**Executive summary of the minor research project**

- **Project Title:** "Preparation and characterization of $Cu_2ZnSnS_4$"
- **Sanction letter: Ref.-** File No. 47-707/08 (WRO) dt. 06/03/2009

## Part-I: Influence of growth temperatures on the properties of photoactive CZTS thin films using spray pyrolysis technique

### Introduction

CZTS has been emerged as a potential candidate for absorber layer in photovoltaic cell, having earth abundant, non-toxic and low cost elements. It exhibits an excellent optical absorption of over $10^4$ $cm^{-1}$, direct optical band gap energy of 1.4-1.5 eV and p-type conductivity, which makes this material especially suited for the development of low-cost, and environmentally non-toxic thin film solar cells (TFSCs) numerous vacuum and non-vacuum based deposition techniques have been employed for the synthesis of CZTS thin films.

Chemical spray pyrolysis (CSP) technique is low cost, non-vacuum, eco-friendly and can be used to large scale deposition of different semiconductor thin films, as well its high potential for achieving a significant reduction of production costs. The composition, morphology and optical and electrical properties of the CZTS films can be tailored by changing the deposition parameters such as the precursor's composition, the substrate temperature, the deposition time duration, the spray rate, the nozzle-to-substrate distance, etc.

In first part, we have synthesisedthe highly crystalline CZTS thin films using spray pyrolysis technique by varying the substrates temperature without sulfurization in toxic atmosphere such as $H_2S$ or 'S' vapor. Furthermore, the influence of different growth temperatures on the physico-chemical properties and photoelectrochemical performance of sprayed CZTS thin films has been investigated.

### Experimental details

CZTS thin films were deposited by spraying the precursor solution on preheated, ultrasonically cleaned soda lime glass (SLG) and fluorine doped tin oxide (FTO) coated SLG substrates at different substrate temperatures. CZTS precursor solution was prepared by dissolving copper chloride, zinc chloride, tin chloride and thiourea in double distilled water and stirring for ten minutes. The concentration of materials was selected as 2:1:1:8. Excess amount of thiourea was required to avoid the precipitate in the solution and also to compensate the loss of sulphur during pyrolysis as sulfur source is volatile at higher temperature [14]. 30 ml solution sprayed with the spray rate of 2 ml/min, and substrate temperature varied from 200˚C to 500˚C with an accuracy of ± 5 $^oC$ using a digital temperature controller. The samples are denoted as 'CZTS-200', 'CZTS-300', 'CZTS-400' and 'CZTS-500', respectively.

### Characterization

The structural properties were studied using X - ray diffractometer (Bruker AXS Model D2 PHASER Analatical Instrument, Germany) and Raman spectroscopy (Bruker AXS Analytical instrument, Germany). The optical absorption of the sprayed thin films was measured by UV-vis spectrophotometer (UV-1800, Shimadze, Germany). The photoelectrochemical performance measured using a Sol2A Oriel New Port Corporation USA, with Keithley-2420 source meter under 1.5 AM.

## Results and Discussion

### XRD analysis

XRD patterns of sprayed CZTS samples as a function of growth temperatureexhibits three major broad peaks at which also correspondsto kesterite type CZTS. The increase in the (1 1 2) peak intensity with increase in the growth temperature has been observed, which indicates that highly crystalline sample can be deposited at high growth temperatures.

### Raman Analysis

The existence of CZTS is confirmed by the presence of major Raman peak at 337 $cm^{-1}$ and the shoulder peaks at 282 and 362 $cm^{-1}$one extra peak at 479 $cm^{-1}$ corresponds to $Cu_{2-X}S$ can be seen for all samples except CZTS-500. This could be attributed to the high substrate temperature, which easily allows the formation ofsecondary phase of $Cu_{2-X}S$.

### Optical studies

The optical band gap energy ($E_g$) obtained 1.87, 1.70, 1.59 and 1.47 eV for CZTS-200, CZTS-300, CZTS-400 and CZTS-500, respectively.

### PEC studies

The photoelectrochemical (PEC) performance of CZTS thin films on FTO substrates has been studied with a two electrode configuration of photoanode, which were immersed in 0.1 M Europium nitrate (Eu (III)$(NO_3)_3$) as a redox mediator under UV (100 mW) illumination. ITO was used as a counter electrode. Illuminated J-V curves for CZTS PEC devices fabricated using CZTS-200, CZTS-300, CZTS-400 and CZTS-500 under dark and light illumination. The gradual increment in the current density ($J_{SC}$) from 4.15 to 7.31 mA/$cm^2$, open circuit voltage ($V_{OC}$) from 0.28 to 0.39 V and photon conversion efficiency (PCE) from 0.30 to 0.86 % with increase in the substrate temperature has been observed. The various solar cell parameters were elucidated in Table 1.

**Table 1** Solar cell parameters of PEC devices fabricated using CZTS-200, CZTS-300, CZTS-400 and CZTS-500 samples

| Sample | $J_{sc}$ (mA/$cm^2$) | $V_{oc}$ (V) | *F. F.* | η (%) | Rs (Ω) | Rsh(Ω) |
|---|---|---|---|---|---|---|
| **CZTS-200** | 4.15 | 0.28 | 0.26 | 0.30 | 292 | 424 |
| **CZTS-300** | 5.53 | 0.31 | 0.29 | 0.50 | 203 | 400 |
| **CZTS-400** | 6.36 | 0.38 | 0.27 | 0.67 | 221 | 400 |
| **CZTS-500** | 7.31 | 0.39 | 0.30 | 0.86 | 190 | 400 |

## Conclusions

CZTS thin films have been successfully deposited by low cost, simple spray pyrolysis technique. The influence of growth temperatures on properties and photoelectrochemical performance of sprayed CZTS thin films has been investigated. The significant improvement has been observed in the crystallinity of spray deposited CZTS thin films having kesterite structure with increase in the growth temperature. The band gap energy of 1.47 eV is obtained for CZTS film sprayed at 500$^o$C. The PEC device based on CZTS-500 sample showed the $J_{SC}$ = 7.31 mA/$cm^2$, $V_{OC}$ = 0.39 V and *F.F* = 0.30, with best power conversion efficiency of 0. 86 %.

## Part II: Influence of copper concentration on sprayed CZTS thin films deposited at high temperature

In this part,it has been attempted to decrease the formation of secondary phases with good morphology. The effect of Cu concentration on the properties of CZTS films at high substrate temperature have been studied and the obtained results are analysed herewith.

**Experimental**

Experimental process is same as discussed above only copper chloride in the solution was varied from 0.15 - 0.30 M in the steps of 0.05 M. The as deposited samples were allowed to cool naturally at room temperature. These samples were further used for structural, optical, morphological and PEC properties. The samples are denoted as 'C1'for copper 0.15M, 'C2' for copper 0.2M, 'C3' for copper 0.25M andC4 for copper 0.30 M, respectively.

**Results and Discussion**

**XRD analysis**

Increase in copper concentration from 0.15 M to 0.25 M in the spraying solution improves the crystallinity of CZTS films as revealed by the sharp and increasing peak intensity along (112), (002), (114), (220), (312), (008) and (332) respectively, indicating the formation of kesterite type CZTS thin film (JCPDS 26-0575).

**Raman Analysis**

In the Raman spectra, peaks are observed at 289, 305, 335, and 373 $cm^{-1}$. The maximum intensity peak at 335 $cm^{-1}$and other low intense peaks observed at 289 and 373 $cm^{-1}$ corresponds to CZTS**,** which are in agreement with the reported results and it confirms the formation of CZTS phase.

**FE-SEM studies**

As the Cu concentration increases, an increase in the average grain size as 142 nm for 0.15 M, 205 nm for 0.20 M and 330 nm for 0.25 M is observed. This increase in the grain size is might be due to agglomeration of grains. Increase in grain size improves the performance of a polycrystalline CZTS thin film with decrease in grain boundaries that increases the effective diffusion length of minority carriers. Thickness of the films is calculated by the cross section of FE-SEM images and found to be 2.05 μm, 2.15 μm and 2.21 μm for C1, C2 and C3 films**,** respectively.

**Optical studies:**

The values of band-gap for CZTS films are determined to be 1.61 eV, 1.52 eV and 1.45 eV for C1, C2 and C3 respectively. The band gap value of C3 sample is near the optimum for photovoltaic solar conversion in a single-band-gap device. The decrease in band gap with increase in the cu concentration may be because of: 1] Increase in the crystallinity 2] The presence of narrow band gap Cu2SnS3 phase in the C3 sample and 3] Increase in thickness of the films

**PEC studies**

Illuminated J-V curves for CZTSbased PEC devices fabricated using C1, C2 and C3 are shown in Fig. 5. The detailed PEC parameters are listed in Table 1. It can be clearly seen from the graph that, the solar cell based on CZTS thin films derived from C1 shows relatively poor performance. This may be due to insufficient Cu concentration during the CZTS deposition process which may create structural defects in the CZTS film. While, the cell derived from C3 exhibits better conversion efficiency of 1.09 %. From the structural analysis, it is observed that the C1 and C2 films does not show any secondary phase where as C3 sample shows very small secondary phase of Cu2SnS3. C1 and C2 films show low efficiency as

compared to C3 film. The photoelectrochemical measurement confirmed the good photo-activity of the CZTS thin film (Table I).

Table 1. Solar cell parameters of PEC devices fabricated for different copper concentration: C1=0.15 M, C2 = 0.20 M, and C3 = 0.25 M

| **Sample** | **$J_{sc}$ ($mA/cm^2$)** | **$V_{OC}$ (V)** | **F.F.** | **η (%)** | **$R_s$ (Ω)** | **$R_{sh}$ (Ω)** |
|---|---|---|---|---|---|---|
| **C1** | **2.84** | **0.23** | **0.31** | **0.21** | **253** | **541** |
| **C2** | **7.31** | **0.39** | **0.30** | **0.86** | **190** | **400** |
| **C3** | **8.88** | **0.51** | **0.23** | **1.09** | **278.49** | **250** |

**Conclusions**

In this part, the effect of copper concentration on structural, morphology, optical and PEC properties of CZTS thin films at high temperature has been investigated. The analysis of XRD patterns indicate that, the CZTS film with copper concentration up to 0.25 M have sharp and intense peak orientation. For higher concentration above 0.25 M amorphous phase was confirmed. Further, Raman studies confirm the phase purity of CZTS films with relatively small peak of $Cu_2SnS_3$ phase. FE-SEM results indicate that as the Cu concentration increases average grain size also increases. Decrease in band gap due to increase in copper concentration was confirmed. Furthermore, the solar cell fabricated with the copper rich CZTS film (C3) showed enhancement in conversion efficiency about 1.09% due to presence of Cu2SnS3 phase in the film.

The results of this work are submitted in the revised format for the publication in the international journal Materials Letters and Ceramics International

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