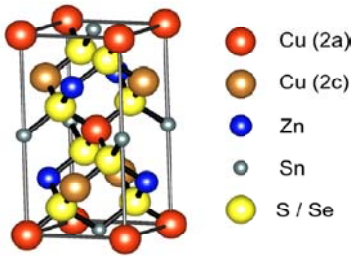
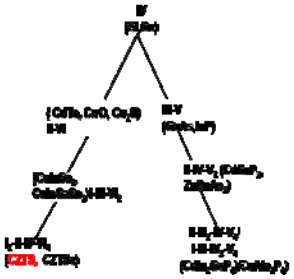
Project Report

PREPARATION AND CHARACTERIZATION OF KESTERITE THIN FILMS FOR SOLAR CELL APPLICATIONS

Introduction

As the energy crisis has become increasingly serious, research on high efficiency, low cost solar cells has become more important. Among numerous types of solar cells, the CIGS thin film solar cell has attracted great interest due to its high power conversion efficiency, small material requirements and stability. However, the low availability of indium and gallium increases the production costs and hinders the development of CIGS thin film solar cells. For years, scientists have been attempting to find a substitute for CIGS that avoids using costly and rare elements. CZTS, the p-type kesterite semiconductor with chemical formula Cu_2ZnSnS_4 is a promising alternate material for photovoltaics because of its many distinguishing properties like ideal band gap around 1.5 eV and the high absorption coefficient of 10^4 cm^{-1}. Most important among its advantages are that it contains only earth abundant and non-toxic elements.





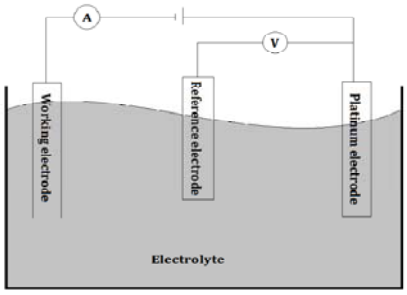
Kesterite films have been prepared using various techniques like sputtering, physical and chemical vapour deposition, spray pyrolysis , spin coating techniques and electro deposition. Cost reduction is a central factor in developing solar cells; we have therefore chosen the electro deposition technique which does not require costly vacuum equipment. Electrochemical deposition is attractive due to cheap capital equipment, low cost source materials, minimum energy input and good control over thickness and composition. It is also an eco friendly synthesis method that is easily scalable to large areas.

Method

A three electrode electro deposition unit was set up with a Pt mesh electrode as counter electrode, ITO coated glass substrate as the working electrode and Ag/AgCl as the reference electrode. Aplab's programmable multi channel power supply was used in the potentiostatic mode as power supply.

Before deposition, the substrates were cleaned in de-ionized water, acetone and iso-propanol ultrasonically. 0.02 M anhydrous $CuSO_4$ solution , 0.01 M $ZnSO_4$ solution, 0.02 M $SnSO_4$ solution and 0.02 M $Na_2S_2O_3$ solutions were mixed in volumetric proportions to prepare the

aqueous electrolyte. 0.2 M trisodium citrate was added as complexing agent and 0.1 M tartaric acid was added to maintain the pH between 4.5 and 5.



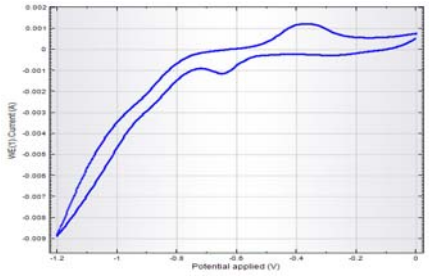


Fig. 1-Schematic diagram of the electro deposition system

Fig. 2- Cyclic voltametry of the deposition process

CZTS thin films were deposited on ITO coated and Mo glass substrates by single step method using the above electrolyte. The potential applied to the working electrode during this single step deposition process was -1.03 V with respect to the Ag/AgCl reference electrode. Deposition of stacked layers of metal sulphides was also attempted. For stacking ZnS/CuS/SnS/CuS order was followed. But single step deposition was found to be easier and more efficient. So single step deposition was chosen for further fabrication. After deposition, the films were rinsed with de-ionized water and dried in air.

XRD studies revealed that the as-deposited films were amorphous. Annealing of the electro deposited films in an inert atmosphere with the presence of sulphur vapour in the the ambience was found to be a must. This was clear from the fact that films annealed in an ordinary muffle furnace at various temperatures from 250 ^{0}C to 550 ^{0}C showed no sign of CZTS peaks in their X ray diffraction patterns. But they contained various peaks of the metal oxides rather than sulphides. Avoiding the presence of oxygen during annealing becomes essential. Also, even though sulphur is deposited on the substrate from the thiosulphate precursor in the electrolyte solution, its vapourization point being 444.5 ^{0}C , it suffers losses due to evaporation. The presence of sulphur in the annealing atmosphere helps to compensate for these losses.

Sulphurization was done in N_2 atmosphere in a vertical chamber furnace at 500 ^{0}C for an hour. The samples were then characterized structurally by XRD, Raman spectroscopy and SEM. Optical characterization was done using uv-visible spectroscopy and thickness measured using a DekTak profilometer. Electrical measurements were also done. The sheet resistance was evaluated using the van der Pauw techniques. The four probe sample holder and contacts were designed for the purpose, satisfying the requirements of small contacts at the sample periphery, thin uniform sample free from holes and other singularities. The currents were supplied by the Keithley 6220 DC

current source and voltages measured by the Keithley 2812 nanovoltmeter. The switching between the current and voltage probes to various points on the sample was achieved with the help of Keithley 7001 switcing system. The various modules were interfaced with the PC programmed by the graphical language labVIEW for data acquisition using the IEEE 488 GPIB cable. The magnetic field for Hall measurements was applied using an electro magnet (from Holmarc) with cylindrical pole pieces.

Results and Analysis

XRD analysis of the sulphurized films revealed peaks from the (112), (220) and (312) planes of CZTS crystals. Raman spectrum confirms the formation of CZTS. But the broad peak reveals the presence of other phases which have to be avoided. The project clearly shows that electro deposition / sulphurization route is an effective method for the deposition of device quality CZTS thin films.

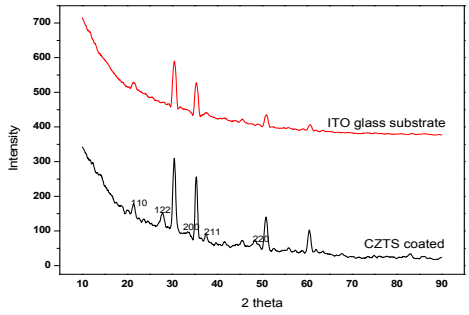


Fig. 3- XRD pattern of the CZTS film

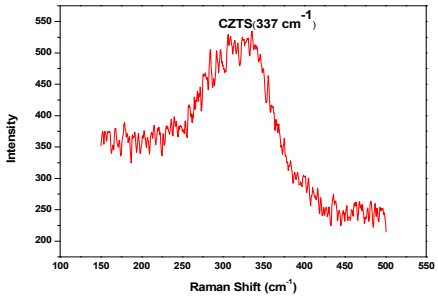


Fig. 4-Raman Spectrum(using Horiba Jobin Yvon LabRAM micro spectrometer

(using Rigaku X-ray diffractometer (employing Cu-K_α line (5405 A °) and Ni filter)

The thickness of the different films measured by a DekTak profiler varied between 200 to 350 m. CZTS is a direct band gap semiconductor. So the optical absorption data was analyzed using the classical relation

$$\propto = \frac{A\sqrt{(h\nu - Eg)}}{h\nu}$$

Thus a plot of $(\alpha h\nu)^2$ against hν is linear and the x- intercept gives the optical band gap- the difference between the top of the valence band and the bottom of the conduction band. This was found to be 1.535 eV for our sample.

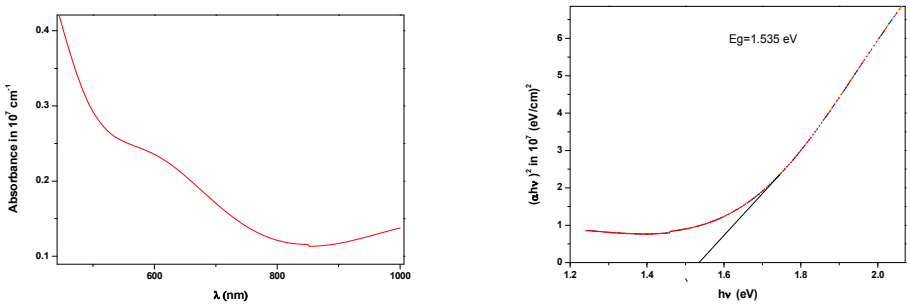
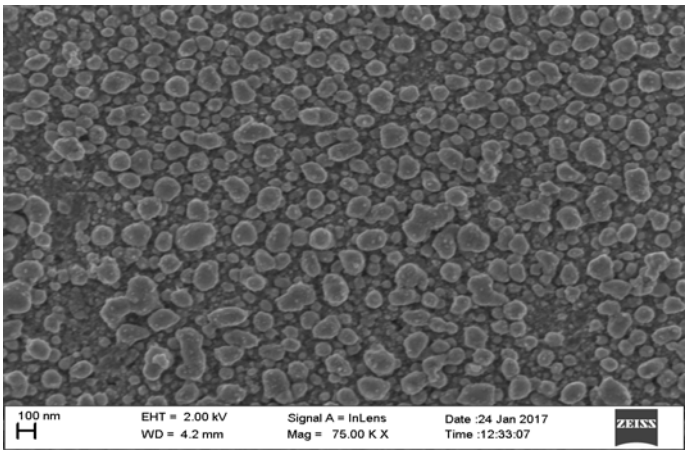


Fig. 5-Uv-visible spectral data **(from** Jasco V-570 Model uv-vis spectro photometer)

The SEM image of the sample at 75 K magnification is given below. The grain size is 100 nm on the average. The formation of larger crystals is essential for device quality films.



The electrical characterization was done by van der Pauw and Hall techniques. Expected values of resistivity were high. The results of measurements are as shown.

Sheet resistance= 1830 Ω/sq. Resistivity=3.6 X 10^{-2} Ωcm

Carrier concentration = 5.623 X 10^{16} /cm^3 Mobility = 681 cm^2/(Vs)

The low values of sheet resistance, resistivity and carrier concentration and the impossibly high value of carrier mobility clearly showed that the van der Pauw and Hall methods could be successfully applied only for films on well insulating substrates like glass. The ITO coatings on the substrates were short circuiting the currents applied to the CZTS films leading to low values of sheet resistance. But it is impossible to produce the films on pure glass substrates in the electro deposition method. The electrical properties being difficult to get and analyze, and kesterite being a solar cell absorber material, it is more important to understand and analyze its optical properties.

Conclusion

It is possible to produce good quality thin films of CZTS with kesterite structure via the cheap and simple electro deposition route. The technique does not require a vacuum and therefore needs minimum capital equipment and has the advantage of scalabilty to large areas. The electrolyte composition is crucial in the formation of good quality films. The sulphurization process also plays a leading role in the formation of CZTS crystals of appreciable size. This cheap and eco-friendly p-type semiconductor material is a very good candidate for the absorber layer of solar cells.

Future Plans

The investigator has plans to further study the properties of the CZTS films by varying the percentage of the different elements deposited in the thin films of the compound and changing the sulphurization conditions. Plans to prepare the complete solar cell device are also under consideration.

Acknowledgement

The Principal Investigator would like to thank the University Grants Commission for the financial support, without which the research work would not have been possible.

References:

1. S. M. Pawar, B. S. Pawar et. al., Electrochemica Acta 55 (2009) 4057-4061
2. J. J. Scragg, P. J. Dale, L. M. Peter, Thin Solid Films 517 (2008) 2481-2484
3. T.K. Todorov, J.Tang, D.B.Mitzi, et. Al., Advanced Energy Materials(2013),3,34-38
4. Septina , et.al., ., Electrochemica Acta 88 (2013), 436-442
5. A. Ennaoui, et.al., Thin Solid Films517(2009),2511-2514
6. H. Katagiri, et.al., Thin solid Films,517,(2009),2455-2460
7. Y. Cui, J. Chu,et.al. Solar Energy materials and solar cells 95,(2011), 2136-2140
8. S. Ahmed,et.al.,Advanced Energy Materials, www.MaterialViews.com
9. S. M. Pawar, B. S. Pawar et. al., ISRN Renewable Energy,Vol 2011, Article ID 934575
10. Ali Aldalbahi, et.al., Scientific Report 6, Article no. 32431(2016), www.nature.com
11. K.A.Borup, et.al., Review of Scientific Instruments 83,123902 (2012)
12. Thin Film Solar Cells from earth abundant materials- S. R. Kodigala, Elsevier Insights