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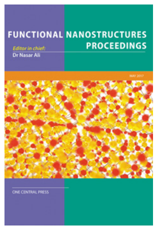

Synthesis of Cu_2ZnSnS_4 Thin Films Prepared by Highly Efficient Convective Deposition Method

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ABSTRACT

Cu_2ZnSnS_4 (CZTS), a *p*-type semiconductor, has received numerous interest for being one of the most promising candidates as an absorber layer in thin film solar cells. In this study, convective deposition method was used to synthesize CZTS thin films. A variation in operating conditions such as deposition speed and annealing temperature were investigated to obtain dense and uniform CZTS thin films, which will be suitable for use in thin film solar cells. The structure, morphology, composition, phase, and optical properties of CZTS thin films were characterized by Scanning electron microscopy (SEM), Energy dispersive X-ray analysis (EDX), X-ray diffraction (XRD), Raman, and UV-Vis spectrophotometer, respectively. According to the results, all CZTS films exhibited a kesterite structure. The films fully cover the surface of the substrate as the deposition speed increases. The grain size of CZTS films increased substantially in the annealing temperature from 340 to 440°C. The optical band gaps of the films are approximately 1.50 eV.

I. INTRODUCTION

CZTS is a *p*-type semiconductor which has a direct band gap of 1.5 eV and a relatively high absorption coefficient (> 10^4 cm^{-1}). Because of its excellent properties, CZTS is a promising candidate for a low-cost absorber layer in thin film solar cells. CZTS thin films can be prepared by both vacuum and non-vacuum based techniques, such as sputtering, thermal evaporation, spray pyrolysis, sol-gel, electrochemical deposition, *etc*. [1]. However, non-vacuum techniques are simpler, low-cost, consume less energy and scalable, therefore it is likely to apply to a large-scale production. Convective deposition method, in particular, involves a moving substrate with respect to a blade, where the precursor solution is stretched into thin film *via* evaporation and capillary attraction, resulting in closed-packed particles. The process consists of two physical processes. Firstly, convection is driven by evaporation, similar to the "coffee ring effect", where flow is generated by the evaporation losses [2]. The other is capillary attraction where particles on liquid interface are drawn into a close-packed structure to minimize the energy, similar to that found in the "cheerio effect" [3].

Herein, we adopted a facile convective deposition technique to synthesize CZTS thin films. Variation in operating conditions such as deposition velocity and annealing temperature were investigated to obtain close-packed stoichiometric CZTS thin films which may be useful for solar cell applications.

II. EXPERIMENTAL

The precursor solution was prepared by dissolving copper (II) chloride, zinc (II) chloride, tin (II) chloride, and thiourea in stoichiometric ratio of 2:1:1:4 in 2-methoxyethanol and triethanolamine (TEA) as a stabilizer, and stirred at 50°C for 30 min. The CZTS films were deposited on glass substrates by convective deposition system at different deposition speeds ranging from 500 – 1500 μm/s. The remaining solvent in the film was dried on a hotplate at 200°C for 10 min. The coating and drying processes were repeated 4 times. Lastly, the films were annealed in a nitrogen atmosphere at different temperatures of 340°C and 440°C, for 30 min.

III. RESULTS AND DISCUSSION

All samples were prepared using 5 different deposition speeds of 500, 750, 1000, 1250, and 1500 μm/s for 4 times. Fig. 1(a-e) show SEM images of CZTS thin films, annealed at 440°C. All samples show a uniform particle size on the substrate, indicating that the convective deposition method could control the surface morphology. Particle sizes prepared at deposition speed of 500 μm/s are decreased from about 500 nm to about 100 nm of those prepared at increasing deposition speed of 1500 μm/s. However, at low to moderate deposition speeds, *i.e.* 500 – 1000 μm/s, the films do not fully cover the substrate surface. While the films prepared at higher deposition speeds, *i.e.* 1250 – 1500 μm/s show a good coverage with a secondary layer. According to these observations, higher deposition speed leads to higher evaporation rate through convective flow from the moving substrate, resulting in a stretched solution as well as a decreasing solution level below the height of individual particles. Consequently, particles are drawn together as a result of capillary forces and formed covered films. Whereas at lower deposition speeds, evaporation rate is relatively lower, resulting in a remaining solution covering on the particles. As a consequence, the remaining solution hinders a formation of close-packed particles by capillary forces, causing nonuniformly covered films. The films annealed at 340°C at corresponding speeds are shown in insets of Fig. 1. It can be seen that the grain size decrease with decreasing annealing temperature as a result of decreasing agglomeration of particles.

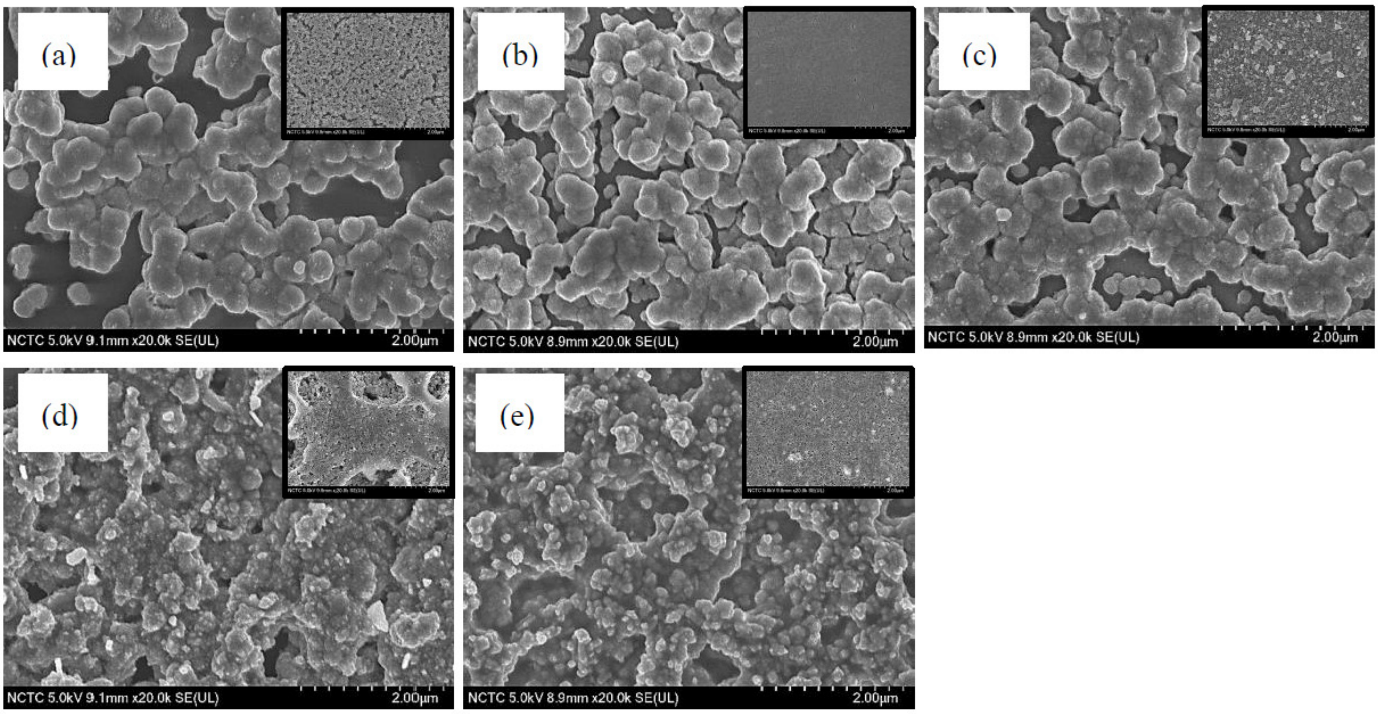

Figure 1 (SEM micrographs of CZTS thin films prepared at deposition speeds of (a) 500 μm/s, (b) 750 μm/s, (c) 1000 μm/s, (d) 1250 μm/s, and (e) 1500 μm/s, annealed at 440°C. Insets show films prepared at corresponding deposition speeds and annealed at 340°C.

The compositions of CZTS thin films, deposited at various deposition speeds and annealing temperatures were examined by EDS. The results revealed that the compositions obtained from various speeds are slightly off stoichiometric of 2:1:1:4 due to a sulfur deficit that may occur at high annealing temperature (results not shown). In terms of phase formation, the crystallinity of CZTS thin films was analyzed by XRD. Figure 2(a-b) show XRD pattern of CZTS thin film deposited at speed of 750 μm/s and annealed at 340°C and 440°C, respectively. The peaks from both conditions were attributed to the (1 1 2), (2 0 0), (2 2 0), and (3 1 2) planes of kesterite phase of CZTS. It can be clearly seen that the intensity of the diffraction peaks increase with increasing annealing temperature, indicating the improvement of the crystallinity of the samples. The formation of CZTS was also confirmed by Raman spectroscopy, measured using a 473 nm laser, as shown in insets of Fig. 2. Raman spectra of the films at corresponding annealing temperatures give evidence of peaks presence at 337 cm-1 which are characteristic of CZTS and close to reported values [4].

The optical properties of the CZTS thin films were measured using a UV-Vis spectrophotometer. The optical band gaps (E_g) of the CZTS films, prepared at various deposition speeds and annealed at 340°C, were estimated from extrapolating the linear region of a plot of the squared absorbance versus the photon energy. Fig. 3 shows that the band gaps of the CZTS thin films in the range of 1.4 – 1.5 eV were obtained. These optical properties of the CZTS thin films are suitable as the absorber layer of thin film solar cells.

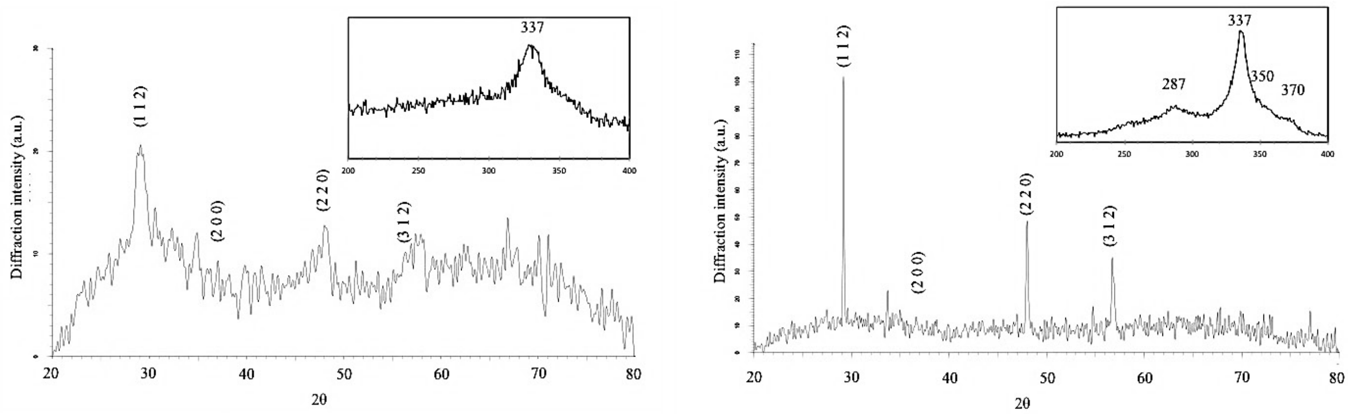

Figure 2 XRD spectra of CZTS thin films prepared at deposition speed of 750 μm/s and annealed at a) 340°C and b) 440°C. Insets show Raman spectra of corresponding CZTS thin films.

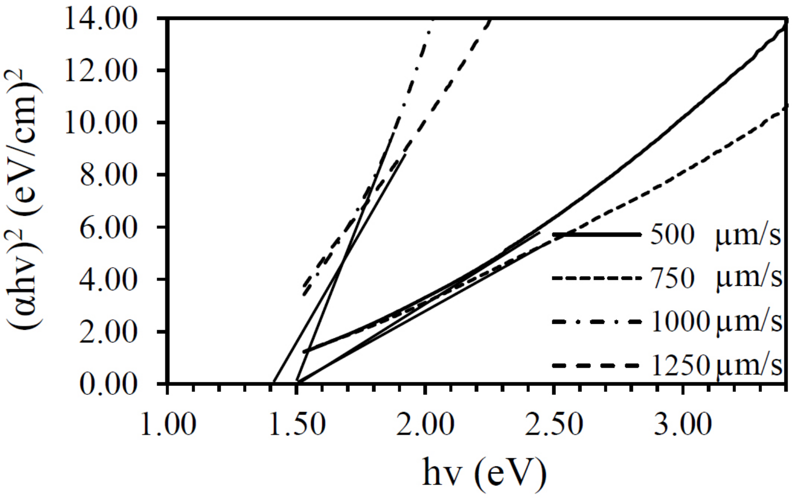

Figure 3 $(\alpha h\nu)^2$ vs. hv of CZTS films, prepared at various deposition speeds annealed at 340°C.

IV. SUMMARY

CZTS thin films have been successfully prepared by the efficient method of convective deposition. The effects of deposition speed and annealing temperature on the morphology, composition, phase, and optical properties of the CZTS thin film were investigated in detail. The films exhibited quite smooth and uniform in particle sizes on glass substrates at higher deposition speed. The formation of kesterite structure CZTS thin film was obtained and the optical band gap of the CZTS thin films was about 1.50 eV. With suitable composition, phase, and optical property, CZTS films prepared by convective deposition method can be used as absorber layers of thin film solar cells.

V. REFERENCES

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