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X-RAY DIFFRACTION ANALYSIS OF THERMALLY EVAPORATED COPPER TIN SELENIDE THIN FILMS AT DIFFERENT ANNEALING TEMPERATURE

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ABSTRACT

Semiconductor thin films Copper Tin Selenide, Cu_2SnSe_3, a potential compound for solar cell applications or semiconductor radiation detector were prepared by thermal evaporation method onto well-cleaned glass substrates. The as-deposited films were annealed in flowing purified nitrogen N_2, for 2 hours in a temperature range from 100°C to 500°C. The structure of as-deposited and annealed films has been studied by X-ray diffraction technique. The semi-quantitative analysis indicated from Reitveld refinement show that the samples composed of Cu_2SnSe_3 and SnSe. These studies revealed that the films were structured in mixed phase between cubic space group F-43m (no. 216) and orthorhombic space group P n m a (no. 62). The crystallite size and lattice strain were determined from Scherrer calculation method. The results show that increasing in annealing temperature resulted in direct increase in crystallite size and decrease in lattice strain.

Keyword: Cu_2SnSe_3, semiconductor, thermal evaporation, X-ray diffraction, thin films

INTRODUCTION

Ternary compound semiconductors are currently being investigated due to their variety of applications in areas like photovoltaic solar cell, electro-optics, opto-electronics, non-linear optics, acousto-optics, etc. The compound semiconductors of I_2–IV–VI_3 family, which are three-fold derivatives of IV–VI binary analogs, have attracted the attention of researchers recently for acousto-optic applications due to their low energy band gaps, low melting points, high mean atomic weight and high refractive indices [Naemen, 2006]. There is a huge range ternary compounds semiconductor with different band gap energy, electrical resistivity, refractive indices, thickness, and other properties to suit the application of interest [Owens, 2004].

Polycrystalline semiconductor of I_2–IV–VI_3 group compounds have come under increased scrutiny because of their potential use in cost reduction of devices for photovoltaic applications. Photovoltaic conversion of solar energy appears to be one of the most promising ways of meeting the increasing energy demands of the future in a time when conventional sources of energy are being depleted. Advantages of thin film solar cells compared to silicon solar cells include their low cost that is attributable to lesser energy for processing and relatively lower costs of materials and its feasibility for large-scale production [Zainal et al., 2004].

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Thermal evaporation deposition technique consists of heating the conducting boat until evaporation of the material to be deposited occurs. The vapor finally condenses in form of thin film on the cold substrates surface. This vacuum thermal evaporation technique is the best method for deposition of Copper Tin Selenide due to its cleanliness and it allows better contact between the layer of deposition material and the surface of glass slide. In addition, the vacuum will prevent major contamination from the atmosphere. This method use high temperature to melt or sublimate the target (source material) into vapor state. The atom or molecule of target is speed up by high temperature. Passing through an almost vacuum space which is required to allow the molecules to evaporate freely in the chamber, and they subsequently condense on substrate surfaces. As the term "thermal" indicated, the thermal high temperature is key role of this method. Previous work on semiconductors Cu_2SnSe_3 thin films was successfully prepared using chemical bath deposition, co-evaporation, MOCVD, spray pyrolysis, molecular beam epitaxy, sputtering, etc. [Zainal et al., 2004; Suresh Babu et al., 2006; Fernandes, 2010]

In this paper we report our work on preparing Copper Tin Selenide via thermal evaporation method. Structure is the most important factors to determine the physical properties of a material. Therefore, X-ray diffraction technique was used to characterize the crystallographic structure or crystallite size (grain size) of Copper Tin Selenide. In this report, we investigate the physical properties of Copper Tin Selenide films annealed at different temperature by using X-ray diffraction technique.

EXPERIMENTAL

Starting materials (Cu, Sn, and Se) (Alfa Aesar) with a nominal purity of 99.99 wt. % in the stoichiometric ratio were mixed together. To coat the Copper Tin Selenide powder was placed in Molybdenum, (Mo) boat and fixed to a holder. The glass slide substrates were placed on the plate containing holes at specific intervals with similar geometry. The setup was then covered with a glass bell jar and was evacuated using a fore pump and then when the vacuum dropped to ~10^{-3} mbar, a diffusion pump will automatically take places. Coating process was started after the chamber pressure reached roughly 1x10^{-5} mbar. Fig. 1 shows the experimental setup for the thermal evaporator (Edward Auto 306 Vacuum Coating Unit). It also shows the location where the substrate and powder were placed.

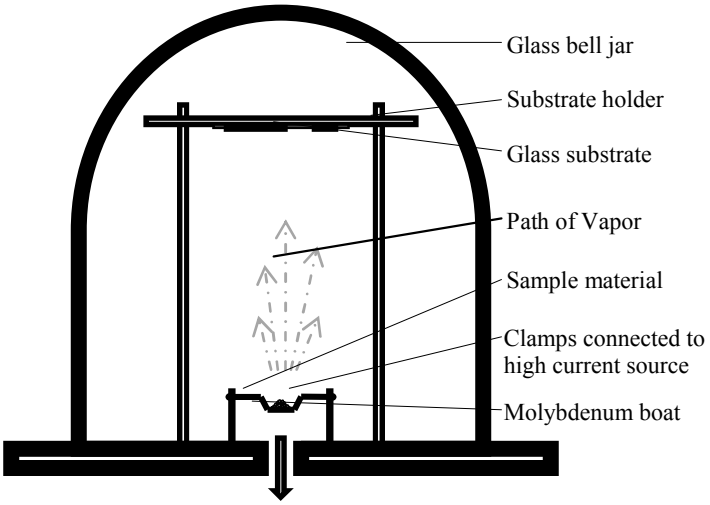

Fig. 1: A simple setup for thermal evaporator vacuum unit

The annealing process was carried out under different temperatures by using a Tube Furnace. The annealing temperatures were 100˚C, 200˚C, 300˚C, 400˚C and 500˚C and flowing purified nitrogen gas, N_2, was run through the furnace to ensure the tin in Copper Tin Selenide thin films did not react with atmosphere and produce tin oxides. The rate for heating and cooling for annealing process was fixed at 3˚C per minutes as shown in Table 1. Then, the specific temperature was maintained at a constant time of 2 hours. The samples were then cooled to room temperature with approximately the same rate as the heating rate.

Table 1: Total time taken to heat up desired temperatures and cooling down

Annealing temperature (°C)	Time taken (minutes)	
	When heating	When cooling*
100	25	25
200	58	58
300	91	91
400	125	125
500	158	158

* The time taken for cooling down from maximum temperature depends on surrounding temperature and could be different from the fixed temperature.

X-ray diffraction data was collected from the annealed thin films that were initially ground. The small thin film sample with diameter of about 1 cm was inserted into the holder and the analysis was carried out by X'pert Pro X-ray Diffractometer model PW 3040 Philips, with CuK_α radiation in the range of 2θ degree from 20^o to 80^o in steps of 0.1˚ with a counting time of 2 s. Working voltage and acceleration current were 40kV and 30mA respectively and the wavelength of X-ray used was 1.54 Å.

RESULTS AND DISCUSSION

Fig.2 shows X-ray diffraction patterns for the films deposited on substrate with different annealing temperatures. Four main peaks at 2θ=38.4°, 44.6°, 65.1°, and 78.2° corresponding to d-spacing values of 2.342 Å, 2.028 Å, 1.432 Å, and 1.221 Å were observed and these are attributed to the (410), (022), (004), and (802) planes. The h k l planes with (410) and (802) which were the most intense, was identified belonging to SnSe peaks (ICSD 98-002-4336). However, appearance of peaks at h k l planes of (022) and (004) are associated to Cu_2SnSe_3 peaks (ICSD 98-007-8211). The observed d-spacing values with its standard data are tabulated in Table 2. When the annealing temperature increases, the intensity of the peaks also increases because temperature will affect the growth of crystals. The X-ray diffraction data in Fig. 2 indicate as grown in intensity of the peaks related to improvement in the crystallinity of the deposited Copper Tin Selenide on the substrate depends on the increasing annealing temperature. This phenomenon was also observed by Dwivedi et al. [2009] on effect of annealing to CdTe/ZnTe heterojunctions thin films.

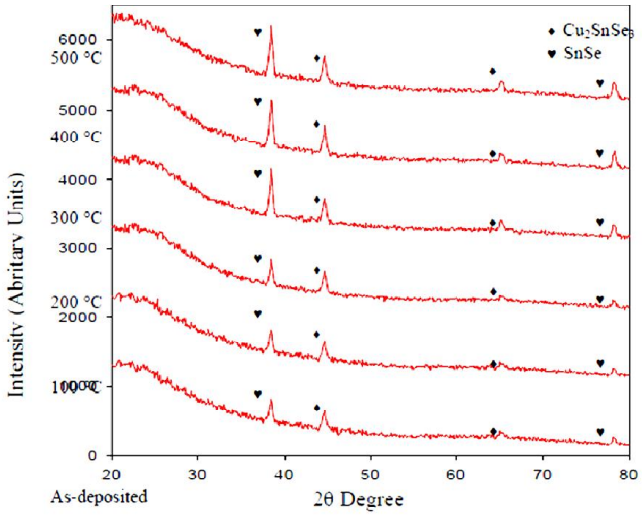

Fig.2. XRD pattern of Copper Tin Selenide thin films annealed at different temperatures.

Table 2: Comparison of the ICSD *d*-spacing data for Cu_2SnSe_3, SnSe to experimentally observed values for the thin film samples annealed at different temperatures

Annealing temperature (°C)	2θ (°)	*d*-spacing (Å)		h	k	l	Compound
		Observed values	Standard values				
As-deposited	38.4	2.35	2.38	4	1	0	SnSe
	44.6	2.04	2.01	0	2	2	Cu_2SnSe_3
	65.1	1.43	1.42	0	0	4	Cu_2SnSe_3
	78.2	1.22	1.22	8	0	2	SnSe
100	38.4	2.35	2.38	4	1	0	SnSe
	44.6	2.04	2.01	0	2	2	Cu_2SnSe_3
	65.1	1.43	1.42	0	0	4	Cu_2SnSe_3
	78.2	1.22	1.22	8	0	2	SnSe
200	38.4	2.34	2.38	4	1	0	SnSe
	44.6	2.03	2.01	0	2	2	Cu_2SnSe_3
	65.1	1.43	1.42	0	0	4	Cu_2SnSe_3
	78.2	1.22	1.22	8	0	2	SnSe
300	38.4	2.34	2.38	4	1	0	SnSe
	44.6	2.02	2.01	0	2	2	Cu_2SnSe_3
	65.1	1.51	1.42	0	0	4	Cu_2SnSe_3
	78.2	1.22	1.22	8	0	2	SnSe
400	38.4	2.34	2.38	4	1	0	SnSe
	44.6	2.03	2.01	0	2	2	Cu_2SnSe_3
	65.1	1.43	1.42	0	0	4	Cu_2SnSe_3
	78.2	1.22	1.22	8	0	2	SnSe
500	38.4	2.34	2.38	4	1	0	SnSe
	44.6	2.02	2.01	0	2	2	Cu_2SnSe_3
	65.1	1.43	1.42	0	0	4	Cu_2SnSe_3
	78.2	1.22	1.22	8	0	2	SnSe

Thin films consist of a mixture of amorphous and sometime crystalline, perhaps depending on the substrate temperature or the film. At lower temperatures films are amorphous. Film deposited at a higher temperature was found to be polycrystalline in nature along the peak intensity direction. It is found that films deposited at higher temperatures will give better crystallinity and crystallization on the materials [Dwivedi, 2009]. The initial hump at lower angle indicates that the structures of the films are amorphous and the four obvious peaks represent the polycrystalline structure of the material. But, there is some equivocalness in the structure of the Copper Tin Selenide that had been studied and reported earlier. Suresh Babu et al. [2006] reported it as sphalerite structure and no peaks corresponding to either the orthorhombic or the monoclinic structures were observed. After few years, Fernandes [2010] reported it as tetragonal (*I-42m*) and cubic (*F-43m*) structure were grown on Cu_2SnS_3 thin films by sulphurization of dc magnetron sputtered Sn–Cu metallic precursors in a S_2 atmosphere.

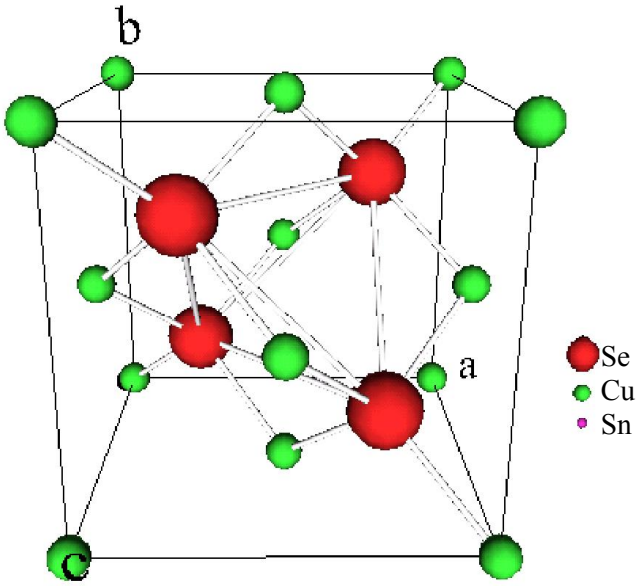

Fig. 3: Unit cell diagram for Cu_2SnSe_3 phase

Table 3: Reitveld refinement details for Cu_2SnSe_3 and SnSe

Molecular formula	Cu_2SnSe_3	SnSe	
Molecular weight (g/mol)	642.8	790.6	
a (Å)	5.81(4)	9.68(6)	R_{exp} (%) = 4.43
b (Å)	5.81(4)	1.84(1)	R_p (%) = 6.32
c (Å)	5.81(4)	5.17(4)	R_{wp} (%) = 10.91
V (Å^3)	196.18	91.89	χ^2 = 2.46
Space group	F-43m (no. 216)	P n m a (no. 62)	
D_{calc} (g/cm^3)	5.44	1.43	
Weight fraction (%)	89.6	10.4	
R_B (%)	2.13	4.97	

$R_p = 100\Sigma|y_{obs} - y_{calc}|/ \Sigma|y_{obs}|$; $R_{wp} = 100[\Sigma_w|y_{obs} - y_{calc}|^2/ \Sigma_w|y_{obs}|^2]^{1/2}$;
$R_B = 100\Sigma_k|I_k - I_{ck}|/\Sigma_k|I_k|$; $\chi^2 = [R_{wp}/R_{exp}]$; $R_{exp} = 100[(N - P + C)/\Sigma w(y_{obs}^2)]^{1/2}$;
$N - P + C$ is the number of degrees of freedom. Delgado et al [2008].

The refinement of crystal structure of Copper Tin Selenide thin films by the Rietveld method from X-ray powder diffraction data indicated that both compounds (Cu_2SnSe_3 and SnSe) crystallize in cubic and orthorhombic space groups [Delgado et al., 2008]. Results of Rietveld refinement for both phases for as-deposited Copper Tin Selenide are summarized in Table 3. Semi-quantitative analysis from Rietveld refinement (see Table 3) indicated that the sample composed of 64.1% Cu_2SnSe_3 and 35.9% SnSe. Fig. 3 shows the unit cell diagram for Cu_2SnSe_3 phase indicating the position of material crystallizes in the cubic space group F-43m (no. 216). This phenomenon was also reported by Ares et al. [2005] on grain and crystallite size in polycrystalline pyrite thin films. Fig. 4 and Fig. 5 show the crystallite size and lattice strain of Copper Tin Selenide as a function of annealing temperatures. The crystallite size and lattice strain were determined by using Scherrer calculator from X'Pert Highscore Plus software. Values of crystallite size and lattice strain were calculated by comparing the profile width of a standard profile with a sample profile according to Scherrer formula based on the tangent formula [Delhez et al., 1982]. Fig. 4 shows that the crystallite size increases with increasing annealing temperatures whereas Fig. 5 shows the lattice strain decreases with increasing annealing temperature [Adawiya et al., 2008].

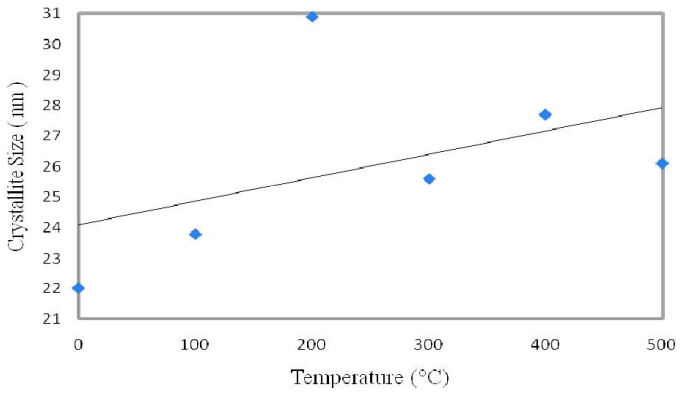

Fig. 4: Variation in crystallite size with anenealing temperature

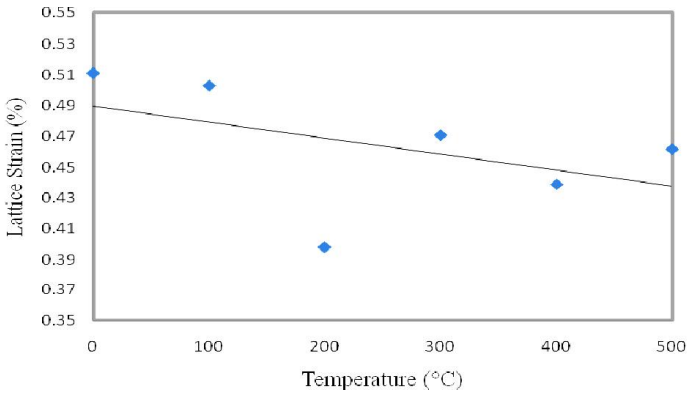

Fig. 5: Variation in lattice strain with annealing temperature

CONCLUSIONS

This study showed that two mixed phases were obtained for thermal evaporation of Copper Tin Selenide thin films deposited using thermal evaporator and annealed at different temperatures. The

refinement of crystal structure of copper tin selenide thin films by Reitveld method indicated that the compound crystallizes in the cubic space group *F*-43*m* and orthorhombic space group P n m a. Annealing caused increase in the crystallinity of resulted structures. From the Scherrer calculations, crystallite size of Copper Tin Selenide increases with increasing annealing temperature and the lattice strain decreases with increasing annealing temperature.

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REFERENCES

Adawiya, J., Haider, Ali M. Mousa, (2008)Annealing Effect on Structural, Electrical and Optical Properties of Cds Films Prepared by CBD Method, *Journal Of Semiconductor Technology And Science 08: 04-08*

Ares, J.R., Pascual, A., Ferrer, I.J. dan Sanchez, C. (2005), Grain And Crystallite Size In Polycrystalline Pyrite Thin Films, *Thin Solid Films,* 480–481:477– 481

Delgado, G.E. and Mora, A.J. (2008), Crystal Structure of $CuFe_2InSe_4$ From X-Ray Powder Diffraction, *Journal Of Alloys And Compounds* 454:306–309

Delhez, R. dan Mittemeijer, E. J. (1982) Determination of Crystallite Size and Lattice Distortions Through X-Ray Diffraction Line Profile Analysis,*Journal of Analytical Chemistry* 312:1-16

Dwivedi, D. K., Dayashankar, and Dubey,M. (2009), Effect of Annealing on The Structural And Electrical Properties of Cdte/Znte Heterojunction Thin Films, *Chalcogenide Letters* 6:71 – 76

Fernandes P. A., (2010), A Study Of Ternary Cu_2SnS_3 And Cu_3SnS_4 Thin Films Prepared By Sulfurizing Stacked Metal Precursors, *Journal Physics D: Applied Physics* 43: 215403

Naemen, D.A. (2006), An Introduction to Semiconductor Devices, McGraw-Hill

Owens, A. and Peacock, A. (2004), Compound Semiconductor Radiation Detectors, *Nuclear Instruments and Methods in Physics Research A* 531 18–37

Suresh Babu, G., Kishore Kumar, Y.B., Bharath Kumar Reddy, Y. and V. Sundara Raja (2006), Growth And Characterization of Cu_2SnSe_3 Thin Films, *Materials Chemistry and Physics* 96 442–446

Zainal, Z., Kasim, A. and Chuah C.C., (2004), Effect of Bath Temperature on The Electrodeposition of Copper Tin Selenide Films From Aqueous Solution, *Materials Letters* 58: 2199– 2202