Study the Structural and Optical Properties Pure Copper Sulfide (CuS) Films Prepared by Pulsed Laser Deposition (PLD)

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Abstract. In this research, thin film copper sulfide (CuS) were prepared by the pulse laser deposition (PLD) on glass substrate with different thicknesses. The structural and optical properties of copper sulfide thin films were studied and the results of X-ray diffraction (XRD) were analysis. It was found that CuS films have a polycrystalline structure with hexagonal system. The optical properties of the CuS films were studied by measuring and calculating Transmittance and absorbance spectrum respectively within the wavelength range (300-1100) nm. The results of the absorbance spectrum showed that absorbance of the films increase with an increase in the number of pulses (increasing thickness) and that the type of the electronic transition are allowed direct type. The energy gap values between (2.2-2.9) eV, and the it decrease with an increasing of thickness.

Key words: copper sulfide, thin films, pulsed laser deposition

1. Introduction

The copper sulfide belongs to an important class of semiconducting compounds called Chalcogenides. It is formed by the interaction of one of the transition metals with one of the sixth group elements in the periodic table such as sulfur or selenium, and these compounds have received great attention because of their great diversity in its various characteristics and the high ability to control on these characteristics [1]. As with most Chalcogenide compounds, CuSx have many phases, depending on the copper-sulfur ratio in the compound, CuS at room temperature has five known stable phases, Chalcocite phase (Cu2S), Djurleite phase, Digenite phase, Anillite phase, and Covellite phase [2]. In nature, it is found as a metal form and Calcite (Cu2S) and Cusylite (CuS) are the most common. The calcite is crystallized as an orthopedic (Orthorhombic) form with a density of 5.5-5.8 (g/cm3), and it has a light grey color on the newly cut surface, but it rusts to black after exposure to the atmosphere. It is found in secondary deposits that originate in areas rich in sulfide deposits. This mineral is used as an important source for the copper. While, the Covelite (CuS) crystallized in a hexagonal form as masses or thin layers, or grains speeded scattered on the copper minerals with a
density of (4.6-4.76) g/cm³. It has a metallic luster and a blue-violet color. The Covellite is one of the uncommon minerals, and is found in similar areas of the Calcite mineral and is not a major source of copper [3].

![Figure 1](image.png)

**Figure 1.** The crystal structure of the CuS phase [1]

### 2. Experimental Work

The pulsed laser deposition system consists of several parts arranged where they are used in preparing thin films deposited on different bases as Figure (1) that showed the pulsed laser deposition system is as follows (laser device, deposition chamber, rotary vacuum pump, vacuum pressure gauge, holder Target, digital thermometer). The laser device is the ND-YAG laser with the following specifications (Huafei Tongda Technology- DIAMOND-288 pattern EPLS). The laser energy (100-2000)mJ, the frequency (1-6)Hz., the wavelength(λ) (532 ,1064)nm, the pulse duration 10 ns cooling method: The presence of an inner girdle that replaces hot water with cold water[4]. The thin-film deposition of the CuS according to the value of (x) that was performed inside the vacuum pump chamber in the laser system (Nd-YAG pulse laser) under vacuum pump. The process of precipitation thin film (10-3 mbar) included as in the following steps:

- The interaction of the pulsed beam laser beam with the target (disc)
- The formation and expansion of the plasma inside the deposition chamber towards the glass slide that is caused by lasers.
- Thin film precipitation on the glass slide at temperature at (275°C) at a vacuum pump pressure of (10-3) mbar, the laser energy was (600) mj, the frequency (6Hz) where the incident laser beam is made at an angle (45°) with the target surface and the slide is fixed (10 cm) from the target.

The thickness of the thin films was measured using the Michelson method of optical interference, and this method is based on the interference of the rays reflected from the surface of the thin layer and the substrate on which the deposition was placed, the He-Ne laser was used with a wavelength (632.8 nm) and at a angle of incidence of 45°.
3. Result & Discussion:

The X-ray diffraction results for the copper sulfide films prepared by the pulsed laser precipitation method showed that the films were of a polycrystalline structure and that the lattices of this structure have a hexagonal system and that the preferred direction of growth was toward (100). Figure (3) shows the diffraction of X-rays of the prepared films, and it is clear that the positions of the peaks corresponding to the reflections at the following angles; for the prepared film with a number of pulses equal to 50 pulses at the angle $(2\Theta=27.2871^\circ)$ and the prepared film with a number of pulses equal to 100 pulses, the reflections corresponding the angles $(2\Theta=16.1320^\circ, 20.7806^\circ, 24.7116^\circ, 27.2847^\circ, 33.1087^\circ)$. While for the film prepared with a number of pulses equal to 150 pulses, the reflections corresponding the angles $(2\Theta=16.0940^\circ, 20.3219^\circ, 24.0728^\circ, 27.2538^\circ, 33.6642^\circ)$. Comparing the results shown in Figure 3 and listed in Table (1) with the ICDD numbered (06-0464) it was found that the results are almost somewhat identical with the observation that the peaks appearing on the prepared membranes are clearly demonstrated by increasing the number of pulses that mean increasing the thickness of the prepared films, which indicates that the degree of crystallization of the prepared films increases with the increase in the thickness of the films. This result is consistent with the published research[5].

![Figure 3. X-ray diffraction spectrum for pure CuS films.](image)
Table 1. Results of XRD of CuS Thin Films Prepared by PLD.

| Sample       | 2θ (Deg.) | d_{hkl} Exp.(Å) | d_{hkl} Std.(Å) | FWHM (Deg.) | C.S(nm) | hkl     | Phase      | card No.         |
|--------------|-----------|-----------------|-----------------|-------------|---------|---------|------------|-----------------|
| CuS 50 Pulse | 27.2871   | 3.2656          | 3.2850          | 0.2400      | 34.0506 | (100)   | Hexagonal  | 00-006-0464     |
| CuS 100 Pulse| 16.1302   | 5.4898          | 5.3400          | 0.2000      | 40.1052 | (121)   | Orthorhombic| 00-042-1278     |
|              | 20.7806   | 4.2710          | 4.5290          | 0.1200      | 67.2837 | (212)   | Orthorhombic| 00-042-1278     |
|              | 24.7116   | 3.5998          | 3.6600          | 0.0400      | 25.0150 | (125)   | Orthorhombic| 00-042-1278     |
|              | 27.2847   | 3.2659          | 3.2850          | 0.3250      | 25.1449 | (100)   | Hexagonal  | 00-006-0464     |
|              | 33.1078   | 2.6265          | 2.7240          | 0.3800      | 21.8022 | (006)   | Hexagonal  | 00-006-0464     |
| CuS 150 Pulse| 16.0940   | 5.5027          | 5.3400          | 0.2840      | 28.2418 | (121)   | Orthorhombic| 00-042-1278     |
|              | 20.3219   | 4.3664          | 4.5290          | 0.0800      | 100.8524| (212)   | Orthorhombic| 00-042-1278     |
|              | 24.0728   | 3.6939          | 3.6600          | 0.1600      | 49.6674 | (125)   | Orthorhombic| 00-042-1278     |
|              | 27.2538   | 3.2695          | 3.2850          | 0.2667      | 30.6395 | (100)   | Hexagonal  | 00-006-0464     |
|              | 33.6642   | 2.6601          | 2.7240          | 0.0300      | 276.5627| (006)   | Hexagonal  | 00-006-0464     |

It was found from the calculated values that the average grain size of the crystals decreases with the increase in the thickness of the prepared thin films, and this result was in agreement with Research No. [7] and did not agree with Research No. [6]. Lattice constants (a₀) and (c₀) were also calculated for all thin films prepared using the relationship of the hexagonal system (\(c₀ = \frac{a₀}{\sqrt{3}}\)) and it was found that there was consistent with the international card and published research and it was at a rate of value equal to (a₀ = 3.792 Å, c₀ = 16.34 Å). The absorption spectrum was measured depending on the wavelength, by the study of the absorbance spectrum, we can find many optical constants. The measurements were made at the wavelength range (300-1100) nm for all (CuS) thin film. The results of the UV-VIS measurements are shown in the figure (4) which represents the change of the absorbance spectrum as a function of the wavelength. The figure showed that the absorbance would increase with an increase in the number of pulses and this leads to the increase in thickness. In another mean, the incident photon can stimulate the electron and transfer from the valence band to the conduction band because the energy of the incident photon is greater than the energy gap of the semiconductor, therefore, the absorbance increases with increasing wavelength and that similar to the previous studies [8] [9].
Figure 4. shows the change of absorption with increasing wavelength.

The transmission measurement was performed within the wavelength range (300-1100) nm of all (CuS) thin film. The results of the UV-VIS measurements showed that the transmission spectrum exhibits a completely different behavior of the absorbance spectrum as shown in Figure (5). The transmission of the thin film decreased with increasing the wavelength; In addition, these results showed that the CuS thin film possess a high transmission in the visible and infrared rays spectrum range area at the value (500-760) nm. This region is called the basic absorption edge, and this edge of absorption forms a curve, that confirms that the material is polycrystalline. The absorption and transmission are affected by several factors such as the type of material, thickness, wavelength radiation, surface nature and the crystal structure. The variation in the transmission of thin film (CuS) depends on the method and conditions for preparing the thin films and that agreement with [10].

Figure 5. Shows change of the transmission spectrum with an increasing number of pulses.
The calculation of the energy gap is of great importance. By its value, we can determine the electro-optical application that appropriates for the use of the prepared thin film in it such as photodiodes, solar cells, detectors, etc. The value of the optical energy gap for direct transmission is calculated by drawing a relationship between \((\alpha h\nu)^2\) with the incident photon energy \((h\nu)\) as in the figure(6). The intersection point gives a value of the energy gap to the direct possible transitions of the thin film. The figure (6) shows that the energy gap for the prepared thin films are decreasing from \((2.9 \text{ eV}-2.2 \text{ eV})\) with increasing of the films thickness from \((50 \text{ nm}–150 \text{ nm})\).

![Graph showing energy gap differences according to the wavelength.](image)

**Figure 6.** Shows the energy gap differences according to the wavelength.

4. Conclusions.
The copper sulfide \((\text{CuS})\) films deposited on glass bases prepared by the method of evaporation by a pulsed laser and with different PULSES where the results of X-ray diffraction showed that the films have a various crystalline structure of the hexagonal type. It was clear from the results of the optical measurements that the nature of the electronic films was direct transitions of the allowed type, and the value of the optical energy gap decreased with the increase of the number of pulses. That is decreases with increasing thickness, and the value of the energy gap was within the range \((2.2\text{ eV}-2.9\text{ eV})\).
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