Structure, surface morphology and optical properties of Cu$_x$Zn$_{1-x}$S/Au NPs layer for photodetector application.

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Abstract. CuZnS and CuZnS/Au NPs layer with different Cu/Zn content thin films have been deposited on heated glass substrate by spray pyrolysis technique at 330 °C and annealed at 450 °C for 1 hour. X-ray diffraction (XRD) results reveals that the structures of all prepared thin films are polycrystalline in nature, with preferential growth orientation along (111) plane corresponding to the cubic ZnS (sphalerite). Two low crystallinity of crystallographic phases corresponding to hexagonal CuS and monoclinic Cu$_2$S were appeared with Cu/Zn different content. Strong diffraction peak of Au NPs appeared in CuZnS/Au NPs layer structure corresponding to the cubic Au gold phase oriented along (111) plane. Structure parameters such as crystallite size and number of crystalline, dislocation density and micro strain have been determined. Scanning Electron Microscopy (SEM) and Atomic force microscope (AFM) images of CZS, and CZS/Au NPs thin films shows smooth, uniform morphology and plated regularly with no detectable micro-cracks. The roughness and r.m.s. roughness was increased with increase of Cu/Zn content from 1.95 nm to 4.36 nm respectively, while it decreased with the exists of Au NPs layer from 20.9nm to 3.99 nm. The energy dispersion x-ray spectroscopy spectra demonstrate the stoichiometry of the deposited films. The optical properties results exhibits red shifted in the fundamental absorption edge towards low energies of CZS (Cu/Zn content) and CZS/Au Nps layer thin films. The optical energy gap has been decreased from (2.56 to 2.34 eV, and 2.62 to 2.32 eV) with respect to Cu/Zn content and Au Nps layer, respectively.

1. Introduction

Chalcogenide semiconductors thin films was attractive large attention last few decades due to their wide range of potential application in the various fields, such as photovoltaic and optoelectronic applications[1]. CuZnS ternary semiconductor with high absorption coefficient ($\alpha > 10^4$cm$^{-1}$) and forbidden energy gap (1.6 eV) was a very suitable for solar cell applications where it can be replaced the silicon, CuInS2 and CZTS in the expensive solar cell. So that CuZns was used in the fabrication of affordable solar cell due its low cost, non-toxic and earth abundant and have a suitable optical and electrical characteristics [2, 3]. CZS was a p- type semiconductor and transparent conducting material TCMs which have a high transmittance in the visible region, high reflectance in the infra-red region with high conductivity [4,5]. These materials attracted considerable attention for optoelectronic and transparent electronics devices such as solar energy cell [6] flat-display panel [7], organic light-emitting diode (OLED) [8] and mobile touch screen [9] and transparent conductors [10]. Thin films of CuZnS TCMs material were successfully deposited by different physical and chemical techniques such as chemical spray pyrolysis (SPD) [11], successive ionic layer adsorption and reaction (SILAR) method [1, 2], pulse laser deposition (PLD) [5], ultrasonic spray technique (UST) [12], chemical bath deposition (CBD) [13] sol- gel method [14], photochemical deposition method [15], RF co-sputtering method [16]. In present work CuZnS and CuZnS/Au NPs layer thin films were deposited on glass substrate by spray deposition method. The effect of Cu/Zn content and Au NPs layer on the structure, optical and electrical properties of CuZnS films were studied.
2. Experimental details

CuZnS Thin films were prepared by spray pyrolysis deposition method SPD from the following starting chemicals: 0.1M of Cupric chloride dihydrat (CuCl₂.2H₂O), with purity of 99.6%, 0.1 M of Zinc chloride (ZnCl₂) with purity 99.8%, and 0.3 M of thiourea [CS(NH₂)₂] with purity 99.6% provided from BDH chemical Ltd poole England, as the source of Cu²⁺, Zn²⁺ and S⁻² ions, respectively. 0.01 M of Chlorogoldsäure (HAuCl₄.xH₂O) Gold(III) chloride hydrate with purity of 99.995% and molecular weight 339.79 g/mol provided from SIGMA-ALDRICH were used as the starting chemicals for the solution preparation of Au NPs layer for CuZnS/ Au NPs layer. CZS films at (1:1:2, 1.2:0.8:2 and 1.4:0.6:2) Cu:Zn:S as volumetric content, and Au NPs thin films layer were deposited on previously cleaned glass substrate. Then CZS films with the same Cu/Zn content were deposited on the Au NPs layer to produce CZS/Au NPs thin films. The deposition parameters was fixed as follows: distance of the spray nozzle 30±1, air flow pressure 1 bar, deposition time 3 minute, at substrate temperature 330 oC. To avoid excessive cooling of the substrate, spraying is achieved in periods of about 15 sec followed by ~2 mins wait, with 5 ml/hour of air flow rate. Clean microscope glass were used as substrate for CuZnS, CuZnS/AuNPs. After the spray process was completed, the deposited films were annealed at 450 °C for 1 hour using CARBOLITE (CWF 1200) furnace. Thickness of CZS & CZS/Au NPs thin films prepared by spray pyrolysis method are recorded by using (Optical Thin film Measurement) model (LIMF-10). It is found that the thickness of CuZnS films was about 150-160 nm whereas for CZS/Au NPs films was about 205-225 nm. Structural properties were studied by x-ray diffraction technique using XPert Pro MPD Diffractometer, by PANalytical of X-Ray radiation is Cu kα radiation with wavelength 1.5406 Å, current 30 mA, and voltage 40 KV. The surface morphology of the samples is recorded by an atomic force microscopy and scanning electron microscopy by using Nanoscope III and Dimension 3100, by Veeco Instruments Inc. and INSPECT-S50 by FEI-Netherlands-Holland respectively. The optical measurements include transmittance and absorbance spectra in the wavelength range (200-1100) nm using (Double Beam UV Spectrophotometer–Model MEGA-2100-SCINCO Company–Korea).

3. Results and discussion

3.1. Structure properties

The crystal structure of the prepared films have been studied from the XRD Pattern of the deposited films on glass substrate at temperature 330°C, and annealed at 450°C for 1 hour. Figure (1) illustrate the XRD pattern of CZS and CZS/Au NPs layer thin films with different Cu/Zn content; (1:1:2), (1.2:0.8:2) and (1.4:0.6:2) respectively. The diffraction pattern indicates that the films have a structure of low crystallinity and with polycrystalline nature. The diffraction peak at (111) plane was refer to the ZnS sphalerite (cubic) phase appeared at 2θ 28.47°, 28.39° and 28.49° for the films at different Cu/Zn content respectively as shown in figure (1a). The results are excellent agreement with the standard values of the (JCPDS) card file data (02-0565 ZnS). Secondary peaks was appeared in the XRD pattern refers to the diffraction from the crystal planes (004), (315) and (220) which corresponding to the hexagonal CuS and monoclinic Cu₂S phases appeared at (2θ, 2θ = 22.35°, 34.14° and 47.64° respectively, the results are in good agreement with standard values (JCPDS) card file data is (02-820 CuS) and (33-490 Cu₂S).
Figure 1. XRD Pattern of a: CZS and b: CZS/Au NPs both at Cu:Zn:S content (1:1:2), (1.2:0.8:2) and (1.4:0.6:2) thin films.

The perceptual orientation was along (111) plane which refers to ZnS phase and its intensity was dedicated with the increasing of Cu/Zn content. The cubic sphalerite ($\beta$-ZnS) crystalline forms at high temperature above 400 °C [3]. In the present work, the films were deposited at 330 °C, and annealed at 450 °C, then high possibility of forming crystalline ZnS [17]. The diffraction pattern of CuAZnS/Au NPs figure (1b) indicates that the crystal structure of the films has good crystallinity for Au-nanoparticle layer related to the high intensity of Au NPs (111) peak, but low crystallinity for other content (Cu/Zn). It was found the diffraction peak (111) corresponding Au the cubic phase appeared at $2\theta = 38.02^\circ$, $38.12^\circ$ and $38.15^\circ$ respectively. The results are in agreement with the card standard values data (JCPDS; 02-1095 Au). In the XRD pattern a secondary peaks (111), (311) and (116) was
appeared at $2\theta = 28.27^\circ$, $55.14^\circ$ and $60.29^\circ$ respectively, as shown in the figure corresponding the cubic ZnS, hexagonal CuS and monoclinic Cu2S phases. The preferential orientation was along (111) plane which to Au NPs layer and its intensity was decreased with the increasing of Cu/Zn content. Interplanar spacing ($d_{hkl}$) were calculated using Bragg's law and the results showed good agreement with the standard values as shown in Table (1). Finally, all these results are good agreement with the literature [18]. The crystallite size $D$ was calculated using Deby Scherrer's equation [3]:

$$D = \frac{k\lambda}{\beta \cos \theta} \quad (1)$$

where $k$ represents the shape factor (0.9), $\lambda$ is the wavelength of the used x-ray and $\beta$ is the full width at half maximum of the peaks in radian. It found that the average of crystallite size in range (21.4 – 71.15 nm), that's refer to the CZS/Au NPs thin films, Table (1) showed that the crystallinity of the film was decreases with increase of Cu/Zn content. The decreases refer to low crystallinity structure, which mean that is crystallite growth in various orientations. Dislocation Density $\delta$ and Number of Crystallites $N$ were calculated by use equations [18, 19].

$$\delta = \frac{1}{D^2} \quad (2)$$

$$N = \frac{t}{D^3} \quad (3)$$

As show in Table (1). The increase of Dislocation Density and Number of Crystallites at lowering of crystallite size prove that the grain boundary is increase in compare with previous result. The results are agreement with the literature [19].

**Table 1. a.** XRD obtained results for CZS thin films with varying Cu/Zn content.

| Sample   | $2\theta^\circ$ | hkl     | $d_{\text{calc}}$ | $d_{\text{stand}}$ | $a$  | $c$  | Crystallite Size (nm) | Dislocation density ($\delta$) $10^{13}$lines/m$^2$ | Number of Crystallites $10^{13}$ m$^{-2}$ |
|----------|-----------------|---------|-------------------|---------------------|------|------|-----------------------|---------------------------------|---------------------------------|
| CZS 1:1:2 | 22.347          | (004)   | 3.98              | 3.97                | 3.8  | 16   | 26.0269               | 148                             | 729                             |
| CZS 1:2:0.8:2 | 28.466        | (111)   | 3.14              | 3.12                | 5.439| 5.439| 28.388                | 69.3858                         | 21                              |
| CZS 1.4:0.6:2 | 28.494        | (111)   | 3.133             | 3.12                | 5.426| 5.426| 28.494                | 17.3542                         | 332                             |

**Table 1. b.** XRD obtained results for CZS/Au NPs layer thin films with varying Cu/Zn content.

| Sample   | $2\theta^\circ$ | hkl     | $d_{\text{calc}}$ | $d_{\text{stand}}$ | $a$  | $FWHM$ | Crystallite Size (nm) | Dislocation density ($\delta$) $10^{13}$lines/m$^2$ | Number of Crystallites $10^{13}$ m$^{-2}$ |
|----------|-----------------|---------|-------------------|---------------------|------|--------|-----------------------|---------------------------------|---------------------------------|
| 1:1:2/Au | 38.015          | (111)   | 2.37              | 2.35                | 4.1  | 0.1968 | 71.1478               | 20                              | 36                              |
| 1.2:0.8:2 | 38.117         | (111)   | 2.36              | 2.36                | 4.1  | 0.1574 | 35.5846               | 79                              | 285                             |
| 1.4:0.6:2 | 38.145         | (111)   | 2.36              | 2.34                | 4.1  | 0.1574 | 21.3563               | 219                             | 1319                            |
3.2 SEM and EDX Analyses

Figure 2 (a, b and c) demonstrates SEM images of CZS thin film (1:1:2, 1.2:0.8:2 and 1.4:0.6:2) respectively, including large and small grain size and has regular shape and dense uniform and homogenous surface with a fine particle size of the roughness and coarse scales are low in thin film sample. Figure (2 d) shows EDX spectra of CZS (1:1:2) thin film, which can prove and demonstrates the existence of elements (copper, Zinc, and Sulfur) constitute the thin films structure and showing good samples stoichiometry. Figure 3 (a, b and c) shows CZS thin films on Au NPs layer CZS/Au NPs, the surface becomes granular structure with low homogeneity than its pure CZS, and it consist of nanocrystalline grains with uniform coverage of the substrate surface. The particles agglomerations are randomly oriented in their morphology with an increment in grain size that has been noticed and agreement with Innocenti et al. [20]. Figure (3d) show EDX spectra of CZS/Au NPs layer thin films at different ratios (1:1:2) which can prove the existence of the elements (Cu, Zn and S) in the thin films structure.

Figure 2. SEM images of a:CZS (1:1:2), b: (1.2:0.8:2) and c: (1.4:0.6:2) and d: EDX of CZS (1:1:2) NPs layer thin films.
3.3 Atomic force microscopy analysis (AFM)

The AFM images of CZS and CZS/Au NPs layer thin films show a uniform granular surface morphology. The surface morphology of CZS thin films with varying Cu/Zn content was illustrated in the figure (4 a and c). It can be seen that the surface morphology results showed that the surface roughness increased from 1.95 nm for CZS (1:1:2) to 4.36 nm for CZS (1.4:0.8:2) thin films as shown in Table (2), the increases could be possibly due to the increasing of copper atoms concentration in the CZS thin films. The root mean square (RMS) of roughness increased with the increase of Cu/Zn content, which is in agreement with the results of researchers Edwin J [21] and Ali A [22]. The average grain diameter was estimated from the plane view images for pure CZS (68.99–92.7 nm) as illustrated in Table (2), where the granularity accumulation distribution shown in the figures (4 and 5)c. These results were in agreement with XRD results. The tilted image exposes grain heights of a few tens of nanometers, as shown in Table (2).
Figure 4. AFM images; (a) 2D, 3D and Granularity distribution of CZS (1:1;2), (1.2:0.8:2) and c: (1.4:0.6:2).

Figure 5. AFM images; (a) 2D, 3D and Granularity distribution of CZS (1:1;2)/Au , b: (1.2:0.8:2)/Au and c: (1.4:0.6:2)/Au NPs layer thin films.

The surface morphology of CZS/Au NPs layer thin films with varying Cu/Zn content was illustrated in the figures (4 and 5). The surface morphology results showed that the roughness decreased from (20.9 to 3.99) for CZS(1:1:2)/Au NPs and CZS(1.4:0.6:2)/Au NPs layer thin films respectively. The root mean square (RMS) (Sq) decreased with decreasing of Cu/Zn content and present of Au NPs layer, it can attributed to the interface between CZS and Au NPs layer, which is in agreement with the results of Vasuhi A [23] and Atanas K [24]. The average grain diameter was estimated from the plane view images for CZS/Au NPs layer (113.74–238.19 nm) as illustrated in Table (2), where the granularity accumulation distribution shown in the figures (4 and 5) c. These results were in agreement with XRD results. Also the images exposes grain heights of a few tens of nanometers, as shown in Table (2).

Finally it can be notice from the results in table (2) that the roughness (Sa), root mean square (Sq) and the average grain diameter of CuZnS (1:1:2) was increased with increase of Cu/Zn content, and with the present of Au NPs layer. Where it can contribute to the modification of the optical and electrical properties.
Table 2. Surface morphology measurements of CZS (1:1:2), (1.2:0.8:2) and (1.4:0.6:2) /Au NPs layer thin films.

| Sample           | C:Z:S content | Average Roughness (nm) | Root mean square (nm) | Tenpoint height (nm) | Average diameter (nm) |
|------------------|---------------|------------------------|-----------------------|----------------------|-----------------------|
| CZS              | 1:1:2         | 1.95                   | 2.47                  | 12.6                 | 68.99                 |
|                  | 1.2:0.8:2     | 3.04                   | 3.85                  | 10.7                 | 97.45                 |
|                  | 1.4:0.6:2     | 4.36                   | 5.1                   | 10.9                 | 92.70                 |
| CZS/Au layer     | 1:1:2/Au      | 20.9                   | 25.9                  | 78.8                 | 113.74                |
|                  | 1.2:0.8:2/Au  | 9.94                   | 13.6                  | 69                   | 238.19                |
|                  | 1.4:0.6:2/Au  | 3.99                   | 4.63                  | 15.4                 | 141.61                |

3.4 Optical properties

The optical Transmittance spectra depend on the chemical structure, crystal structure, the film thickness and the surface morphology of the films. Figure (6 a and b) shows the optical transmittance spectra of the CuZnS thin films as a function of wavelength. The spectra exhibit high transmittance value in the visible region and decreases from 57% to 51% beyond the absorption edge after increasing of Cu/Zn content. From the figure it can be notice that the optical transmittance is influenced by Cu/Zn content and absorption edge red shifted towards the long wavelength [21]. The transmittance was decrease with the increase of Cu/Zn content where the film with higher Cu content shows lower transmittance while the films with higher Zn content shows higher transmittance [3, 21]. The effect of increasing of Cu/Zn content in CZS thin film leads to formed structural defects [3, 24], and that agreement with XRD Result.

![Figure 6. Optical transmittance spectra of a. CZS, b. CZS/Au NPs layer thin films.](image)

The optical energy band gap for allowed direct transition of the prepared films (figure 7. a and b) is evaluated from the plot of $(\alpha h\nu)^2$ versus $h\nu$ using Tauc relation [25]:

\[
\alpha h\nu = \frac{E_g}{h\nu} \exp\left(\frac{E_g}{2k_B h\nu}\right)
\]
\[ ahv = B(hv - Eg)^r \]  

(4)

Where \( B \) is constant, \( r \) values for allowed direct and indirect transitions are 1/2 and 2 respectively. Where it was estimated by extrapolating the straight line portion of the Plot to the point \( \alpha = 0 \). The optical energy gap of the prepared CuZnS thin film was found to be decreases from (2.56 to 2.34 eV, and 2.62 to 2.32 eV) with respect to Cu/Zn content, and present of Au NPs layer. The lower band gap value corresponds to CuS phase and the higher band gap confirms the alloy nature of material [3, 26].

The decrement of the energy gap after increment of Cu/Zn content and the presence of Au NPs layer can be attributed to the redshift of the absorption edge and to the low crystallinity of the films, where the crystallite size of the prepared films is found to decreased with the increase of Cu/ Zn content, resulting in the decrease of the band gap of the samples. The obtained optical band gaps for CZS thin films are agreement with those reported by Sreejith M S [3], Mehdi A [17] and Sreejith M S [26].

4. Conclusions
In this study CZS and CZS/Au NPs layer thin films were successfully deposited by spray pyrolysis technique. From the structural, optical properties results, it can be concluded:
1. The crystal structure is satisfied with a cubic (sphalerite) for ZnS preferential orientation along (111) direction, while the CuS was crystallized in two phases (hexagonal CuS) and (monoclinic Cu2S). The film structures show low crystallinity, and it enhanced by Au NPs layer thin films. The crystallite size was increased with the increase of Cu/Zn Content.
2. The surface morphology of CZS and CZS/Au NPs layer thin film from SEM images seems relatively smooth and plated regularly and the stoichiometric ratio was proved by EDX spectra.
3. The atomic force microscope (AFM) images shows uniform and granular surface morphology thin films. The average roughness and the root mean square roughness (RMS) are decreased with the increasing of Cu/Zn content.
4. From the optical properties, the transmittance decreased with the increasing of Cu content and presence of Au NPs layer in the visible wavelength range 600-750 nm.
5. The optical results reveals that CZS thin films have direct energy gap (Eg), decreased with the increase of Cu/Zn content and with presence of Au NPs. The absorption edge red shifted towards long wavelength and the optical energy gap decreases to low values towards the middle of the visible region which make it suitable for optoelectronic and photodetector applications.
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