OPTICAL PROPERTIES OF SELENIZED Cu₂ZnSnSe₄ FILMS FROM A Cu-Zn-Sn METALLIC PRECURSOR

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Cu₂ZnSnSe₄ thin films compound were prepared by selenization of sputtered metallic alloy precursor. The as-selenized films were characterized by X-Ray diffractometer (XRD), scanning electron microscopy (SEM), energy dispersive X-ray spectrometry (EDS), and atomic force microscopy (AFM). The optical constants of CZTSe films were estimated from the analysis of the transmission and reflection spectra measured by UV-Vis-NIR double beam spectrophotometer in the wavelength region of 300–2000 nm. It was found that the direct optical band gap values of CZTSe were around 1.0 eV with absorption coefficient more than 10^4 cm⁻¹ for all CZTSe samples. The other optical properties of CZTSe films such as refractive index dispersion, single oscillator parameters, the high-frequency dielectric constant, the carrier concentration to the effective mass ratio and the electric free carrier susceptibility were discussed and found to be affected by impurities and microstructure of films as a result of different selenization temperatures applied.

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1. Introduction

Research in thin films solar cells using chalcopyrite semiconductor materials has shown significant progress in recent years. Solar cells based on polycrystalline-CuInGaSe₂ (CIGS) already achieved a record of efficiency greater than 20% [1]. Other promising chalcopyrite material is Cu₂ZnSn(Se,S)₄ which is relatively inexpensive compared to CIGS since it consists of earth-abundant zinc and tin. To date, the highest efficiency reported for Cu₂ZnSn(Se,S)₄ thin film solar cells is 10.2 %, for those fabricated by a hydrazine solution based process [2].

In this report we studied pure $Cu_2ZnSnSe_4$ (CZTSe) compound without any incorporated sulfur. CZTSe has semiconducting properties such direct *p*-type semiconductor, absorption coefficient that is larger than 10^4 cm⁻¹, and optical band gap of 1.0 eV [3–4].

The common method to grow CZTSe films is by vacuum growth techniques which have advantages such as scalability and controllability. Various vacuum-based processes have been applied to prepare CZTSe such as one-step deposition of CZTSe thin films using blended targets by radio frequency (RF) magnetron sputtering [4], pulsed laser deposition [5], and co-evaporation [6]. In these reports, physical properties of CZTSe compounds were presented. However, studies concerning the optical properties of CZTSe are not much available.

In this work, we prepared CZTSe compounds by selenization of metallic precursor deposited from single target of Cu-Zn-Sn (CZT) alloy. The structural and optical properties of the selenized CZTSe films were discussed. Furthermore, the effect of thermal annealing on the estimated optical constants such as the refractive index, high frequency dielectric constant (ϵ_0) and carrier concentration to the effective mass ratio (N/m*) were also presented.

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2. Experimental details

Polycrystalline CZTSe films were grown by two stages process comprising vacuum deposition of metallic precursor and its sequential selenization. CZT bulk target was employed as source of the metallic elements for metallic precursor deposition by RF magnetron sputtering on soda-lime glass (SLG) substrates. Prior to deposition, SLG substrates were cleansed with acetone, ethanol, and distillated water and then were dried with nitrogen gas. The as-deposited metallic precursors were ~700 nm in thickness and compositional ratio of Cu/(Zn+Sn) = 0.8 and Zn/Sn = 0.9. The selenization process was done inside quartz tube furnace in an inert argon atmosphere using Se pellets as selenium source. The heat treatment profile included evaporation of Se pellets to produce selenium ambiance at 250 °C, followed by solid state reaction at different temperatures of 350 °C, 400 °C, 450 °C and 500 °C. Hereafter, as-selenized samples will be named as CZTSe350, CZTSe400, CZTSe450, and CZTSe500 according to the substrate temperatures applied. Following the end of the process, an unforced cooling down to room temperature was carried out. The heating rate for each step was 10 °C/min with holding time of 30 minutes.

The structural characterization of as-selenized films were examined by X-Ray diffractometer (XRD; PANalytical, Netherlands). The microstructural observation was carried out by scanning electron microscopy (SEM; Hitachi S-4200, Japan). In addition, surface topography and roughness was examined by atomic force microscope (AFM; NanoScopeIIIa, UK). The compositions of the samples were determined by energy dispersive X-ray spectrometry (EDS; Horiba, Japan) attached to SEM instrument. The optical transmissions and reflections spectra were measured by UV-Vis-NIR double beam spectrophotometer (Cary 500, Varian, USA) at room temperature.

3. Results and discussion

XRD patterns of as-selenized CZTSe films at different temperatures are shown in Fig. 1. All patterns showed peaks corresponding to CZTSe phase [JCPDS no. 70-8930] with main peaks at $2\theta^{\circ} = 27.2^{\circ}$, 45.1° , 53.4° , 72.4° , and 83.14° were well-observed. The CZTSe films grew in (112) orientation with good crystallinity as indicated by sharp peaks of patterns. However, secondary phases of binary copper selenides, i.e., CuSe [JCPDS no. 049-1457] and CuSe₂ [JCPDS no. 071-0046] were detected in the diffraction pattern of CZTSe350 films. This result indicates the incomplete reaction of CZTSe formation from binary selenides. It is well-known that binary selenides acts as educts in CZTSe compound formation.

Figure 2 shows the SEM micrographs and the corresponding AFM surface images for all CZTSe samples. The evolutions of microstructure and grain growth were affected by selenization temperatures as depicted in Fig. 2. The SEM image of CZTSe350 samples (Fig. 2(a)) shows homogenous surface with grain size of around 600 nm. However, AFM images of CZTSe350 (Fig. 2(b)) shows distinguishable large grain which indicated the presence of copper selenide phase. The grain sizes were further increased to be around 2000 nm after selenization at 500 °C (Fig. 2(g)). Roughness analysis by AFM showed that the value of root mean square (rms) of the film surface was found to increase with increasing selenization temperature, from 134.04 nm of CZTSe350 to 176.47 nm of CZTSe400, and improved to 214.03 nm for CZTSe450 film. Yet, the rms roughness of CZTSe500 film was decreased to 175.01 nm due to increasing temperature at 500 °C gave sufficient energy for particles to consolidate and to grow homogenously in all direction. As result, CZTSe500 film is composed of denser film with smoother surface than CZTSe450 film.



Fig. 1. XRD patterns for CZTSe samples with different substrate temperatures.

Chemical compositions of CZTSe films were analyzed by EDS and the result is shown in Fig. 3. All films possessed near stoichiometric composition with incorporated selenium contents increasing with the increase of substrate temperatures. The slight increased value of Cu at high temperature can be explained by the loss of tin and zinc due to low melting temperature of 231.9 °C and 419.53 °C for tin and zinc, respectively.

The optical transmission and reflection spectra measured by double beam spectrophotometer in the range of 300–2000 nm are presented in Fig. 4a–b. The highest transmission was obtained around 50% for CZTSe350 sample. CZTSe350 film, which has smooth surface as depicted by SEM and AFM results, showed high transmission and more interference fringes. The transmission of CZTSe samples were decreased as substrate temperature was increased; hence reflection of samples was increased. These occurrences were related to the roughness of films surface.



Fig. 2. SEM and AFM images for selenized CZTSe at (a-b) 350 °С, (c-d) 400 °С, (e-f) 450 °С, (g-h) 500 °С.



Fig 3. Chemical composition of CZTSe films with different substrate temperatures.

The value of optical constants was estimated using Swanepoel's method from the normal incidence transmission, T and reflection, R of a weakly absorbing thin film on a nonabsorbing substrate in the air interface [7–8]. The refractive index, n in the transparent region where absorption coefficient, $\alpha = 0$ is estimated by solving the equation:

$$n = \left[H + \left(H^2 - s^2 \right)^{\frac{1}{2}} \right]^{\frac{1}{2}}$$
(1)

$$H = \frac{4s^2}{(s^2 + 1)T_{\alpha}^2} - \frac{s^2 + 1}{2}$$
(2)

While in the region of weak and medium absorption when $\alpha \neq 0$, n is estimated by using the following expression:

$$n = \left[N + \left(N^2 - s^2 \right)^{\frac{1}{2}} \right]$$
(3)

$$N = \frac{s^2 + 1}{2} + 2s \frac{T_{\text{max}} - T_{\text{min}}}{T_{\text{max}} T_{\text{min}}}$$
(4)

where T_{max} and T_{min} are the envelopes of the maximum and minimum position of a fringe in the transmission spectrum, and *s* is the refractive index for transparent substrate. The sets of refractive index values, *n* calculated from experimental data can be fitted to the theoretical model of first-order Sellmeier dispersion equation:

$$n^{2}(\lambda) = A + \frac{\lambda^{2}}{\lambda^{2} - B}$$
(5)

where A and B are the fitting parameters, to give extrapolation of the refractive index to shorter wavelengths.



350

Fig. 4 (a) Transmission spectra and (b) reflection spectra from normal incidence of CZTSe films at room temperature.

The relation of transmission, *T* and reflection, *R* in all wavelengths λ can be expressed by [9]:

$$\alpha = \frac{1}{d} \ln \left[\frac{(1-R)^2}{2T} \right] + \left(\frac{(1-R)^4}{2T^2} + R^2 \right)^{\frac{1}{2}}$$

$$k = \lambda \alpha / 4\pi$$
(6)
(7)

The relation between absorption coefficient, α and the incident photon energy, hv can be written as:

$$(\alpha h \nu) = A (\alpha h \nu - E_g)^p \tag{8}$$

where A is a constant, E_g is the optical band gap, and $p = \frac{1}{2}$ for direct allowed transition. The value of E_g was estimated by extrapolating the straight line portion of $(\alpha h v)^2$ versus hv graph to x-axis. Figure 5 (a) and (b) show the refractive index, n and the extinction coefficient, k respectively, for CZTSe thin films. The refractive indices for all samples were found to decrease with the increase in wavelength of the incident photon and tend to be constant at higher wavelength. The values of refractive index for CZTSe350 sample were found to be lower than other samples due to difference in grain size and film's roughness. Furthermore, the extinction coefficient values of CZTSe films decreased until 1200 nm, and showed nearly same values at higher wavelength.



Fig. 5 (a) the refractive index, n and (b) the extinction coefficient, of CZTSe thin films.

Fig. 6 (a) and (b) show absorption coefficient spectra and plot of $(ahv)^2$ versus hv from which the values of optical band gap were estimated for all CZTSe samples. All films showed high absorption coefficients greater than 10^4 cm⁻¹ at energies higher than 1.2 eV. The estimated values of the optical band gap from Fig. 6 (b) were 0.97 eV, 1.18 eV, 1.20 eV, and 1.22 eV for CZTSe350, CZTSe400, CZTSe450, and CZTSe500, respectively. The slight band gap deviation in CZTSe350 sample was due to the existence of secondary phases.



Fig. 6 (a) Absorption coefficient spectra and (b) plot of $(\alpha h v)^2$ versus h v of CZTSe thin films.

The single-effective oscillator can be approximated using the results of refractive index dispersion according to the Wemple-DiDomenico [10–11]:

$$n^{2}(h\nu) = 1 + \frac{E_{d}E_{0}}{E_{0}^{2} - (h\nu)^{2}}$$
(9)

where E_0 is the single oscillator energy and E_d is the dispersion energy. The oscillator energy, E_0 is related by an empirical formula to the optical gap value E_g in close approximation by $E_0 \approx 2 E_g$. The dispersion energy, E_d is a measure of the average strength of interband optical transition. The values of E_0 and E_d can be obtained from the slope and intercept of the plot $(n^2-1)^{-1}$ versus photon energy squared as shown in Fig. 7. It was calculated that the value of E_0 lies between 1.71 eV and 2.81 eV and the value of E_d ranges from 4.76 eV to 46.59 eV for CZTS thin films.



wavelength of CZTSe thin films.

The electrical susceptibility of free carrier, χ_c and its contribution to the real dielectric constant, ε can be estimated by using calculated optical constants based on the model proposed by Spitzer–Fan [12]:

$$\chi_c = -\frac{Ne^2}{m_c \omega^2} ; \omega = 2\pi c/\lambda$$
⁽¹⁰⁾

$$\varepsilon = \varepsilon_0 + 4\pi \chi_c = n^2 - \kappa^2 \tag{11}$$

where N/m_s is the carrier concentration to the effective mass ratio, *e* is the electronic charge, ω is the angular velocity, and ε_0 is the high-frequency dielectric constant in the absence of any contribution from free carriers. The value N/m_s and ε_0 were estimated by plotting $\varepsilon = n^2 - k^2$ versus λ^2 and fitting to a straight line (Fig. 8 (a)). Figure 8 (b) shows graph of $-4\pi\chi_e$ versus wavelength which fits good to a straight line, and were plotted to estimate the free carrier susceptibility values at the extreme of the specified range. The values of χ_e increased to some extent and became large, reducing the refractive index and dielectric constant in the near-infrared range. Table 1

summarizes the values of estimated optical constants. All samples showed relatively similar values, with the exception of CZTSe350 sample which may be caused by the existence of copper selenide.

CZTSe	n(0)	E ₀ (eV)	E _d (eV)	E _g ^{dir} (eV)	${{ m E_0/}\atop { m E_g}}$	$\epsilon_0^{\ a}$	$\epsilon_0^{\ b}$	N/m_{s} (×10 ³⁵ cm ⁻³)	$-\chi_{c}$ (×10 ²)
350	2.20	1.71	4.76	0.97	1.76	2.78	5.10	2.79	1.57
400	2.60	2.06	10.43	1.18	1.75	5.06	7.40	2.45	1.61
450	2.80	2.45	13.60	1.20	2.04	5.56	8.05	3.73	2.36
500	2.90	2.81	46.59	1.22	2.30	5.90	8.06	2.82	3.93

Table 1. Optical constants of CZTSe thin films.

a) estimated ε_0 from Wemple–DiDomenico model.

b) estimated ε_0 from Spitzer-Fan model.

4. Conclusions

CZTSe thin films were prepared by selenization of sputtered metallic alloy precursor in the range of temperatures from 350 °C to 500 °C. Secondary phases of binary copper selenide were detected in CZTSe films selenized at 350 °C, while single CZTSe compounds were obtained after higher temperature selenization. The optical properties of CZTSe films were discussed and found to be affected by impurities and microstructure of films as a result of different selenization temperatures applied. The direct optical band gap values were estimated to be around 1.0 eV with absorption coefficient more than 10^4 cm⁻¹ for all CZTSe samples. The refractive index dispersion and single oscillator parameters were calculated and discussed using Wemple-DiDomenico model. In addition, the high-frequency dielectric constant, the carrier concentration to the effective mass ratio and the electric free carrier susceptibility were also estimated by Spitzer–Fan model.

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