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Morphological, Structural, Optical Properties of Stannous and Stannic Chloride CZTS Thin Film

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Abstract: CZTS thin film prepared on glass substrate by spray pyrolysis technique using copper chloride (0.0185M),zinc acetate (0.0117 M), thiourea (0.7692 M), stannous chloride (0.0135 M).The same molarity of stannic chloride were used as the precursor for tin in order to study the properties of CZTS film. The substrate temperature was maintained at 350°C. CZTS thin films properties of stannous and stannic chloride were characterized by using XRD, FESEM, EDAX and UV-Vis characterization. From the results, morphological image shows the nanorod film was obtained only for stannous chloride. Compare to stannic chloride, the stannous chloride film composition of Cu, Zn, S was high. The bandgap of both stannous and stannic chloride films were found to be 2.0 eV, 1.5 eV.
Keywords: CZTS; XRD; FESEM; EDAX; UV-Vis characterization and Nano rod.

Introduction and Experimental Method:

Cu_2ZnSnS_4 (CZTS) (I_2-II-IV-VI_4) is a quaternary thin film with good excellent optical and electrical properties similar to CIGS (copper indium gallium selenide). The CZTS thin film is one of the promising candidates for low cost absorber layer in thin film solar cells and has ess environmental pollution. With high absorption coefficient (~10^4 cm^{-1}) it is considered to be a suitable material in many applications such as solar cells, PEC cell, etc. CZTS is a p type semiconductor material with a direct band gap value of 1.5eV. The efficiency of the CZTS solar cells was reported to be 6.7% [1]. CZTS can be prepared by various deposition methods such as spray pyrolysis [2], electrodeposition [3], RF sputtering [4], SILAR [5] etc. Among the various deposition method Spray pyrolysis techniques was adopted for film deposition. In this case spray pyrolysis method, the film properties can be controlled by varying the deposition parameters such as pressure of the carrier gas, distance between nozzle to the substrate, substrate temperature and solution spray rate and volume sprayed. The objective of the present work is to prepare a p-type CZTS quaternary semiconducting thin film sing stannous and stannic chloride which was compared by the morphological, structural and optical properties.

Copper chloride(0.0185M), Zinc acetate(0.0117 M), thiourea(0.7692 M), stannous chloride, stannic chloride(0.0135 M) was used as precursors for the deposition of CZTS film. All the chemicals were dissolved in de-ionized water. The glass substrates were cleaned well to before deposition using chromic acid for 24 hrs. The substrate temperature was maintained at 350°C. The substrate and the nozzle distance between 5 cm. The carrier gas was maintained at a pressure of 1 bar. The structural properties of the CZTS thin films were determined by using an X-ray diffraction (XRD). The optical properties of the films deposited on glass substrates were recorded using a UV–Vis spectrophotometer jasco V670. The surface morphology and the elemental composition of the sample was analyzed by FESEM (Oxford X-act tescan instrument).

Results and Discussion:

Fig.1 shows the diffraction peak both stannous and stannic chloride at 2θ =28.53°, (112) plane of the Cu_2ZnSnS_4 and it's well matched with JCPDS card no. 26-0575 and the deposited film shows the kesterite structure. It was observed that no secondary phase was found in the XRD pattern for both stannous and stannic chloride. Using the Scherer's formula, grain size of the CZTS thin film was calculated 31nm for nanorod thin film .The result close agreement with the study conducted by O B.Uma Maheshwari et.al 2012[6]. The morphology of the as-deposited films shows the both stannous and stannic chloride was shown in the Fig 1. It was observed that the CZTS film has non-uniform distribution of nano rods on the surface of thin film using stannous chloride, for stannic chloride uniform distribution of grains was achieved rather than nanorod formation. Table 1 shows the composition of stannous and stannic chloride CZTS film. Compare to stannic chloride, the stannous chloride film composition of Cu, Zn, S was high. From the Fig 2 Absorbance of the film was quite high for stannic chloride compared to stannous chloride CZTS film also the transmittance was quite high for stannous chloride CZTS film. Fig 3 shows the extrapolating the linear portion of $(\alpha h\gamma)^2$ versus hγ curve, the band gap of the as-deposited film was found to be 2.0eV for stannous chloride and stannic chloride 1.5eV. Compared to the theoretical value, the band gap value little high, blue shift transpired in the stannous chloride CZTS film due to the nanorod formation.

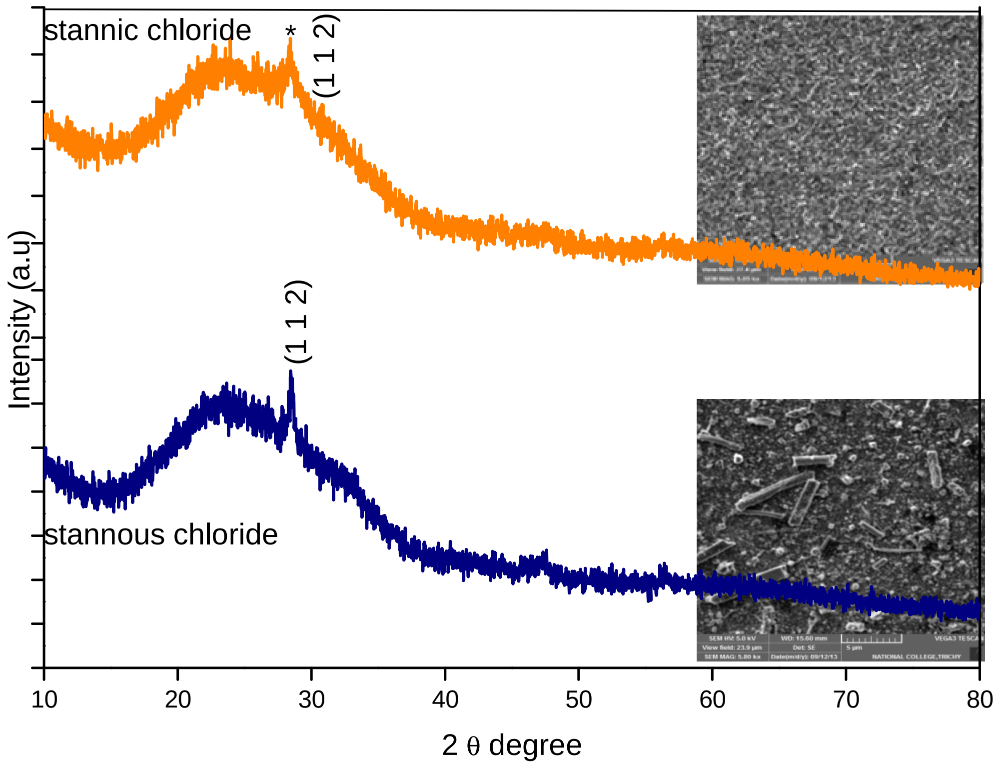

Fig 1: XRD and FESEM image of Stannous and stannic chloride of CZTS thin film

Table 1: Composition of Stannous and stannic chloride of CZTS thin film

Element	Wt %-Stannous chloride	At %	Wt%-Stannic chloride	At%
Cu	31.82	29.01	24.19	24.14
Zn	27.31	24.21	16.20	15.71
Sn	20.52	10.01	39.99	21.36
S	20.35	36.77	19.62	38.79

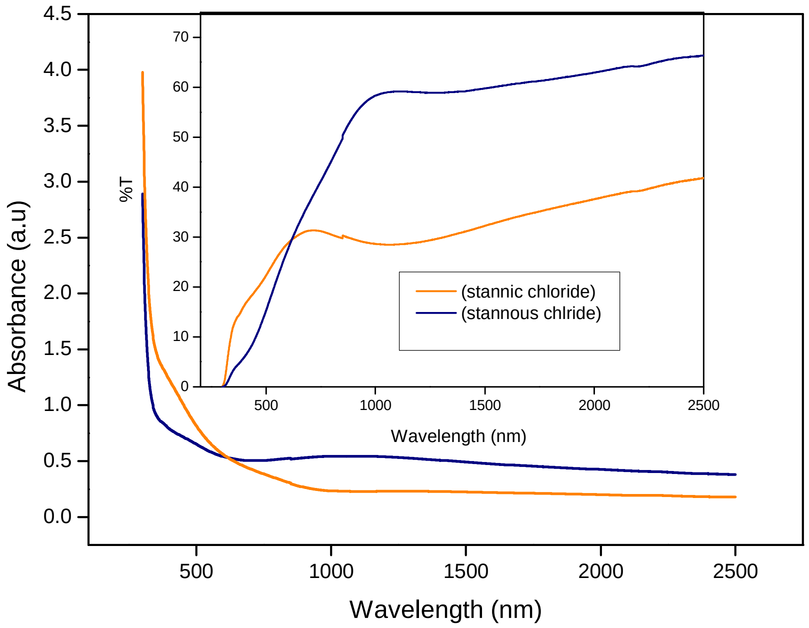

Fig : 2 Absorbance and transmittance spectrum of the stannous and stannic chloride CZTS films

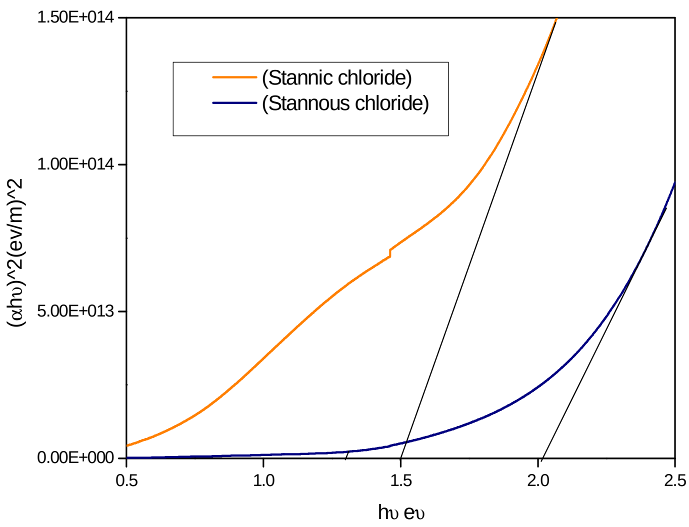

Fig : 3 Band gap of the stannous and stannic chloride CZTS films

Conclusion:

CZTS thin film prepared by stannous and stannic chloride using spray pyrolysis technique. From the XRD, it was inferred that film intensity of stannous was high compared to stannic chloride and the peak position of both the film were same. Optical study shows the transmittance was quite high for stannous chloride CZTS film. Morphology of the deposited stannous chloride film shows the nanorod on the surface of the film. Due to the morphological effect, the bandgap for stannous chloride film was found to be 2.0eV and for stannic chloride film E_g = 1.5eV due to the occurence of blue shift.

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