

Journal of Photonics for Energy

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Abstract. Cu₂ZnSnS₄ (CZTS) was obtained from a sol-gel precursor which consists of copper chloride, zinc chloride, tin chloride, and thiourea. CZTS thin films were prepared by spin-coating the sol-gel precursor followed by annealing in a nitrogen atmosphere. The morphology, composition, and structure of the absorber layer were studied by scanning electron microscopy, energy dispersive spectroscopy, x-ray diffraction, and Raman scattering. The optical measurement shows the bandgap of these films is ~ 1.51 eV, and the optical absorption coefficient is on the order of 10^4 cm⁻¹. CZTS solar cells with a structure of low-alkali glass/Mo/CZTS/CdS/i-ZnO/ZnO:Al/Al grid were tentatively fabricated. The best solar cell showed a short-circuit current density of 5.06 mA/cm², an open-circuit voltage of 358 mV, a fill factor of 34.66%, and an efficiency of 0.63% under AM1.5 (100 mW/cm²) illumination. These results demonstrate the CZTS thin films were successfully deposited by a cheap sol-gel technique. © 2011 Society of Photo-Optical Instrumentation Engineers (SPIE). [DOI: [10.1117/1.3628450](https://doi.org/10.1117/1.3628450)]

Keywords: CZTS; photovoltaic material; spin-coating; sol-gel.

Paper 11185LR received Mar. 22, 2011; revised manuscript received Jul. 15, 2011; accepted for publication Aug. 4, 2011; published online Sep. 2, 2011.

1 Introduction

Research on thin film photovoltaic (PV) technologies, such as CdTe and Cu(In,Ga)(S,Se)₂ (CIGS), have recently made tremendous progress academically¹ and industrially.² It was claimed by First Solar that manufacturing costs ranging from \$0.59/W to \$0.62/W has already been realized at the end of 2009.³ However, the scarcity and toxicity of raw materials will become obstacles for CdTe and CIGS to significantly snatch PV market share from dominant silicon wafer-based PV technologies. Kesterite Cu₂ZnSnS₄ (CZTS) has gained broad interest due to its abundant raw materials and semiconductor properties comparable to chalcopyrite CIGS.⁴⁻⁷

Several methods have been employed to deposit CZTS thin films. These include direct current/radio-frequency magnetron sputtering deposition,⁸ thermal evaporation,⁹ electron beam evaporation,¹⁰ spray pyrolysis deposition,¹¹ sol-gel deposition,¹² electrodeposition,¹³ photochemical deposition,¹⁴ pulsed laser deposition,¹⁵ screen-printing,¹⁶ and nanoparticle-based method.¹⁷ Katagiri et al. reported a promising conversion efficiency of 6.77% in 2008 CZTS thin film solar cell (TFSC) which was fabricated by sputtering elements and metal sulfides followed by annealing in H₂S.¹⁸ In 2010, IBM slightly improved the efficiency to 6.81% using a co-evaporation process.¹⁹ However, the high vacuum employed by both teams requires expensive equipment, complicated operations, and significant maintenance. It is generally promoted that nonvacuum deposition techniques are to manufacture low-cost PV modules.

In this work, we report on a different route, using sol-gel as CZTS precursors. In this process, the CZTS polycrystal thin films were deposited on soda lime glass and low-alkali glass substrates by the spin-coating of CZTS sol-gel followed by annealing in nitrogen atmosphere. Densely packed crystal domains were observed with these annealed films. Results from absorber and device characterization demonstrated the feasibility to fabricate a CZTS PV device by an inexpensive sol-gel process.

2 Experimental Procedures

Copper chloride (2 M), zinc chloride (1.2 M), tin chloride (1 M), and thiourea (8 M) were added in a mixture solvent water/ethanol (v/v 70:30). Clear yellow sol-gel was formed after being stirred at room temperature for tens of minutes. The spin-coating process was used to deposit CZTS sol-gel on substrates. Solvents in the as-coated films were removed by drying at 110°C. Preannealing at 250°C was employed in nitrogen to decompose CZTS precursors for generating metal sulfides (copper sulfide, zinc sulfide, and tin sulfide) nanocrystals.²⁰ The spin-coating and drying processes as well as preannealing were repeated twice to deposit relatively thick CZTS thin films (>2 μm). Finally, the annealing temperature was elevated to 550°C for growing polycrystalline CZTS thin films.

The optical property of the prepared thin films was examined by a UV-visible-infrared spectrophotometer. Surface and cross section morphologies of CZTS thin films were investigated using scanning electron microscopy (SEM). The composition of the films was analyzed by energy-dispersive x-ray spectroscopy (EDX). X-ray diffraction (XRD) spectrum and room temperature Raman spectrum were recorded to examine the crystal structure.

3 Results and Discussion

Figure 1(a) shows the SEM surface image of a CZTS film preannealed at 250°C. Due to volume contraction arising from the evaporation of volatile products, cracks exist in the film. Organic binders in the CZTS precursor sol-gel could prevent the formation of cracks.²¹ The grain boundaries are difficult to be delineated because a preannealed sample is mainly composed of nanoparticles of metal sulfides (copper sulfide Cu_xS, zinc sulfide Zn_xS, and tin sulfide Sn_xS). These sulfides react to form a CZTS nanocrystal during heating. High temperature annealing could improve the crystallinity and increase the grain size of thin films.²² Moreover, the efficiency of TFSC increases with increasing crystal size of the absorber layers.²² A CZTS thin film containing large densely packed grains with size of more than 400 nm was achieved after annealing at 550°C in nitrogen atmosphere [Fig. 1(c)]. The cross section images of a CZTS thin film are shown in Figs. 1(b) and 1(d). The thickness of a CZTS thin film is decreased by ~200 nm after the annealing process in comparison to a preannealed thin film. This was attributed to nanocrystals congregation at high temperature for forming larger crystalline domains.

The compositional ratios of Cu/(Zn+Sn), Zn/Sn, and S/metals examined by EDX are shown in Table 1. A preannealed CZTS film is copper-poor, zinc-rich, and slightly sulfur-poor, which are beneficial to prevent the formation of binary phases such as Cu₂S, and to induce self-doped

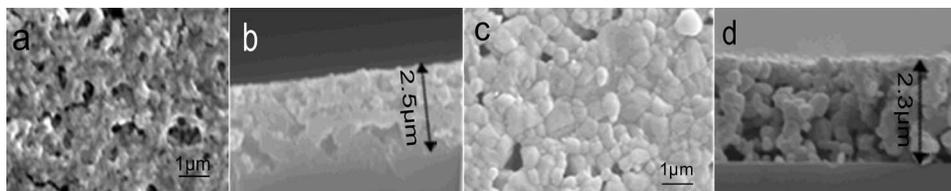


Fig. 1 SEM images of CZTS films (a) surface after preannealing, (b) cross section after preannealing, (c) surface after annealing, and (d) cross-section after annealing.

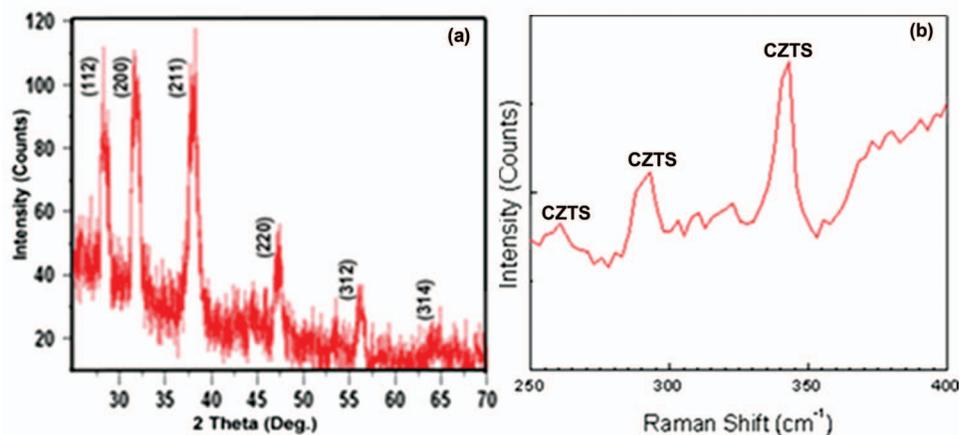
Table 1 Chemical composition of the CZTS films.

	Mass percentage (%)						Atomic percentage		
	Cu	Zn	Sn	S	Cl	C	Cu/(Zn+Sn)	Zn/Sn	S/(Cu+Zn+Sn)
Preannealing	26.38	17.80	28.28	27.07	0.47	0	0.81	1.15	0.91
Annealing	24.68	19.82	25.20	30.29	0	0	0.75	1.43	1.05

p-type conductivity.²³ A minute quantity of chlorine remained after preannealing and was totally removed after annealing. The preannealing process could fully remove carbon as a form of carbon dioxide. As verified by EDX results, a loss of Sn was recorded during annealing at higher temperature. Similar phenomena was observed by Weber et al. who suggested that a CZTS thin film should be deposited at a temperature lower than 550°C to suppress the evaporation of tin sulfide.²⁴ It remains unresolved to what extent loss of tin could be endured without detrimental effects on CZTS TFSC since CZTS TFSCs have been successfully fabricated with a large variation of composition.¹⁹ Moreover, the versatility of the sol-gel method provides a simple way to optimize the composition which can be fine-tuned by changing the molar concentration of reagents when preparing the CZTS sol-gel precursor.

Figure 2(a) shows an XRD pattern of a CZTS film annealed at 550°C. All peaks can be assigned to kesterite CZTS.²⁵ The phenomenon of three strong peaks is attributed to the polycrystallinity of a deposited CZTS thin film. Three continuous strong peaks were also observed by Lu et al. on as-synthesized wurtzite CZTS nanocrystals.²⁶ The existence of CZTS is further confirmed by the presence of Raman peaks at 256 to 257 cm⁻¹, 288 cm⁻¹, and 338 to 339 cm⁻¹. These are in good agreement with the reported data.^{27,28} From both the elemental and structural analysis, a total reaction, 2CuCl₂ + ZnCl₂ + SnCl₂ + 4SC(NH₂)₂ + 8H₂O → Cu₂ZnSnS₄ + 4CO₂ + 8NH₄Cl, may be suggested to the presented process.

Figure 3 shows the optical transmittance of CZTS thin films preannealed at 250°C and annealed at 550°C. It is reported that Cu_xS, Sn_xS, and Zn_xS have direct bandgap of 2.35 eV,²⁹ 2.0 eV,³⁰ and 2.99 to 3.80 eV,³¹ respectively, all of which are larger than that of CZTS.⁸ Therefore, the transmittance of an annealed CZTS thin film was observed with redshift. The optical absorption coefficient is approximately derived from the transmittance data and shown in Fig. 3 as a function of photon energy. The absorption coefficient is larger than 10⁴ cm⁻¹ in the photon energy range greater than 1.2 eV, which agrees well with those reported in literature.^{11,32,33}

**Fig. 2** (a) XRD pattern and (b) Raman spectrum of CZTS film annealed at 550°C.

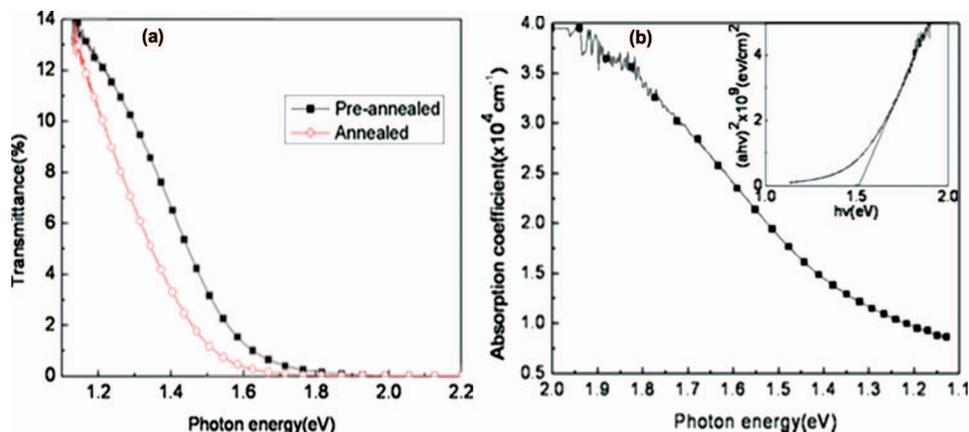


Fig. 3 (a): Transmittance of CZTS films and (b) absorption coefficient of CZTS film annealed at 550°C.

The insert in Fig. 3(b) shows the square of the product of the absorption coefficient and photon energy ($h\nu$) as a function of the photon energy. The bandgap is estimated to be 1.51 eV by extrapolating the straight line part of the $(\alpha h\nu)^2$ versus $h\nu$ curve to the intercept of the horizontal axis as depicted in Fig. 3(b). This value is quite close to the theoretical optimal value for a single-junction solar cell.³⁴ From the perspective of optical properties, the CZTS film deposited using spin-coating of sol-gel followed by annealing can be considered a suitable photovoltaic material.

CZTS solar cells with an active area of 0.46 cm² were fabricated and characterized. All cell parameters were relatively low. The current density-voltage (J - V) characteristic of the best solar cell is presented in Fig. 4. The performance parameters were as follows: a short circuit current density (J_{sc}) of 5.06 mA/cm², an open-circuit voltage (V_{oc}) of 358 mV, a fill factor of 34.66%, and an efficiency (η) of 0.63% under simulated AM1.5 illumination. Shunt and series resistances, R_{sh} and R_s , were 99.78 and 31.30 $\Omega \cdot \text{cm}^2$, respectively, which caused the quite low fill factor.

4 Conclusions

CZTS thin film was successfully deposited by a sol-gel method. The annealed film showed large densely packed grains. This film possesses a high optical absorption coefficient and optical bandgap near to the ideal bandgap of the absorber for single junction solar cells. The film could be

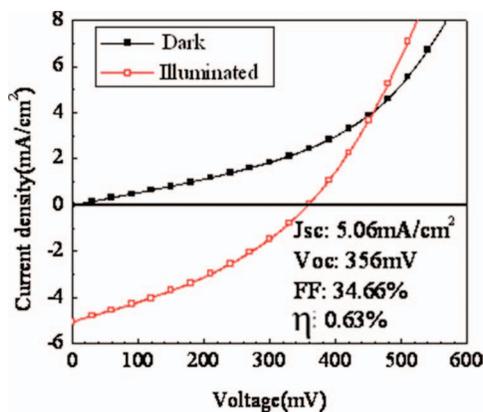


Fig. 4 J - V characteristic of the best CZTS solar cell.

a suitable photovoltaic material from the perspective of optical properties. Desired composition was achieved for the CZTS thin film after preannealing at low temperature. Loss of tin was observed after annealing at higher temperature, as should be solved for high-performance TFSCs. The best solar cell showed a low conversion efficiency of 0.63%. Optimization experiments are in progress and expected to lead to a significant improvement.

Acknowledgments

We acknowledge the financial support from the NASA EPSCoR through Contract NNX09AU83A and SDSU EE PhD program. We are also grateful to OPTORUN Co. Ltd. (Japan) for providing Mo-coated low-alkali glass substrates for this project.

References

1. P. Jackson, D. Hariskos, E. Lotter, S. Paetel, R. Wuerz, R. Menner, W. Wischmann, and M. Powalla, "New world record efficiency for Cu(In,Ga)Se₂ thin-film solar cells beyond 20%," *Prog. Photovoltaics* (2011).
2. SOLAR FRONTIER (2011, April 20). Solar Frontier Officially Opens World's Largest CIS Solar Module Plant, <http://www.solar-frontier.com/MainMenu/News/19>.
3. M. A. Green, "Learning experience for thin-film solar modules: First Solar Inc. case study," *Prog. Photovoltaics* **19**(4), 498–500 (2010).
4. S. H. Han, F. S. Hasoon, H. A. Al-Thani, A. M. Hermann, and D. H. Levi, "Effect of Cu deficiency on the optical properties and electronic structure of CuIn_{1-x}Ga_xSe₂," *J. Phys. Chem. Solids* **66**, 1895–1898 (2005).
5. O. Lundberg, M. Bodegard, J. Malmstrom, and L. Stolt, "Influence of the Cu(In,Ga)Se₂ thickness and Ga grading on solar cell performance," *Prog. Photovoltaics* **11**, 77–88 (2003).
6. H. Katagiri, K. Jimbo, W. S. Maw, K. Oishi, M. Yamazaki, H. Araki, and A. Takeuchi, "Development of CZTS-based thin film solar cells," *Thin Solid Films* **517**, 2455–2460 (2009).
7. H. Katagiri, "Cu₂ZnSnS₄ thin film solar cells," *Thin Solid Films* **480–481**, 426–432 (2005).
8. H. Yoo and J. Kim, "Comparative study of Cu₂ZnSnS₄ film growth," *Sol. Energy Mater. Sol. Cells* **95**, 239–244 (2011).
9. B. Schubert, B. Marsen, S. Cinque, T. Unold, R. Klenk, S. Schorr, and H. W. Schock, "Cu₂ZnSnS₄ thin film solar cells by fast coevaporation," *Prog. Photovoltaics* **19**, 93–96 (2010).
10. H. Katagiri, K. Saitoh, and T. Washio, "Development of thin film solar cell based on Cu₂ZnSnS₄ thin films," *Sol. Energy Mater. Sol. Cells* **65**, 141–148 (2001).
11. Y. B. Kumar, P. U. Bhaskar, G. S. Babu, and V. S. Raja, "Effect of copper salt and thiourea concentrations on the formation of Cu₂ZnSnS₄ thin films by spray pyrolysis," *Phys. Status Solidi A* **207**, 149–156 (2010).
12. K. Tanaka, M. Oonuki, N. Moritake, and H. Uchiki, "Cu₂ZnSnS₄ thin film solar cells prepared by non-vacuum processing," *Sol. Energy Mater. Sol. Cells* **93**, 583–587 (2009).
13. J. J. Scragg, D. M. Berg, and P. J. Dale, "A 3.2% efficient Kesterite device from electrodeposited stacked elemental layers," *J. Electroanal. Chem.* **646**, 52–59 (2010).
14. K. Moriya, K. Tanaka, and H. Uchiki, "Characterization of Cu₂ZnSnS₄ thin films prepared by photo-chemical deposition," *Jpn. J. Appl. Phys.* **44**, 715–717 (2005).
15. K. Moriya, K. Tanaka, and H. Uchiki, "Cu₂ZnSnS₄ thin films annealed in H₂S atmosphere for solar cell absorber prepared by pulsed laser deposition," *Jpn. J. Appl. Phys.* **47**, 602–604 (2008).

16. Z. Zhou, Y. Wang, D. Xu, and Y. Zhang, "Fabrication of Cu₂ZnSnS₄ screen printed layers for solar cells," *Sol. Energy Mater. Sol. Cells* **94**, 2042–2045 (2010).
17. C. Chory, F. Zutz, F. Witt, H. Borchert, and J. Parisi, "Synthesis and characterization of Cu₂ZnSnS₄," *Phys. Status Solidi C* **7**, 1486–1488 (2010).
18. H. Katagiri, K. Jimbo, S. Yamada, T. Kamimura, W. S. Maw, T. Fukano, T. Ito, and T. Motohiro, "Enhanced conversion efficiencies of Cu₂ZnSnS₄-based thin film solar cells by using preferential etching technique," *Appl. Phys. Express* **1**, 041201 (2008).
19. K. Wang, O. Gunawan, T. Todorov, B. Shin, S. J. Chey, N. A. Bojarczuk, D. Mitzi, and S. Guha, "Thermally evaporated Cu₂ZnSnS₄ solar cells," *Appl. Phys. Lett.* **97**, 143508 (2010).
20. N. Nakayama and K. Ito, "Sprayed films of stannite Cu₂ZnSnS₄," *Appl. Surf. Sci.* **92**, 171–175 (1996).
21. T. Todorov and D. B. Mitzi, "Direct liquid coating of chalcopyrite light-absorbing layers for photovoltaic devices," *Eur. J. Inorg. Chem.* **2010**(1), 17–28 (2010).
22. L. Zhang, Q. He, W. Jiang, F. Liu, C. Li, and Y. Sun, "Effects of substrate temperature on the structural and electrical properties of Cu(In,Ga)Se₂ thin films," *Sol. Energy Mater. Sol. Cells* **93**, 114–118 (2009).
23. S. Chen, J. Yang, X. Gong, A. Walsh, and S. Wei, "Intrinsic point defects and complexes in the quaternary kesterite semiconductor Cu₂ZnSnS₄," *Phys. Rev. B* **81**, 245204 (2010).
24. A. Weber, R. Mainz, and H. W. Schock, "On the Sn loss from thin films of the material system Cu-Zn-Sn-S in high vacuum," *J. Appl. Phys.* **107**, 013516 (2010).
25. W. Schafer and R. Nitsche, "Tetrahedral quaternary chalcogenides of the type Cu₂-II-IV-S₄ (Se₄)," *Mater. Res. Bull.* **9**, 645–654 (1974).
26. X. Lu, Z. Zhuang, Q. Peng, and Y. Li, "Wurtzite Cu₂ZnSnS₄ nanocrystals: A novel quaternary semiconductor," *Chem. Commun.* **47**, 3141–3143 (2011).
27. F. Liu, K. Zhang, Y. Lai, J. Li, Z. Zhang, and Y. Liu, "Growth and characterization of Cu₂ZnSnS₄ thin films by DC reactive magnetron sputtering for photovoltaic applications," *Electrochem. Solid-State Lett.* **13**, H329–H381 (2010).
28. M. Grossberg, J. Krustok, J. Raudoja, K. Timmo, M. Altosaar, and T. Raadik, "Photoluminescence and Raman study of Cu₂ZnSn(Se_xS_{1-x})₄ monograins for photovoltaic applications," *Thin Solid Films* **519**, 7403–7406 (2010).
29. H. M. Pathan, J. D. Desai, and C. D. Lokhande, "Modified chemical deposition and physico-chemical properties of copper sulphide (Cu₂S) thin films," *Appl. Surf. Sci.* **202**, 47–56 (2002).
30. M. Khadraoui, N. Benramdane, C. Mathieu, A. Bouzidi, R. Miloua, Z. Kebbab, K. Sahraoui, and R. Desfeux, "Optical and electrical properties of Sn₂S₃ thin films grown by spray pyrolysis," *Solid State Commun.* **150**, 297–300 (2010).
31. S. D. Sartale, B. R. Sankapal, M. Lux-Steiner, and A. Ennaoui, "Preparation of nanocrystalline ZnS by a new chemical bath deposition route," *Thin Solid Films* **480–481**, 168–172 (2005).
32. P. M. P. Salome, P. A. Fernandes, A. F. da Cunha, J. P. Leitão, J. Malaquias, A. Weber, J. C. González, and M. I. N. da Silva, "Growth pressure dependence of Cu₂ZnSnSe₄ properties," *Sol. Energy Mater. Sol. Cells* **94**, 2176–2180 (2010).
33. H. Katagiri, N. Sasaguchi, and S. Hando, "Preparation films by and evaluation of Cu₂ZnSnS₄ thin sulfurization of E-B evaporated precursors," *Sol. Energy Mater. Sol. Cells* **49**, 407–414 (1997).
34. T. Zdanowicz, T. Rodziewicz, and M. Zabkowska-Waclawek, "Theoretical analysis of the optimum energy band gap of semiconductors for fabrication of solar cells for applications in higher latitudes locations," *Sol. Energy Mater. Sol. Cells* **87**, 757–769 (2005).