VARIATION OF CHARACTERISTIC PROPERTIES OF Cu_2ZSnS_4 DEPOSITED BY ELECTRODEPOSITION LAYERING OF CZT METHOD COUPLED WITH CHEMICAL BATH IN Na_2S SOLUTION TECHNIQUE WTH ANNEALING TEMPERATURE

Obila J. O

Department of Physics
School of Physical Sciences
University of Nairobi
Kenya

Domtau D. L

Taddy E. N

Durodola O. M

Madaki A. Y

Chagok N. M. D

Department of Physics
Faculty of Natural Sciences
University of Jos
Nigeria

Dawuk N. D

Department of Science Laboratory Technology
Federal Polytechnic Nasarawa
Nigeria

Abstract

Cu2ZSnS4 (CZTS) solar technology is considered as a viable replacement to copper indium gallium selenide (CIGS) solar technology. Though CIGS technology has achieved high efficiency, 20%, it is faced with problems of material scarcity and toxicity. Therefore, CZTS which contains earth abundant and nontoxic materials is a best alternative. In this study, properties of CZTS deposited by low cost electrodeposition, layering of CZT with Sn as the underneath layer and a composite of Zn and Cu as the top layer, coupled with chemical bath in Na2S solution and then annealed under sulphur rich atmosphere were investigated. The optical band gaps of the annealed samples ranged between 1.59 to 1.94 eV with absorption coefficient in the order of ~104 cm-1 in the visible and near infrared range of the solar spectrum. The electrical sheet resistivity of the samples was observed to decrease with annealing temperature. The quality of the deposited CZTS was determined using Raman Spectroscopy, main peak at 338 cm-1 was observed for films annealed at 550 oC.

Keywords: Variation, Electrode position layering, CTZ method, chemical bath and annealing temperature

Introduction

Due to the increase in fossil fuel energy consumption and the gradual environmental crisis, due to CO2 gas emission during their use, researchers have been attracted to solar cells (Song *et al.*, 2014). Solar energy is one of the energy sources that can address the energy problems such as; energy security, energy equity and environmental sustainability since it is abundantly available and accessible. Development and commercialization of thin film solar cells has been growing over the past decade due to their low cost and scalability (Ananthan and Mahalaksmi, 2014). The currently available and commercialized thin film solar technology is the CdTe and CIGS which have achieved a conversion efficiency of 20% (Walsh *et al.*, 2011).

In and Ga are expensivecomponents of CIGS and therefore a replacement which CZTS is considered viable (Chen *et al.,* 2009). CZTS is a non-toxic form of CIGS, it is obtained by substituting In with Zn, Ga with Sn and Se with S (Mkawi *et al.,* 2013). CZTS is a promising material for absorber layers of the thin film solar cells due to its appropriate properties. CZTS has a suitable optical optical band gap of 1.4 – 1.5 eV and large optical absorption coefficient of ~104 cm-1. In addition, the materials for CZTS are abundant in the earth crust and nontoxic (Katagiri *et al.,* 2008).

CZTS can be synthesized using a number of methods which can be classified as vacuum and non vacuum based methods. In this study, elecrodeposition and chemical bath was used to achieve CZTS films. Electrodeposition is a promising technique for the low cost deposition of semiconductors films (Wang, 2011). In this research, CZT was electrodeposited in layers with Sn as the underlying layer and the composite of Zn and Cu as the top layer. This was followed by a low cost chemical bath and annealed to obtain CZTS film.

Methods

The chemicals used in this study were of analytical grade and were procured from Alpha Chemica, India. Electrodeposition of CZT thin films was performed using a three electrode electrochemical cell with a saturated calomel electrode (SCE) as a reference electrode, a precleaned TCO coated glass as a working electrode and platinum as a counter electrode at room temperature (23oC). This was done by the use of Autolab PG STAT 12. Electrodeposition of CZT was performed in layers with Sn as the underlying layer and composite of Cu/Zn as the top layer. Sn layer and Cu/Zn composite layer were deposited by performing a Cyclic voltammograme (CV) scan on 260 mM of SnCl4.5H2O solution and a mixture of 47 mM of CuSO4.5H2O and 450 mM of ZnSO4.7H2O solution, respectively, with the beginning potential at 1.00 V and end potential at -1.00 V, the rate of scan was 0.10 V/s while step potential was 3.05 mV.

Sulphurization of the samples was done using chemical bath technique together with annealing step in sulphur rich atmosphere, at dfferent temperatures. Chemical bath technique was implemented by dipping and leaving the samples in a 50 mM Na2S solution for 5 minutes each.

To determine the elemental composition of the deposited CZT film, Laser Induced Breakdown Spectroscopy (LIBS) (in the University of Nairobi) was used to analyze the deposited CZT film. The scan was done on sampled areas of each film with optical distance from the film of 3 mm, and laser energy of 7.5 mJ.

The optical characterization of CZTS was carried out using *Shimadshu UV-VIS-NIR*, Japan spectrophotometer in the wavelength range of 300 – 2500 nm, in the University of Nairobi. Electrical characterization was done by using four point probe system, Guardian (SRM-232- 100), in the University of Nairobi. This was done by use of contact technique where a four point probe system was brought into contact with the sample and its sheet resistivity recorded.

Quality determination of CZTS film was done by the use of Raman spectroscopy (in the University of Nairobi) at room temperature at excitation wavelength of 785 nm, exposure time of 10 s, number of accumulation 5 s, center wavelength of 1050 nm, objective ×50 and intensity of 50%

Results

Figure 1 and 2 showing typical CV scans of SnCl4.5H2O, and mixture of CuSO4.5H2O and ZnSO4.7H2O respectively. From the data collected the oxidation potential of Sn is -0.33 V verses Ag/AgCl which is a deviation from the expected -0.13 V verses Ag/AgCl (Scragg, 2011). This deviation is due to the presence of acetic acid in the electrolyte, which could have resulted in formation of complex ions with tin ions. The CV scan performed on electrolyte containing a mixture of CuSO4.5H2O and ZnSO4.7H2O showed two oxidation peaks, as shown in Figure 2. The oxidation peaks, at -0.12 V verses Ag/AgCl and 0.30 V verses Ag/AgCl, are the oxidation peaks of Zn and Cu, respectively. The reduction potentials are at higher negative potential compared to the redox potential of the individual metals. The results of oxidation and reduction potential of mixture CuSO4.5H2O and ZnSO4.7H2O are in accordance to results reported in other studies (Grujicic and Pesic, 2002).

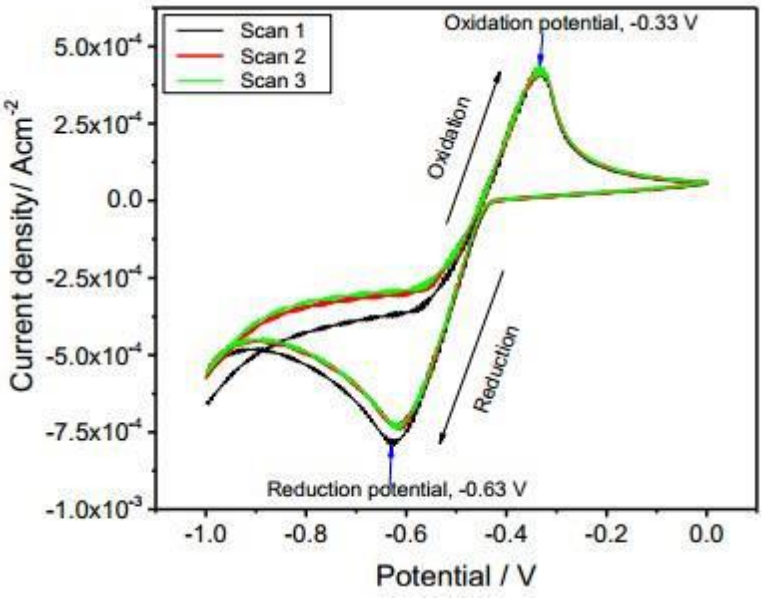


Figure 1: CV scans response of Sn electrodeposited on TCO glass electrode in solution containing 260 mM SnCl4.5H2O. Potential limit -1.00 V to 0.00 V, Scan rate
0.10 V/s, pH 3 and temperature of 23oC.

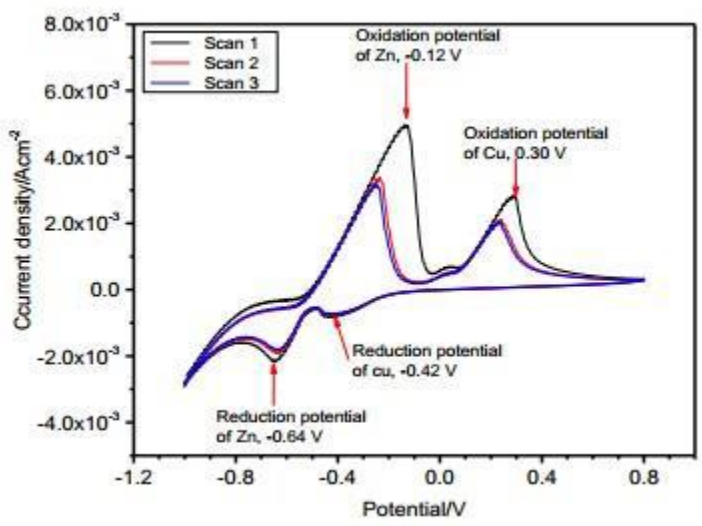


Figure 2: CV scans response of Cu and Zn electrodeposited on TCO glass electrode in solution containing a mixture of 47mM CuSO4.5H2O and 450mM ZnSO4.7H2O. Potential limit -1.10 V to 0.80 V, Scan rate 0.10 V/s, pH 3 and temperature of 30oC.

Elemental analysis of the deposited CZT thin film was done by Laser induced breakdown spectroscopy (LIBS). The results showed the presence of the three metals forming CZT as shown in Figure 3.

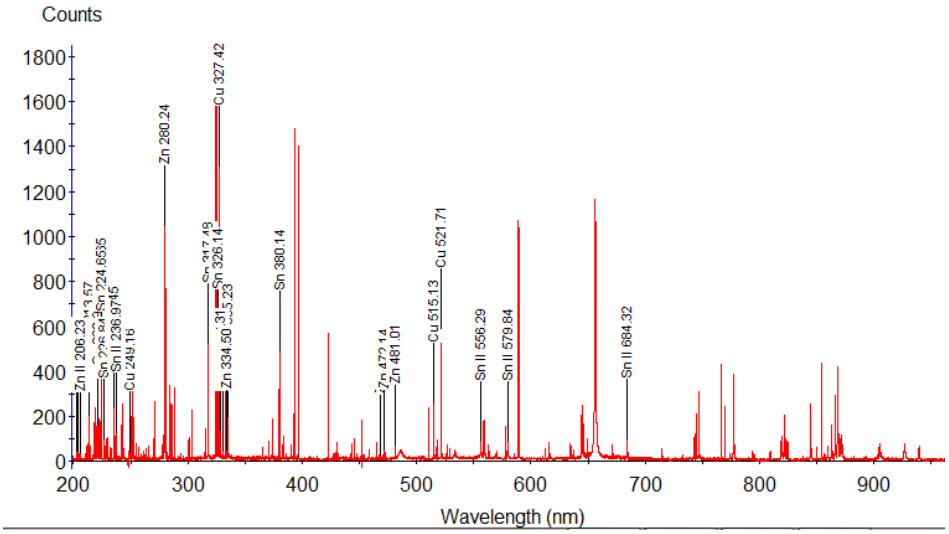
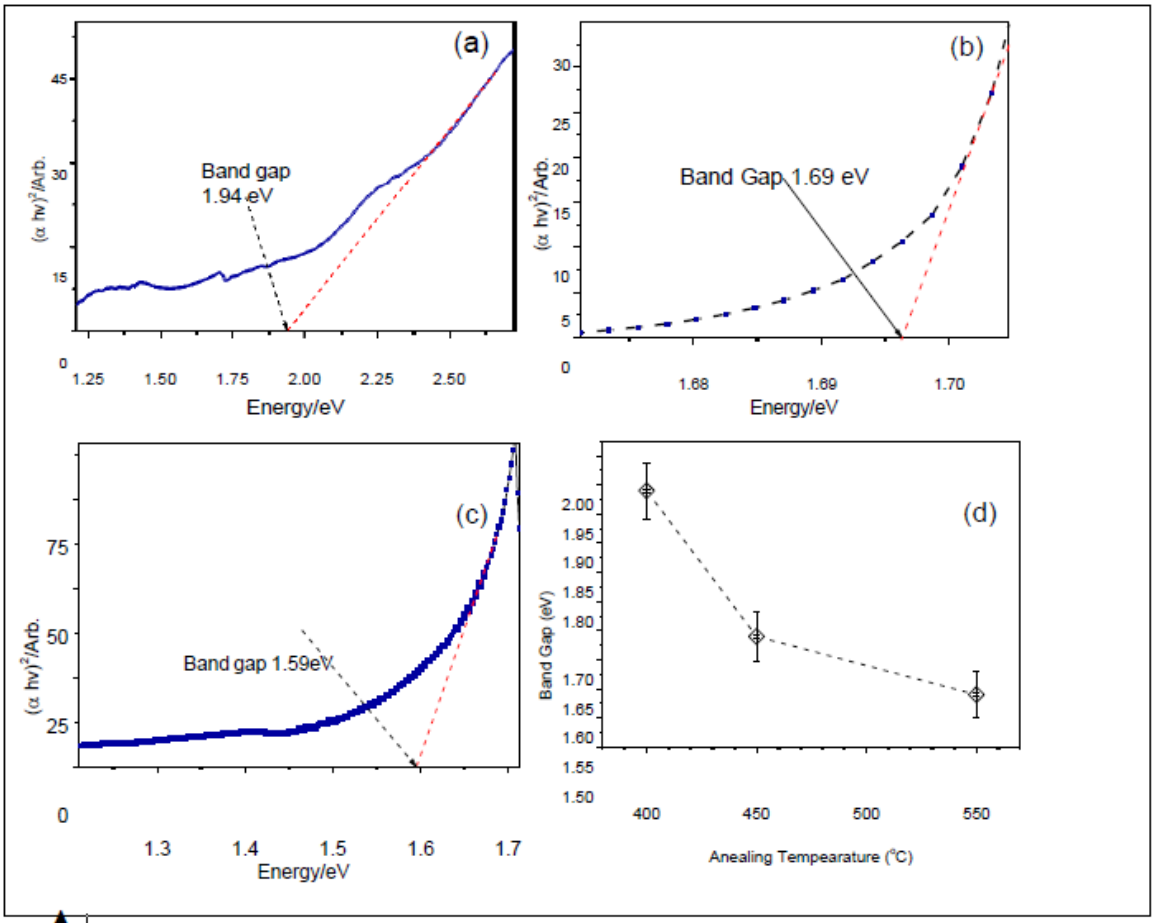


Figure 3: Spectral lines of deposited CZT film using LIBS spectroscopy. Energy 7.5 mJ, integration time 0.42 µS, shot counts 1, single count, Q switch delay time 150 µS and optical distance 3 mm.

The band gap of the CZTS thin film deposited and annealed at various temperatures were determined and the results were as shown in Figure 4(A). Figure 4(A (d)) is the summary variation of the determined band gap with annealing temperature. Variation of absorption coefficient of the sample at annealing temperature of 550 oC is as shown in Figure 4(B).



A

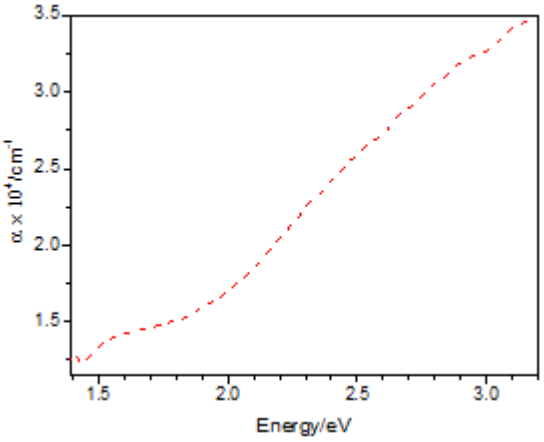


Figure 4: (A) variation of band gap with annealing temperature. (B)The absorption coefficient of annealed CZTS deposited by layering method followed by chemical bath in Na2S annealed at 550Oc

The reduction of band gap with increase in annealing temperature is as a result of significant transformation of the binary phases and the formation of crystalline CZTS (Pawar *et al.*, 2014). For example from Raman peaks diagrams, Figure 6 – 8, it is observed that at 550oC only a small peak of ZnS appears. The band gap obtained was still within the desired optimum range (Sheng *et al.*, 2014). Other researchers have tried etching using toxic KCN to get rid of ZnS completely from their samples (Tiong *et al.*, 2014), which was to ensure that a band gap range of between
1.41 - 1.51 eV was obtained. Based on this study and theoretical knowledge, it is without doubt that band gap depends very much on the impurities in the film as well as secondary phases and annealing temperatures. Band gap also reduces due to increase in grain size at high annealing temperatures; this increase in grain size was predicted from the electrical resistivity of the deposited films (Tumuluri *et al.*, 2012).

It is observed that absorption coefficient is in the range of ~104 to ~105 cm-**1** within the region

≥1.50 eV. The high value of absorption coefficient obtained in this study was within the range observed in other studies, and shows that CZTS is a viable solar cell absorber (Singh *et al.*, 2015).

Figure 5 shows the variation of sheet resistivity with annealing temperature.

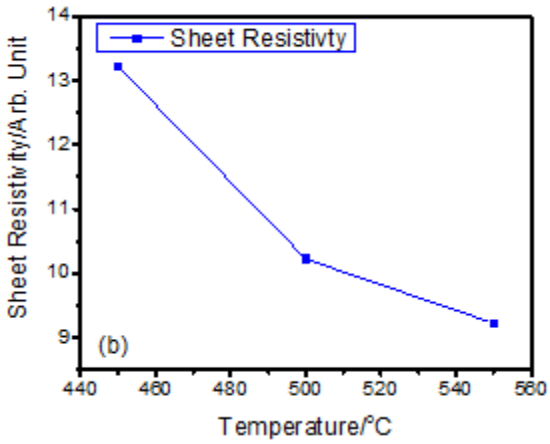


Figure 5: Sheet resistivity variation with temperature.

The decrease in sheet resistivity with annealing temperature, Figure 5, is because of grain size increase which increases with the annealing temperature (Shinde *et al.*, 2013).
The shape and position of Raman peaks are strongly influenced by the presence of defects in the sample, either in the form of structural inhomogeneity or secondary phases. Typical Raman spectra for CZTS films annealed at different temperatures are given in Figure 6 – 8.

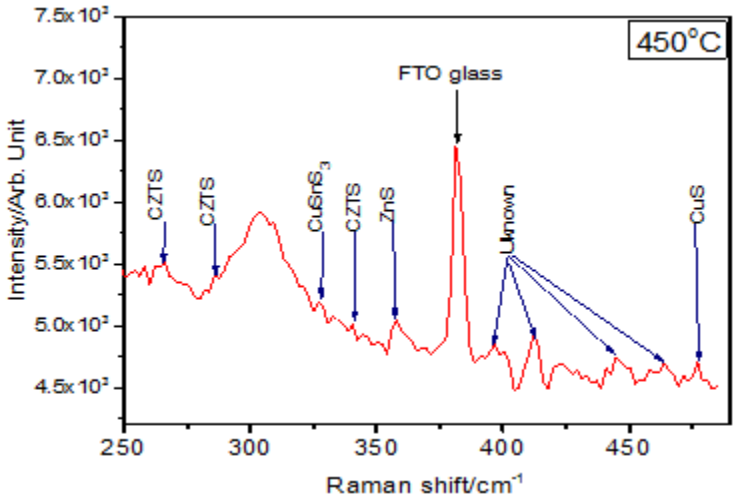


Figure 6: Raman peaks of CZTS film deposited by layering method followed by chemical bath in Na2S solution annealed at 450oC.

Several Raman peaks were observed at 266 cm-1, 287 cm-1, 334 cm-1, 333 cm-1, 359 cm-1, and 477 cm-1 for sample annealed at 450oC. Of these peaks, three peaks at 266 cm-1, 286 cm-1 and one at 341 cm-1 were identified to be CZTS as shown in the spectrum. The 359 cm-1 peak is attributed to ZnS binary phase while 477 cm-1 peak was due to CuS. Similar observations hadbeen reported by Dimitrievska *et al.*, (2014). These peaks could be due to other binary and ternary produced during the formation of CZTS film.
In Figure 7, the intensities of ZnS and CuS were reduced in sample annealed at 500oC compared to those annealed at 450oC.

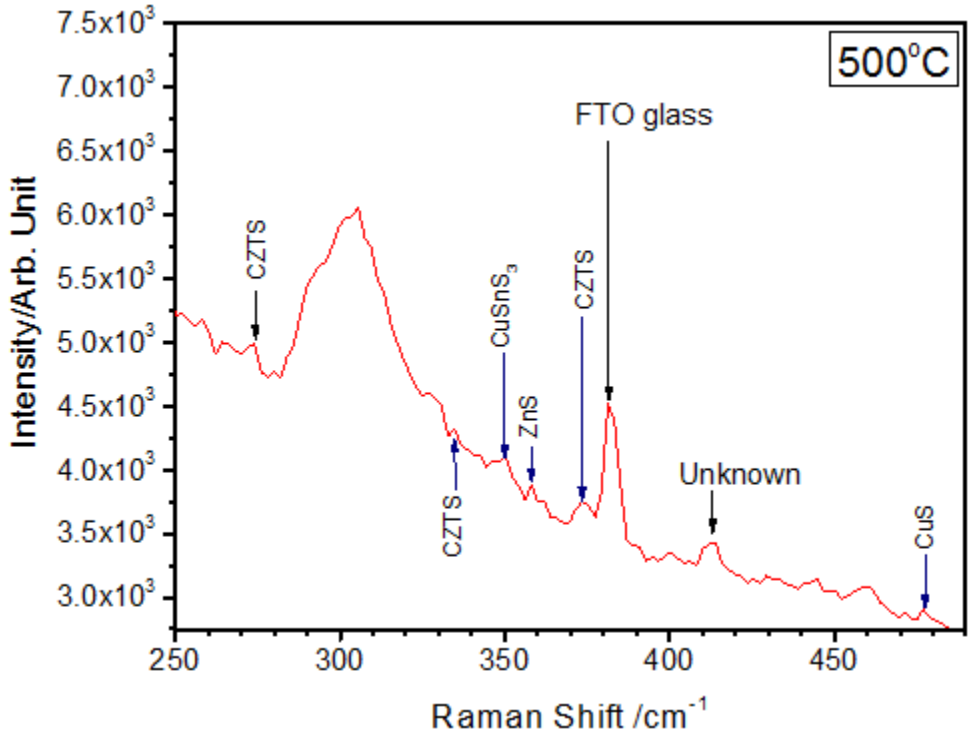


Figure 7: Raman peaks of CZTS film deposited by layering method followed by chemical bath in Na2S solution annealed at 500oC.

From Figure 7, the Raman peaks observed at 335 cm-1, 351 cm-1, 356 cm-1 373 cm-1 and 475 cm- 1 were for the sample annealed at 500oC. The peaks at 335 cm-1 and 373 cm-1 peaks were as a result of CZTS structure, while those at 356 cm-1, 351 cm-1 and 475 cm-1 were as a result of ZnS, CuSnS3 and CuS phases respectively.

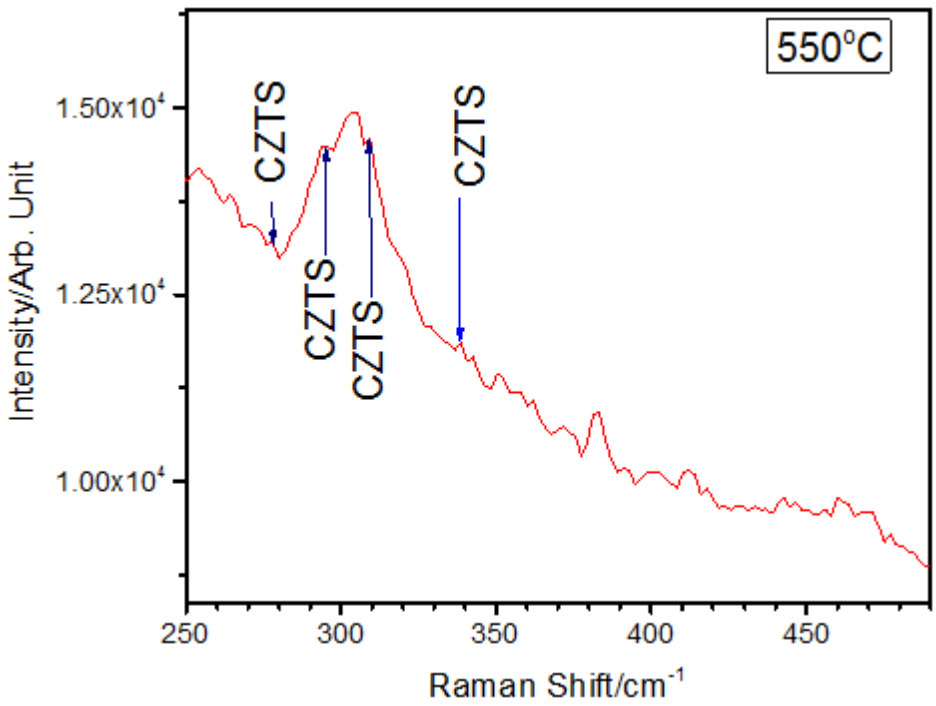


Figure 8: Raman peaks of CZTS film deposited by layering method followed by chemical bath in Na2S solution annealed at 550oC.

From Figure 8, the Raman peaks were observed at 278 cm-1, 293 cm-1, 310 cm-1 and 338 cm-1 were for sample annealed at 550oC under the flow of nitrogen gas. The peaks at 278 cm-1, 293 cm-1, 310 cm-1 and 338 cm-1 were attributed to CZTS crystalline structure (Dimitrievska *et al.*, 2014, Lydia and Reddy, 2013).

The shift in the main CZTS peak position which were 333 cm-1, 335 cm-1 and 337 cm-1 for samples annealed at 450oC, 500oC and 550oC respectively could be due to local inhomogeneities with high degree of disorder in the cation of sublatice of CZTS film and the wavelength of laser excitation used which was 785 cm-1. There was a very small peak at 256 cm-1 which was an indicator of the presence of ZnS. The presence of ZnS in the sample annealed at 550oC indicated that the CZTS thin film deposited was rich in Zn (Dimitrievska *et al.*, 2014) as expected for a best performing CZTS film. Zn rich prevents formation of Cu-Sn-S ternary phases, which was readily converted to CZTS under heat treatment (Singh *et al.*, 2015).

The intensities of optical Raman modes of CZTS could vary depending on the excitation wavelength of the sample. Raman modes such as 302.1 cm-1 which has not been identified by researchers could be due to low intensities produced by the excitation wavelength chosen (Dimitrievska *et al.*, 2014).

Conclusion

CZTS can be deposited by electrodeposition coupled with chemical bath followed by annealing under sulphur atmosphere, and the formation of secondary phases suppressed by increasing annealing temperatures to 550oC.

References

Ananthan M. R. and Mahalaksmi B., (2014), Review on CZTS based solar cells, *Advances in Natural and applied sciences*, **8**(21) 72-75

Chen S., Gong X. G., Walsh A. and Wei S., (2009), Crystal and electronic band structure of Cu2ZnSnX4 (X=S and Se) photovoltaic absorbers: First-principles insights, *Applied Physics Letters*, **94**, 041903 1-3

Dimitrievska M., Fairbrother A., Fontane X., Jawhari T., Izquierdo-Roca V., Saucedo E. and Perez-Rodriguez A., (2014), Multiwavelength excitation Raman scattering study of polycrystalline kesterite Cu2ZnSnS4 thin films, *Applied Physics Letters*, **104** 021901 (5pp)

Grujicic D. and Pesic B., (2002), Electrodeposition of copper; the nucleation mechanisms, *Electronic Acta, 47 2901-2912*

Katagiri H., Jimbo K., Yamada S., Kamimura T., Maw W. S., Fukano T., Ito T. and Matohiro T., (2008), Enhanced conversion efficiencies of Cu2ZnSnS4-based thin film solar cells by using preferential etching technique, *Applied Physics Express*, **1**(4) 1-2

Mkawi E. M., Ibrahim K., Ali M. K. M., Farrukh M. A. and Mohamed A. S., (2013), Synthesized and characterization of Cu2ZnSnS4 (CZTS) thin films deposited by electrodeposition method, *Applied Mechanics Materials* **343** 85-89

Pawar S. M., Pawar B. S., Moholkar A. V., Choi D. S., Yun J. H, Moon J. H., Kolekar S. S. and Kim J. H., (2010), Single step electrosynthesis of Cu2ZnSnS4 (CZTS) thin films for solar cell application, *Electrochimica Acta*, **55** 4057-4061Scragg J. J., (2011), Copper Zinc Tin Sulfide thin films for photovoltaics: Synthesis and characterization by electrochemical methods, *Springer theses*, page 9-66

Sheng C. Y., Jun Y. W., Rui L., Hua G. J., Xiao L. J., and Shi E. Y., (2014), Preparing Cu2ZnSnS4 films using the co-electrodeposition method with ionic liquids, *China Physics B*, **21**(5) **058801** 1-4

Shinde N.M., Deokate R. J., and Lokhande C. D**.,** (2013), Properties of spray deposited Cu2ZnSnS4 (CZTS) thin films, *Journal of Analytical and Applied Pyrolysis*, **100** 12-16

Singh O. P., Muhunthan N., Singh N. V. and Singh B. P**.,** (2015), Effect of annealing time on the composition, microstructure and band gap of copper zinc tin sulfide thin films, *Research Article*, **6**(1) 2-7

Song X., Ji X., Li M., Luo X. and ZhangH., (2014), A review on development prospect of CZTS Based Thin Film Solar Cell, *international Journal of Photoenergy*, Article ID 613173, 11pages

Tiong V. T., Bell J., and Wang H., (2014), One-step synthesis of high quality kesterite Cu2ZnSnS4 nanocrystals-a hydrothermal approach, *Beistein Journal of nanotechnology*, **5** 438-446

Tumuluri A., Naidu K. L., and Raju K. C. J., (2014), Band gap determination using Tauc's plot for LiNbO3 thin films, I

Walsh A., Chen S., Gong X. and Wei S., (2011), Crystal structure and defect reactions in the kesterite solar cell absorber Cu2ZnSnS4 (CZTS): Theoritical insights, *AIP conference proceedings* **1399** 63

Wang H., (2011), Progress in thin film solar cells based on Cu2ZnSnS4, *International Journal of photoenergy*, Article ID 801292 10pages