Hydrothermal Synthesis of Cu$_2$ZnSnS$_4$ Nanostructure and Their Application as H$_2$S Gas Sensor

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Abstract. In this study, Cu$_2$ZnSnS$_4$ (CZTS) nanostructure are successfully synthesized by using hydrothermal method. Structural, morphology, optical properties have been studied for thin films (CZTS) deposited via spin-coating method. X-ray diffraction show that the films have pure tetragonal- kesterite structure preferred orientation along (112). The FE- SEM shows that (CZTS) have a nano-sphere like structure, consist with diameters less than 35 nm. UV-Vis spectroscopy measurement showed that absorption coefficient ($\alpha > 10^4$ cm$^{-1}$) and the band gap energy is equal to 1.42 eV. The Sensitivity properties of (CZTS) samples for H$_2$S gas was tested at various operating temperature and found that the highest sensitivity is (83.63 %) at T=150 ºC.

Keywords: Cu$_2$ZnSnS$_4$; different solvent; hydrothermal; FE-SEM; optical properties; H$_2$S gas sensor.

1. Introduction
The Due to a rise in atmospheric pollution, there is a want to manufacture sensitive devices to discover and measure various hazardous gases. Actually, popular air pollution measurements are based on gas chromatography methods and steeply-priced optical spectroscopy. These methods are big, pricey and slow in interval of response times[1, 2]. Many articles had been centered on air pollutant gases, like CO, H$_2$, NH$_3$, NO$_2$, C$_3$H$_8$,CH$_4$, and H$_2$S, that make a contribution to the damage to human health, global warming and climate change[3]. The semi-conductor gas sensors are being used on Widely due to the little cost, simple manufacturing and high level of sensing as compared to the several sensor kinds such as, bio-chemical acoustic, optical in addition to different gas sensor devices [4].

Sensors play an essential role by the fields of ecological safeguard, emission notice, human health and general safety [5]. So, there is an urgent want to development more stable p-type material and it's used to design and manufacture cheap gas-sensors to detect various toxic explosive gases. Cu$_2$ZnSnS$_4$ is the suitable materials for ecological-appropriate application, because it's The elements are available in the Earth's crust , little-cost and non toxicity [6-8]. The Cu$_2$ZnSnS$_4$ combination is a good material having p-type electrical conductivity and It's also possess absorbance coefficient >104 /cm with direct band gap energy is between 1.4 –1.6 eV , It is an approximation to the optimal value to use in solar cells and good electrical properties suitable for photovoltaic applications [9,10].

Cu$_2$ZnSnS$_4$ can be manufactured easily by different methods [11-16 ], such as sol-gel, sputtering, thermal evaporation, spray pyrolysis, electro-deposition, hydrothermal method. also, the prime hurdle of these manufacture methods is a need of costly production, high annealing temperature, controlled
weather circumstances and condition of a more secure to clear the unsteadiness of as fabricated output. Though for dispose of those optimal conditions And get a good cost effective crystalline product an alternate hydro-thermal method is very favorite and it's an excellent choice of manufacture of CZTS. Also, this method provides smaller grain size, faster kinetics, easy setup, and low produce charge to synthesis of high quality Nano-crystalline add to individual morphology, structures [17].

Cu2ZnSnS4 has also been studied as a gas sensor however just for LPG gas sensor. Several groups of articles have achieved their behavior in gas sensing through the manufacture of polyaniline/(CZTS) [18], (PANI/CZTS) [19], (CZTS/ZnO) hetero-junctions [20] and Cu2ZnSnS4 thin films [21]. To our knowledge, no researches available on the use of Cu2ZnSnS4 nanostructure for H2S gas sensors. Being highly toxic gas H2S is a dangerous problem[22]. So as to contribution to the application of Cu2ZnSnS4 instead of the area of solar cells, we used them to monitor toxic gases. We present for the first time a report on the application of Cu2ZnSnS4 thin films in the H2S gas sensing. These films were characterized using X-ray diffraction (XRD) , Field emission scanning electron microscopy (FESEM) and UV-Vis spectroscopy. Characteristics of CZTS H2S gas sensor were studied at different operating temperatures with concentration of (25 ppm).

2. Experimental details
Cupric chloride (CuCl2), Zinc acetate dihydrate (Zn(CH3COO)2·2H2O), Tin(II) chloride dehydrate (SnCl2·2H2O) and thiourea (CS(NH2)2) were of analytical grade, used without any further purification. 2-methoxethanol was used for thin films preparation and characterization. Pure (CZTS) was synthesized by using hydrothermal method. In a typical synthesis, CuCl2 (0.112 mmol), Zn(CH3COO)2·2H2O (0.046 mmol), SnCl2·2H2O (0.044 mmol), and CS(NH2)2 (0.355 mmol) were added into 2-methoxethanol (30 mL) under continuous stirring to obtain a yellow solution. Then, the solution was transferred into a stainless steel autoclave (100 ml), heated to (200 °C) for (7 hours). Thereafter, the auto-clave was cooled at room temperature naturally. The centrifugation method was used to collect black precipitates after being washed with ethanol and deionized water and then dried in a vacuum at (70 °C) for (2 hours) to obtain CZTS nanoparticle powder and used for further experiments.

(0.01 g) of CZTS powder was dissolved in (15 ml) of 2-methoxyethanol and put these solutions in ultrasonic for (2 hours) to be well dispersed. Finally, these solutions are deposited on glass and silicon substrates by spin-coating technique to prepare thin film.

3. Results and discussion

3.1. Structural and morphology Properties
The XRD pattern of (Cu2ZnSnS4) thin film prepared from hydrothermal method is shown in Figure 1. The diffraction peaks are at 20 values of 28.5603°, 32.88°, 47.5644° and 56.1057° were identified to originate from (112), (200), (220 and (312) planes. All the peaks are indexed and found to be well matched to kesterite structure of (Cu2ZnSnS4) having tetragonal phase. The noticed diffraction peaks correspond to ASTM data (card number:26-0575). In addition, the most intense peak at 2θ=(28.5603°) which is referred to (112) plane[16,23-25].
The lattice parameter \((a, c)\) was found about 0.5403 nm and 1.0843 nm, respectively. These values of lattice parameter \((a,c)\) are consistent with the theoretical parameters [26,27].

**Table 1.** X-ray diffraction analysis of Cu$_2$ZnSnS$_4$ thin film.

| 2θ (degree) | (hkl) | \(d(Å^0)\) | \(β(\text{rad})\) | \(D_{\text{av}}\) (nm) | \(S\) | \(c\) |
|------------|-------|-------------|-----------------|-----------------|---|---|
| 28.5603    | (112) | 3.1229      | 0.0194          | 7.4             | 0.006 | 0.54028 | 1.08429  |

The grain size \((D_{\text{av}})\) of the thin films was calculated for the maximum intense peak (112) by the Debye–Scherrer formula [28]:

\[
D_{\text{av}} = \frac{0.9λ}{β\cosθ} \tag{1}
\]

where \(λ\) : wavelength of XRD (1.54056 Å for Cu Kα), \(θ\) : angle of Bragg diffraction and \(β\) : full width at half-maxima. The \(D_{\text{av}}\) by Scherrer of the sample are observed as 7.4 nm. To determine The average crystallite size \((D_{\text{av}})\) and micro-strain\((S)\) for the sample, the Williamson-Hall (WH)equation is generally used [29]

\[
β\cosθ = \frac{kλ}{D_{\text{av}}} + 4S\sinθ \tag{2}
\]

If \(β\cosθ\) along Y- axis is plotted versus \(4\sinθ\) along X-axis for all peaks, The \(D_{\text{av}}\) by W-H and \(S\) for film can be found from the y-intercept and slope respectively, which is shown in Figure 2. Values of the average crystallite size and micro-strain obtained from W-H plot have been tabulated in Table1.

The values of micro-strain were positive for the sample as illustrated in Table 1, which means the signature of tensile strain [30].
Field emission scanning electron microscopy (FESEM) is a versatile technique for studying morphology of materials. FESEM images prove the formation of nano-sphere structure as shown in Figure 3 with diameter less than 35 nm. The images disclose agglomeration of nano-sphere.

**Figure 3.** FE-SEM image of (Cu₂ZnSnS₄) thin film.

### 3.2. Optical Properties

The optical absorption and transmission spectra of the film have been studied by using UV-Vis-NIR absorbance spectra in the wavelength range (300–1100) nm at room temperature, the transmittance versus wavelength for the film as shown Figure 4a and It was found that The thin film has highly transmittance value of about (60%) in the visible area and near the infrared region of the electromagnetic spectrum. In addition to, Figure 4b shows that the optical absorbance value decreases with increasing wavelength.
Figure 4. Optical properties for (Cu$_2$ZnSnS$_4$) film.

The optical absorption coefficient ($\alpha$) versus photon energy ($h\nu$) of Cu$_2$ZnSnS$_4$ film as shown Figure 4c. It was observed that the prepared thin film has a high value of $\alpha > 10^4$ cm$^{-1}$, This indicates has an allowed direct transition.

The band gap energy ($E_g$) can be calculated by using the Tauc formula:

$$ (\alpha h\nu) = A(h\nu - E_g)^r $$

where $h\nu$ is the photon energy, $\alpha$ is the absorption coefficient, $E_g$ is the band gap energy, $A$ is a constant and $r$ is a number which indicates the transition type where $r$ is 2 for direct transition and $r$ is 1/2 for indirect transition [31]. (CZTS) has an allowed direct transition optical band gap ($r = 2$) [32]. Figure 4d shows the variation of $(\alpha h\nu)^2$ versus ($h\nu$) for the (Cu$_2$ZnSnS$_4$) thin film. The band gap energy ($E_g$) is found to be about 1.42 eV. This value is consistent with the band gap values of Cu$_2$ZnSnS$_4$ thin films reported in previous studies [33,34], and it's near to the best for solar cells and photovoltaic applications.

3. 3. Gas sensing results

Thin film sample is tested for H$_2$S toxic gas sensing at operating temperatures (RT, 100 and 150) °C with concentration of 25 ppm. Figure 5 show the change of resistance versus time with (on/off )gas valve at RT, 100 and 150 °C. The resistance increased when the gas valve is on, while, the resistance is decreases rapidly when the gas is off.
Figure 5. The change of resistance versus time at different operating temperatures for (Cu$_2$ZnSnS$_4$) thin film.

Table 2 shows the sensitivity value of the Cu$_2$ZnSnS$_4$ gas sensors to H$_2$S gas was calculated from equation[35]:

$$S = \left| \frac{R_g - R_a}{R_a} \right| \times 100\%$$  \hspace{1cm} (4)

Where, $R_g$ : the resistance of the sensor in target gas, $R_a$ : the resistance in air atmosphere.

Table 2. the sensing results of (Cu$_2$ZnSnS$_4$) thin film gas sensor at different operating temperatures ($T_{op}$).

| Operating Temperature ($^\circ$C) | Response Time (sec) | Recovery Time (sec) | Sensitivity % |
|-----------------------------------|---------------------|---------------------|---------------|
| RT                               | 4.68                | 0.86                | 4.38          |
| 100                              | 1.54                | 0.81                | 65.79         |
| 150                              | 0.78                | 1.58                | 83.63         |

With different temperatures (RT, 100 and 150 $^\circ$C). It was shown that the sensitivity increases with increasing operating temperature as shown Figure 6, reaches a maximum value about 83.63 % corresponding to an optimum operating temperature which is 150$^\circ$C for the sample. Table 2 also shows the relation between the response and the Recovery time as a function of operation temperature for Cu$_2$ZnSnS$_4$ thin film. The results obtained that the response time decreases with increasing the operation temperatures and showed the shorter time response about 0.78 s at 150 $^\circ$C. The response time is a very
important parameter at the gas sensor device, in addition to the sensitivity. The results shown above reveal the Cu$_2$ZnSnS$_4$ thin film is a promising candidate for H$_2$S sensor.

![Figure 6](image.png)

**Figure 6.** The sensitivity of (Cu$_2$ZnSnS$_4$) thin film at different operating temperatures.

### 4. Conclusion

In this paper, Cu$_2$ZnSnS$_4$ nanostructure are successfully synthesized via hydrothermal method. XRD results showed that all prepared films had a tetragonal structure, with preferred orientation of (112) for Cu$_2$ZnSnS$_4$. FESEM images confirmed the formation of CZTS nano-sphere. From Optical properties, it's found that the energy gap is about 1.42 eV. The maximum sensitivity was found about 83.63 % and the best response time is equal to 0.78 s, while, recovery time 15.8 s for the sample at 150 °C.

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