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Research Article

Effect of Annealing Atmosphere on the Properties of Electrochemically Deposited Cu_2ZnSnS_4 (CZTS) Thin Films

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The Cu_2ZnSnS_4 (CZTS) thin films have been electrochemically deposited from a weak acidic medium (pH 4.50∼5.00) onto Mo-coated and ITO-coated glass substrate by using single-step electrodeposition method. Trisodium citrate was used as a complexing agent. The effect of annealing atmospheres such as Ar, N_2, N_2+H_2S on the structural, morphological, compositional, and optical properties of CZTS thin films has been investigated by using X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), and optical absorption techniques, respectively. XRD studies reveal that the as-deposited CZTS film is amorphous in nature. Upon annealing in different atmospheres, a relatively more intense and sharper diffraction peaks (112), (200), (220), and (312) of kesterite crystal structure with uniform and densely packed surface morphology are observed in N_2+H_2S atmosphere. Absorption study shows that the band gap energy of as-deposited CZTS thin film is 2.8 eV whereas after annealing, it is found to be 1.48, 1.76, and 1.53 eV for Ar, N_2, N_2+H_2S atmospheres.

1. Introduction

To meet the ever-increasing demand for energy and to cope with the limited fossil resources available, photovoltaic solar-energy production will become increasingly important. While the solar cells based on single-crystal silicon or III-V semiconductors exhibit already very high efficiency, the cost of electricity produced by crystalline silicon panels however is still significantly higher than the cost of today's grid power (\$0.27/kW·hr versus \$0.06/kW·hr). Therefore, in order to increase the use of solar power, there is a need for new technologies to both decrease the cost and increase the efficiency of photovoltaics (PVs) [1–3]. Thin film solar cells offer the opportunity to lower the price of solar energy by using small amounts of materials and low cost manufacturing technologies. The ternary chalcopyrites, such as Cu(In, Ga)Se_2, have attracted much attention in this respect, and the efficiency of this material has already improved above 20% [4]; however, this compound contains expensive materials such as In and Ga and the toxic element such as Se. This could lead to a shortage in the supply of these elements and would inhibit a cost-effective large-scale production. To overcome these limitations, alternative materials are heavily researched in order to substitute the expensive elements, In and Ga. Therefore, there have been efforts to replace alternative compounds which contain more abundant elements. The quaternary semiconductor Cu_2ZnSnS_4 (CZTS) is a relatively new photovoltaic material and expected to be interesting for environmentally amenable solar cells, as its constituents are nontoxic and abundant in the earth's crust [5–7]. CZTS thin films show *P*-type conductivity, a direct band gap of 1.44–1.51 eV, and high optical absorption ($\sim 1 \times 10^4$ cm^{-1}) [8–11]. Recently, a conversion efficiency of 6.7% has been achieved in CZTS-based solar cells by growing CZTS thin films using cosputtering system equipped with an annealing chamber [12].

A variety of techniques have been used to prepared CZTS thin films for absorber layers, such as atom beam sputtering [11], RF (radio frequency) magnetron sputtering [8], hybrid sputtering [13], thermal evaporation [14], photochemical deposition [15] electrodeposition [10, 16–19], spray pyrolysis [20], pulsed laser deposition [21–23], and sulfurization of electron -beam-evaporated precursors [7, 24]. Among these, electrodeposition is a potentially suitable preparation method to obtain low-cost precursor films. The electrodeposition process could provide (i) a high-quality film with very low capital investment; (ii) a low-cost, high-rate process; (iii) use of very low-cost starting materials (e.g., low purity salts, solvents), based on automatic purification of the deposited materials during plating; (iv) a large-area, continuous, multicomponent, low-temperature deposition method; (v) deposition of films on a variety of shapes and forms (wires, tapes, coils, and cylinders); (vi) controlled deposition rates and effective material use (as high as 98%); (vii) minimum waste generation (i.e., solution can be recycled). Ennaoui et al. Have fabricated thin film solar cells based on CZTS absorbers by solid state reaction in H_2S atmosphere of electrodeposited Cu-Zn-Sn precursors, resulting in a solar cell with a conversion efficiency of up to 3.40% [18]. Araki et al. have fabricated thin film solar cell using electrodeposited (Cu/Sn/Zn) staked and Cu-Zn-Sn precursor layers by sulfurizing at 600°C for 2 hours with conversion efficiency 0.98% and 3.16% [17, 25]. Scragg et al. have fabricated CZTS thin films solar cell using sequential electrodeposition of metallic stack in the order Cu/Sn/Cu/Zn and subsequent annealing of the stack in an sulfur-containing atmosphere, with the best cell having an efficiency of 3.2% [26]. It is well known that the efficiency of polycrystalline thin film solar cell increases with increasing grain size of the absorber layer, and therefore, the larger grains are required for the fabrication of high efficiency solar cells, and the morphology of the absorber layer depends on the preparation method and postannealing treatments [5, 22, 27–29]. In our previous study, we have reported the synthesis of CZTS thin films by single-step electrodeposition technique using trisodium citrate as a complexing agent and studied the effect of postannealing treatment on the structural, morphological, compositional, and optical properties of the CZTS thin films in Ar atmosphere [16, 30]. The stoichiometry is the very important factor to maintain during the synthesis of absorber layer for the solar cell devices. In CZTS-related absorber layers, the S loss and compensation during deposition and the annealing atmosphere have been a critical factor to have cells with good performance. To maintain S composition, annealing in the H_2S atmosphere is done by many of the research groups.

In the present paper, we propose the synthesis of Cu_2ZnSnS_4 (CZTS) thin films using single-step electrodeposition technique and subsequently study the effects of annealing in Ar, N_2, and $N_2 + H_2S$ atmospheres on its structural, morphological, compositional, and optical properties.

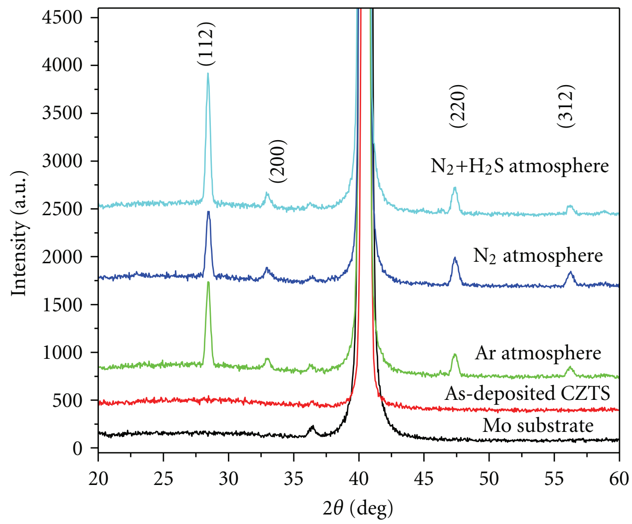

Figure 1: X-ray diffraction patterns of as-deposited precursor film and annealed CZTS thin films annealed at 550°C in various annealing atmosphere.

2. Experimental Details

The Cu_2ZnSnS_4 (CZTS) precursors thin films were prepared from aqueous electrolytic bath containing 0.02 M $CuSO_4$, 0.01 M $ZnSO_4$, 0.02 M $SnSO_4$, and 0.02 M $Na_2S_2O_3$ using a single-step electrodeposition method at room temperature without stirring in a conventional three-electrode electrochemical cell assembly. The electrochemical cell contains a saturated calomel electrode (SCE) as a reference electrode, a platinum electrode as an inert counter, electrode, and Mo-coated glass and ITO substrate with a deposition area $2 \times 2\,cm^2$ were used as the working electrode. The Mo film on glass substrate was about 1 μm thick and was deposited by DC sputtering. The Mo film surface was chemically etched in an ammoniac solution, since as-deposited Mo films had poor adhesion with the precursors. The 0.2 M trisodium citrate was used as complexing agent. The pH of electrolytic solution was 4.5–5.0 (adjusted by using 0.1 M tartaric acid). Analytical regent grade (AR) chemicals (supplied by SIGMA-ALDRICH) were used for the precursor solution preparation. The Mo-coated glass substrates were cleaned ultrasonically in detergent, acetone, methanol, isopropanol, and distilled water and finally dried under flowing nitrogen. The uniform and well-adherent CZTS thin films were deposited using WonATech, WMPG1000 Multichannel Potentiostat/Galvanostat ver. 1.11 at −1.05 V versus SCE in potentiostatic mode at room temperature for 45 min. After deposition, the films were rinsed in doubly deionized water. The as-deposited precursor films were annealed in different annealing atmospheres such as Ar, N_2, and N_2+H_2S atmosphere at optimized annealing temperature of 550°C for 1 hour. After annealing, the films were allowed to cool naturally and were further characterized for their structural, morphological, compositional, and optical properties.

The structural properties of the as-deposited and annealed thin films were studied using high resolution X-ray

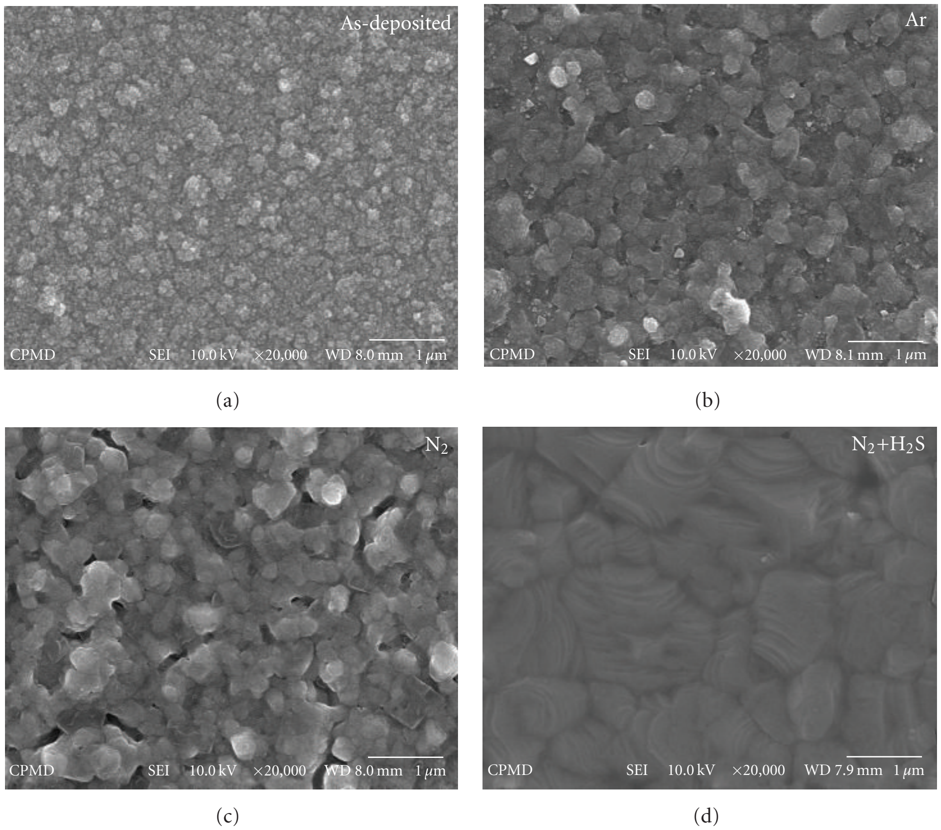

FIGURE 2: FE-SEM micrographs of (a) as-deposited precursor film, and annealed CZTS thin films (b) in Ar, (c)N_2, (d) N_2+H_2S annealing atmosphere.

diffraction (XRD) with Ni-filtered CuKα radiation (X'pert PRO, Philips, Eindhoven, Netherlands). The surface morphology and compositional study of films were observed by using FE-SEM (field emission scanning electron microscopy, Model: JSM-6701F, JEOL, Japan) attached with an energy-dispersive X-ray analysis (EDAX) analyzer to measure the sample composition. Optical absorption studies of the films deposited on ITO glass substrates were carried out in the wavelength range 350–800 nm by using UV-Vis-NIR spectrophotometer (Cary 100, Varian, Mulgrave, Australia).

3. Results and Discussion

Figure 1 shows X-ray diffraction patterns of Mo-coated glass substrates, as- deposited CZTS film and the films annealed at 550°C for 1 hour in different atmospheres, that is, Ar, N_2, and N_2+H_2S, respectively. From XRD patterns, the as-deposited CZTS films showed amorphous nature, whilst the crystalline nature is observed for the films annealed in different atmospheres. In particular, the films annealed in Ar atmosphere showed kesterite structure with major diffraction peaks towards (112), (200), (220), and (312) directions (JCPDS card: 26–0575). Decrement in to the intensity of (112) peak is observed for the films annealed in N_2 atmosphere. But the films annealed in N_2+H_2S atmosphere, a relatively more intense and sharper diffraction peaks are observed than the other two annealing atmospheres. From these above results, it is concluded that N_2+H_2S annealing atmosphere is the suitable medium to get crystalline CZTS films due to activeness of H_2S gas, which accelerates the reactions than the inactive gases like Ar and N_2, thus observed the improved crystallinity in CZTS thin films [22].

Figure 2 shows FE-SEM micrographs of as-deposited and annealed CZTS thin films. The as-deposited CZTS thin films showed nonuniform distribution of agglomerated small particles with well-defined boundaries. The annealed CZTS thin film in Ar atmosphere showed compact larger flat grains, whereas the films annealed in N_2 atmosphere showed well-defined crystallites with an average grain size less than 0.5 μm with some voids on the surface. The uniformity of the films produced from the N_2+H_2S annealing is much improved as compared to N_2 atmosphere. The films annealed in N_2+H_2S atmosphere are densely packed with compact faceted grain structure and having grain size about 1 μm is observed, which will be beneficial in photovoltaic applications as the recombination rate of the photo-generated electron will be reduced [31]. The compositional analysis of as-deposited and annealed CZTS thin film at 550°C in different annealing atmospheres is presented in Figure 3. From EDS study, it is seen that nearly stoichiometric CZTS thin film can be deposited using single-step electrodeposition method. The sulfur quantity of the film annealed in Ar and N2 atmosphere

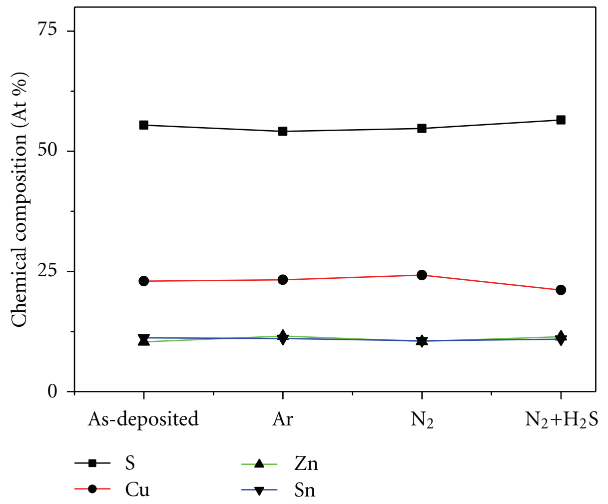

FIGURE 3: Plot of chemical compositions (At %) of CZTS thin films of as-deposited precursor film and annealed CZTS thin films annealed in various annealing atmosphere.

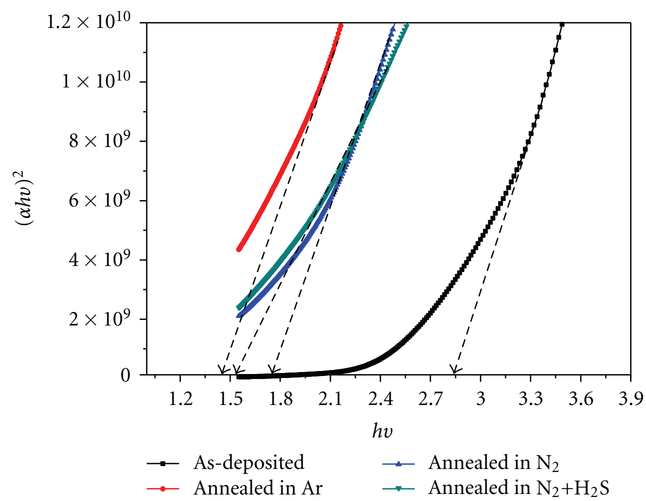

FIGURE 4: Variation of $(\alpha hv)^2$as a function of photon energy (hv) for as-deposited precursor film and annealed CZTS thin films in various annealing atmosphere.

is slightly decreased whereas in N_2+H_2S atmosphere, the annealed film becomes slightly sulfur rich. The optical absorption spectra for the CZTS thin films were recorded in the wavelength range of 350–800 nm at room temperature. The optical absorption data was analyzed using the following classical relation (1) of optical absorption in semiconductor near band edge [23]:

$$\alpha = \frac{A\left(hv - E_g\right)^n}{hv}, \tag{1}$$

where E_g is the separation between bottom of the conduction band and top of the valence band, hv is the photon energy, and n is a constant. The value of n depends on the probability of transition; it takes values as 1/2, 3/2, 2, and 3 for direct allowed, direct forbidden, indirect allowed, and indirect forbidden transitions, respectively. Thus, if the plot of $(\alpha hv)^2$ versus (hv) is linear, the transition is direct allowed. Also the value of absorption coefficient in the present case is of the order of $10^4\,\mathrm{cm}^{-1}$, which supports direct band gap nature of the deposited CZTS material. Extrapolation, of the straight line to zero absorption coefficient $(\alpha = 0)$, leads to estimation of band gap energy (Eg) values. Figure 4 shows variation of $(\alpha hv)^2$ as a function of photon energy (hv) for as-deposited precursor film and annealed CZTS thin films. The band gap energy of the as-deposited CZTS thin film is about 2.8 eV. After annealing, it is found to be 1.48, 1.76, and 1.53 eV for Ar, N_2, N_2+H_2S atmospheres. [16, 22, 32]. This value is quite close to the optimum band gap energy for thin film solar cell and is appropriate for the application of thin film solar cells with high conversion efficiency.

4. Conclusions

The Cu_2ZnSnS_4 (CZTS) thin films have been synthesized using cost-effective and convenient single-step electrodeposition method and the effects of different annealing atmospheres, that is, Ar, N_2, and N_2+H_2S on the structural, morphological, compositional, and optical properties of the CZTS thin films are reported. XRD studies revealed that the as-deposited CZTS film is amorphous in nature. Upon annealing in different atmospheres, a relatively more intense and sharper diffraction peaks (112), (200), (220), and (312) of kesterite crystal structure with uniform and densely packed surface morphology are observed in N_2+H_2S atmo sphere. The absorption study shows that the band gap energy of as-deposited CZTS thin films is 2.8 eV. After annealing, it is found to be 1.48, 1.76, and 1.53 eV for Ar, N_2, N_2+H_2S atmospheres.

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References

[1] J. Paier, R. Asahi, A. Nagoya, and G. Kresse, "$Cu_2\,ZnSnS_4$ as a potential photovoltaic material: a hybrid Hartree-Fock density functional theory study," *Physical Review B*, vol. 79, no. 11, pp. 115126–115134, 2009.

[2] D. B. Mitzi, M. Yuan, W. Liu et al., "A high-efficiency solution-deposited thin-film photovoltaic device," *Advanced Materials*, vol. 20, no. 19, pp. 3657–3662, 2008.

[3] M. Kaelin, D. Rudmann, and A. N. Tiwari, "Low cost processing of CIGS thin film solar cells," *Solar Energy*, vol. 77, no. 6, pp. 749–756, 2004.

[4] P. Jackson, D. Hariskos, E. Lotter et al., "New world record efficiency for Cu(In,Ga)Se_2 thin film solar cell beyond 20%," *Progress in Photovoltaics: Research and Applications*. In press.

[5] K. Jimbo, R. Kimura, T. Kamimura et al., "Cu_2ZnSnS_4-type thin film solar cells using abundant materials," *Thin Solid Films*, vol. 515, no. 15, pp. 5997–5999, 2007.

[6] H. Katagiri, "Cu_2ZnSnS_4 thin film solar cells," *Thin Solid Films*, vol. 480-481, pp. 426–432, 2005.

[7] H. Katagiri, K. Saitoh, T. Washio, H. Shinohara, T. Kurumadani, and S. Miyajima, "Development of thin film solar cell based on Cu_2ZnSnS_4 thin films," *Solar Energy Materials and Solar Cells*, vol. 65, no. 1, pp. 141–148, 2001.

[8] J. S. Seol, S. Y. Lee, J. C. Lee, H. D. Nam, and K.-H. Kim, "Electrical and optical properties of Cu_2ZnSnS_4 thin films prepared by rf magnetron sputtering process," *Solar Energy Materials and Solar Cells*, vol. 75, no. 1-2, pp. 155–162, 2003.

[9] H. Matsushita, T. Maeda, A. Katsui, and T. Takizawa, "Thermal analysis and synthesis from the melts of Cu-based quaternary compounds Cu-III-IV-VI4 and Cu_2-II-IV-VI_4 (II = Zn, Cd; III = Ga, In; IV = Ge, Sn; VI = Se)," *Journal of Crystal Growth*, vol. 208, no. 1, pp. 416–422, 2000.

[10] J. J. Scragg, P. J. Dale, and L. M. Peter, "Towrds sustainable materials for solar energy conversion: preparation and photoelectrochemical characterization of Cu_2ZnSnS_4," *Electrochemistry Communications*, vol. 10, pp. 639–642, 2008.

[11] K. Ito and T. Nakazawa, "Electrical and optical properties of stannite-type quaternary semiconductor thin films," *Japanese Journal of Applied Physics*, vol. 27, no. 11, pp. 2094–2097, 1988.

[12] H. Katagiri, K. Jimbo, S. Yamada et al., "Enhanced conversion efficiencies of Cu_2ZnSnS_4-based thin film solar cells by using preferential etching technique," *Applied Physics Express*, vol. 1, no. 4, pp. 041201–041202, 2008.

[13] T. Tanaka, T. Nagatomo, D. Kawasaki et al., "Preparation of Cu_2ZnSnS_4 thin films by hybrid sputtering," *Journal of Physics and Chemistry of Solids*, vol. 66, no. 11, pp. 1978–1981, 2005.

[14] K. Oishi, G. Saito, K. Ebina et al., "Growth of Cu_2ZnSnS_4 thin films on Si (100) substrates by multisource evaporation," *Thin Solid Films*, vol. 517, no. 4, pp. 1449–1452, 2008.

[15] K. Moriya, K. Tanaka, and H. Uchiki, "Characterization of Cu_2ZnSnS_4 thin films prepared by photo-chemical deposition," *Japanese Journal of Applied Physics*, vol. 44, no. 1 B, pp. 715–717, 2005.

[16] S. M. Pawar, B. S. Pawar, A. V. Moholkar et al., "Single step electrosynthesis of Cu_2ZnSnS_4 (CZTS) thin films for solar cell application," *Electrochimica Acta*, vol. 55, no. 12, pp. 4057–4061, 2010.

[17] H. Araki, Y. Kubo, K. Jimbo et al., "Preparation of Cu_2ZnSnS_4 thin films by sulfurization of co-electroplated Cu-Zn-Sn precursors," *Physica Status Solidi (C)*, vol. 6, no. 5, pp. 1266–1268, 2009.

[18] A. Ennaoui, M. Lux-Steiner, A. Weber et al., "Cu_2ZnSnS_4 thin film solar cells from electroplated precursors: novel low-cost perspective," *Thin Solid Films*, vol. 517, no. 7, pp. 2511–2514, 2009.

[19] J. J. Scragg, P. J. Dale, L. M. Peter, G. Zoppi, and I. Forbes, "New routes to sustainable photovoltaics: evaluation of Cu_2ZnSnS_4 as an alternative absorber material," *Physica Status Solidi (B)*, vol. 245, no. 9, pp. 1772–1778, 2008.

[20] Y. B. Kishore Kumar, G. Suresh Babu, P. Uday Bhaskar, and V. Sundara Raja, "Preparation and characterization of spray-deposited Cu_2ZnSnS_4 thin films," *Solar Energy Materials and Solar Cells*, vol. 93, no. 8, pp. 1230–1237, 2009.

[21] K. Moriya, K. Tanaka, and H. Uchiki, "Fabrication of Cu_2ZnSnS_4 thin-film solar cell prepared by pulsed laser deposition," *Japanese Journal of Applied Physics*, vol. 46, no. 9 A, pp. 5780–5781, 2007.

[22] K. Moriya, K. Tanaka, and H. Uchiki, "Cu_2ZnSnS_4 thin films annealed in H_2S atmosphere for solar cell absorber prepared by pulsed laser deposition," *Japanese Journal of Applied Physics*, vol. 47, no. 1, pp. 602–604, 2008.

[23] S. M. Pawar, A. V. Moholkar, I. K. Kim et al., "Effect of laser incident energy on the structural, morphological and optical properties of Cu_2ZnSnS_4 (CZTS) thin films," *Current Applied Physics*, vol. 10, no. 2, pp. 565–569, 2010.

[24] H. Katagiri, N. Sasaguchi, S. Hando, S. Hoshino, J. Ohashi, and T. Yokota, "Preparation and evaluation of Cu_2ZnSnS_4 thin films by sulfurization of E-B evaporated precursors," *Solar Energy Materials and Solar Cells*, vol. 49, no. 1–4, pp. 407–414, 1997.

[25] H. Araki, Y. Kubo, A. Mikaduki et al., "Preparation of Cu_2ZnSnS_4 thin films by sulfurizing electroplated precursors," *Solar Energy Materials and Solar Cells*, vol. 93, no. 6-7, pp. 996–999, 2009.

[26] J. J. Scragg, D. M. Berg, and P. J. Dale, "A 3.2% efficient Kesterite device from electrodeposited stacked elemental layers," *Journal of Electroanalytical Chemistry*, vol. 646, no. 1-2, pp. 52–59, 2010.

[27] K. Tanaka, N. Moritake, and H. Uchiki, "Preparation of Cu_2 $ZnSnS_4$ thin films by sulfurizing sol-gel deposited precursors," *Solar Energy Materials and Solar Cells*, vol. 91, no. 13, pp. 1199–1201, 2007.

[28] K. Ramanathan, G. Teeter, J. C. Keane, and R. Noufi, "Properties of high-efficiency $CuInGaSe_2$ thin film solar cells," *Thin Solid Films*, vol. 480-481, pp. 499–502, 2005.

[29] P. J. Dale, K. Hoenes, J. Scragg, and S. Siebentritt, "A review of the challenges facing kesterite based thin film solar cells," in *Proceedings of the 34th IEEE Photovoltaic Specialists Conference (PVSC '09)*, pp. 002080–002085, 2009.

[30] B. S. Pawar, S. M. Pawar, S. W. Shin et al., "Effect of complexing agent on the properties of electrochemically deposited Cu_2ZnSnS_4 (CZTS) thin films," *Applied Surface Science*, vol. 257, no. 5, pp. 1786–1791, 2010.

[31] K. Ramanathan, M. A. Contreras, C. L. Perkins et al., "Properties of 19.2% efficiency ZnO/CdS/$CuInGaSe_2$ thin-film solar cells," *Progress in Photovoltaics: Research and Applications*, vol. 11, no. 4, pp. 225–230, 2003.

[32] Y. Cui, S. Zuo, J. Jiang, S. Yuan, and J. Chu, "Synthesis and characterization of co-electroplated Cu_2ZnSnS_4 thin films as potential photovoltaic material," *Solar Energy Materials and Solar Cells*, vol. 95, no. 8, pp. 2136–2140, 2011.