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Influence of film thickness on the structural properties of copper zinc tin sulphide absorber materials

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Abstract
Copper Zinc Tin Sulphide (Cu_2ZnSnS_4, CZTS) thin films absorber materials were deposited onto soda-lime glass substrates by sol-gel dip-coating technique, a simple and low-cost process. The Cu_2ZnSnS_4 precursor solution contains copper (II) acetate precursor, Zinc (II) acetate precursor, Tin (II) Chloride precursor, Thiourea solution, and a mixture of ethanol and water. The prepared films were annealed in the presence of sulphur gas at a temperature of 500 ºC for one hour. The influence of film thickness on the structural properties and composition of the synthesized CZTS thin film absorbers was investigated. The prepared films were analyzed by X-ray diffraction (XRD), Raman spectroscopy, Atomic force microscopy (AFM) and Energy Dispersive X-ray fluorescence (EDXRF). The thickness of the film of each sample was determined with the aid of a surface profiler. The XRD and Raman spectroscopy measurements exhibited the formation of polycrystalline kesterite structure of CZTS thin films. AFM showed increasing grain density, growth and compactness as film thickness increases.

Keywords: Cu_2ZnSnS_4, thin film absorbers, sol-gel dip-coating method, structural, composition

Introduction

Copper Zinc Tin Sulphide (Cu_2ZnSnS_4), thin film material, a potential candidate for the absorber layer of photovoltaic systems exhibits unique characteristics such as low cost of production, non-toxicity, easy handling, suitable optical band-gap of about 1.5 eV and its large absorption coefficient of over 10^4 cm^{-1} [1]. These features make Cu_2ZnSnS_4 one of the most interesting materials for absorber layer of thin-film solar cells compared to those utilizing hazardous elements in Cadmium Telluride (CdTe) and the expensive or rare elements (In and Ga) in Copper Indium Gallium Selenide (CIGS). As a preference to CIGS for thin film solar cells absorber, quarternary compound Cu_2ZnSnS_4 has resemblant structure and properties of the chalcogenide type semiconductor CIGS [2]. Since the discovery of Cu_2ZnSnS_4 as a feasible absorber material in solar cells, several groups have investigated Cu_2ZnSnS_4 utilizing different techniques of fabrication such as dip coating method [3], spin coating method [4], co-evaporation method [5], electro-deposition techniques [6], spray pyrolysis technique [7], electron beam evaporation [8], and pulsed layer deposition [9], Magnetron sputtering [10], sol-gel sulphurisation technique [11], successive ionic layer adsorption and reaction (SILAR) method [12].

Sol-gel dip-coating technique is a simple and inexpensive process where the substrate to be coated is immersed in the precursor sol and then withdrawn with a well-defined withdrawal speed under controlled temperature and atmospheric conditions to form a film. The advantage of this deposition process over other methods is in its ability to tailor the microstructure of the deposited material [13]. This simple method also offers the possibilities of producing thin film materials that are nearly stoichiometric in composition with a desired thickness in a relatively short time.

However, studies have shown that the structural, optical, electrical, compositional and mechanical properties of Cu_2ZnSnS_4 depend on method of fabrication, film thickness and composition. In this work, sol-gel dip-coating method has been employed to produce sulphur rich films with controlled thickness values between (100 – 1000 nm) with the aim of determining the influence of film thickness on the morphological properties of the synthesized CZTS thin film absorber materials.

Materials and Method

1. Materials

Copper (II) acetate (Cu $(C_2H_3O_2)_2$, 99.0%), Zinc (II) acetate (Zn $(C_2H_3O_2)_2$, 99.0%), Tin (II) chloride ($SnCl_2$, 99.0%), Thiourea (CH_4N_2S, 99.0%), Ethanol (C_2H_5OH, 99.0%), de-ionized water (H_2O) and soda-lime glass (SLG) substrate. The ethanol acts as a dispersion agent to prevent several unidentified peaks displaying in the XRD analysis.

2. Preparation OF CZTS precursor sol

Analytical reagents grade (AR) chemical Cu (C2H3O2)2, Zn (C2H3O2)2, SnCl2, and Thiourea were used as the precursor in a mixture solvent containing water and Ethanol (70%: 30%). The solution was stirred for 1 hour at room temperature to produce a homogenous, clear and transparent solution using a magnetic stirrer. The CZTS precursor solution consists of metal ions.

The Cu2ZnSnS4 formation is according to the below equation:

2Cu (CH3CO2)2 + Zn (CH3CO2)2 + SnCl2 + 4CH4N2S + 8H2O □ Cu2ZnSnS4 + 6NH4 (CH3CO2) + 2NH4Cl + 4CO2

The Cu2ZnSnS4 precursor sol was formed by adding 15ml of 0.2M copper acetate precursor, 15ml of 0.1M zinc acetate precursor, 15ml of 0.1M Tin chloride precursor and 15 ml of 0.4M Thiourea solution in a beaker. The mixture was stirred gently for one hour at room temperature to produce a yellow, clear and homogenous Cu2ZnSnS4 sol-gel precursor.

3. Cu_2ZnSnS_4 Thin film fabrication

Dip-coating method was employed to prepare the thin film samples as shown in fig.1. Well cleaned SLG substrates were dipped into the CZTS sol and withdrawn at a constant speed of 0.80mm/sec, and then dried at room temperature. This was followed by air-drying using a hand-dyer and thermal treatment at a temperature of 100 °C for 5 minutes resulting in a very thin black film. The process of dipping, withdrawal, air-drying and thermal treatment were each repeated in cycles to obtain film thickness of 0.20 µm on sample A, 0.34 µm on sample B, 0.51 µm on sample C, 0.70 µm on sample D, 0.86 µm on sample E, and 0.98 µm on sample F. The samples were further annealed in the presence of sulphur gas at a temperature of 500 °C for one hour using SVG 2610 Base Horizontal Diffusion Furnace system. The fabricated CZTS thin film absorbers were analyzed by studying their structural and compositional properties using x-ray diffraction, atomic force microscopy, Raman spectroscopy and energy dispersive x-ray spectroscopy.

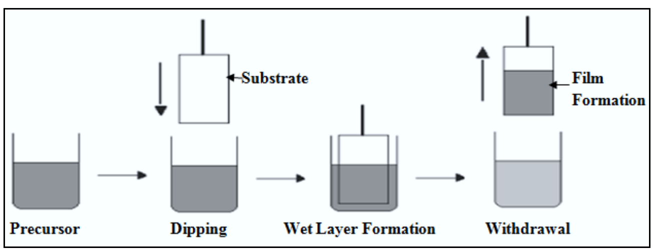

Fig 1: Representation of film fabrication technique

Results and Discussion

1. X-Ray Diffraction Studies

The XRD patterns of the thin film samples (A, B, C, D, E and F) are shown in fig. 2. It is confirmed that a polycrystalline CZTS thin films with Kesterite type structure was obtained in the samples as shown by the diffractions at (011), (110), (112), (004), (211), (220) and (116) observed in the XRD pictograph. The results of the lattice parameters were: a = 5.4320Å and c = 10.8460Å, which are in good agreement with the reported values [14]. The average grain size of the thin film samples (A, B, C, D, E and F) calculated using Debye-Scherer's formula [3] were 4.72, 4.05, 5.61, 5.00, 4.94 and 4.46 nm respectively. The CZTS diffraction planes were observed to become sharper as the film thickness increases indicating an increase in crystallinity. With increasing thickness values, more CZTS phases were also seen to grow in the samples as depicted in sample B with (004) diffraction plane while (011) and (211) planes started from sample E. However, CZTS is a quarternary compound and the presence of secondary phases is always expected in its formation. The peaks at diffraction planes (001) and (121) indicate the presence of CuSn phase [15]. Diffraction planes (010), (013) and (200) show the presence of Wurtzite (ZnS) phase [16]. The planes (002) and (113) indicates CuS phase [17] and (131) SnS phase [18] in the samples they are seen. The CuS phase can be effectively removed by immersing the samples in potassium cyanide (KCN) solution and the SnS phase has been reported to have no considerable effects on the performance of the thin film absorber materials.

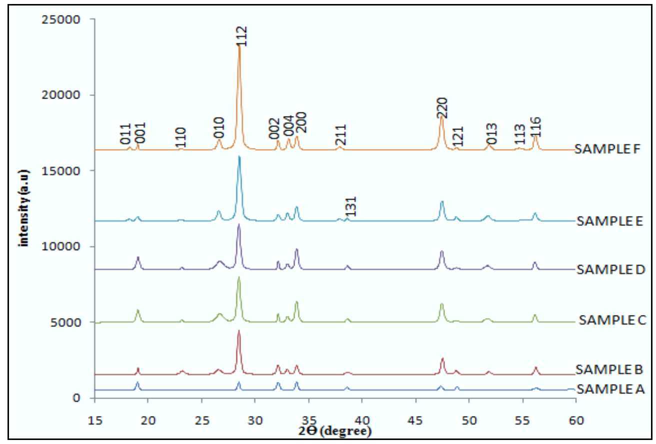

Fig 2: XRD pattern of CZTS/SLG substrate samples

2. Raman Scattering Analysis

Raman spectroscopy provides a better explanations of the presence of secondary phases in the samples since each phase in the CZTS material depicts a peak position in Raman scattering which is more diverse compared to X-ray diffraction pattern. The Raman scattering measurement was performed with a Pro-Raman-L Enwave Optronic using a wavelength of 750 nm for excitation. The Raman spectra of the samples are shown in fig 3. In the Raman spectra, peaks are observed at 264, 286, 338 and 374 cm^{-1}. The maximum intensity at 338, 286 and 374 cm^{-1} further confirms the formation of Kesterite CZTS [19] which is in good agreement with the XRD results. The Cu_xS and ZnS phases which were observed in the XRD analysis were also observed for the samples in the Raman spectra with small peaks at 264 cm^{-1} [3]. Cu_xS phases are known to form at low synthesizing temperature. The Cu_xS phase was observed to decompose slowly with increasing thickness and crystallinity of the samples as observed in the XRD and Raman scattering analysis. However, the CZTS Raman spectrum displayed no evidence for the presence of SnS and SnS_2 binary phases in the samples.

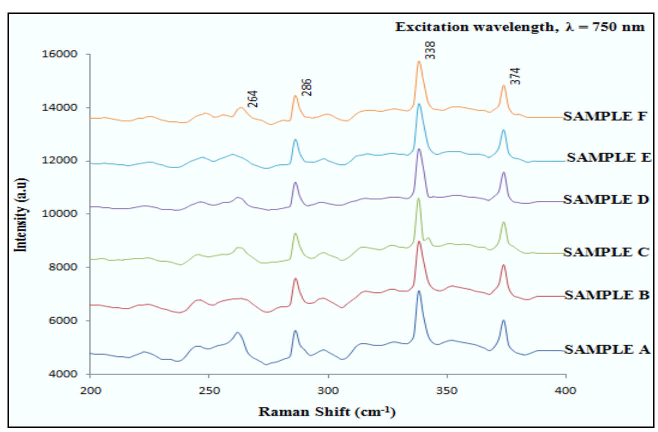

Fig 3: Raman spectra of the CZTS thin film samples

3. Microstructural Analysis

In order to achieve a direct insight into the surface morphology features of the samples, AFM was utilized to study the evolution and growth CZTS thin films. The root mean square (RMS) roughness was found to in the range of 1.25nm to 1.45nm for the samples indicating the formation of smooth and compact films.

The AFM pictographs (fig. 4) showed large agglomeration of spherical grains homogenously throughout the film as the thickness increases, this is beneficial in photovoltaic applications as the recombination rate of the photo-generated electron will be reduced [20].

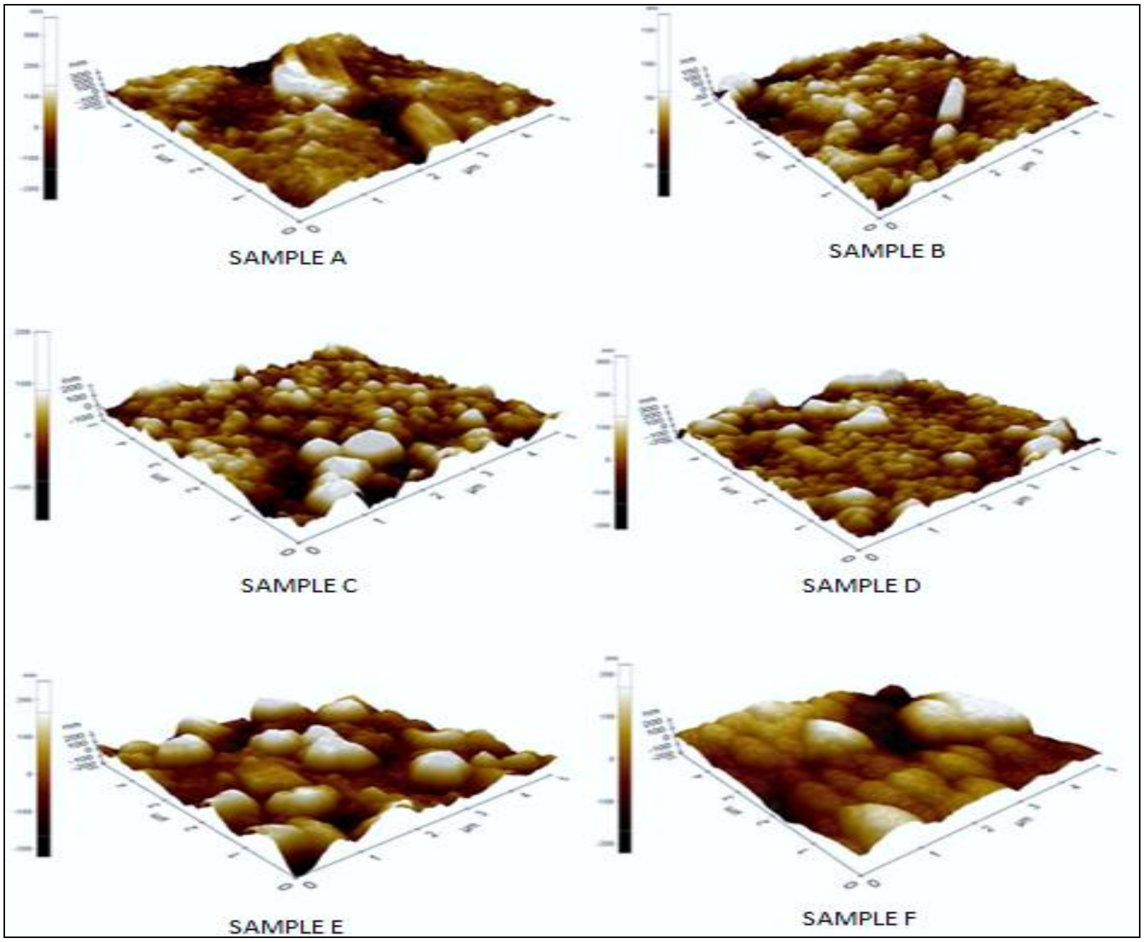

Fig 4: AFM pictographs of the CZTS Thin film samples

4. Compositional Studies

The atomic stoichiometry and compositional analysis of the samples were performed by energy dispersive analysis of X-ray (EDAX). The atomic stoichiometries of constituent elements are given in table 1. The elemental composition of copper was observed to increase from 15.81 – 18.10 as the film thickness increases while the elemental compositions of Zn and Sn both decreased from 22.20 – 20.40 and 14.81 – 12.80. The decrease in Sn composition could be attributed to the high volatile nature of Sn at very high temperature of 450 ^{o}C and its poor incorporation efficiency **[21]**. The Cu/(Zn + Sn), Cu/Zn and Zn/Sn ratios showed that the films are Cu-poor and Zn-rich which is the preferable elemental composition to obtain a highly efficient CZTS based thin film absorber materials **[22]**. However, all the CZTS thin film samples possess nearly the same amount of sulphur (between 0.87 – 0.92) with S/metal ratios less than 1 for all the samples indicating that S was sufficiently incorporated with the other metals in the precursors.

Table 1: Elemental composition of the CZTS thin films

Samples	Film Thickness (µm)	Elemental composition (%)				Atomic ratio (%)				
		Cu	Zn	Sn	S	Cu/Zn	Cu/Zn	Zn/Sn	Cu/(Zn+Sn)	S/Metal
A	0.20	15.79	22.20	14.81	45.92	1.07	0.71	1.50	0.43	0.87
B	0.34	16.33	21.80	14.32	45.97	1.14	0.74	1.52	0.45	0.88
C	0.51	16.61	21.32	14.00	46.80	1.17	0.78	1.52	0.47	0.91
D	0.70	17.22	21.11	13.71	46.71	1.26	0.82	1.54	0.49	0.90
E	0.86	17.80	20.72	13.42	46.64	1.33	0.86	1.54	0.52	0.90
F	0.98	18.10	20.40	12.80	47.14	1.41	0.89	1.59	0.52	0.92

Conclusion

CZTS thin film absorber materials with different film thickness were successfully deposited on SLG glass substrate by sol-gel dip-coating technique. The XRD patterns of the films showed that the films were polycrystalline with tetragonal type kesterite structure having orientations along

(011), (110), (112), (004), (211), (220) and (116) diffraction planes. The XRD analysis also showed increase in crystallinity with increase in film thickness. Raman scattering analysis further confirmed the presence of CZTS in the samples with peaks at 338, 286, and 374 cm^{-1}. The microstructural analysis showed increasing grain density and formation of smooth and compact films as thickness increases with root mean square (RMS) roughness in the range of 1.25nm to 1.45nm for the samples. The atomic ratio of sulfur in all the films reaches about 48 (%) which indicates that sufficient sulphurisation was achieved. The ratios of Cu/(Zn + Sn) and Cu/Zn were below 1.0 for all the samples and were observed to increase as the film thickness increase indicating that the films are Cu-poor and Zn-rich and thus have high p-type conductivity that results in high efficiency thin film solar cells.

References

1. Tanaka K, Moritake N, Uchiki H. Preparation of Cu_2ZnSnS_4 Thin Films by Sulphurizing Sol-gel Deposited Precursors. Solar Energy Materials and Solar Cells,2007:91:1199–1201.
2. Woo K, Kim Y, Moon J. A Non-toxic Solution Processed, Earth Abundant Absorbing Layer for Thin Film Solar Cells. Energy and Environmental Science,2012:5:5340–5345
3. Rajesh G, Muthukumarasamy N, Subramaniam EP, Agilan S, Velanthapillai D. Synthesis of Cu_2ZnSnS_4 Thin Films by Dip Coating Method without Sulphurisation. Journal of Sol-Gel Science and Technology, 2013, 0928-0707.
4. Yeh M, Lee C, Wuu D. Influence of Synthesizing Temperatures on the Properties of Cu_2ZnSnS_4 Prepared by Sol-gel Spin-coated Deposition. Journal of Sol-Gel Science and Technology,2009:52:65–69
5. Tanaka K, Kawasaki D, Nishio M, Guo Q, Ogawa H. Fabrication of Cu_2ZnSnS_4 Thin Films by Co-evaporation. Physics Status Solidi,2006:(C)3:2844–2847
6. Scragg JJ, Dale PJ, Peter LM. Synthesis and Characterization of Cu_2ZnSnS_4 thin film Solar Cell Absorber Layers by an Electro-Deposition Annealing route. Thin Solid Films,2009:517:2483.
7. Kumar YBK, Babu GS, Bhaskar PU, Raja VS. Preparation and Characterization of Spray-Deposited Cu_2ZnSnS_4 Thin Films. Solar Energy Materials and Solar Cells,2009:93:1230-1237.
8. Katagiri H, Sasaguchi N, Hando S, Hoshino S, Ohashi J, Yokota T. Preparation and Evaluation of Cu_2ZnSnS_4 Thin Films by Sulphurisation of E-B Evaporated Precursors, Solar Energy Materials & Solar Cells,1997:49:407–414.
9. Sekiguchi K, Tanaka K, Moriya K, Uchiki H. Epitaxial Growth of Cu_2ZnSnS_4 Thin Films by Pulsed Layer Deposition. Physics Status Solidi,2006:(C)3:2618–2621.
10. Salome PMP, Malaquias J, Fernandes PA, Ferreira MS, Leitao JP, Da Cunha AF *et al*. The Influence of Hydrogen in the Incorporation of Zn during the Growth of Cu_2ZnSnS_4 Thin Films. Solar Energy Materials and Solar Cells,2011:95:3482–2489.
11. Tanaka K, Oonuki M, Moritake N, Uchiki H. Cu_2ZnSnS_4 Thin Film Solar Cells Prepared by Non-vacuum Processing Method. Solar Energy Materials and Solar Cells,2009:93:583–587
12. Henry J, Mohanraj K, Sivakumar G. Electrical and Optical Properties of CZTS Thin Films Prepared by SILAR Method. Journal of Asian Ceramic Society,2016:4:81–84.
13. Brinker CJ, Frye GC, Hurde AJ, Ashley CS. Fundamentals of Sol-gel Dip-coating. Thin Solid Films,1991:201:97–108.
14. ICSD Card: 98 – 026 – 2388
15. ICSD Card: 98 – 065 – 3103
16. ICSD Card: 98 – 065 – 1446
17. ICSD Card: 98 – 005 – 7213
18. ICSD card: 98 – 070 – 7090
19. Fernandes PA, Salome PMP, Da Cunha AF. Growth and Raman Scattering Characterization of Cu_2ZnSnS_4. Thin Solid Films,2009:517(7):2519–2523.
20. Seol JS, Lee SY, Lee JC, Nam HD, Kim KH. Electrical and Optical Properties of Cu_2ZnSnS_4 Thin Films Prepared by RF magnetron Sputtering Process. Solar Energy Materials and Solar Cells,2003:75:155–162.
21. Patel KK, Shah DV, Kheraj V. Effects of Annealing on Structural Properties of Copper Zinc Tin Sulphide (CZTS) Material. Journal of Nano- and Electronic Physics,2013:5:02031
22. Tanaka K, Fukui M, Moritake N. Chemical Composition Dependence of Morphological and Optical properties of Cu_2ZnSnS_4 Thin Films Deposited by Sol-gel Sulphurisation and Cu_2ZnSnS_4 Thin Film Solar Cell Efficiency. Solar Energy Materials and Solar Cells,2011:95:838–842.