt}} \times \frac{1000}{V} \]  

Where \( M_\text{O} \) molar concentration, \( W_t \) weight in grams (g), \( M_{wt} \) molecular weight of the substance (g / mol) \( V \) volume of distilled water (ml)

The weights calculated are (0.2283, 0.3806, 0.6089) gm in (100 ml) from distilled water. The solution was deposited on glass substrates to prepare thin films with solution temperature (75 °C). The deposition solution were prepared by dissolving appropriate amounts of copper chloride (CuCl2·2H2O) (99% purity) and equipped with the German company (Fluka) and Thiourea (NH2)2CS (99% purity) into distilled water and equipped with the Spanish company (Sharlve). The molar ratio of Copper chloride to Thiourea was varied from 1:3, 1:5 and 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, 0.05, 0.08)M). The prepared solution of hydrous copper chloride and thorium with PH value (2) and added by drops of sodium hydroxide. The glass substrates were cleaned using alcohol (Methyl ethyl ketone C4H8O) (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-kα radiation (\( \lambda =1.5404 \text{ Å} \)) 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 Texture Analysis (NanosulrF Flex AFM).

3. Results and discussion

3.1. Structural Properties

The result of X-ray diffraction showed that thin film (CuS) prepared by mixing solution of Thiourea (NH2)2CS (TU) and copper chloride (CuCl2·2H2O) with molar ratio (1:3) showed that the film were polycrystalline with hexagonal phase and we can see Three characteristic diffraction peaks corresponding to the (204), (111) and (220) reflections at Bragg angles 26; (31.7078 °), (25.8278 °) and (43.7627 °) respectively, which undoubtedly indicate that the structure of the
films is polycrystalline. The figure also shown that another phases of copper sulfide (Cu$_{1.92}$S) are grown as shown in the reflection (410). Figure (1-a) also shown that the concentrations of Thiouria (0.05, 0.08) the films to be amorphous structure. On the other hand, after annealing of the films in air at constant temperature (120 °C) for two hour showed that the film prepared with Thiouria concentration (0.03 M) has polycrystalline structure with characteristic reflections belong to peaks (204) and (111), and the digenite phase (Cu$_{1.92}$S) was observed with reflection (410). While the results of the diffraction of X-ray for the films with concentration (0.05 M) has polycrystalline with characteristic diffraction peaks corresponding to the (204) and (220) thin films corresponding well with standard crystallographic data (ICDD-00-019-0381. The result of the film with construction of the Thiouria (0.08 M) has amorphous structure fig (1-e,f).

The crystallite size (D) of CuS thin films calculated from the full width at half maximum (FWHM) from XRD patterns by using Deby–Scherrer's equation [4].

\[
D_{ave} = \frac{0.9 \lambda}{\beta \cos \theta}
\]

Where \( \lambda \) (1.5404 Å) is wavelength of X-ray, \( \beta \) is full width at half maximum in radian, and \( \Theta \) is brag. The crystallite size (grain size). It was found that the granular size after the annealed process was in a state of decrease as a result of the increase of the molar concentrations of the sulfur source Thiouria from (225-96 nm).
Figure 1. XRD pattern of CuS thin films (CuCl$_2$·2H$_2$O + TU) for different molar concentration (a, c, e) for as-deposited films and for (b, d, f) annealed films (T= 120 °C for 2 h).
Figure 2. Shows the AFM images of CuS thin films deposited at (75 °c) The study of the topography of the thin film surfaces and the effect of changing the proportions involved in the Film structure is done using the AFM technique, which has the ability to capture and analyze these surfaces and give accurate statistical values on the particle size and distribution and the surface roughness values based on the root . The mean square root of surface roughness (RMS) as well as providing us with a lot of other important information. The results shown in Figure (2) showed that Film materials, through binary and three-dimensional diagnosis, are homogeneous to a certain extent and homogeneous vertical heights, The surface of the material is equalivent [6] .

Figure 2. Results of (AFM) for CuS thin films; as deposited films for molar concentration ratio (1:3 and 1:5)
3-2 Optical Properties

Optical experiments provide a good way of examining the properties of semiconductor, practically measuring the absorption coefficient for various energies gives information about band gaps of materials. The optical transmission spectra of CuS films obtained by CBD are presented in fig. 3. 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 films. Fig. 3. shows The absorbance spectra of these films with different molar ratio for as deposited films. The spectra shows that the absorption of the films decreases with increasing of molar ratio consistent with the previous study [7].

Figure 3. Shows Transmission(T) & Absorbance(A) spectra of the CuS thin films as deposited films with different molar ratio.
Figure 4. 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 ($\alpha > 10^4 \text{ cm}^{-1}$)

The band gap energy of the film can be estimated from the absorption spectrum using the

$$\alpha h\nu = P(h\nu - E_g)^r$$  \hspace{2cm} (2)

Where $h\nu$ 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 ($\alpha h\nu$)$^2$ and photon energy falling ($h\nu$), and through the extension of the straight part of the curve to determine the intersection with the axis point ($X$) special photon card where ($\alpha h\nu$)$^2 = 0$ (which represents the value of the optical energy gap, and as shown in the fig(6) this figure represents the case of the as deposited and annealed thin films and for four molar concentrations of sulfide source (TU)). Table (1) shows us clearly that the optical energy gap for three molar concentrations 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 ($1.3-2.2$ eV), these increasing of the values of energy gap can be attributed to elimination of the local and extended levels in the energy gap. These results are consistent with previous studies [9] [10].

![Figure 4](image_url)

Figure 4. Shows the optical energy gap $E_g$ for allowed direct transitions CuS thin films; as deposited films different molar concentration ratio.
The direct optical band gaps in the CuS thin films with different Cu to S molar concentration ratios (0.03, 0.05, 0.08) have been deposited on glass substrates by chemical bath method using an aqueous solutions of copper chloride and Thio urea at substrate temperature of 75°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 (1.3-2.2) eV.

| Molar ratio | Optical band gap (Eg(ev)) |
|-------------|--------------------------|
| As deposited films |
| 1:3         | 1.3                      |
| 1:5         | 2                        |
| 1:8         | 2.2                      |

Copper sulphide (CuS) thin films with different Cu to S molar concentration ratios (0.03, 0.05, 0.08) have been deposited on glass substrates by chemical bath method using an aqueous solutions of copper chloride and Thiourea at substrate temperature of 75°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 (1.3-2.2) eV.

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