Supporting Information for

"The synergistic influence of anionic bath immersion time on the photoelect rochemical performance of CZTS thin films prepared by modified SILAR s equence"

M. P .Suryawanshi[a,b], P. S. Patil[b], S. W. Shin[c], K. V. Gurav[a], G. L. Agawane[a],
M. G. Gang[a], J. H. Kim[a]*, A. V. Moholkar[b]**

[a]*Photonics Technology Research Institute, Department of Materials Science and Engineering, Chonnam National University, 300, Yongbong-Dong, Buk-Gu, Gwangju 500-757, South Korea*

[b]*Thin Film Nanomaterials Laboratory, Department of Physics, Shivaji University, Kolhapur 416-004, (MH) India*

[c]*Department of Materials Science and Engineering, KAIST, Gwahangno, Daejeon 305-701, South Korea*

Corresponding author:A. V. Moholkar

Email ID: ***avmoholkar@gmail.com***

Co-corresponding author: J. H. Kim

Email ID: ***jinhyeok@chonnam.ac.kr***

Keywords: Cu_2ZnSnS_4 (CZTS), TFSCs, SILAR with modified sequence, anionic bath immersion time, 2.33 % conversion efficiency

S1. DETAILED EXPERIMENTAL PROCEDURE:

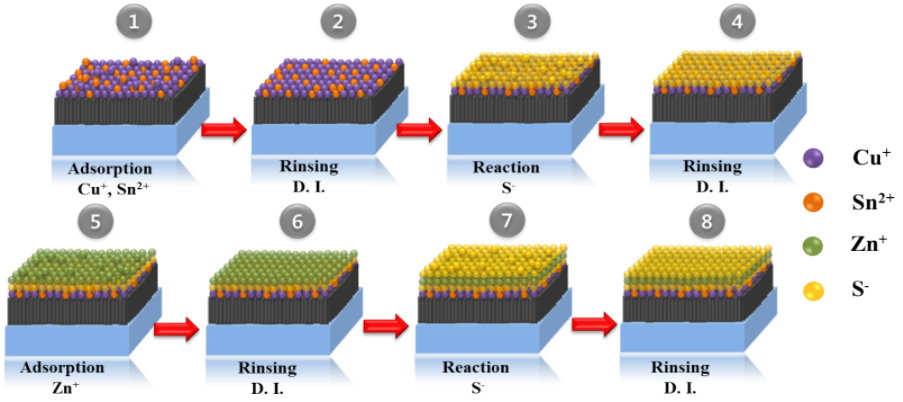
S1.1 Materials

Chemicals of copper (II) sulfate ($CuSO_4$), Zinc sulfate ($ZnSO_4$), Tin (II) sulfate ($SnSO_4$) and sodium sulfide (Na_2S) were commercially available from Aldrich. Europium (III) nitrate ($Eu(NO_3)_3$) was also purchased from Aldrich. All reagents were used as received. Aqueous solutions were prepared with water purified by a Millipore Milli-Q system.

S1.2 Deposition of CZTS precursor films

For a traditional SILAR method used for binary chalcogenides thin films like CdS, ZnS etc., one cycle contains four steps: the substrates is i) immersed in a reaction solution containing the aqueous cationic precursors, ii) rinsed with water, (iii) immersed in the anionic solution, and finally (iv) rinsed once again with water. However, for quaternary compound thin film like CZTS, developing SILAR cycle is a real challenge, due to different specific adsorptivities. Moreover, the judicious limitation of cationic solution concentration is conductive. The solution concentration adjusted according to the stoichiometric ratio of Cu_2ZnSnS_4 as 2Cu:Zn:Sn:4S failed to produce high quality CZTS thin films. Hence we attempted SILAR deposition from several combinations and found that, 0.02 M of $CuSO_4$, 0.5 M of $ZnSO_4$, 0.08 M of $SnSO_4$ and 0.16 M of Na_2S is the best suitable one for the deposition of the CZTS precursor films.

Further, the bath containing 3 cations together also didn't work out well and hence we have modified the process and separated cationic solutions. Nevertheless, making the separate chemical baths for all the three cations and anion becomes too cumbersome due to increase in deposition time and decrease in the growth rate. We used following combination: Cationic bath-1 contains Cu^{2+}, Sn^{2+} species, cationic bath-2 contains Zn^{2+} species, and anionic bath contains S^{2-} species. Hence our modified SILAR cycle contains following steps: the substrate is (1) Immersed in cationic solution containing Cu^{2+} & Sn^{2+} species for 30 sec, (2) rinsed with deionized (D. I.) water for 10 sec (3) Immersed in anionic solution, (4) rinsed with D.I. water for 10 sec, (5) immersed in cationic solution of Zn^{2+} for 30 sec. (6) rinsed with D.I. water for 10 sec. (7) immersed in anionic solution, and finally (8) rinsed with D.I. water again for 10 sec. The steps (1) - (4) caused approximate monolayer coverage of the Cu-Sn-S formation due to adsorption of Cu, Sn and then reaction with 'S', while the deposition of Zn-S layer is accomplished during the steps (5)-(8). The successive layers of Cu-Sn-S and Zn-S are formed on to the Mo substrates. Fig.1 shows the schematics illustration of modified SILAR sequences to deposited CZTS precursor thin films. To obtain smooth and adherent CZTS precursor thin film, utmost care has been taken to remove the loosely bound particles that would form dendritic like or rough films. Finally films were grown by repeating SILAR cycles 80 times in an air to achieve a desired film thickness.



S1.3 Sulfurization treatment:

It is well known that the phase pure CZTS film with high PEC is formed after anneal (at ~ 580 oC) under 'S' atmosphere. Several attempts were made to sulphurize ~ 1 μm thick Cu-Zn-Sn metallic precursor layers to obtain CZTS films. This evinces the incorporation of 'S' vapor into these precursor layers and formation of CZTS during the sulfurization.

Therefore, we carried out the sulfurization treatment for CZTS precursor films with different anionic bath immersion time in H_2S (5 %) + N_2 (95 %) atmosphere at 580 ^oC for 1 h. We varied anionic bath ('S' solution) immersion time (5, 10 and 15 sec) and controlled the uptake of 'S' into the precursor films during the SILAR cycle, and found that lower the amount of 'S', better is the quality of CZTS films, after anneal in H_2S (5 %) + N_2 (95 %) atmosphere at 580 ^oC.

S1.4 Fabrication of Photoelectrochemical (PEC) device.

The photoelectrochemical solar cells were fabricated using a standered two electrode configration, co mprising the sulfurized CZTS used as photoanode and indium doped tin oxide (ITO) was used as a counter elect rode which is sealed with the working electrode using a spacer (~ 1 mm) of polyacrylamide. The distance betwe en the CZTS photoeletrode and ITO counter electrode was 0.4 cm. The 0.1 M Europium nitrate [Eu(III)$(NO_3)_3$], which acts as a redox mediator was used as the redox electrolyte and injected into the interelectrode space from t he counter electrode side through a pre-drilled hole. The photoelectrochemical (PEC) characteristics were measu red by Sol2A Oriel New Port Corporation USA, with Keithley-2420 source meter under 1.5 AM.

2S CHARACTERIZATON DETAILS:

The structural properties of sulfurized CZTS thin films were studied by X-ray Diffractometry recorded using X-ray diffractometer (Philips, PW 3710, Holland) operated at 40 kV, 30 mA with CuKα radiation (λ = 1.5406 Å) and Raman spectroscopy recorded using Raman microscope (LabRam HR800 UV, Horiba Jobin-Yvon, France) with excitation wavelength of 514 nm. The surface morphology was observed using Field emission scanning electron microscopy (FE-SEM) (Model Hitachi S4800, Japan). X-ray florescence spectroscopy (XRF) studies were carried out to determine the compositional ratio of sulfurized CZTS thin films using a Wavelength Dispersive X-ray Fluorescence (ZSX Primus II, Rigaku Corporation, Japan) operated at room temperature. The generator power is 4 kW (60kv, 150 mA) and window type Rh target wavelength dispersive XRF spectrometer used. The sample diameter of detected area was 20 mm. The calculation procedures includes following three steps. i) The measurement of the standard sample with known the chemical composition to calibrate. ii) The measurement of the sulfurized CZTS samples, with unknown chemical composition which is to be determined iii) Comparing the sulfurized sample with the standard sample, the composition of sulfurized CZTS samples was found directly in atomic percent (at %).

S 3 EXPERIMENTAL RESULTS:

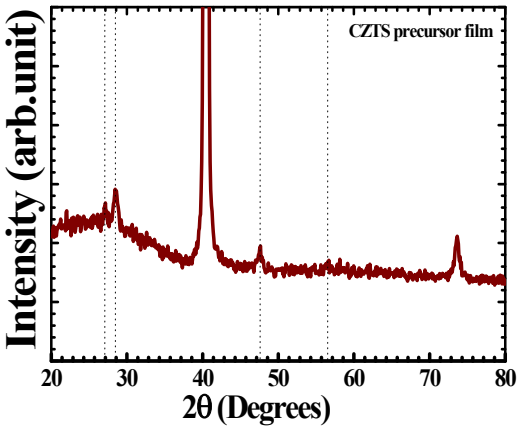


Fig. SI-1 XRD pattern for CZTS precursor film.

Sample	F. W. H. M. (°)	Grain Size (nm)
CZTS-5	0.207	41.40
CZTS-10	0.187	45.84
CZTS-15	0.179	47.89

Table SI-1 FWHM values and grain sizes of (112) orientation of the CZTS-5, CZTS-10 and CZTS-15 samples

S3.1 Compositional Analysis:

	Sample	Cu (at %)	Zn (at %)	Sn (at %)	S (at %)	Cu/(Zn+Sn)	Zn/Sn	S/(metal)
As deposited	**$CZTS_5$**	24.2	13.3	12.9	38.4	0.92	1.03	0.76
	$CZTS_{10}$	24.9	13.5	12.3	44.5	0.97	1.09	0.88
	$CZTS_{15}$	24.7	12.9	12.8	49.2	0.96	1.01	0.98
Sulfurized	**$CZTS_5$**	23.9	12.3	12.1	51.7	0.97	1.02	1.07
	$CZTS_{10}$	24.1	13.1	12.1	50.7	0.96	1.08	1.02
	$CZTS_{15}$	24.8	12.5	11.9	50.8	1.02	1.05	1.03

Table SI-2. Elemental compositions of CZTS thin films before and after sulfurization for different anionic bath immersion time.

S3.2 FE-SEM Results (Top and cross-section view)

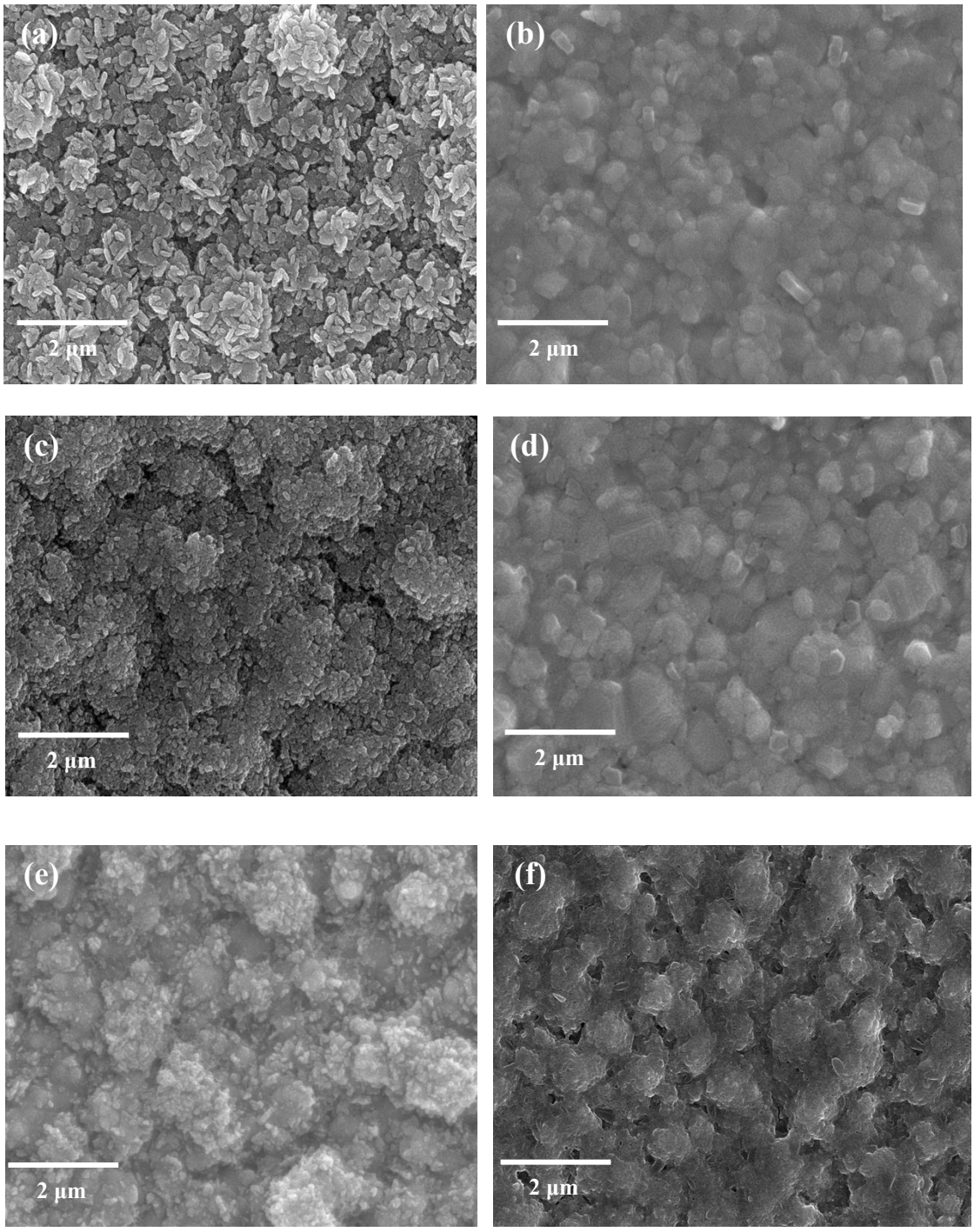


Fig. SI-2 Top view FE-SEM images of precursors (a, c, e) and sulfurized (b, d, e) CZTS-5, CZTS-10 and CZTS-15 samples, respectively

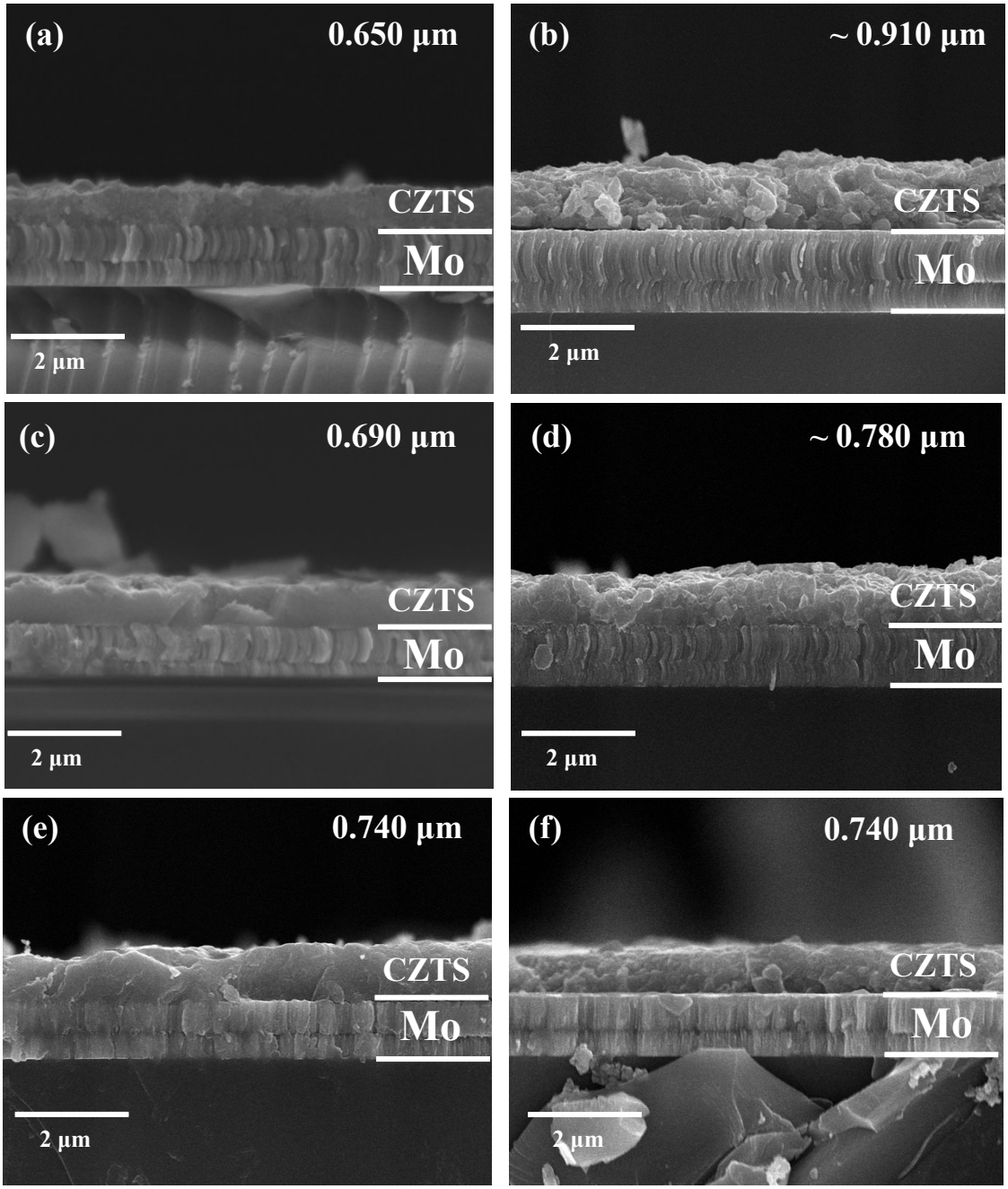


Fig. SI-3 Cross-sectional FE-SEM images of precursors (a, c, e) and sulfurized (b, d, e) CZTS-5, CZTS-10 and CZTS-15 samples, respectively

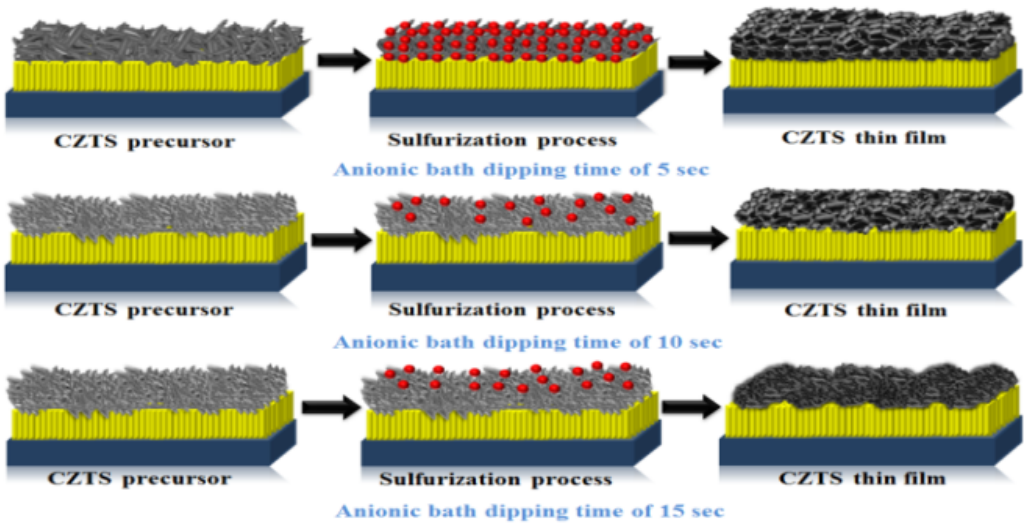


Fig. SI-4 Schematic of growth mechanism for CZTS-5, CZTS-10 and CZTS-15 samples

To investigate an influence of sulfurization process on the kinetics of film formation and growth mechanism, FE-SEM images (Top and cross-section view) were recorded for the as-deposited (precursor films) and sulfurized films. As shown in Fig. SI-3 (a, c & e), the as deposited films have different thickness ranging from 0.653, 0.697 and 0.740 μm for CZTS-5, CZTS-10 and CZTS-15 samples, respectively. The CZTS-5 sample has less amount of 'S' content and hence the growth of the film is limited. As the 'S' content in the as-deposited samples increases, (by increasing the immersion times from 10 to 15 sec.) the film thicknesses of as-deposited samples increased. The adsorption of cations and subsequent reaction with anions form miniscule building blocks often each SILAR cycle. Further, the growth of building blocks takes place due to events of 'adsorption-reaction-growth' after each successive SILAR cycle. Finally, larger self-assembled building blocks mature to form the bigger grains. However, if 'S' content is insufficient reaction of cations with anions become incomplete, leaving unreacted species on the substrates without forming the building blocks, In this case, the growth would heterogeneous with formation of fewer building blocks and unreacted nanoparticles conconittently. The subsequent growth is given graphically illustrated in the Fig. SI-4

S3.3 Optical results:

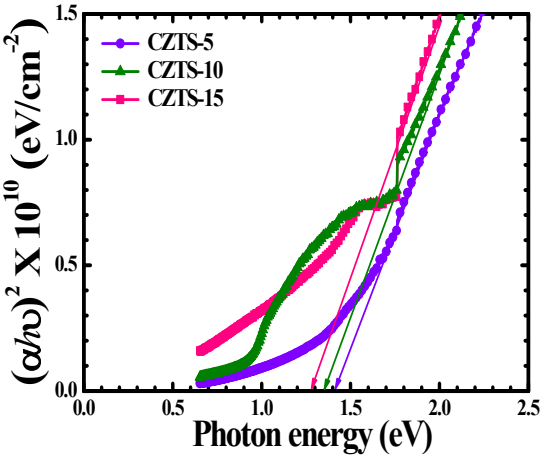


Fig. SI-5 Plot of (αhυ)2 versus hυ for CZTS-5, CZTS-10 and CZTS-15 samples

S3.2 Solar cell parameters:

Sample	J_{sc} (mA/cm^2)	V_{OC} (V)	*F. F.*	Efficiency η (%)	R_s (Ohm)	R_{sh} (ohm)	Ideality Factor (A)	Diode Saturation Current density (J_o) (mA/cm^2)
CZTS-5	12.88	0.42	0.43	2.33	63	500	1.63	1.29 X 10^{-5}
CZTS-10	7.02	0.38	0.42	1.22	77	667	2.86	2.21 X 10^{-5}
CZTS-15	6.49	0.38	0.39	0.96	257	693	2.56	7.95 X 10^{-5}

Table SI-3 Device parameters for CZTS-5, CZTS-10 and CZTS-15 thin films based PEC devices

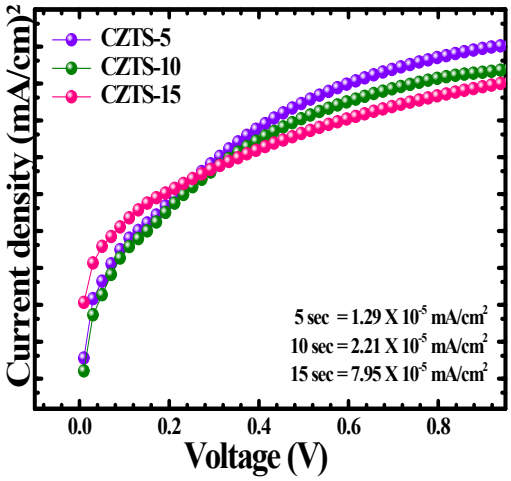


Fig. SI-6 Semi-logarithmic plot of J against V for CZTS-5, CZTS-10 and CZTS-15 thin films based PEC devices under illumination