



## ZnS/Cu<sub>2</sub>ZnSnS<sub>4</sub>/CdTe/In Thin Film Structure for Solar Cells

M.A. Jafarov, E.F. Nasirov, S.A.Jahangirova,

Baku State University, Baku, Azerbaijan, maarif.jafarov@mail.ru

### Abstract

A solar cell with glass/ITO/ZnS/Cu<sub>2</sub>ZnSnS<sub>4</sub>/CdTe/In structure has been fabricated using all-electrodeposited ZnS, Cu<sub>2</sub>ZnSnS<sub>4</sub> and CdTe thin films. The three semiconductor layers were electrodeposited using a two-electrode system for process simplification. The incorporation of a wide bandgap amorphous ZnS as a buffer/window layer to form ITO/ZnS/Cu<sub>2</sub>ZnSnS<sub>4</sub>/CdTe/In solar cell resulted in the formation of this 3-layer device structure. This has yielded corresponding improvement in all the solar cell parameters resulting in a conversion efficiency >12% under AM1.5 illumination conditions at room temperature. These results demonstrate the advantages of the multi-layer device architecture over the conventional 2-layer structure.

**Keywords:** solar cell, ZnS, Cu<sub>2</sub>ZnSnS<sub>4</sub>, CdTe, thin film, electrodeposition

Language: English

Date of Submission: 06-05-2018

Date of Acceptance: 20-05-2018

Date of Publication: 31-05-2018

DOI: It will be added at the time of publication.

ISSN: 2347-3487

Volume: 14 Issue: 2

Journal: Journal of Advances in Physics

Publisher: CIRWORLD

Website: <https://cirworld.com>



This work is licensed under a Creative Commons Attribution 4.0 International License.



## INTRODUCTION

II–VI semiconducting materials have emerged with high potential in applications for fabricating optical devices which include short wavelength emitting laser diodes and light emitting diodes operating in the blue region due to their wide direct band gap properties. It is a subject of great interest in regard to chalcogenide-based semiconducting materials which are used in making devices like photodetectors and photovoltaic devices [1-4].

Zinc sulfide (ZnS) is a wide direct band gap, high optical absorption coefficient, reasonable work function. It has attracted considerable attention due to its excellent electrical and optical properties with its distinct properties has become the potential candidate for many applications [5-8].

Solar cells based on thin films of polycrystalline materials are very promising in order to achieve better efficiency/cost ratios than the other counterparts. Among the thin film cells, CdTe based solar cells is the most promising candidate for photovoltaic energy conversion because of the high potentiality to realize low cost, high efficiency, reliable and stable solar cells. Firstly, the CdTe cell is produced from polycrystalline materials on glass, which are potentially much cheaper and involve simpler processes [9-12].

## EXPERIMENTAL

ZnS layers were electrodeposited from an aqueous electrolyte containing 0.3 M ZnCl<sub>2</sub> and 0.03 M (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>3</sub> in 800 mL of de-ionized water. Electropurification of the ZnCl<sub>2</sub> was carried out for 48 h prior to the addition of (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>3</sub> in order to remove any possible impurity ions present in the solution. Finally, the pH of the electrolyte containing both precursors was adjusted to 3.00 ± 0.02. The temperature of the electrolyte was 30°C. Uniform and transparent ZnS layers were cathodically deposited on cleaned glass/ITO substrates using a simple two-electrode deposition system at a cathodic potential of 1550 mV established using a cyclic voltammogram. The deposited layers using an average deposition current density of ~65 μA·cm<sup>-2</sup> and deposition time of 60 min have thickness of ~150 nm. These were then annealed in air at 350 °C for 10 min.

Prior to the deposition of Cu<sub>2</sub>ZnSnS<sub>4</sub>, the glass/ITO/ZnS substrates were cleaned with methanol and deionised water. The deposition of Cu<sub>2</sub>ZnSnS<sub>4</sub> layers was also done using a two-electrode system at a cathodic deposition potential of 1450 mV also established using a cyclic voltammogram. The Cu<sub>2</sub>ZnSnS<sub>4</sub> deposited on glass/ITO had a thickness ~300 nm while that deposited on glass/ITO/ZnS had a thickness ~150 nm. This therefore brings the total thickness of the ZnS/Cu<sub>2</sub>ZnSnS<sub>4</sub> bi-layer to ~250 nm comparable to the ~300 nm of Cu<sub>2</sub>ZnSnS<sub>4</sub> grown on glass/ITO.

The CdTe deposition electrolyte contained 1 M CdSO<sub>4</sub> (99.0%) and 1 mM TeO<sub>2</sub> (99.999%) in 800 mL of de-ionized water. To do this, a cyclic voltammogram was recorded using the two-electrode system, to determine the reduction potential of Cd<sup>2+</sup>. The TeO<sub>2</sub> was first dissolved in H<sub>2</sub>SO<sub>4</sub> and then added into the bath after the electro-purification of CdSO<sub>4</sub>, and the pH of the electrolyte adjusted to 2.00 ± 0.02.

After depositing and characterizing few CdTe samples on glass/ITO substrates, the final cathodic deposition potential for CdTe was taken as 2038 mV. CdTe thin layers with thickness of ~1.70 μm were then deposited on annealed glass/ITO/CdS and glass/ITO/ZnS/CdS substrates previously cleaned with methanol and de-ionised water. Typical deposition time for the CdTe used in this work was 4 h, with an average deposition current density of ~176 μA·cm<sup>-2</sup>. To complete the solar cell fabrication, the annealed glass/ITO/Cu<sub>2</sub>ZnSnS<sub>4</sub>/p-CdTe 2-layer structure and glass/ITO/n-ZnS/n-Cu<sub>2</sub>ZnSnS<sub>4</sub>/p-CdTe 3-layer structure were etched for 5 s in aqueous solution of 1.0 g of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> acidified with 10 mL of dilute H<sub>2</sub>SO<sub>4</sub> in 10 mL of deionised water, rinsed in deionized water and then etched in a warm solution containing 0.5 g each of NaOH and Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> in 50 mL of deionised water for 2 min. The thickness of the gold contacts was ~100 nm each with a diameter of 2 mm. Optical absorption and transmittance measurements on the various deposited thin film layers were carried out using a Carry 50 Scan UV-VIS spectrophotometer in order to determine their energy bandgaps. X-Ray diffraction measurements were carried out using an X'Pert Pro diffractometer with CuKα excitation wavelength of 1.5406 Å. Scanning electron microscopy (SEM) images of the various semiconductor layers were



obtained using FEI-SEM NOVA NANO equipment. A computerized 619 Electrometer/Multimeter was used to measure the current-voltage (I-V) characteristics of the resulting solar cells using a solar simulator with light intensity corrected to a power density of  $100 \text{ mW}\cdot\text{cm}^{-2}$  (AM1.5).

### 3. Results and Discussion

This amorphous nature of ZnS is viewed as an advantage in the sense that it provides a more uniform coverage of the ITO substrate by ZnS without gaps between the grains so that the next layer (polycrystalline  $\text{Cu}_2\text{ZnSnS}_4$ ) will not come into direct contact with the ITO front contact through any possible gaps between ZnS grains (Fig.1a.)

The electrodeposited  $\text{Cu}_2\text{ZnSnS}_4$  layers are polycrystalline in nature with hexagonal structure as shown in Fig.1b. Figure 1c shows that the electrodeposited CdTe is highly oriented in the  $\langle 111 \rangle$  direction with a cubic structure.

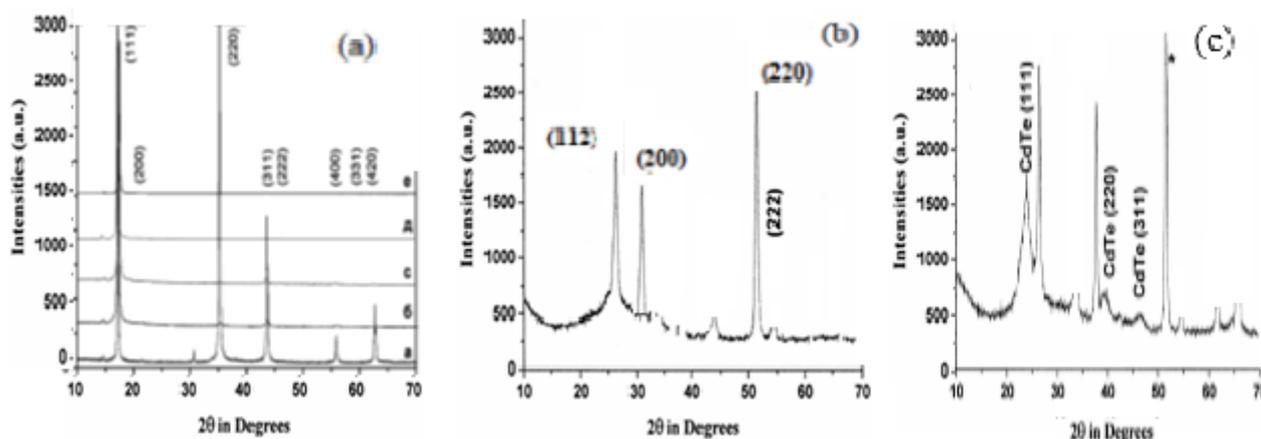


Figure 1. X-ray diffraction patterns of electrodeposited (a) amorphous ZnS;

(b) polycrystalline  $\text{Cu}_2\text{ZnSnS}_4$  and (c) highly oriented CdTe thin layers on glass/ITO substrates.

The preferred orientation of the structure is in the  $\langle 002 \rangle$  direction with the corresponding XRD peak at  $2\theta = 26.3^\circ$ . As a result, the next higher peak which is the (101) peak at  $2\theta \sim 28.1^\circ$  was used for this purpose. The d-spacing obtained for the annealed sample was  $3.186 \text{ \AA}$ . The corresponding  $2\theta$  and d-spacing for the reference file are  $28.2^\circ$  and  $3.164 \text{ \AA}$  respectively.

Figure 2a–c shows the scanning electron micrographs of the electrodeposited ZnS, CdS and CdTe layers, respectively. Figure 4a shows ZnS with uniform coverage of the glass/ITO substrate without any visible pinholes at the magnification of  $60,000\times$  used. The estimated sizes of the grains are in the range  $208\text{--}417 \text{ nm}$ . In Figure 4b, the nature of CdS growth is revealed. The estimated grain sizes are in the  $167\text{--}375 \text{ nm}$  range.

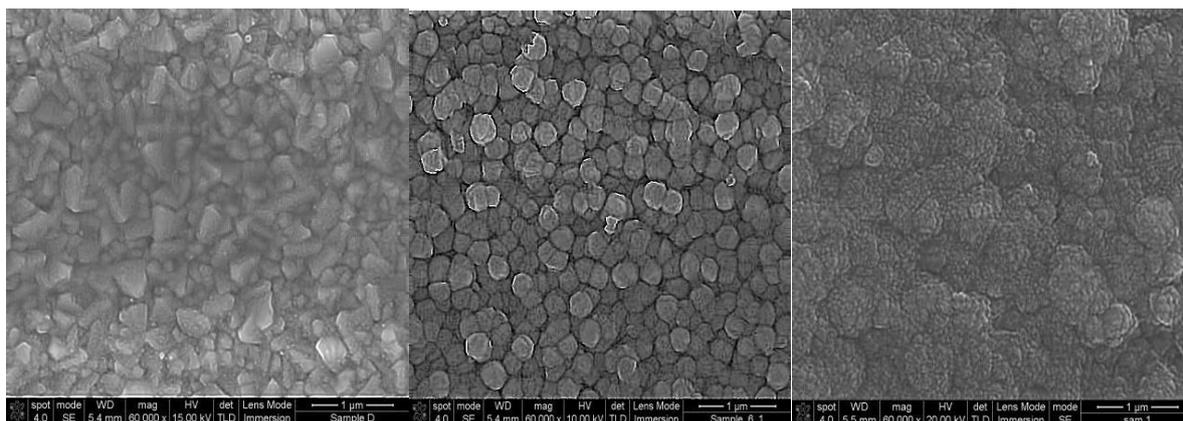


Figure 2. Scanning electron micrographs of electrodeposited (a) amorphous ZnS; (b) polycrystalline  $\text{Cu}_2\text{ZnSnS}_4$  and (c) highly oriented CdTe thin layers.

However, due to the large thickness grown compared to  $\text{Cu}_2\text{ZnSnS}_4$ , the grains touch each other towards the surface of the layer and tend to close up the gaps between them so that the micrograph shows no visible pinholes or gaps between the grains as shown in Figure 4c. What is seen therefore are clusters of tightly-packed grains with these clusters of grains touching each other. The grains are also made up of tightly-packed smaller crystallites. The estimated grain sizes (or clusters) in Figure 4c are in the 217–870 nm range.

The results of optical absorption measurements for the electrodeposited ZnS,  $\text{Cu}_2\text{ZnSnS}_4$  and CdTe layers are presented in Figure 3a–c, respectively. The figures show that the electrodeposited ZnS,  $\text{Cu}_2\text{ZnSnS}_4$  and CdTe layers have energy bandgaps of 3.70 eV, 2.42 eV and 1.45 eV, respectively. This makes ZnS a suitable candidate for use as effective buffer/window layer in CdTe-based multilayer graded bandgap solar cells.

It is important to note what happens to the ZnS/ $\text{Cu}_2\text{ZnSnS}_4$ /CdTe structure in the annealing process. The glass/ITO/ZnS/ $\text{Cu}_2\text{ZnSnS}_4$ /CdTe/In solar cell is also similar to the glass/ITO/ZnS/ $\text{Cu}_2\text{ZnSnS}_4$ /CdTe/In counterpart in structure and is used as a control experiment in this work to compare the advantages of the architecture with ZnS as wide bandgap buffer/window layer. layers, respectively.

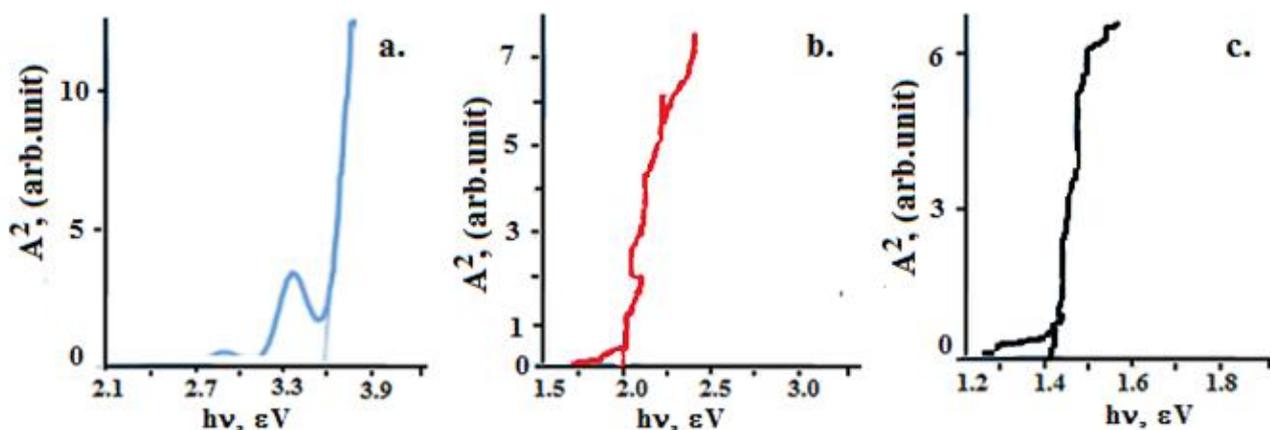


Fig.3. Optical absorption for the electrodeposited ZnS,  $\text{Cu}_2\text{ZnSnS}_4$  and CdTe layers

Figure 4a,b shows the  $\text{Log}I$  vs.  $V$  graphs under dark conditions for the ITO/ZnS/ $\text{Cu}_2\text{ZnSnS}_4$ /CdTe/In solar cell, respectively. Each of the figures is a combination of  $\text{Log}I$ - $V$  for both forward and reverse bias conditions. The diode parameters under dark condition (such as barrier height,  $\phi_B$ , ideality factor,  $n$ , rectification factor, R.F., and reverse saturation current density,  $J_0$ ) are obtained from these graphs. The Schottky barrier heights



estimated for the two device structures were  $>1.13$  eV and  $>1.10$  eV for glass/ITO/ZnS/Cu<sub>2</sub>ZnSnS<sub>4</sub>/CdTe/In and glass/ITO/CdS/CdTe/Au devices, respectively.

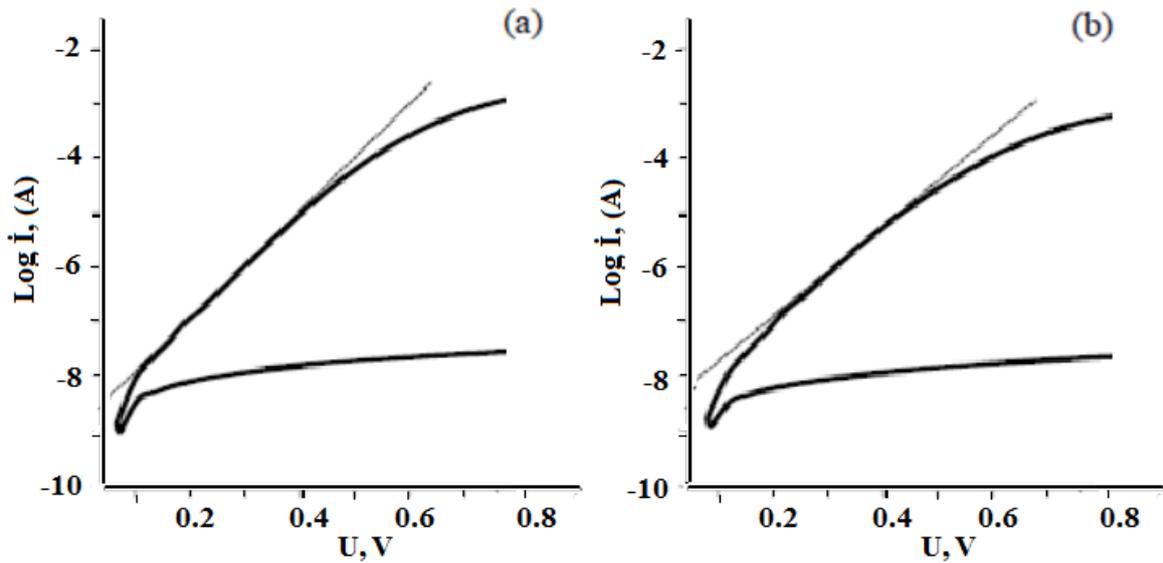


Figure 4. Log I vs. voltage under dark conditions for (a) glass/ITO/ZnS/Cu<sub>2</sub>ZnSnS<sub>4</sub>/CdTe/In solar cell and (b) glass/ITO/Cu<sub>2</sub>ZnSnS<sub>4</sub>/CdTe/In 2-layer solar cell.

For comparison Figure 6a,b shows the linear-linear I-V characteristics of the best

glass/ITO/ZnS/Cu<sub>2</sub>ZnSnS<sub>4</sub>/CdTe/In solar cell under AM 1.5 illumination conditions at room temperature, respectively. The result of using ZnS as the buffer/window layer is directly reflected in the improved high short-circuit current density ( $J_{sc}$ ) as well as improved open-circuit voltage ( $V_{oc}$ ), fill factor (FF) and ultimately, the conversion efficiency ( $\eta$ ) of the 3-layer device, compared to the device as shown in Figure 5a,b. The measured  $V_{oc}$  values of 640 mV and 630 mV are not as large as expected and are indicative of the presence of leakage paths which is also evident in the low fill factor values obtained. The low  $V_{oc}$  values can also arise due to low-purity chemicals used to deposit some semiconductors in this work.

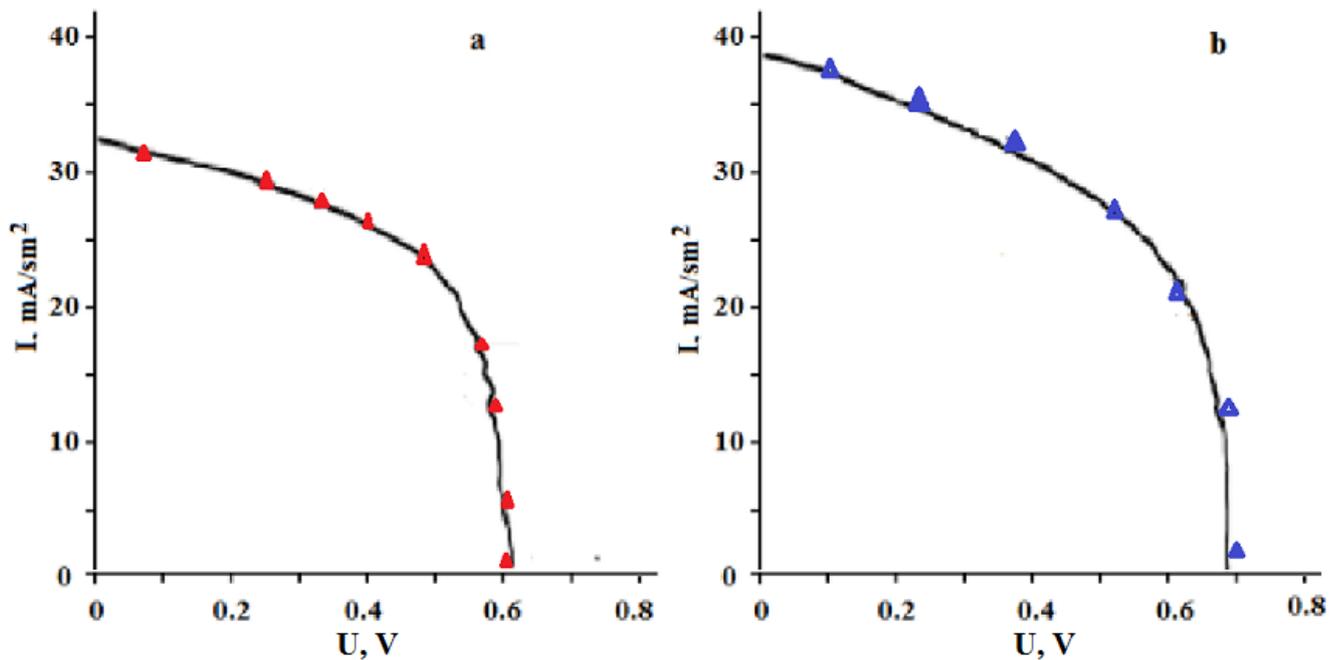




Figure 5. I-V characteristics of glass/ITO/ Cu<sub>2</sub>ZnSnS<sub>4</sub>/CdTe/In 2-layer solar cell (a) and glass/ITO/ZnS/Cu<sub>2</sub>ZnSnS<sub>4</sub>/CdTe/In solar cell (b)

However, to ensure that the observed high  $J_{sc}$  values are genuine, the diodes producing them were isolated by carefully removing the CdTe material around them and repeating the I-V measurements. It is therefore possible in these solar cells for photons with energy lower than the energy bandgap of CdTe to create useful electron-hole pairs that contribute to photo-generated current. The capacitance-voltage (C-V) relationship of the glass/ITO/ZnS/Cu<sub>2</sub>ZnSnS<sub>4</sub>/CdTe/In devices at a frequency of 1 MHz and the corresponding Mott-Schottky plots of these devices are shown in Figure 6.

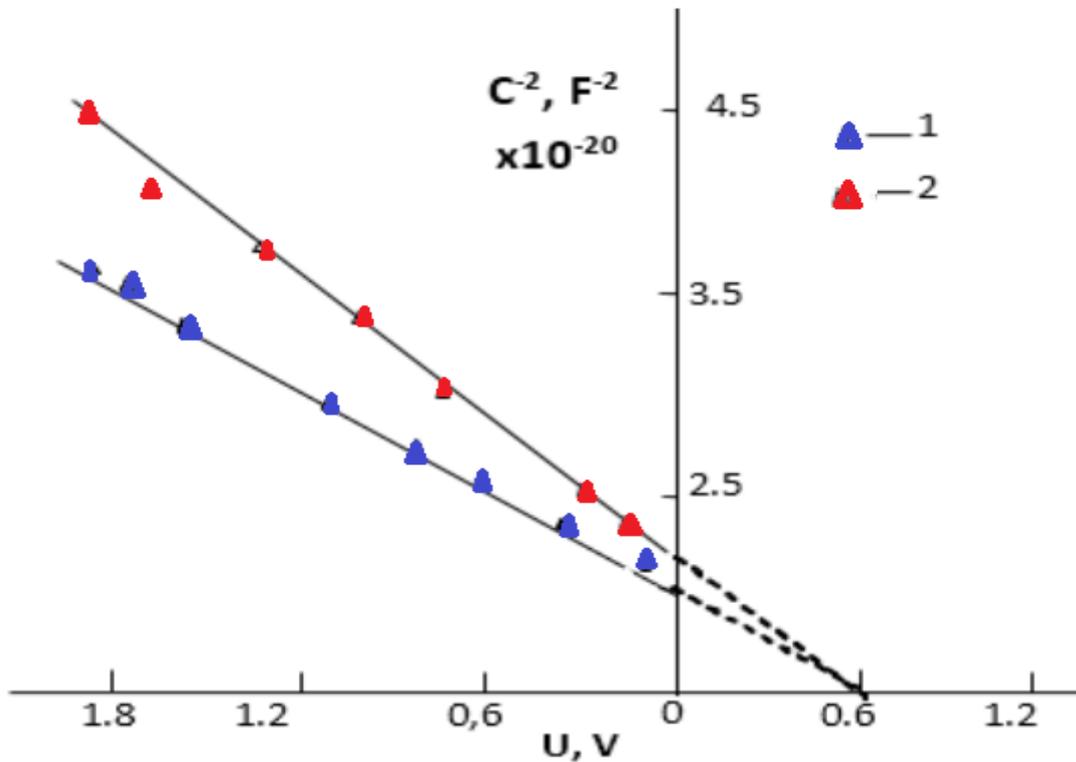


Figure 6. C-V characteristics of glass/ITO/ZnS/Cu<sub>2</sub>ZnSnS<sub>4</sub>/CdTe/In (a) and glass/ITO/Cu<sub>2</sub>ZnSnS<sub>4</sub>/CdTe/In (b) solar cell

For the glass/ITO/ZnS/Cu<sub>2</sub>ZnSnS<sub>4</sub>/CdTe/Au structure, The depletion capacitance measured for this device at zero applied bias was  $C_0 \sim 151$  pF. The depletion capacitance obtained for the glass/ITO/Cu<sub>2</sub>ZnSnS<sub>4</sub>/CdTe/In device was  $C_0 \sim 179$  pF. These capacitance values suggest that the glass/ITO/ZnS/Cu<sub>2</sub>ZnSnS<sub>4</sub>/CdTe/In solar cell has a wider depletion region compared to the glass/ITO/ Cu<sub>2</sub>ZnSnS<sub>4</sub>/CdTe/In 2-layer solar cell. Both figures display a slow response of  $1/C^2$  with applied reverse bias voltage. For the glass/ITO/ZnS/Cu<sub>2</sub>ZnSnS<sub>4</sub>/CdTe/In device in Figure 7a, there is a more rapid drop in the value of  $1/C^2$  as forward bias increases from 0 V to  $\sim 0.35$  V than in the reverse bias. More so, the complex nature of the device structures reported in this paper can result in significant deviation of the C-V and  $1/C^2$ -V responses from those of simple structures.

#### 4. Conclusions

The use of a low-cost, scalable and manufacturable electrodeposition technique for the deposition of device-grade thin film semiconductors for fabrication of glass/ITO/ZnS/Cu<sub>2</sub>ZnSnS<sub>4</sub>/CdTe/In solar cell has been demonstrated. A simplification of the electrodeposition process using two-electrode system is an interesting feature of this process as has been shown. The solar cell structure has been implemented as a means of improving the device parameters and ultimately the conversion efficiency of the CdTe-based solar cells, using ZnS, Cu<sub>2</sub>ZnSnS<sub>4</sub> and CdTe, all of which are II-VI semiconductors. These doping concentrations and the



associated capacitance values obtained for the two solar cell devices suggest that the device has a wider and hence a healthier depletion region compared to the 2-layer device.

## References

- [1] P.Babu, M.V. Reddy, N. K. Revathi, T.R. Reddy. Effect of pH on the physical properties of ZnIn<sub>2</sub>Se<sub>4</sub> thin films grown by chemical bath deposition. *Journal of Nano- and Electronic Physics*, **3**, P. 85–91 (2011).
- [2] E. Bacaksiz, S. Aksu, I. Polat, S. Yilmaz, M. Altunbas. The influence of substrate temperature on the morphology, optical and electrical properties of thermal evaporated ZnSe thin films. *Journal of Alloys and Compounds*, **487**, P. 280–285 (2009).
- [3] A.S. Abidinov, M.A. Jafarov, N.M. Mekhtiev. Photosensitivity of the CdSSe films near the JR region *Proc. of SPIE*, **4340**, P. 107–111 (2000).
- [4] A. Dumbrava. Zinc sulfide fine particles obtained at low temperature. *Chalcogenide Letters*, **6**(9), P. 437–443 (2009).
- [5] J. Yang, G. Wang, H. Liu, X. Chen. Controlled synthesis and characterization of ZnSe nanostructures via a solvothermal approach in a mixed solution. *Mater. Chem. Phys.*, **115**, P. 204–208 (2009).
- [6] J.B. Chaudhari, N.G. Deshpande, Y.G. Gudage, A. Ghosh, V.B. Huse, R. Sharma. Studies on growth and characterization of ternary CdS<sub>1-x</sub>Se<sub>x</sub> alloy thin films deposited by chemical bath deposition technique. *Applied Surface Science*, **254**, P. 6810–6816 (2008).
- [7] A. Apolinar-Iribe, M.C. Acosta-Enriquez, M.A. Quevedo-Lopez, R. Ramirez-Bon, A. De-Leon, S.J. Castillo. Acetylacetone as complexing agent for CdS thin films grow chemical bath deposition. *Chalcogenide Letters*, **8**, P. 77–82(2011).
- [8] L.Y. Chen, D.L. Zhang, G.M. Zhai, J.B. Zhang. Comparative study of ZnSe thin films deposited from modified chemical bath solutions with ammonia-containing and ammonia free precursors. *Materials Chemistry and Physics*. **120**, P. 456–460 (2010).
- [9] T.P. Kumar, P.D. Ramesh, B.J. Abaraj. Effect of ethylenediamine tetraacetic acid concentration on the photoluminescence behavior of CdZnS thin films. *Chalcogenide Letters*, **8**, P. 207–212 (2011).
- [10] Gopakumar, N.P. Anjana, P.P. Vidyadharan. Chemical bath deposition and characterization of CdSe thin films for optoelectronic applications. *J. Materials Sci.*, **45**, P. 6653–6656 (2010).
- [11] W.C. Song, J.H. Lee. Growth and characterization of ZnxCd<sub>1-x</sub>S films prepared by using chemical bath deposition for photovoltaic devices. *Journal of the Korean Physical Society*, **54**, P. 1660–1665 (2009).
- [12] D. Patidar, K.S. Rathore, N.S. Saxena, T.P. Sharma. Determination of optical and electrical properties of ZnSe thin films. *Journal of Modern Physics*, **55**, P. 3041–3047 (2008).