Aviskaar – A Xaverian Journal of Research
Volume 13, February 2021

ANALYSIS OF ADSORPTION OF IONS UNDER DIFFERENT PREPARATIVE PRECURSORS

Shaunak Guha, Md Sahil Haque, Arnab Gon, Gayatri Banerjee*

Department of Physics

St. Xavier's College (Autonomous), Kolkata, West Bengal, India

*dalieban@gmail.com

ABSTRACT

A smart alternative to conventional crystalline silicon and existing thin film solar cells are CZTS thin film cells. CZTS stands for Copper-Zinc-Tin-Sulphide ($\mathbf{Cu_2ZnSnS_4}$). Since all its ingredients are abundantly available on Earth and the synthesis process is simple, it is much easier and cheaper to manufacture than conventional solar cells. In this report we tried to prepare CZTS thin films on regular glass slides using SILAR (Successive Ionic Layer Adsorption and Reaction) method to study the amount of deposition of ions when the ingredients of the precursor solutions are varied.

Keywords. *SILAR, CZTS, SEM-EDX*

---

1. INTRODUCTION

At present the whole world is using energy at the rate of approximately 4.27×10^{27} J/year. This is equivalent to a power consumption of 15 terawatts (TW). This huge energy demand is primarily satisfied by fossil fuels, which are almost depleted. Of the possible sources of renewable energy, Solar Energy perhaps has the most potential. This is because of the sheer size of the solar energy resource when compared to wind, wave, or tidal power. Thin film solar cells made of CdTe and CIGS are being commercially used. Unfortunately, Cadmium is toxic, and Indium and Tellurium are scarce. Copper-Zinc-Tin-Sulphide (CZTS) on the other hand uses materials that are abundant and are non-toxic. Being a quaternary compound, its methods of synthesis are complicated and expensive. In this report we have studied the SILAR method of synthesis which is cost effective and can be performed at ambient conditions.

2. PROCEDURE

The ***SILAR (Successive Ionic Layer Adsorption and Reaction)*** method involves dipping the substrate, silica glass slide in this case, into the cation and anion solutions separately and

ISSN (Print): 2277-8411
ISSN (Online): 2278-1048

washing it in distilled water in between. This process is repeated any number of times for a smooth coating of the material on the substrate. The details of the process are given below.

2.1 Steps of SILAR

The step-by-step procedure to obtain the CZTS coating at ***room temperature*** on the glass slide is as follows [1][2]:

- Dipped in beakers containing ***cationic solution for 30 seconds***
- Rinsed in ***distilled water for 10 seconds***
- Dipped in the ***anionic solution for 30 seconds***
- Rinsing in ***distilled water for another 10 seconds***

The whole cycle is repeated ***40-50 times*** to get a ***dark-brownish, greenish-black*** or ***brownish-yellow coating*** of thin film CZTS on the glass substrate depending on the reacting agents. Sometimes an effect called ***competitive adsorption*** comes into play, which we encountered while performing the experiment. It is the phenomenon that prioritizes adsorption of one ion over the other; more specifically the preferential adsorption of Sn^{2+} ions over Zn^{2+} ions, which gave an erroneous result in the percentage composition of elements on the thin film. This problem is tackled by using the ***Modified SILAR Sequence*** which has a separate cationic solution bath **consisting** of Zn^{2+} ions.

3 EXPERIMENT AND RESULTS

3.1 Sample 1

Cationic Solution: $CuSO_4$, $ZnCl_2$, $SnCl_2$, ***pH:*** 1.5;

Anionic Solution: Na_2S, ***pH :***> 11.5

Number of Cycles: 30

ISSN (Print): 2277-8411
ISSN (Online): 2278-1048

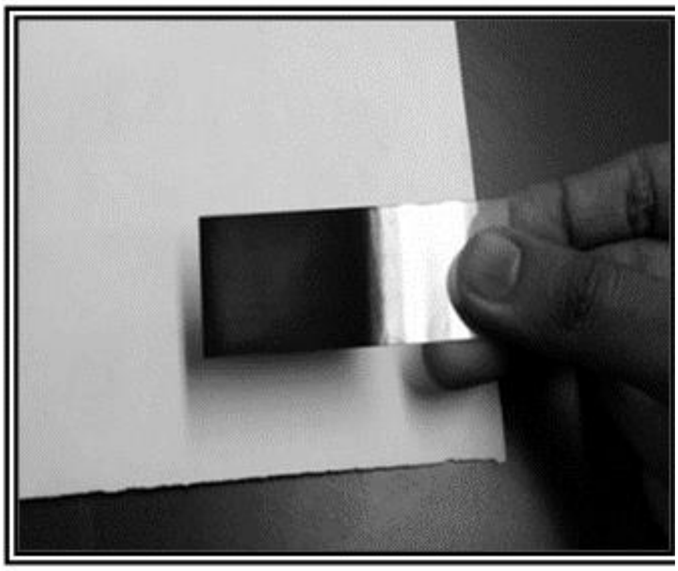

Fig. 1 Dark-Brownish Thin Flim

High resolution ***Image*** obtained from the ***Scanning Electron Microscope*** is shown below:

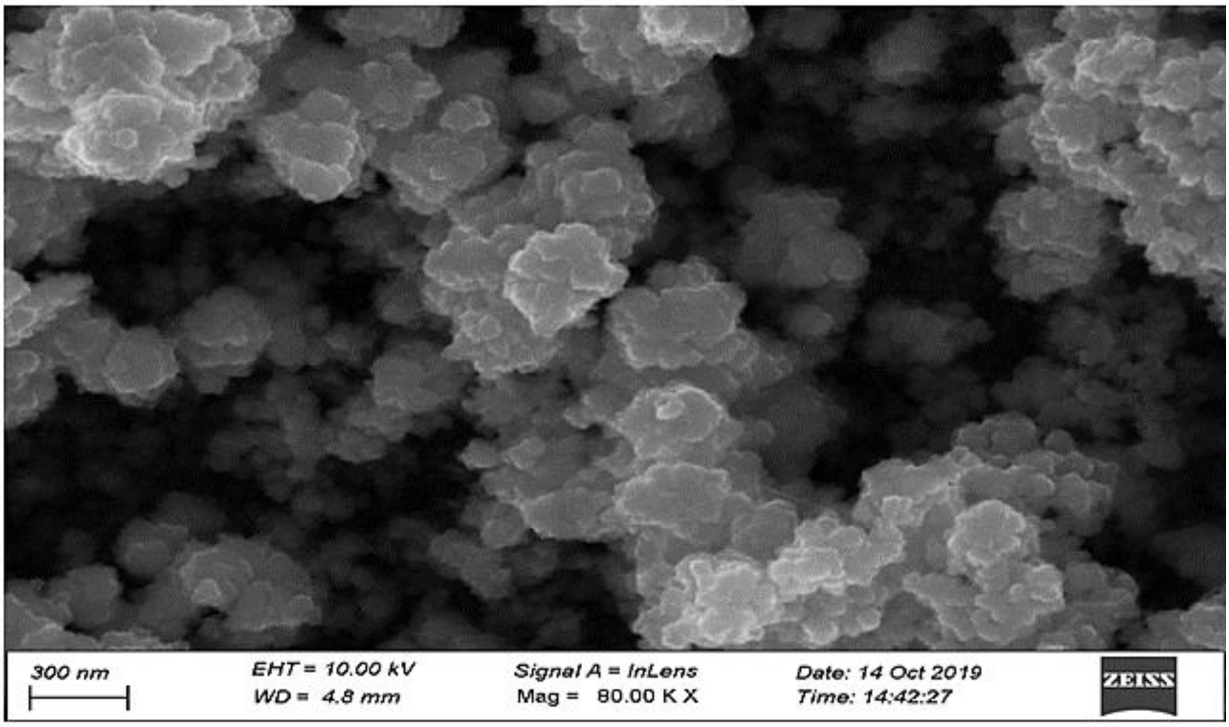

Fig. 2 Magnification- 80.00 KX

Table 1. Percentage Composition of Different Elements for Sample 1

Element	App Conc.	Intensity Corr.	Weight %	Weight % σ	Atomic%
S	9.36	0.8558	15.40	0.13	30.46
Cu	36.68	0.9830	52.52	0.24	52.41
Sn	19.11	0.8385	32.08	0.22	17.14
Total			100.00		

3.2 Sample 2

Cationic Solution: $CuSO_4$, $ZnCl_2$, $SnCl_2$, ***pH:*** 1.5

Anionic Solution: C_2H_5NS, ***pH :***> 5.5

Number of Cycles: 25

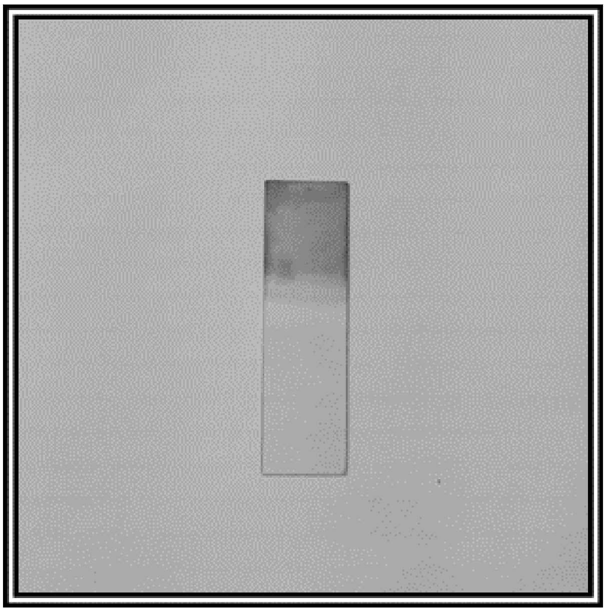

Fig. 3 Brownish-Yellow Thin film

High resolution ***Image*** obtained from the ***Scanning Electron Microscope*** is ***given below.***

ISSN (Print): 2277-8411
ISSN (Online): 2278-1048

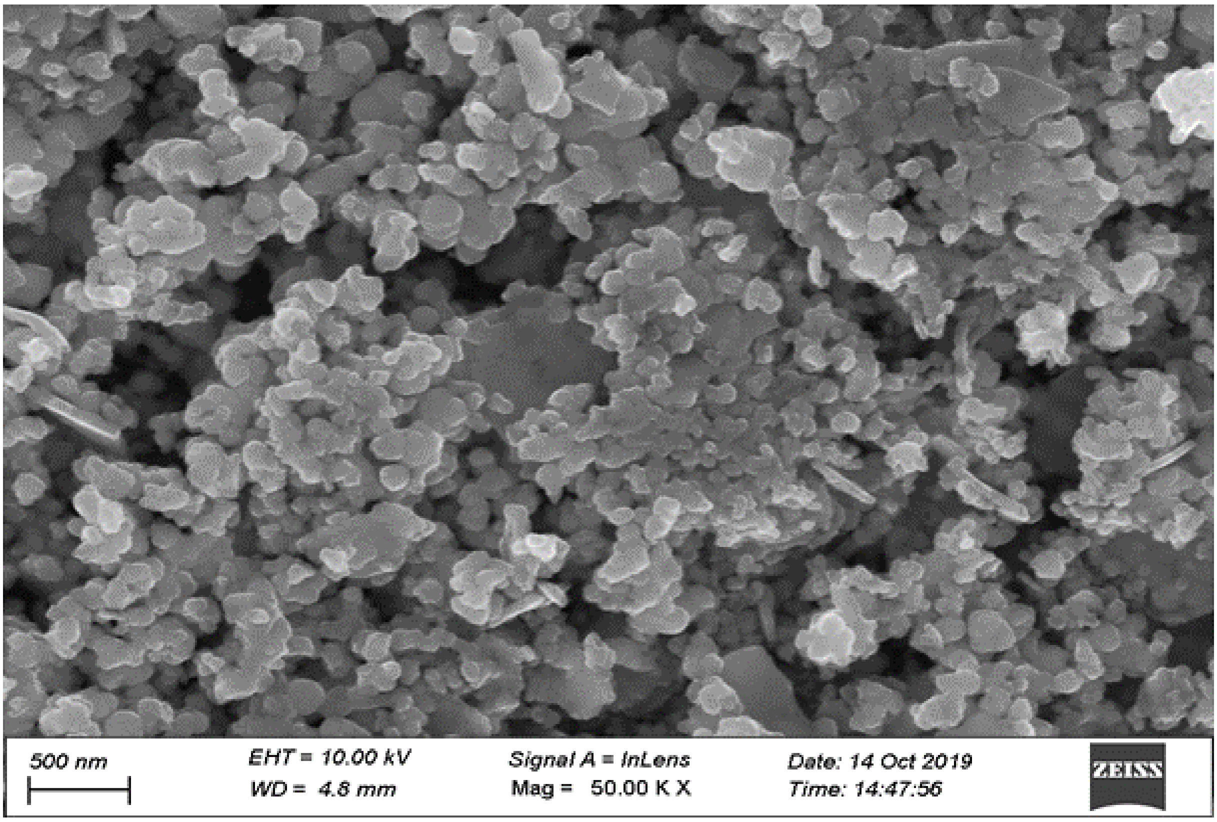

Fig 4: Magnification-50.00 KX

Table 2. Percentage Composition of Different Elements

Element	App Conc.	Intensity Corr.	Weight %	Weight % σ	Atomic%
S	2.64	0.9748	7.16	0.15	21.57
Cu	1.60	1.0334	4.09	0.28	6.21
Sn	31.99	0.9520	88.75	0.30	72.21
Total			100.00		

3.3 Sample 3

Cationic Solution: $CuSO_4$, $ZnCl_2$, $SnCl_2$, ***pH:*** 3.0

Anionic Solution: Na_2S, ***pH :*** > 11.5

Number of Cycles: 40

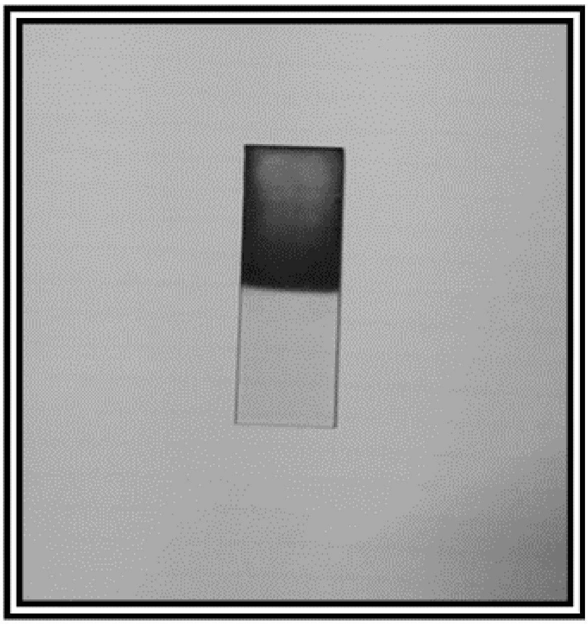

Fig. 5 Dark-Brownish Thin film

The high-resolution ***Image*** obtained from the ***Scanning Electron Microscope*** is ***given below:***

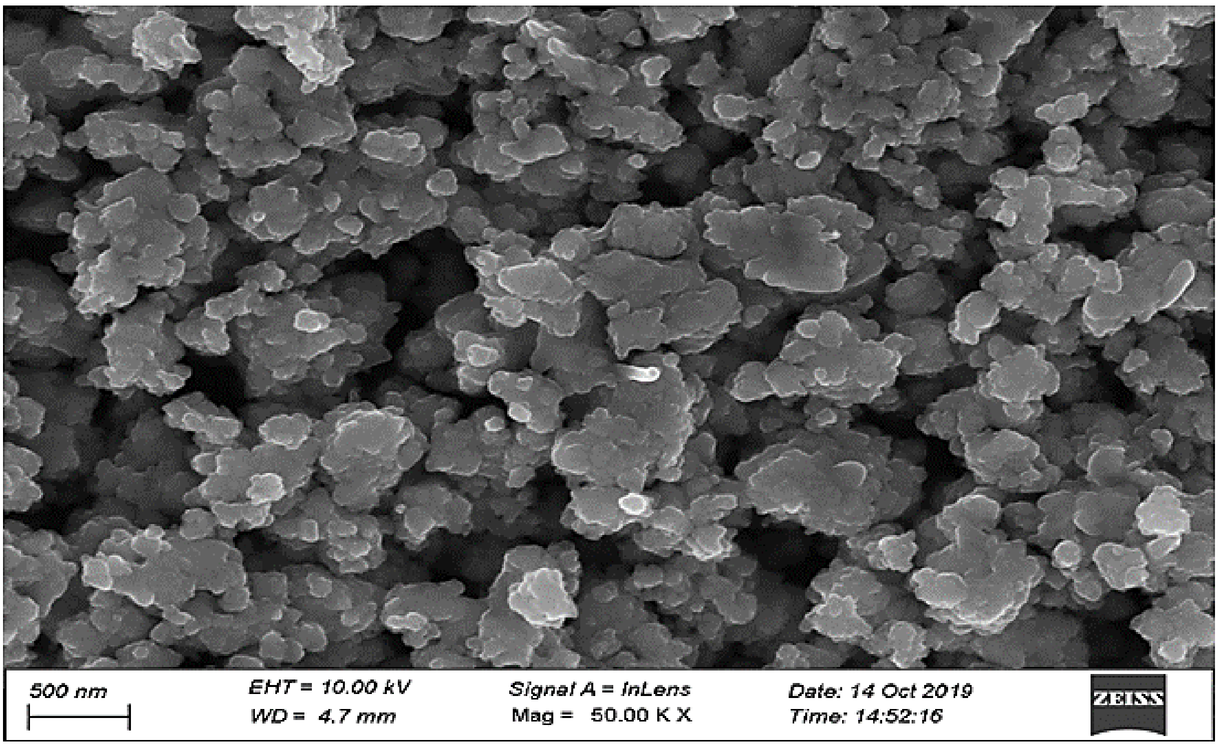

Fig 6 Magnification- 50.00 KX

ISSN (Print): 2277-8411
ISSN (Online): 2278-1048

Table 3. Percentage Composition of Different Elements

Element	App Conc.	Intensity Corr.	Weight %	Weight % σ	Atomic%
S	10.99	0.8661	15.94	0.13	31.86
Cu	37.96	0.9836	48.49	0.24	48.92
Sn	23.83	0.8416	35.57	0.22	19.21
Total			100.00		

3.4 For the following samples the Modified SILAR method as mentioned earlier was used and the sample was then annealed in a sulphurized atmosphere

3.4.1 Sample 4

Cationic Solution: $CuSO_4$, $ZnCl_2$, $SnCl_2$, ***pH:*** 1.5

Anionic Solution: Na_2S, ***pH :***> 11.5

Number of Cycles: 50

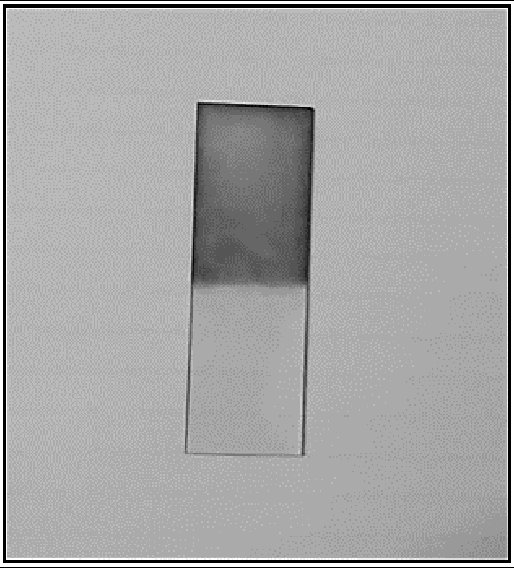

Fig. 7 Brownish-White Thin Film

ISSN (Print): 2277-8411
ISSN (Online): 2278-1048

3.4.2 Sample 5

Cationic Solution: $CuCl_2$, $ZnCl_2$, $SnCl_2$, ***pH:*** 1.5

Anionic Solution: Na_2S, ***pH :***> 11.5

Number of Cycles: 50

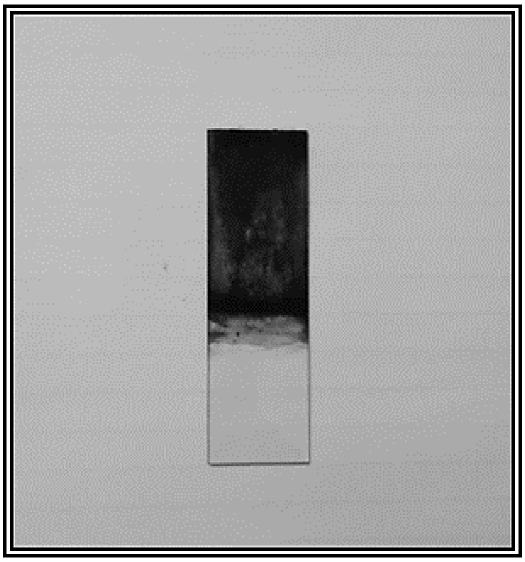

Fig. 8 Greenish-Black Thin Film

Due to some unfortunate circumstances (Covid19), ***SEM-EDX*** analysis ***could not*** be performed on Samples 4 and 5. As a result the percentage composition of elements adsorbed on these is still a speculation. However, we aspire to get the analysis results done as soon as the opportunity presents itself to us.

4 INFERENCE

- Zinc is absent in the samples 1, 2, 3. The probable cause for this might be ***competitive adsorption*** which prioritizes Cu^{2+} and Sn^{2+} ions over Zn^{2+} ions. This shortcoming was dealt with by using the ***Modified SILAR sequence*** approach.

- Tin was found to have a ***huge percentage*** of 72.21% presence for Sample 2 where we had used Thioacetamide as the anionic solution. This might be because of the low pH of the anionic solution.

- Copper ***dominated*** in presence when the base used was Sodium Sulfide, having percentages of 52.41 and 48.92 respectively in Samples 1 and 3.

ISSN (Print): 2277-8411
ISSN (Online): 2278-1048

- There are indications of certain ***peaks being omitted*** from the EDX analysis, due to very low intensities. These peaks might be those of Zinc, which appear marginally in the CZTS thin film.

- Changing the pH from 1.5 to 3.0 saw the ***decrease*** in percentage of Cu deposited by 3.49% and ***increase*** in Sn and Su deposition by 2.07% and 1.40% respectively.

- The pH-dependence remains inconclusive as the percentage changes are small and fall within the domain of experimental inaccuracy and error.

5 CONCLUSION

The COVID-19 outbreak of 2020 has doused most of the plans this year due to institutions and labs all across the nation being shutdown to avoid risking contamination. During future opportunities, we intend to make sure that no peaks are omitted in the SEM-EDX analysis and Zinc is investigated in addition to Copper, Tin and Sulphur. We also hope to study the pH-dependence of deposition amounts of the elements in a more robust manner with more samples and a broader range of pH, as the main hurdle in this endeavour is the inability to examine all the samples because SEM-EDX analysis is expensive and in very high demand by the entire experimental science community.

ACKNOWLEDGEMENT

We acknowledge the help of our friend Utsab Sarkar in procuring materials for our experiment. We thank Dr. R.N. Basu, Chief Scientist & Head, Fuel Cell & Battery Division of CSIR-Central Glass & Ceramic Research (CSIR-CGCRI) for analysis of our samples at the SEM-EDX facility. We are indebted to late Dr. D.N. Bose for his guidance and unparalleled enthusiasm. Ms. G. Banerjee acknowledges the role of Dr S. Ghosh of St. Xavier's College for introducing her to the topic. We offer thanks to our institution, St. Xavier's College, Kolkata, for providing necessary source materials and instruments from her laboratories.

REFERENCES

1. M.P. Suryawanshi, (2015), Deposition of Kesterite Cu2ZnSnS4 (CZTS) Thin Films by Successive Ionic Layer Adsorption and Reaction Method and Their Application in Photo-electrochemical PEC Solar Cells, Shivaji University, Kolhapur, India

2. G. Banerjee, S. Das & S. Ghosh, **Mat. Today. Proc.,** 494, **18**, 2, (2019).

#First three authors have equal contribution to this work.

****