Study of the structural and Optical Properties of Composite (PbS/CuS) Thin Films prepared by Thermal Evaporation Method.

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Abstract

In this research, thin films of composite of PbS/CuS were prepared by means of thermal evaporation in different proportions of copper sulfide (CuS). The structural and optical properties of these prepared films were studied. The structural properties using X-ray diffraction showed that the prepared films of this composite are polycrystalline with cubic phase and the granular size of the prepared films decreases by increasing the thickness of the prepared films and by increasing the proportion of copper sulfide in the composite. The same behavior was also observed when examining thin films using the atomic force microscope (AFM) and the scanning electron microscope (FESEM). The optical properties showed that the absorption of composite films decreased by increasing the ratio of copper sulfide (CuS) in the composite, as well as decreasing with increasing thickness of the prepared films. Optical properties represented by the absorption coefficient, the refractive index, and the energy gap were calculated. It was found that the value of the energy gap of the prepared films was within the limits of (1.6-2.2) eV.

Key words: Thermal evaporation, Composite materials, Structural properties, Optical properties

INTRODUCTION

The recent increased interest in the properties of metal - metal Chalcogenide materials, is due to their efficient solar energy conversion ratio, and as such a potential candidate for photo - electrochemical solar cells fabrication[1,2,3,4,5,6]. Thermal evaporation in a vacuum used in this research is not necessary due to its relative cheapness (and as such the most available for research in developing countries where other highly expensive and technically advanced methods are not readily available) but because, it is a simple way of depositing and fabricating large area metal Chalcogenide thin films [7,8,9,10,11,12], easy coating process of complex
shaped substrates and possibility of using high purity starting materials for the growth of the thin film. Thermal evaporation in a vacuum method also offers wider choices of materials to be used (insulators, semiconductors or metals) since it is a low temperature process which avoids oxidation and corrosion of substrates, and facilitates better orientation of crystallites with improved grain structure [2]. The material property that is of interest in these films are normally the optical properties within the range of UV-Visible and near infrared (NIR) which strongly depends on the dielectric constants, refractive index, and the energy band gap of the thin film and also to some extent on the properties.

In this research thin films of composite of (PbS/CuS) were prepared by means of thermal evaporation in different proportions of copper sulfide (CuS). Structural and optical properties of these films were studied.

**EXPERIMENTAL WORK**

The composite thin films (PbS/CuS) was prepared with specific ratios of CuS which are (10%, 15%, 20%). These films were deposited on corn glass substrate by home made thermal evaporation coating unit with ultimate pressure of vacuum chamber 1x10⁻⁶ mbar. Lead Sulfide (PbS) and Copper Sulfide (CuS) powders with purity 99.999% supplied from Laboratory Reagents company are considered as source materials and were taken into Tungsten boats which are connected to the respective electrodes. The pressure of the vacuum chamber was maintained at 2 x 10⁻⁵ mbar, target-substrate separation of 10 cm was maintained during the entire deposition process. Before the deposition, the glass substrate was thoroughly cleaned with cleaning liquid soap and then with acetone to remove organic particles on the surface and then washed with distilled water. To prevent local hydrolysis the substrates were then soaked in diluted isopropyl alcohol for 10 minutes and then dried. The crystal structure of the composite thin films (PbS/CuS) were determined by X-ray diffraction using the Philips model, (PW/6000) diffract meter, with monochromatic Cu-Kα radiation (λ = 1.541 Å at 40 KV and 30 mA) and 2θ ranges from 10° to 80°. The optical properties of thin films are measured by using UV-VIS. Shimadzu 1800PC Spectrometer in range of wavelength (300 - 1100) nm.

**RESULT AND DISCUSSION**

The structural analysis of composite (PbS/CuS) thin films with different ratio of (CuS) (10% - 15% - 20%) was carried out by using x-ray diffractometer that the diffraction angle 2 varied from 10° to 80°. The X-ray diffraction patterns of these thin films on glass substrates are shown Fig.1. The data analysis showed that all the prepared films have a polycrystalline structure and that the films have cubic phase. The favorite direction of growth of the films is (111) when the adding ratio of CuS is (10%) while the favorite direction of growth is (222) for the CuS ratios (15%) and (20%). To find the predominant average crystallite size (Dave) in polycrystalline samples we used Scherrer's formula [13].

\[ \text{Dave} = \frac{K \lambda}{\beta \cos \theta} \]

Where \( \lambda \) is the x-ray wavelength, \( \beta \) is (FWHM) (Full Width at Half Maximum) and \( \theta \) 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 (10.53 - 39.90) nm and through the results listed in Table (1),
FIGURE 1. X-ray diffraction spectrum for composite films (PbS/CuS)

TABLE 1. Synthetic parameters of composite (PbS/CuS) thin films.

| Composite   | Sample | 2θ (Deg.) | d_{hkl} Exp (Å) | d_{hkl} Std (Å) | FWHM (Deg.) | G.S (nm) | hkl | Phase | card No. |
|-------------|--------|-----------|-----------------|-----------------|-------------|----------|-----|-------|---------|
| PbS/CuS 10% |        | 25.82     | 3.44            | 3.30            | 0.42        | 19.26    | 111 | Cubic | 00-0120174 |
|             |        | 29.93     | 2.98            | 2.85            | 0.48        | 17.08    | 200 | Cubic | 00-0120174 |
|             |        | 42.87     | 2.10            | 2.09            | 0.38        | 22.26    | (220)| Cubic | 00-005-059  |
| PbS/CuS 15% |        | 50.50     | 1.80            | 1.79            | 0.22        | 39.90    | 311 | Cubic | 00-0050592 |
|             |        | 52.86     | 1.73            | 1.71            | 0.24        | 36.94    | 222 | Cubic | 00-005-059  |
| PbS/CuS 10% |        | 25.90     | 3.43            | 3.30            | 0.62        | 13.05    | 111 | Cubic | 00-0120174 |
|             |        | 29.97     | 2.97            | 2.85            | 0.56        | 14.55    | (200)| Cubic | 00-012-017  |
| PbS/CuS 15% |        | 42.90     | 2.10            | 2.96            | 0.81        | 10.53    | (220)| Cubic | 00-005-059  |
|             |        | 50.82     | 1.79            | 1.79            | 0.58        | 15.15    | 311 | Cubic | 00-0050592 |


**FIGURE 2.** Grain size change relative to Weight ratios of films

**TABLE 2.** Values of the synthetic parameters at the dominant direction (200) of the compound (PbS/CuS) and in different ratios at films thickness of 200nm.

| Sample | Hkl | e | PbS/CuS 10% | PbS/CuS 15% |
|--------|-----|---|-------------|-------------|
|        | 2θ (deg) | |             |             |
|        | d_{hkl} (Å) | |             |             |
|        | FWHM (Å) | |             |             |
|        | Lattice constant | |             |             |
|        | a=b=c (Å) | |             |             |
|        | D (nm) | |             |             |
|        | t (a₀) (Å) | |             |             |
|        | N_e (cm⁻²) (×10⁻¹²) | |             |             |
|        | T_c (hkl) (cm⁻²) (×10⁻¹⁴) | |             |             |

Table No. (1) and Figures (2, 3, 4 and 5) show calculation of some of the structural parameters of the composite thin films (PbS/CuS) with different ratios of copper sulfide (CuS), where it is found that the average grain size (D_{ave}) falls within the range (11.41-17.08) nm, and is considered within the nanoparticles range, where the average grain size tends to decrease with an increase in the ratio of addition of copper sulfide (CuS). This can be attributed to the increase in the ratio of addition of copper sulfide may be reduce the process of nucleation and thus leads...
to a decrease in the granular size and in turn leads to an increase in crystal defects and a crystallization of the material as this is also shown in Figure (3, 4). The results of calculating the intensity of the dislocation density ($\delta$), the number of crystals ($N_o$) and texture coefficient ($T_c$) showed a decrease in their values by increasing the ratio of addition of copper sulfide (CuS), and this result is also consistent with the previous results for calculating the average granular size. These results clearly indicate that the increase in the percentage of addition of copper sulfide led to an increase in granular boundaries and consequently leads to a reduction in dislocation within these limits, and this could lead to a decrease in strain at the crystalline levels. These results are compared with the previous results, and it was found that the results are consistent with [14, 15].

**FIGURE 3.** The number of crystals with the ratio of the (CuS) in composite (PbS / CuS)

**FIGURE 4.** Shows the change in the number of crystals with the ratio of (CuS) in the composite films (PbS/CuS)
FIGURE 5. shows the change Micro Strain with the ratio of CuS in composite (PbS/CuS)

Table No. (3) and Figure (6) show the results of the atomic force microscopy examinations (AFM) for composite thin films (PbS/CuS) prepared with a specific mixing ratio of copper sulfide (CuS), where it was clear that the surface roughness and root mean square values for the prepared films change for all the prepared films, noting the average grain size values for the prepared films decrease with an increase in the ratio of addition of copper sulfide (CuS). This may be attributed to the difference in the mobility of the atoms of the additive compared to the base or hosts atoms. It appears from the microscope images shown in Figure (7) that the increase in the ratio of addition led to a decrease in the rate of surface roughness, and in the figure also shows the curves of the volumetric distribution of the crystal nanoparticles as the granular distribution varies according to the ratio of the added material and these results are consistent with [14, 15].

| Sample       | Surface roughness (nm) | RMS (nm) | $\lambda$ |
|--------------|-------------------------|----------|-----------|
| PbS/CuS 10%  | 3.77                    | 5.71     |           |
| PbS/CuS 15%  | 1.98                    | 2.94     |           |
| PbS/CuS 20%  | 3.36                    | 4.70     |           |
FIGURE 6. AFM images and volumetric distribution for composite (PbS/CuS) films prepared with different ratios of CuS.
Table No. (4) and Figure (7) shows the results of the scanning electron microscopy (FESEM) tests for prepared composite thin films (PbS/CuS) with different addition ratios of copper sulfide (CuS). It is clear from the table that the values of the granular size ratio decrease with increasing the ratio of addition of copper sulfide, and this results is in consistent with the results of the structural results mentioned in the previous paragraphs. From the microscope images shown in Figure (8), the films surfaces consist of semi-spherical nanoparticles arranged regularly, with an important observation that the prepared thin films with a ratio of additives (10%), that the grains take a distinct shape and are in the form of flowers.

TABLE 4. Average grain size values for composite thin films (PbS/CuS) films with different ratio of (CuS).

| Sample PbS/CuS | PbS/CuS 10% | PbS/CuS 15% |
|---------------|-------------|-------------|
| Average Grain Size( nm) | 35.36 | 27.92 |

FIGURE 7. FESEM images of the thin (PbS/CuS) composite films prepared in different mixing ratios.
The figures (8, 9, 10 and 11) represent the results of the optical properties for the composite thin films (PbS/CuS) prepared with different ratio of addition of copper sulfide (CuS). Where figures (8 and 9) represents the absorption and Transmission spectrum of the thin films and within the wavelengths (300-1100 nm), it is clear from these figures that the absorbance of the films decreases by increasing the ratio of addition of copper sulfide to form the composite (PbS/CuS). This decrease in the films absorption can be attributed to the apparent decrease in the crystallization of the material and the decrease in the average granular size, and thus an increase in the crystalline boundaries, as was clearly shown in the results of the structural tests.

**FIGURE 8.** the absorption spectra as a function of the wavelength of the composite (PbS/CuS) thin films

**FIGURE 9.** The Transmission spectra curve as a function of the wavelength of the composite (PbS/CuS) thin films.
The values of the absorption coefficient and the optical energy gap are calculated and the results are clear in Figures (10) and (11) respectively. In these figures, it appears that the absorption coefficient of the prepared thin films has a value greater than (104 cm\(^{-1}\)) and this indicates that the electronic transitions in these films are of direct type. Generally, the absorption coefficient decreases with increasing wavelength. While we find that the energy gap that is of the permissible direct type and its value decreases with increasing the ratio of addition of the copper sulfide compound (CuS), the value of which ranged within the range (1.6-2.2) eV, table (5) showed the values of the optical energy gap as a function of the ratio of addition of copper sulfide.

![Figure 10](image1.png)

**FIGURE 10.** Change of absorption coefficient as a function of wavelength of the composite (PbS/CuS) thin films.
FIGURE 11. the value of the optical energy gap for the composite (PbS/CuS) thin films.

TABLE 5. shows the values of the energy gap of the composite (PbS/ CuS) thin films

| Sample     | $E_{g}^{opt}$ (eV) |
|------------|-------------------|
| PbS/CuS10% | 2.2               |
| PbS/CuS15% | 1.8               |
| PbS/CuS20% | 1.6               |

CONCLUSIONS

In this study, the researchers successfully managed to collect superposed compounds of important and promising materials in a method of thermal evaporation under conditions of high vacuum, and thin films with nanoparticles were obtained that could be used better in many important scientific applications.

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