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FABRICATION AND CHARACTERIZATION OF ELECTRO-DEPOSITED Cu_2ZnSnS_4 THIN FILM ABSORBER LAYER FOR SOLAR POWER ENGINEERING APPLICATIONS

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Cu_2ZnSnS_4 (CZTS) thin film absorber layer was fabricated using electro-deposition method. This electro-deposited CZTS thin film absorber layer was cleaned to remove loosely bounded CZTS particles using ultra sonic bath contain ultra pure water. This CZTS thin film layer is subjected for room temperature hot plate annealing at temperature 80 °C to remove moisture and unwanted water molecules. The structural, surface morphology, optic, elemental and electrical studies were carried out on the fabricated CZTS thin film absorber layer. The observed scientific results on the electro-deposited CZTS sample were presented and discussed in the present research article.

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1. Introduction

Thin film solar cells were enormously investigated for the fabrication of low-cost manufacturing and renewable energy sources. Particularly, $Cu(In,Ga)Se_2$ (CIGS) thin film solar cells are being importantly addressed [1-9] for present market opening because of its high photo conversion efficiency. The possibilities of $Cu_2ZnSn(S,Se)_4$ (CZTSSe) solar cells being issued for further reduction of manufacturing cost by use of earth abundant materials. Further this CZTS and CZTSSe have very wide band gap than CIGS thin film absorber material so that CZTS and CZTSSe can cover a wide range of visible spectral wavelength [10-15]. Fundamentally, fabrication of the quaternary thin film solar cells depends on platform technologies. For the fabrication of platform technologies, there are several available methods such as vacuum-based, electrochemical, and other solution-based depositions [10-18]. In the present work we utilized electro-deposition method for the fabrication of CZTS thin film absorber layer.

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2. Experimental

All the chemicals were purchased from the sigma aldrich with the purity of 99% for the CZTS thin film absorber layer fabrication process. An appropriate amount of ultra pure water and tartaric acid ($HOOC(CHOH)_2COOH$) mixture 5 : 0.6 was taken in to a well cleaned borosilicate glass beaker. Further the ammonium citrate ($HOC(CO_2NH_4)(CH_2CO_2NH_4)_2$) of 0.045 M was added to the above reaction mixture. Then the reaction was stirred until the whole mixture was dissolved without any precipitation and the final solution becomes transparent. After few minutes the copper sulfate of 0.023 M, zinc sulfate of 0.005 M and tin sulfate of 0.015 M ratio respectively. Finally the reaction mixture was completed with the sulfur source sodium thiosulfate 0.03-0.04 M injection.The complete reaction mixture was mild stirred to promote the reaction rate and to avoid the residuals settled down on the bottom of the reaction vessel and the deposition process was carried out at room temperature. Prior to the electro-deposition process, the sputter deposited molybdenum (Mo) of 800 nm coated soda lime glass substrates were cleaned ultrasonically by methanol, acetone and then water for 5 min and dried by nitrogen air and was kept inside the evacuated chamber to avoid the air contact on the surface of the Mo substrate. Here Mo metal is the working electrode and it was immersed inside the above said electro-deposition bath mixture. After several minutes one can get CZTS thin film absorber layer with very uniform thickness. The electro-deposited CZTS finally cleaned using ultra pure water and was dried in air atmosphere.

3. Results and discussion

The compete electro-deposition reaction mixture was set in to a predesigned three electrode electro-deposition system and here platinum mesh of 5 cm^2 were served as a counter electrode and saturated KCl as a reference electrode and Mo metal substrate served as a main working deposition electrode. The deposition was carried out cathodically at the applied voltage range between of -0.9 to -0.95 V. The fabricated CZTS film were taken out and washed by the flowing de-ionized water and dried by nitrogen air then further the CZTS film were annealed in air atmosphere at 80 °C for several minutes and then cool down naturally to the room temperature. The structural property of our electro-deposited CZTS thin film absorber layer was investigated through powder X-ray diffraction method at low scan rate. Figure 1 showed the X-ray diffraction spectra of our electro-deposited CZTS thin film absorber layer. The investigated XRD pattern of our electro-deposited CZTS layer showed very high crystalline quality and the predominant XRD peak was observed at diffraction angle 2Θ = 40.5.

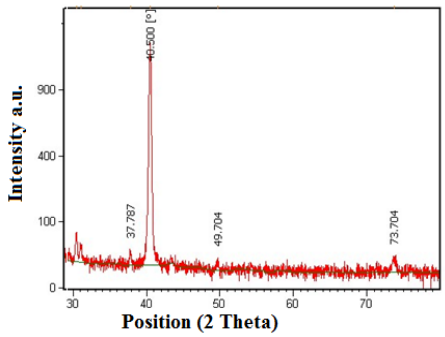

Fig. 1. X-ray diffraction spectra of our electro-deposited CZTS thin film.

The elemental and surface morphology cross-section view with top view focus of our fabricated CZTS thin film absorber layer was investigated using EDX (Energy dispersive X-ray analysis) and SEM (Scanning electron microscopy) analysis. The observed EDX measurement showed all the Cu, Zn, Sn and S elements presence in the fabricated CZTS thin film absorber

layer. This result evident that our electro-deposited CZTS compound formation is confirmed. Fig. 2 shows the EDX analysis of our electro-deposited CZTS thin film absorber layer.

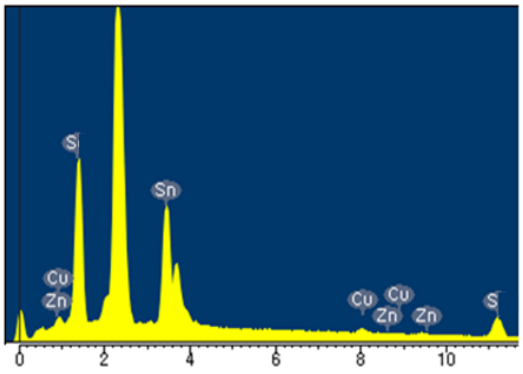

Fig. 2. Shows the EDX analysis of our electro-deposited CZTS absorber layer.

Fig. 3 shows the cross-sectional and top view focused SEM image of our fabricated CZTS thin film absorber layer. The fabricated CZTS thin film absorber layer thickness is nearly 1.42 µm. This thickness is more than enough for the fabrication of CZTS thin film solar cell.

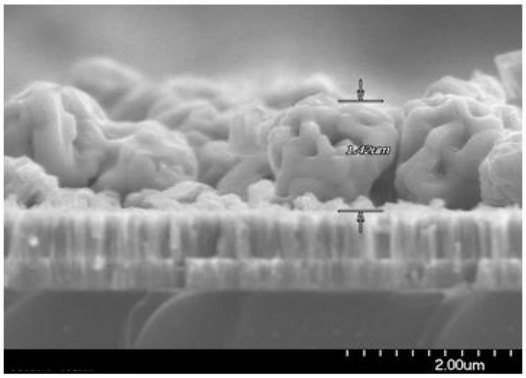

Fig. 3. The cross-sectional and top view focused SEM image of our electro-deposited CZTS thin film absorber layer.

The SEM top standing view showed the CZTS grains are agglomerated and formed very large sized granules. So that we got very good grain continuity and this is important for getting uniform structural, optic, electrical and opto-electronic property of CZTS material layer. Raman spectroscopy measurement was taken on our electro-deposited CZTS thin film absorber layer. Figure 4 showed the Raman spectra of our electro-deposited CZTS layer and vacuum co-sputtered standard CZTS thin film absorber layer.

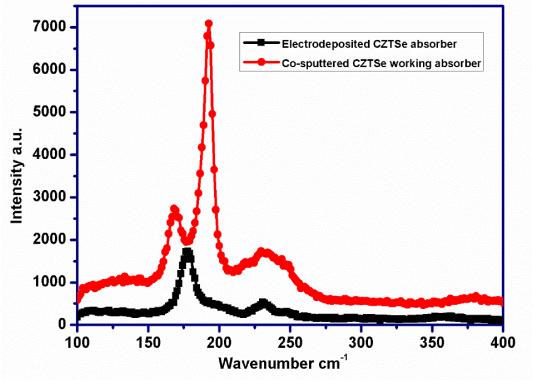

Fig. 4. Raman spectra of our electro-deposited CZTS layer and vacuum co-sputtered standard CZTS thin film absorber layer.

Then this electro-deposited CZTS Raman spectrum was compared with vacuum co-sputtered CZTS thin film absorber layer for checking the optic quality of our electro-deposited CZTS thin film layer. Both the electro-deposited and vacuum sputtered CZTS thin film absorber layer showed the Raman shift 175 cm^{-1} and 190 cm^{-1}. So the Raman shift variation between our present electro-deposited CZTS and vacuum sputtered CZTS thin film absorber layer was just 15 cm^{-1}. But both the -deposited CZTS and vacuum sputtered CZTS thin film absorber layer Raman spectra showed relatively similar Raman shift.

Electrical resistivity of our electro-deposited CZTS thin film absorber layer was measured using a simple resistivity measurement meter. The resistivity measurement of our electro-deposited CZTS thin film sample using 2 point probe method showed nearly 13.44 kΩ (when hard probing) to 30 kΩ (gentle probing)). Electrical resistivity of our CZTS sample (when gentle probing) showed nearly 30 kΩ and this measurement were conducted on various places of our electro-deposited CZTS thin film and we got 29 kΩ to 31 kΩ. So our electro-deposited CZTS thin film resistivity variation between various place to place was ± 1 kΩ and this indirectly showed the uniformity of our fabricated CZTS thin film absorber layer.

4. Conclusions

Copper zinc tin sulfide (CZTS) thin film absorber layer was fabricated successfully using electro-deposition method. The investigated XRD spectra on our electro-deposited CZTS sample showed very high crystalline quality. EDX measurement on our CZTS sample showed the presence of all the Cu, Zn, Sn and S elements which confirms the CZTS compound formation. The SEM image of our CZTS sample showed the thickness 1.42 µm and the standing top view SEM coverage showed very large sized integrated grains.

Raman spectra of our fabricated CZTS thin film showed 15 cm^{-1} red shift than the standard vacuum co-sputtered CZTS thin film absorber layer. Electrical resistivity of our electro-deposited CZTS thin film absorber layer showed the average value 30 kΩ/Sq and showed very uniform resistivity throughout whole CZTS sample. This good quality electro-deposited CZTS thin film sample is very useful for making high efficiency CZTS thin film solar cells.

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