Impact of Solvent type on the Structural, Surface morphology and Optical energy gap of Kesterite Cu$_2$ZnSnS$_4$ thin films deposited by solvothermal method

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Abstract. In present work kesterite quaternary Cu$_2$ZnSnS$_4$ (CZTS) semiconductor thin films were prepared on fluorine-doped tin oxide (FTO) substrate by solvothermal method using different solvent types Ethylene glycol (EG), polyethylene glycol (PEG), and Ethylenediamine (ED). Crystal structure, surface morphology and optical characteristics of the prepared thin film were characterized by x-ray diffraction (XRD), Field emission scanning electron microscopy (FESEM), energy-dispersive X-ray spectroscopy (EDS) and UV–Vis absorption spectroscopies. X-ray diffraction results reveal that the deposited films have polycrystalline nature and in a kesterite phase (tetragonal structure). the crystallite size is in the rang (20-27) nm and the largest one is for the prepared by using PEG solvent. The films surface morphology shows smooth and uniform surface with well distributed spherical particles with largest particles for the films deposited by EG solvent. The EDS spectra confirmed the the existence of the elements Cu, Zn, Sn and S of the films composition. The direct optical energy gap shows different values caused by using different solvent type, where the lower band gap is about 1.56 eV and the largest is about 1.9 eV for the films using ED and EG respectively.

1. Introduction
Cu$_2$ZnSnS$_4$ Copper zinc tin sulfide CZTS or is a quaternary semiconductor which has attracted much attention for photovoltaic applications due to its special properties such as high absorption coefficient greater than (104 cm$^{-1}$) and direct band gap energy in the range 1.4–1.5 eV [1, 2]. There are many methods have been successfully used to prepare kesterite CZTS thin films and nanoparticles, such as RF magnetron sputtering and sulfurization by sulfur powder [3, 6], thermal co-evaporation [4], spray pyrolysis [5] sol–gel [6] hydrazine-based method [7], hydrothermal [8] solvothermal [9]. Kesterite CZTS is composed of relatively abundant and can be synthesized by a variety of vacuum based and nontoxic and solution-based techniques [10]. Due to its direct band gap this quaternary semiconductor is promising for solar energy conversion and photocatalysis applications [11]. The performance of the optical and electrical properties which mainly depend upon the crystal structure and composition of the absorber material it improves the performance e of is very sensitive a solar cell. in this paper, we report the influence of solvents on the preparation of CZTS semiconducting thin film on the structural, compositional and optical properties. This method is very suitable for large-scale fabrication of good-quality crystals while maintaining good control over their morphology and composition [12]. So the influence of solvent significantly affects the composition and structure of thin film which in turn affect the optical and electrical properties. It is generally assumed that the solvents act directing agents
as structure or soft templates, which can control the morphology and size of the particles formed in the solvothermal reaction through influencing their growth process and nucleation. In this study, the influence of solvents type on the preparation and characterization of CZTS semiconductor thin films was investigated for different applications.

2. Experimental part

At first the solution is prepared by adding 2 mmol of copper (II) chloride dihydrate (CuCl₂·2H₂O), 1 mmol of zinc (II) chloride (ZnCl₂) (v), 1 mmol of tin chloride dihydrate (SnCl₂·H₂O) (IV) and 4 mmol of thiourea (CH₄N₂S) to a baker containing 60 ml of Ethylene glycol. The solution was well mixed for a period of 60 min at room temperature using a magnetic stirrer until it well dissolved and transparent. The fluorine-doped tin oxide FTO substrates were cleaned using the following steps; immersed in a beaker containing isopropanol, acetone and distilled water respectively in ultrasonic cleaner for 10 min for each one. Finally the FTO substrates dried using air drier. The mixture is transferred in 50 ml Teflon containing FTO substrate placed inside a stainless steel autoclave in an oven at a temperature of 180°C for 5 h. The autoclave was naturally cooled at room temperature then a black color CZTS films were taken out from the Teflon-liner and rinse by double distilled water and dried in oven at temperature of 80 °C for 2 h. A similar experiment was carried out in another solvents Ethylenediamine and polyethylene glycol instead of Ethylene glycol to study the effect of solvent type on the properties of the CZTS thin films. The deposited thin films crystal structure were characterized by X-ray diffraction (XRD) technique using DX-2700BH multi-function diffractometer CuKα radiation. The morphological and compositional analysis of the deposited films were carried out using Hitachi SU3500 scanning electron microscopy SEM with EDX and the optical studies of the samples were performed using Mega 2100 debacle beam spectrometer.

3. Results and discussion

3.1. XRD analysis

Figures (1) the XRD patterns of CZTS thin films prepared using Ethylene glycol, Ethylenediamine and polyethylene glycol as solvents. The patterns showed a polycrystalline structure nature and exhibits a diffraction peaks at 2θ of 29.56°, 28.38° and 27.46° corresponding to the (103) and (112) diffraction planes and the peaks at 2θ of 37.90°, 37.65° and 38.73° corresponding to the (211) reflection plane of CZTS kesterite (tetragonal) structure for CZTS films prepared using EG, ED and PEG solvents respectively. Whereas a diffraction peak at 2θ of 16.44° corresponding to the (002) plane and a new phase of Cu₂S was observed at 2θ of 13.88° corresponding to the (111) plane in the CZTS film using PEG solvent. All diffraction peaks of CZTS and Cu₂S were confirmed using the standard data of JCPDS using (Card No. 26-0575) and (33-0490) respectively. The lattice constant were calculated and found to be a= 5.32 Å, 5.41 Å and c=10.77 Å, 10.87 Å for the samples prepared using EG, ED and PEG solvents respectively as shown in Table 1. This results show that solvent plays a crucial role in the formation of CZTS compound [13]. The mean crystallite size D is determined according to the Scherer’s equation [16]:

\[ D = \frac{k \lambda}{\beta \cos \theta} \]  

Where k is the shape factor (0.9), \( \lambda \) is the X-ray wavelength (for CuKα radiation \( \lambda = 1.5406 \) Å), \( \beta \) is the full width half maximum (FWHM) in radian and \( \theta \) is the diffraction angle. The calculated mean crystallite sizes are 20.95 nm, 20.93 nm and 27.51 nm for CZTS thin film prepared using EG, ED and PEG solvent respectively as shown in Table 1. This results show that solvent plays a crucial role in the formation of CZTS compound [13]. The other structural property is the dislocation density (δ) which defined as the number of dislocation lines per unit area in the crystal and can be determined using the formula below [17]:
As shown in Table (1), the highest and the lowest values of dislocation were found in the CZTS film prepared using ED and PEG solvents respectively and related to the crystallinity of the films structure and present of more crystal defects in the CZTS lattice. The lattice micro-strain (ε) is the percentage of deformation of the material during the growth of the film or arises from expansion or compression and can be calculated from the following relation [18,19]:

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

Where (β) is the peak full-width half maximum, and (θ) is Bragg's angle of the peaks. It can be noticed that the lattice micro-strain (ε) has a large value in the lattice of the prepared films using EG and ED solvent while the lowest strain value in the lattice of that prepared using PEG as a solvent. Where the type of the micro-strain changes can be attributed to the crystallization process in polycrystalline thin films [19, 20].
Figure 1. X-ray diffraction pattern of CZTS thin films deposited using PEG, EG and ED solvents.

Table 1. Structural Parameters of CZTS thin film Obtained from XRD Data as a Function of Preparation Solvents.

| Solvents | Crystallite Size D (nm) | Dislocation Density (δ) (lines/m²) × 10^{15} | Micro Strain(ε) × 10^{-3}nm^{-2} | FWHM |
|----------|------------------------|---------------------------------------------|---------------------------------|-------|
| P.E.G    | 27.519                 | 1.32                                        | 1.26                            | 0.306 |
3.2. Surface morphology analysis
All the film surfaces appear to be smooth and densely packed with grains uniformly distributed. The improved surface morphology could be attributed to the relationships between growth, and activation energy of the thin films. The films surface morphology shows smooth and uniform surface with well distributed spherical particles with largest particles for the films deposited by EG solvent. The EDS spectra confirmed the existence of the elements Cu, Zn, Sn and S of the films composition as shown in figure 3.

![Figure 2. SEM image with two scale of magnification for CZTS thin films deposited using PEG, EG and ED solvents.](image-url)
3.3 Optical Properties of CZTS Nanostructures Thin Films

Absorbance spectra of CZTS thin films prepared by solvothermal method using different types of solvents EG, ED and PEG are shown in figure 4. The spectra revealed high absorbance at the visible spectrum between (500-700) nm corresponding to absorption edge of CZTS thin films. It can be seen the prepared films using Ethylenediamine ED solvent has the highest absorbance and the absorption edge shifted towards the long wavelength and low energies, while the absorbance of the film prepared using PEG solvent shows the lower absorbance. This absorbance behavior can be attributed to the crystal of the different, where the sample from ED solvent has lowest crystallite size and highest dislocation density where the defects state play important role increase the a the absorption of the film. In the other hand the CZTS film prepared using PEG solvent has the crystal size and lowest dislocations which leads to lower absorbance and higher transmittance and band gap, these results are in consistence with the literature [9, 13]. Also the variation in the surface topography and surface texture which formed different growth mechanisms leads to different surface texture and different particles and grains shape as shown in figure (2).

Physically, Eg is the energy required to break a bond in the semiconductor to free an electron to the conduction band and leave a hole in the valence band. The optical energy band gap for allowed direct transition of the prepared films Figure (5) is estimated from the plot of $(\alpha h\nu)^{2}$ versus $h\nu$ using Tauc relation [20]:

$$a\nu = A(h\nu - E_g)^{\frac{1}{2}}$$

(4)
Where α is the absorption coefficient and A is a constant. The direct energy gap of CZTS films is determined by extrapolating the straight-line portion of the Plot to the point α = 0. The optical energy band gap of CZTS Nanostructures thin films prepared using ED, EG and PEG solvent was found to be (1.52, 1.6 and 1.78) eV respectively. As previously discussed the energy gap value was depended on the growth mechanism which depend on the solvent type affect growth chemical reaction inside the autoclave with the present of high temperature and high pressure which produced a certain structure, morphology and particle shape. The CZTS film with high crystallinity and high crystallite size (low defects) exhibits broadened energy gap as in the CZTS (PEG) film (1.78 eV) whereas the CZTS films using ED and EG solvent with low crystallite size and high dislocation (defects) exhibits lower bang gap of be (1.52, 1.6) eV respectively. The results was in a good agreement with the literature [9, 13, 21].

![Figure 5. The variation of (αhυ)^2 Vs. hυ (Tauc relation) for CZTS thin films prepared using Eg, ED and PEG solvents.](image)

4. Conclusions
In this work one-pot solvothermal route to synthesize Cu$_2$ZnSnS$_4$ (CZTS) nanocrystalline thin films are reported and a low-cost, non-toxic and convenient method. The effects of solvothermal solvent on the structure, morphology and optical properties of the synthesized films were investigated. The results showed that the crystallinity, morphology and surface texture of the CZTS thin film was influenced by the solvothermal type solvent. Where by the solvent type it can be controlled the optical energy gap and the absorption edge which in turns leads to control the application quality and efficiency such as the optoelectronic devices and solar cell conversion e efficiency.

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