



## Structural and optical properties of $\text{Cu}_2\text{ZnSnS}_4$ films deposition by screen coating technique of sol-gel process

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### Abstract

$\text{Cu}_2\text{ZnSnS}_4$  films have been successfully made by Sol-Gel process. Precursors of  $\text{CuCl}_2$ ,  $\text{ZnCl}_2$ ,  $\text{SnCl}_2$  and  $\text{SC}(\text{NH}_2)_2$  were mixed in 2-methoxyethanol with monoethanolamine added to stabilizer.  $\text{Cu}_2\text{ZnSnS}_4$  film was deposited on glass slides by screen coating technique and annealed temperature at 473 K, 573 K, 673 K and 773 K without sulfurization to study formation the phase. The result was tetragonal kesterite crystal structure at the planes (1 1 2), (2 0 0), (2 2 0), (3 1 2) and (1 1 2) show tetragonal structure and peak according to PDF Card-00-026-0575. The lattice constants were  $a = 5.413 \text{ \AA}$  and  $c = 10.771 \text{ \AA}$  and crystallite size 30.931 nm at annealed temperature 773K are in good agreement value as close to the values reported. Absorbance spectrum results not found pronounced peak at temperature under 773 K.

**Keywords:** CZTS, Copper Zinc Tin Sulfide, TFSCs, Wet-gel, Absorb layer

### 1. Introduction

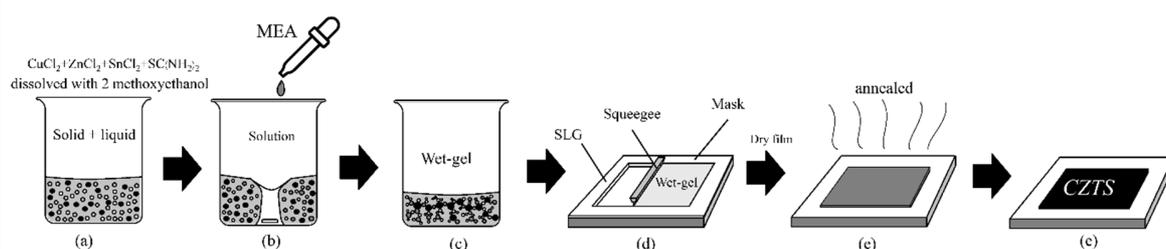
The  $\text{Cu}_2\text{ZnSnS}_4$  (CZTS: copper zinc tin sulfide) thin film is an absorb layer of thin film solar cells (TFSCs). The CZTS comprising only abundant and non-toxic elements thus making has received attracting significant attention for low-cost photovoltaic applications [1]. The CZTS is good absorption the photon of wavelengths ranges of visible light almost entirely over  $10^4 \text{ cm}^{-1}$  [2], p-type semiconductor, direct optical band gap energy of 1.4–1.5eV [3] and can also deposition on flexible substrate [4] can be used in various applications. The optical and electronic properties similar to  $\text{CuInGaS}_2$  (CIGS: copper indium gallium selenide) including crystal structure. The crystal structure of CIGS is chalcopyrite structure and crystal structure of CZTS is kesterite structure and stannite structure. The high price and availability of indium in CIGS thus the CZTS have been studied to replace

CIGS [13]. The numerous techniques can synthesis of CZTS thin films in the based deposition techniques of vacuum co- sputtering [14], RF magnetron sputtering [15], thermal evaporation [16], pulsed laser deposition [17] and non-vacuum such as sol–gel process [6], spin coating [7, 18], spray pyrolysis dip coating [8] and nanoparticles ink [10]. In recently, we have tried to prepare CZTS solution report by but the Chung,et.al [6] experimental result, we got a wet-gel of sol-gel process. Therefor the technique that is possible and reasonable to make the film by screen coating technique.

In this research, we study CZTS film by screen coating technique with wet-gel from sol-gel process. Gel was mixed form chloride precursor such as copper (II) chloride dehydrate, zinc (II) chloride, tin (II) chloride and thiourea dissolved with 2-methoxyethanol (2-metho) and monoethanolamine (MEA) to evaluate the possibilities of film CZTS to applied as an absorb layer of photovoltaic applications in the further.

## 2. Materials and Methods

Firstly, mixed chloride precursor consists of copper (II) chloride dehydrate ( $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ ) 99% , zinc (II) chloride ( $\text{ZnCl}_2$ ) 98%, tin (II) chloride ( $\text{SnCl}_2$ ) 98% and thiourea ( $\text{SC}(\text{NH}_2)_2$  ( $\text{C}_3\text{H}_8\text{O}_2$ ) 99.8% [6] stirrer at 1500 RPM for 30 minute, temperature control at  $80^\circ\text{C}$ , drop by drop monoethanolamine (MEA) 99% to stabilizer until the precursor solution transform to wet-gel. After complete the process we will got turbid yellow wet-gel and leave it 12 hr. Secondly, the glass substrate size of  $2.5 \times 2.5 \text{ cm}^2$  was clean by deionized water and acetone before coating. The wet-gel was deposited on the glass by screen coating technique. After screen coat, film was being dried with hot air. Then, the samples were annealing in the vacuum tube furnace under argon atmosphere at temperature 473K, 573K, 673K and 773K for 30 min. to study the formation phase and gradually rising  $10\text{K}/\text{min}$ . Finally, the phase formation patterns of CZTS film were studied by using an X-ray diffractometer (Shimadzu, XRD-6100) with  $\text{CuK}\alpha$  radiation (  $1.54056 \text{ \AA}$  ) at range between  $20^\circ$ – $80^\circ$  and studied the spectral absorbance by UV-Vis Spectrophotometer (Shimadzu, UV-1800). The experinetal detials show in Fig.1.



**Fig.1** the experimental detail of CZTS screen coating technique (a) mixed the precursor by solid-liquid process (b) drop the monoethanolamine (MEA) to stabilizer (c) the wet-gel product (d) coat wet-gel on soda lime glass (SLG) inside the mask (e) annealed the wet-gel in furnace vacuum tube in sulfurization atmosphere (e) the CZTS film

### 3. Results and Discussion

#### Characteristics of crystal structure

The XRD analysis of CZTS film synthesized by using sol-gel process shown in Fig. 2 the samples annealed at temperature 473 K, 573 K, 673 K and 773 K for 30 have peaks corresponding to the planes (112), (200), (220), (312) and (112), the peak show good crystallinity and confirms the formation of CZTS phase according to PDF Card-00-026-0575. Besides, the phase formation of CZTS film shows tetragonal crystal lattices types which observed with (112) and (220) plane each of samples, indicating kieserite crystal structure. In the Fig. 2, the XRD pattern of sample annealed at temperature 473 K have best match peak but the sample annealed at temperature 573 K have a peak broadens show phase formation not yet fully and the higher temperature have peak moves shown a uniform strain peak increased. The interestingly pattern of sample annealed at 773 K show characteristics phase formation to sharp peak demonstrates the larger grains size when the higher temperature and the formation of the film increases. The lattice constant was  $a = 5.413 \text{ \AA}$  and  $c = 10.771 \text{ \AA}$  at annealed temperature 773 K are in good agreement value as close to the values reported lattice parameter  $a = 5.427 \text{ \AA}$  and  $c = 10.848 \text{ \AA}$  of PDF Card - 00-026-0575. The unit cell volume was calculated from equation;

$$V = a^2c \tag{1}$$

The observed hkl planes in shown tetragonal structure of CZTS in Table 1. The presence of the sharp peaks in diffractogram of annealed at higher temperatures suggests the polycrystalline and a larger crystallite size of the film. There is also the formation of CZTS have peak similar CZTS crystal structure The grain size or crystallite size of CZTS films was calculated by Scherer's equation;

$$D = \frac{K\lambda}{\beta \cos \theta} \tag{2}$$

Where D is grain size, K is a shape factor,  $\lambda$  is the wavelength of X-ray radiation,  $\beta$  is the full width at half maximum (FWHM) of the peak (radian) and  $\theta$  is the Bragg's angle. The strain ( $\epsilon$ ) was calculated by equation;

$$\epsilon = \frac{\beta \cos \theta}{4} \tag{3}$$

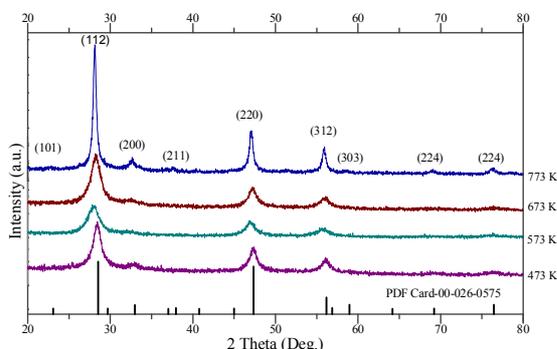


Fig. 2 XRD pattern of CZTS films annealed at 473 K, 573 K, 673 K and 773 K show the phase to tetragonal crystal structure types.

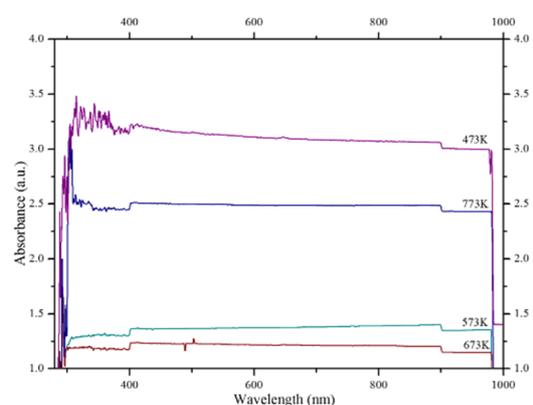


Fig. 3 the absorption spectra of the CZTS film in the wavelength range from 280 nm to 1000 nm.

**Table 1** Detail about quantity precursor [6]

Precursor	Quantity	Unit
Copper (II) chloride dehydrate (CuCl <sub>2</sub> ·2H <sub>2</sub> O)	7.4661	g
Zinc (II) chloride (ZnCl <sub>2</sub> )	3.0561	g
Tin (II) chloride (SnCl <sub>2</sub> )	4.1652	g
Thiourea (SC(NH <sub>2</sub> ) <sub>2</sub> )	13.4261	g
2-methoxyethanol (2-metho) (CH <sub>3</sub> OCH <sub>2</sub> CH <sub>2</sub> OH)	50	ml
Monoethanolamine (MEA) (NH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> OH)	5	ml

### Characteristics of the optical properties

Absorbance spectra of CZTS film are shown in Fig. 3. The topography of the film is thick and opaque. The CZTS film was studied for absorption of light wavelength in the range between 280 nm to 1000 nm. The pattern spectra reveal that have low absorbance in the visible and near infrared regions. The absorbance spectrum was calculated by equation;

$$A = \log_{10} \%T \quad (4)$$

After annealed, the film has very thick ness and porous on surface film. May result in the effects of the gel stiffness for coating has air bubble on surface on sample and coated film in a normal atmosphere, as a result of deviation analysis, Which are also the bubbles in the gel. The absorbance spectrum hasn't found pronounced peak, which are shows characteristic of the film is very thick. However, this process can be improved in the future.

### 4. Conclusion

The CZTS wet-gel was deposited on glass slides by a screen coating technique. The XRD pattern show tetragonal structure of planes (112), (200), (220), (312) and (112) and peaks according to PDF Card-00-026-0575. The lattice constants were  $a = 5.413 \text{ \AA}$ ,  $c = 10.771 \text{ \AA}$  and crystallite size 30.931 nm at annealed temperature 773 K are in good agreement value. The physical surface of CZTS films have a porous on sample annealed at temperature 573 K. The CZTS film has larger grains size when the higher temperature. The UV-Vis spectra does not show pronounced peak and demonstrated very thickness of the film observes by physical surface. However, there is still a possibility to bring the CZTS gel of sol-gel process to coat the film by screen coating technique, if annealing at higher temperature between about 773 K -823 K and control the thickness of film to will be phase of CZTS to nearby more.

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