

Effects of the sulfurization temperature on sol gel-processed $\text{Cu}_2\text{ZnSnS}_4$ thin films

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Abstract

As a promising and alternative solar absorber material, the copper–zinc–tin–sulfide compound ($\text{Cu}_2\text{ZnSnS}_4$) has been drawing attention in recent years for the production of cheap thin-film solar cells owing to the high natural abundance and non-toxicity of all the constituents, a tunable direct-band-gap energy and a large optical absorption coefficient. In addition, to overcome the problem of expensive vacuum-based methods, solution-based approaches are being developed for $\text{Cu}_2\text{ZnSnS}_4$ deposition. In this study, we have produced $\text{Cu}_2\text{ZnSnS}_4$ thin films via the sol–gel technique and subsequent sulfurization. The effects of the sulfurization temperature on the structural, morphological, compositional and optical properties of the films were investigated. X-ray diffraction and Raman spectroscopy analyses confirmed the formation of phase-pure CZTS films. The crystallinity of the films increased with an increasing sulfurization temperature. From the surface images and the results of the composition analysis, it was found that the films are uniform, composed of homogeneously distributed grains and have compositions with Cu deficit. The values of the optical absorption coefficients for the films were found to be 10^4 cm^{-1} based on absorbance spectroscopy. The optical band-gap values were estimated to be between 1.32 and 2.27 eV depending on the sulfurization temperature.

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1. Introduction

The development of green-energy resources as an alternative to carbon-based fuels has become one of the most important duties assigned to researchers in recent years. Among the diverse forms of renewable energy sources, solar energy is the best option, as it can meet the energy demands of modern society [1]. Lately, the production of solar cells has increased significantly due to a rapid increase in demand for renewable energy sources. In order to make photovoltaic devices more widespread, cheaper, more efficient, green solar cells have to be developed [2]. Silicon is the most commonly

used material in commercial solar cells: about 80% of the photovoltaic market is silicon-based devices. The production of highly efficient silicon solar cells requires the use of mono-crystal silicon wafers, which dramatically increases the production costs. Moreover, silicon is an indirect-band-gap semiconductor and its absorption coefficient is relatively low, requiring the absorption layer to be at least 100 μm thick in order to absorb a significant fraction of the incoming solar spectrum. As a result of these problems, the electricity produced by solar cells is still expensive compared to that produced by fossil fuels [2,3].

Thin-film chalcogen materials, especially CuInSe_2 (CIS), $\text{CuInGa}(\text{S},\text{Se})_2$ (CIGS) and CdTe , are currently used in the production of large-scale, commercial photovoltaic devices. However, the scarcity of indium and tellurium in the earth's crust limits the future of CIGS- and CdTe -based solar cells. In addition, the price of In and related solar-cell production

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costs will increase in the near future due to the extensive use of indium in display technologies and opto-electronic devices. Another problem with CdTe-based solar cells is that the cadmium (Cd) is very toxic to health and the environment. This problem has led researchers to search for more abundant and greener materials. Because of its similar properties to the CIGS compound, the $I_2-II-IV-VI_4$ group has been receiving attention as a new-generation absorber material. The Cu_2ZnSnS_4 (CZTS) compound is a good candidate for photovoltaic applications as an absorber layer [4–7]. CZTS has a direct band gap ranging from 1.4 to 1.6 eV which is close to the optimum value required for a single junction solar cell's absorber layer, a high absorption coefficient at the visible solar spectrum wavelengths and a p-type conductivity [8]. However, even though it is a promising absorber material, the studies on CZTS-based solar cells are at an early stage [3]. An efficiency of 9.6% has been reported for CZTS-based solar cells in laboratory conditions [9]. But in view of the fact that the theoretical efficiency of CZTS is about 32.2% [10], more studies are required to increase the efficiency and to develop economical production methods, which would ensure successful commercialization [11]. CZTS thin films have been prepared via various methods such as physical vapor deposition [3,5,7,12–20], electrochemical deposition [2,21–23], sol–gel [24–33] and successive ionic layer adsorption–reaction methods [34–38]. Aqueous solution deposition methods have several advantages, very important one being that a variety of thin films can be grown at low temperatures using cheap manufacturing equipment. The sol–gel method is a very simple and low-cost process based on hydrolysis and poly-condensation reactions. Sulfide films can be directly obtained by sulfurizing oxyhydrate precursors. To date, several groups have reported CZTS thin films produced via the sol–gel method. To the best of our knowledge, the first sol–gel-grown CZTS films were reported by Tanaka et al. [31]. They prepared CZTS films by annealing oxyhydrate precursors in a N_2+H_2S toxic gas atmosphere. Yeh et al. [32] prepared CZTS films by using metal chlorides with thiourea and investigated the effects of annealing between 160 and 320 °C in air. Fischereder et al. [29] deposited CZTS films on ITO-coated glass substrates by using thioacetamide as a source of sulfur. They studied the influence of vacuum annealing temperatures (180–450 °C) and the concentration of thioacetamide in precursor solutions. Park et al. [31] fabricated CZTS thin films via the sol–gel method and then annealed the samples at temperatures above 500 °C in a N_2 atmosphere without any sulfur source. However it is still necessary to improve the quality of sol–gel-processed CZTS films and to find non-toxic ways to tolerate sulfur loss during annealing. In our study, we prepared high-quality, dense CZTS thin films on quartz-glass substrates using the sol–gel spin-coating method. To tolerate sulfur loss during annealing, the annealing process was carried out in a vacuumed quartz tube containing elemental sulfur which is a non-toxic material. We investigated the effects of sulfurization temperature on the structural, morphological, compositional and optical properties of the films.

2. Experimental

The CZTS precursor solution was prepared by dissolving copper (II) acetate monohydrate (0.3 M, 98+%), zinc (II) acetate dihydrate (0.3 M, 99.99%), tin (II) chloride (0.3 M, 98%) from Sigma Aldrich and thiourea (1.2 M, 99.0+%) from Sigma Aldrich into 2-methoxyethanol (20 ml, 99.8% from Sigma Aldrich). The final solution was stirred at 45 °C, 850 rpm for 1 h to dissolve the metal compounds completely. During stirring, 2 ml of diethanolamine (DEA) was dropped slowly into the solution as a stabilizer. A quartz glass slide was used as a substrate which was ultrasonically cleaned in turn with detergent, nitric acid (1:4), acetone and ethanol for 10 min.

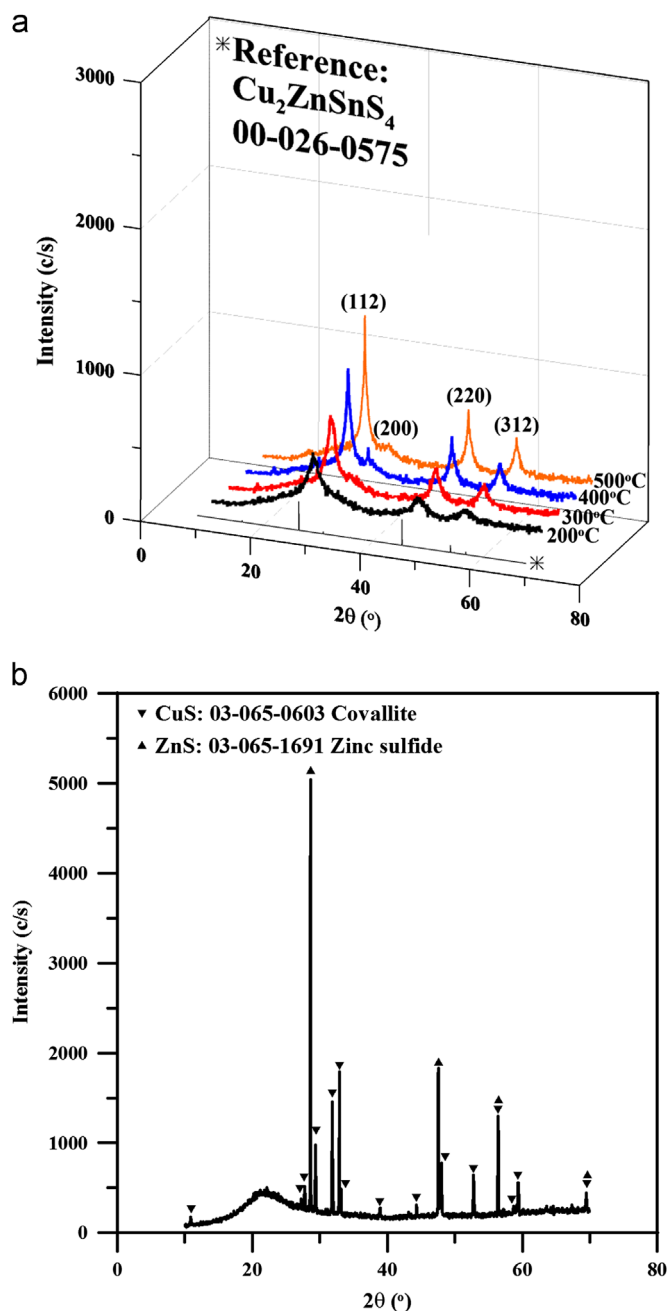


Fig. 1. XRD patterns of the CZTS samples sulfurized at (a) 200 °C, 300 °C, 400 °C and 500 °C and (b) 700 °C.

Table 1
Illustrative elemental compositions of the CZTS films obtained by semi-quantitative energy-dispersive X-ray spectroscopy (EDXS) analysis.

Elements	200 °C		300 °C		400 °C		500 °C		700 °C	
	a.f. (%)	N=8 ^a	a.f. (%)	N=8 ^a	a.f. (%)	N=8 ^a	a.f. (%)	N=8 ^a	a.f. (%)	N=8 ^a
Cu	19.1	1.5	19.4	1.6	19.1	1.5	20.1	1.6	30.2	1.6
Zn	16.2	1.3	14.5	1.2	15.0	1.2	16.2	1.3	26.0	1.3
Sn	16.5	1.3	16.4	1.3	15.8	1.3	14.6	1.2	0.0	0.0
S	48.3	3.9	49.7	4.0	50.2	4.0	49.2	3.9	43.8	3.9
Cu/(Zn+Sn)	0.6		0.6		0.6		0.7			
Zn/Sn	1.0		0.9		0.9		1.1			

^aComposition normalized on 8 atoms per formula unit of Cu₂ZnSnS₄.

To produce the CZTS film, the prepared solution was spin-coated onto a quartz substrate at 3000 rpm for 30 s followed by solvent-drying at 175 °C for 10 min on a hot plate. The spin-coating and solvent-drying processes were repeated 10 times to obtain the desired thickness of the film. The sample was cut into five pieces for the investigation of the effects of the sulfurization temperature. Finally, the samples were subjected to an annealing process for 2 h at a temperature between 200 and 700 °C in a quartz tube containing 10 g of elemental sulfur. Before the annealing, the tube furnace was evacuated to 5×10^{-4} mbar. The heating rate was 5 °C/min. After the annealing process, the samples were allowed to cool naturally to room temperature.

The crystal structure, surface morphology, chemical composition and optical properties of the samples were examined by field-emission-scanning electron microscopy (FEG-SEM, Jeol JSM-7600F), energy-dispersive X-ray spectroscopy (EDS, Oxford Instruments ISIS 300), X-ray diffraction (XRD, PANalytical X'Pert PRO MPD with the wavelength of 1.5418 Å Cu K α radiation), Raman spectroscopy (Confocal raman spectrometer, Witec alpha 300 with 532 nm light source), and absorbance spectroscopy (UV/vis/NIR spectroscopy, Lambda 950 with a 150 mm integrating sphere) methods.

3. Results and discussions

3.1. Structural studies

The structural characterization was performed using X-ray diffraction (XRD) and Raman techniques. The diffraction patterns were obtained with a 40 kV operating voltage and a current of 35 mA. The step size and scan step time were 0.0330° and 1 s, respectively. Fig. 1 shows the obtained XRD patterns of the CZTS samples sulfurized at temperatures between 200 and 700 °C. In the patterns of the samples sulfurized at 200–500 °C

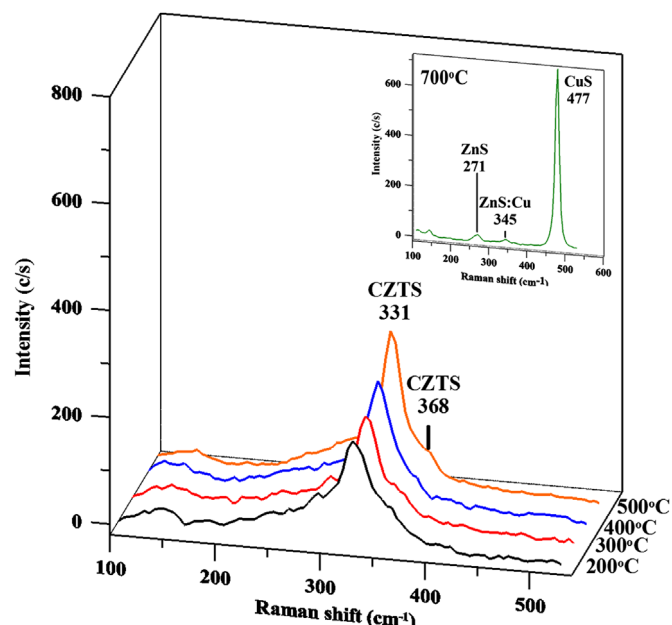


Fig. 2. Raman spectroscopy analyses of the samples.

(Fig. 1a), four clear peaks were observed at $2\theta=28.49^\circ$, 32.17° , 47.37° and 56.15° . The patterns of the samples match very well with $\text{Cu}_2\text{ZnSnS}_4$ (JCPDS 00-026-0575: Tetragonal, $a=b=5.427$ nm, $c=10.848$ nm, and I-42m). Peaks corresponding to the (112), (200), (220) and (312) planes indicate the polycrystalline nature of the films. No other prominent peaks were observed, which suggests that no secondary phases were present.

From Fig. 1a we can see that the degree of crystallinity of the CZTS films increased with the sulfurization temperature. A part of the resulting CZTS was sulfurized at 700°C to see how temperatures above 500°C affect the structure of the CZTS film. Fig. 1b shows the XRD pattern of the sample sulfurized at 700°C . It is clear that this pattern is completely different from the XRD patterns of other samples sulfurized at lower temperatures.

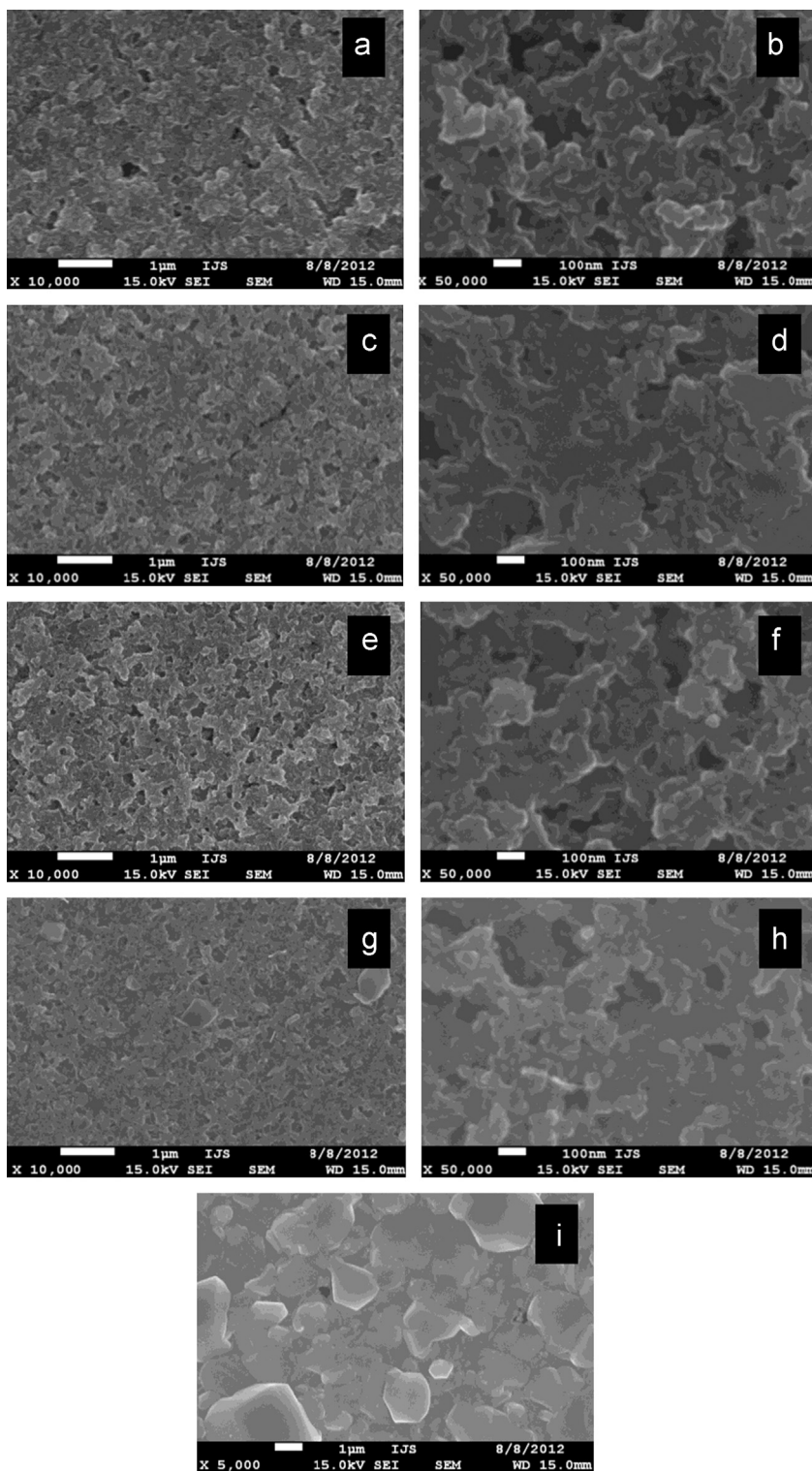


Fig. 3. Top view FEG-SEM images of the CZTS films sulfurized at (a, b) 200°C , (c, d) 300°C , (e, f) 400°C , (g, h) 500°C and (i) 700°C .

All the peaks observed in Fig. 1b can be attributed to CuS (JCPDS 03-065-0603, covallite) and ZnS (JCPDS 03-065-1691, zinc sulfide). According to previous studies on CZTS [39–41], tin losses with significant rates occur at temperatures of 550 °C and above. Therefore, the changes at 700 °C can be attributed to tin loss from the CZTS lattice. The results of the EDXS analysis also support this attribution (Table 1). The mean crystallite sizes of the CZTS films were estimated using Scherrer's formula [42]

$$D = \frac{0.94\lambda}{\beta \cos \theta} \quad (1)$$

where λ is the wavelength of the X-ray radiation, θ is the Bragg angle of the related peak, and β is the angular width of the peak at FWHM. The estimated results are 3.6, 6.0, 9.3 and 11.9 nm for the samples sulfurized at 200, 300, 400 and 500 °C, respectively. The increasing crystallite size with sulfurization temperature can be attributed to an enhancement occurring in the lattice structure of the films. Binary or ternary sulfides such as ZnS, Cu_{2-x}S and Cu_2SnS_3 have similar diffraction patterns to those of CZTS owing to their similar zinc blende-type structures. To prove the phase purity or to detect the presence of other possible secondary phases, Raman spectroscopy analyses of the samples over the range 200–500 cm^{-1} were also made and the results are given in Fig. 2. In the Raman spectrum, an obvious major peak at 331 cm^{-1} and a minor peak at 368 cm^{-1} can be clearly seen. This spectral data is in good agreement with the reported Raman spectra of CZTS [43–45] and confirms the formation of the CZTS phase. Moreover, the strong major peak is an indication of the good crystalline quality of the compound. It is noticeable that the peaks at 351 and 274 cm^{-1} corresponding to ZnS, the peak at 475 cm^{-1} corresponding to Cu_{2-x}S and the peak at 345 cm^{-1} corresponding to ZnS:Cu [13,15,46] do not appear, suggesting the absence of these compounds. The Raman spectra of the sample sulfurized at 700 °C are seen in the inset of Fig. 2. The peaks indicate the formation and presence of Cu–Zn–S phases. This spectrum also proves the decomposition of the CZTS resulting from tin loss.

3.2. Surface morphology and compositional study

Top-view FEG-SEM images of the CZTS films are shown in Fig. 3. They reveal that the CZTS films sulfurized at temperatures between 200 and 500 °C are uniform and composed of homogeneously distributed grains with a size of about 100 nm. As discussed in the previous section, the sample sulfurized at 700 °C is composed of Cu–Zn–S phases due to tin loss. It is clear from Fig. 3 that this decomposition deteriorates the surface morphology of the sample. The results of the semi-quantitative, energy-dispersive X-ray spectroscopy (EDXS) analysis, which just illustrate the elemental composition of the CZTS films, are presented in Table 1. They clearly indicate that the CZTS films sulfurized at temperatures between 200 and 500 °C have a deficit of Cu. Several groups reported that Cu–Zn–Sn–S compounds should be grown under slightly Cu-poor and Zn-rich conditions to

improve the optoelectronic properties of the film and to prevent the formation of Cu_{2-x}S or other binary/ternary phases. Katagiri et al. [5,16,47,48] achieved efficiencies of 1.08%, 3.93%, and 6.77% using Cu-poor absorber layers. Chen et al. [49] found that Cu-poor conditions improved the efficiency of CZTS solar cells. The Cu deficit enhances the formation of Cu vacancies, which give rise to shallow acceptors. Another reason to use a copper-poor composition is the loss of tin, mainly in the form of SnS, which occurs during the sulfurization process [50].

3.3. Absorption behavior

The absorption coefficient (α) of the films was calculated from the measured values of the reflectance (R) and transmittance (T) data using the relation [51]

$$\alpha(\lambda) = \frac{1}{t} \ln \left[\frac{1-R(\lambda)}{T(\lambda)} \right] \quad (2)$$

where α is the absorption coefficient, t is the thickness of the sample and λ is the photon wavelength. The calculated absorption coefficient values are on the order of 10^4 cm^{-1} . Near the absorption edge or in the strong absorption zone of the transmittance spectra, the absorption coefficient is related to the optical energy gap E_g by the power-law behavior of Tauc's relation [52]

$$(\alpha h\nu) = B(h\nu - E_g)^m \quad (3)$$

where B is an energy-independent constant, E_g is the optical band-gap energy and m is an index that characterizes the optical absorption process and is theoretically equal to 2 and 1/2 for the indirect and direct allowed transitions, respectively. Figs. 4 and 5

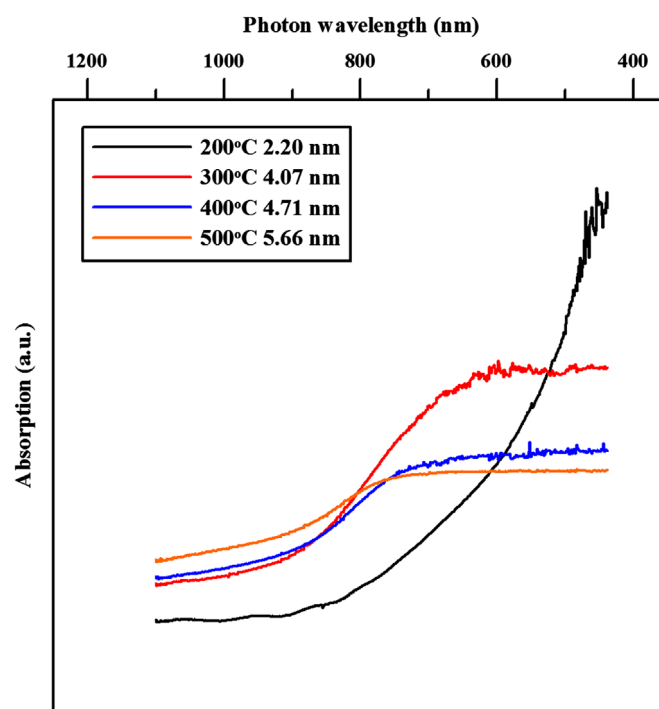


Fig. 4. Plots of optical absorption vs photon wavelength of the CZTS films sulfurized at different temperatures. Estimated crystallite sizes are given in the legend.

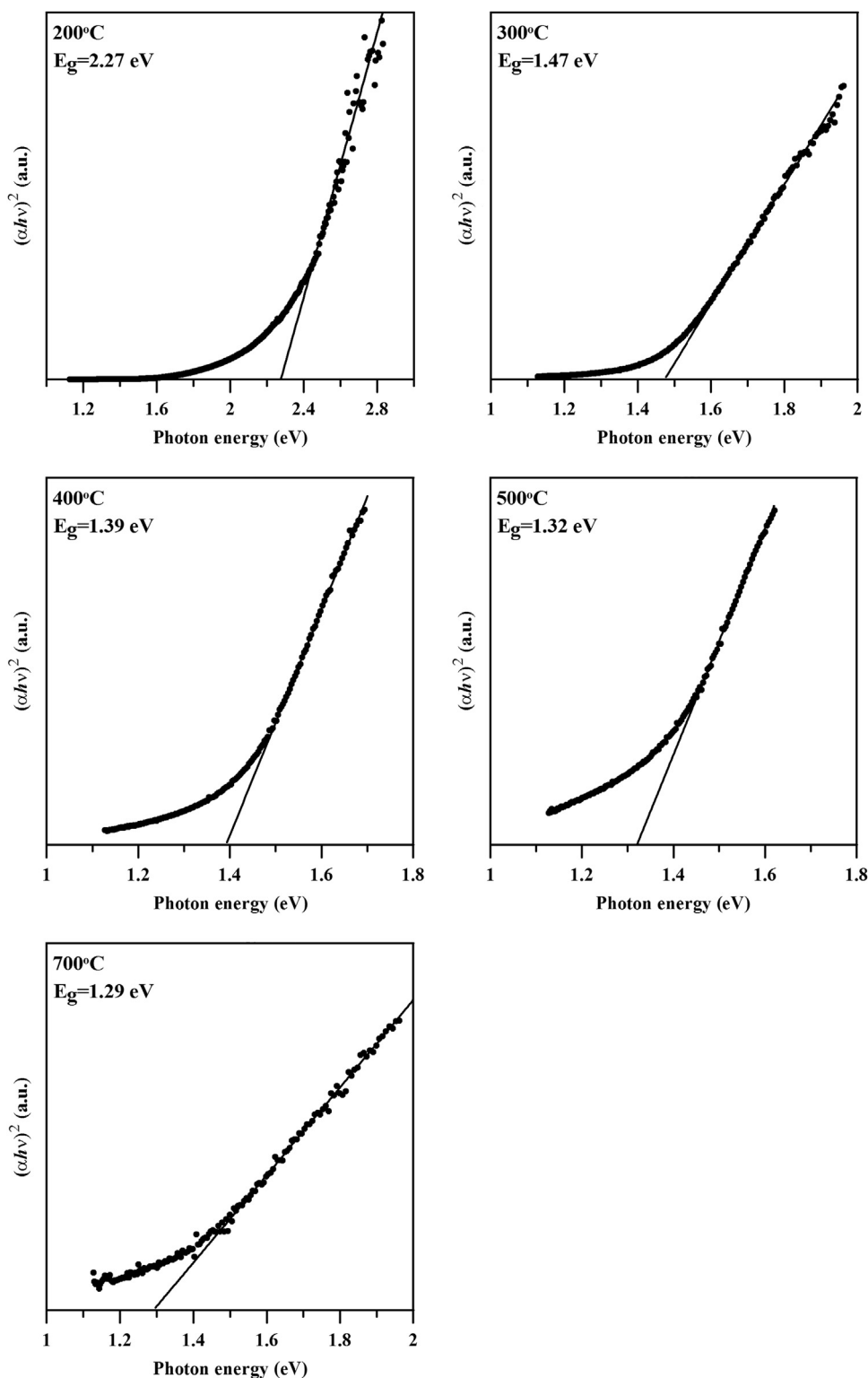


Fig. 5. The plots of $(\alpha h\nu)^2$ vs photon energy ($h\nu$) of the CZTS films sulfurized at different temperatures.

show the absorption behavior and the band-gap photon-energy estimations of the CZTS films, respectively. The band-gap estimations were performed by extrapolating the linear region of the plot of $(\alpha h\nu)^2$ vs $h\nu$ to the horizontal axis and considering the intersecting point. As can be seen from Fig. 5, the samples exhibit a linear dependence which indicates the directly allowed nature of

the films. Thus we can choose m as $1/2$. By plotting the graph of $(\alpha h\nu)^2$ against the photon energy $h\nu$, the band gap values were estimated as 2.27 eV, 1.47 eV, 1.39 eV, 1.32 eV and 1.29 eV for the samples sulfurized at 200 °C, 300 °C, 400 °C, 500 °C and 700 °C, respectively. The E_g value of the CZTS compound, as a p-type direct-band-gap semiconductor, has been reported to be

between 1.4 and 1.5 eV [3,5,17,19]. The high band gap may be attributed to residual organic precursor compounds of the sample at relatively low sulfurization temperatures. It can be said that the estimated results are quite close to the optimum band gap for a solar cell. The crystallite size of the films can also be estimated with UV–vis spectroscopy. By using an effective mass model [53] the crystallite sizes of the samples were estimated to be 2.2 nm, 4.1 nm, 4.7 nm and 5.7 nm for the samples sulfurized at 200 °C, 300 °C, 400 °C and 500 °C, respectively. A similar trend in crystallite size was obtained from the XRD analysis.

4. Conclusions

We prepared high-quality, dense CZTS thin films on quartz-glass substrates via the sol–gel spin-coating method and subsequent sulfurization, which was carried out in a vacuumed quartz tube containing elemental sulfur, a non-toxic material. The effects of the sulfurization temperature on the structural, morphological, compositional and optical properties of the films were investigated in detail. From the XRD results, the diffraction patterns of the samples matched very well with the reference PDF cards and indicated the polycrystalline nature of the films. No other prominent peaks were observed which suggests the absence of any secondary phase. The degree of crystallinity and the crystallite sizes of the CZTS films increased with sulfurization temperature. In the Raman spectrum, only the characteristic CZTS peaks were observed and confirmed the formation, phase purity and good crystalline quality of the CZTS films. From the FEG-SEM images and EDS results, it was found that the films were uniform, textured and composed of homogeneously distributed ~ 100 nm grains and have the preferable Cu-poor composition. The values of the optical absorption coefficients of the CZTS films were found to be about 10^4 cm^{-1} via absorbance spectroscopy. The optical band gap values were estimated to be between 1.32 and 2.27 eV depending on the sulfurization temperature. It was concluded that producing high-quality, homogeneous CZTS thin-film absorbers via the sol–gel spin-coating technique and subsequent sulfurization is a non-toxic and effective way to produce cheap and green solar cells.

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