ZnS/Cu_2ZnSnS_4/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_2ZnSnS_4/CdTe/In structure has been fabricated using all-electrodeposited ZnS, Cu_2ZnSnS_4 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_2ZnSnS_4/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_2ZnSnS_4, CdTe, thin film, electrodeposition

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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 ZnCl2 and 0.03 M (NH4)2S2O3 in 800 mL of de-ionized water. Electropurification of the ZnCl2 was carried out for 48 h prior to the addition of (NH4)2S2O3 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/İTO 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 $\mu A \cdot cm^{-2}$ 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_2ZnSnS_4, the glass/İTO/ZnS substrates were cleaned with methanol and deionised water. The deposition of Cu_2ZnSnS_4 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_2ZnSnS_4 deposited on glass/İTO had a thickness ~300 nm while that deposited on glass/İTO/ZnS had a thickness ~150 nm. This therefore brings the total thickness of the ZnS/Cu_2ZnSnS_4 bi-layer to ~250 nm comparable to the ~300 nm of Cu_2ZnSnS_4 grown on glass/İTO.

The CdTe deposition electrolyte contained 1 M CdSO4 (99.0%) and 1 mM TeO2 (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^{2+}. The TeO2 was first dissolved in H2SO4 and then added into the bath after the electro-purification of CdSO4, and the pH of the electrolyte adjusted to 2.00 ± 0.02.

After depositing and characterizing few CdTe samples on glass/İTO 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/İTO/CdS and glass/İTO/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 $\mu A \cdot cm^{-2}$. To complete the solar cell fabrication, the annealed glass/İTO/Cu_2ZnSnS_4/p-CdTe 2-layer structure and glass/İTO/n-ZnS/n-Cu_2ZnSnS_4/p-CdTe 3-layer structure were etched for 5 s in aqueous solution of 1.0 g of K2Cr2O7 acidified with 10 mL of dilute H2SO4 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 Na2S2O3 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 $mW \cdot cm^{-2}$ (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 İTO substrate by ZnS without gaps between the grains so that the next layer (polycrystalline Cu_2ZnSnS_4) will not come into direct contact with the İTO front contact through any possible gaps between ZnS grains (Fig.1a.)

The electrodeposited Cu_2ZnSnS_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 <111> direction with a cubic structure.

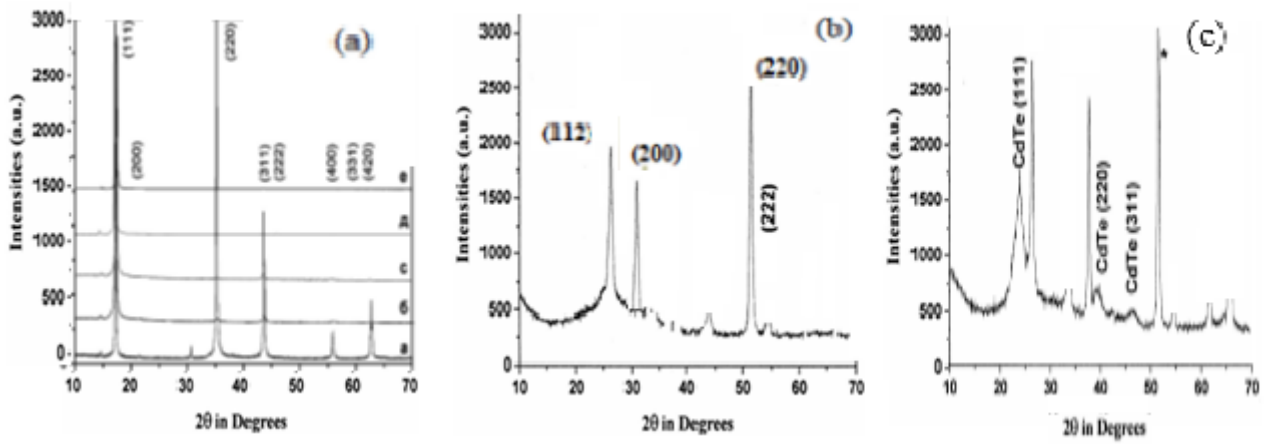

Figure 1. X-ray diffraction patterns of electrodeposited (a) amorphous ZnS;

(**b**) polycrystalline Cu_2ZnSnS_4 and (**c**) highly oriented CdTe thin layers on glass/İTO substrates.

The prefered orientation of the structure is in the <002> direction with the corresponding XRD peak at 2θ = 26.3°. As a result, the next higher peak which is the (101) peak at 2θ ~ 28.1° was used for this purpose. The d-spacing obtained for the annealed sample was 3.186 Å. The corresponding 2θ and d-spacing for the reference file are 28.2° and 3.164 Å 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/İTO substrate without any visible pinholes at the magnification of 60,000× used. The estimated sizes of the grains are in the range 208–417 nm. In Figure 4b, the nature of CdS growth is revealed. The estimated grain sizes are in the 167–375 nm range.

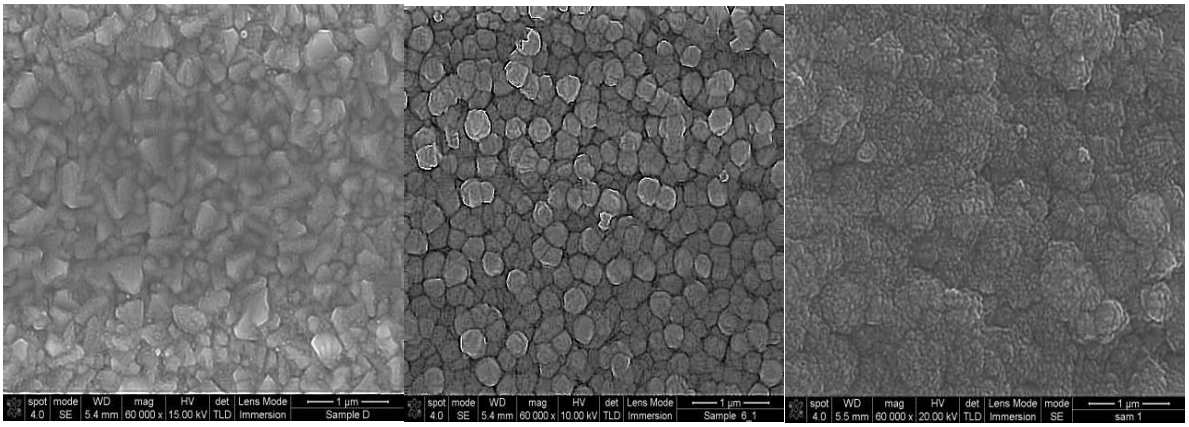

Figure 2. Scanning electron micrographs of electrodeposited (a) amorphous ZnS;

(**b**) polycrystalline Cu_2ZnSnS_4 and (**c**) highly oriented CdTe thin layers.

However, due to the large thickness grown compared to Cu_2ZnSnS_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, Cu_2ZnSnS_4 and CdTe layers are presented in Figure 3a–c, respectively. The figures show that the electrodeposited ZnS, Cu_2ZnSnS_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/Cu_2ZnSnS_4/CdTe structure in the annealing process. The glass/ITO/ZnS/Cu_2ZnSnS_4/CdTe/In solar cell is also similar to the glass/ITO/ZnS/Cu_2ZnSnS_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.

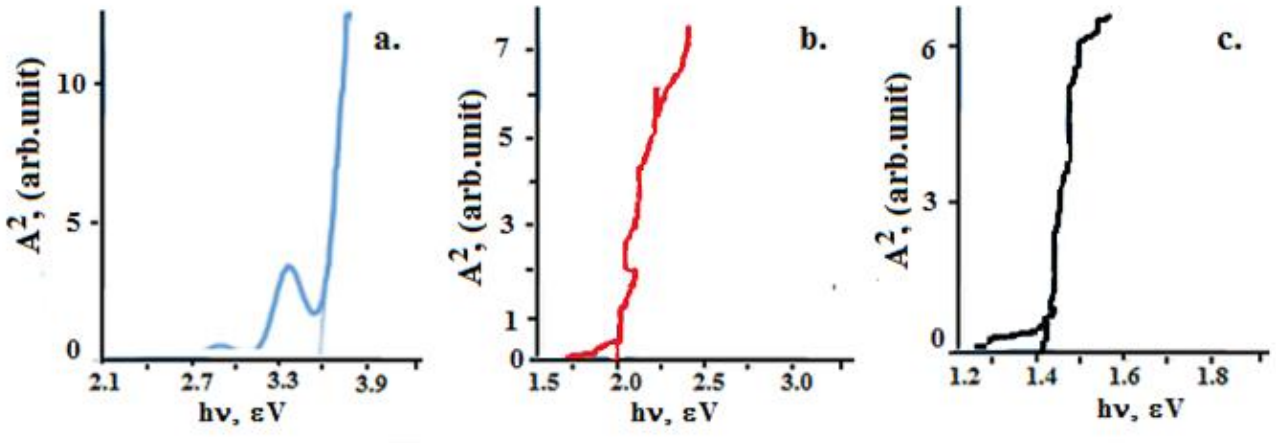

Fig.3. Optical absorption for the electrodeposited ZnS, Cu_2ZnSnS_4 and CdTe layers

Figure 4a,b shows the LogI vs. V graphs under dark conditions for the ITO/ZnS/Cu_2ZnSnS_4/CdTe/In solar cell, respectively. Each of the figures is a combination of LogI-V for both forward and reverse bias conditions. The diode parameters under dark condition (such as barrier height, ϕB, ideality factor, n, rectification factor, R.F., and reverse saturation current density, J0) 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_2ZnSnS_4/CdTe/In and glass/İTO/CdS/CdTe/Au devices, respectively.

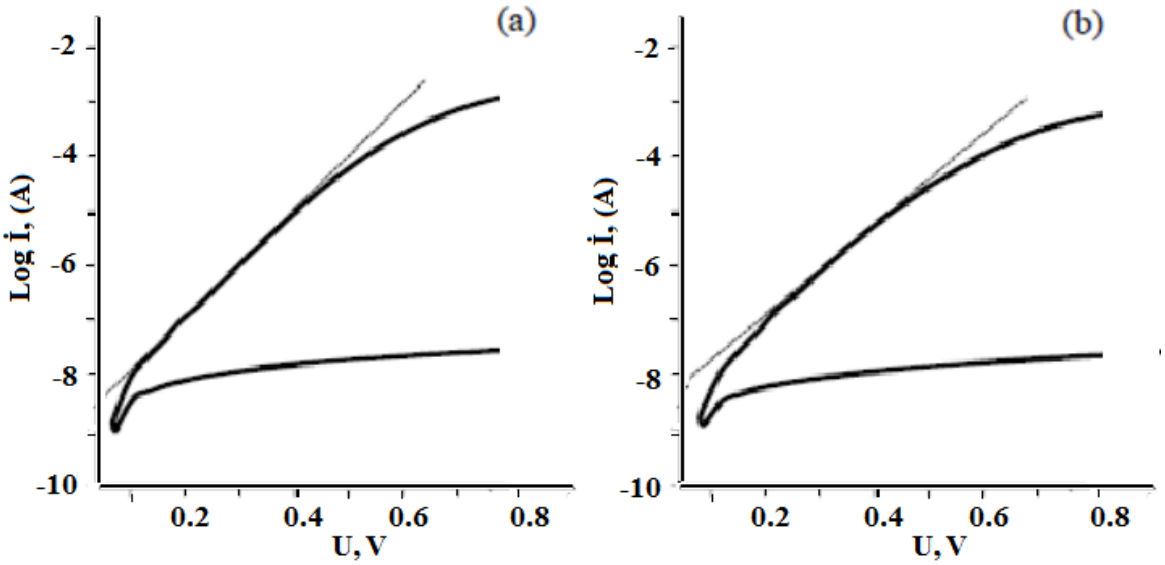

Figure 4. LogI vs. voltage under dark conditions for (a) glass/ITO/ZnS/Cu_2ZnSnS_4/CdTe/In solar cell and (b) glass/İTO/Cu_2ZnSnS_4/CdTe/İn 2-layer solar cell.

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

glass/ITO/ZnS/Cu_2ZnSnS_4/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 (Jsc) as well as improved open-circuit voltage (Voc), fill factor (FF) and ultimately, the conversion efficiency (η) of the 3-layer device, compared to the device as shown in Figure 5a,b. The measured Voc 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 Voc values can also arise due to low-purity chemicals used to deposit some semiconductors in this work.

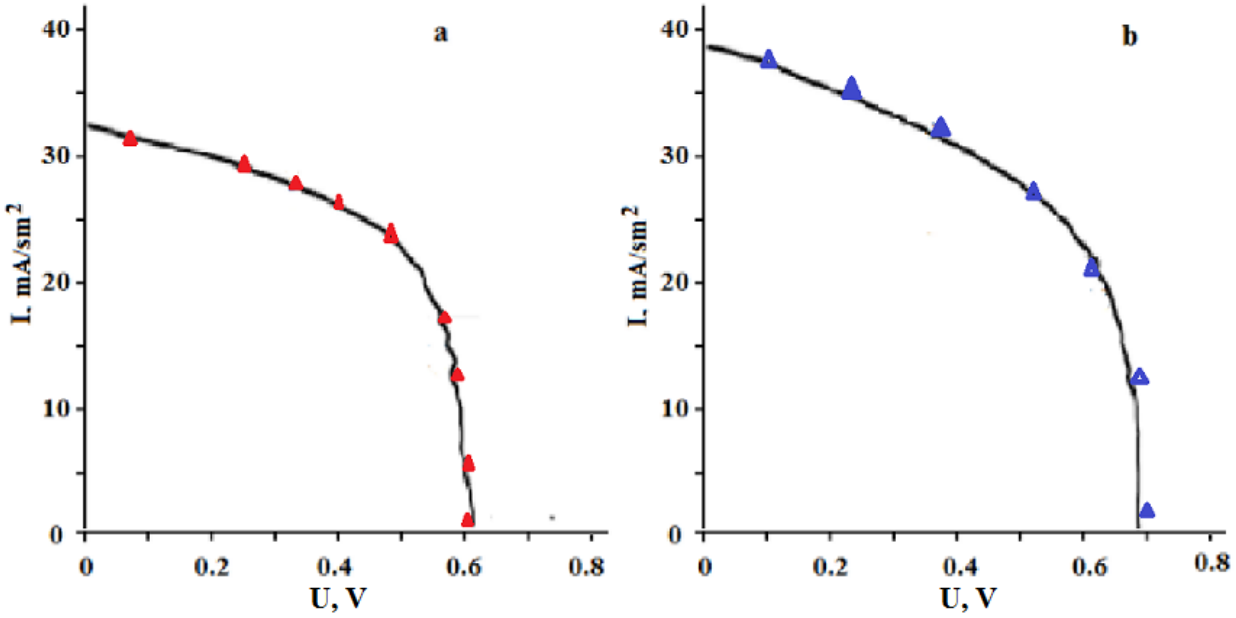

Figure 5. I-V characteristics of glass/İTO/ Cu_2ZnSnS_4/CdTe/İn 2-layer and glass/ITO/ZnS/Cu_2ZnSnS_4/CdTe/In (a) solar cell (b) solar cell

However, to ensure that the observed high Jsc 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_2ZnSnS_4/CdTe/In devices at a frequency of 1 MHz and the corresponding Mott-Schottky plots of these devices are shown in Figure 6.

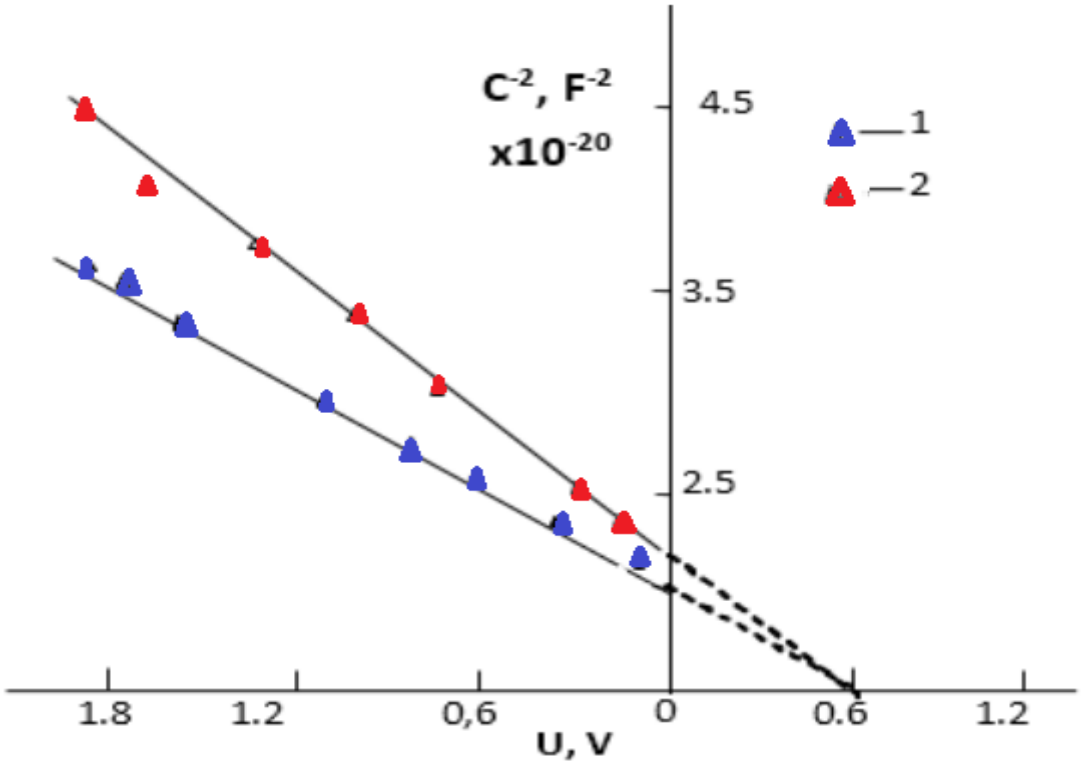

Figure 6. C-V characteristics of glass/ITO/ZnS/Cu_2ZnSnS_4/CdTe/In (a) and glass/İTO/Cu_2ZnSnS_4/CdTe/İn (b) solar cell

For the glass/İTO/ZnS/Cu_2ZnSnS_4/CdTe/Au structure, The depletion capacitance measured for this device at zero applied bias was Co~151 pF. The depletion capacitance obtained for the glass/İTO/Cu_2ZnSnS_4/CdTe/İn device was Co~179 pF. These capacitance values suggest that the glass/ITO/ZnS/Cu_2ZnSnS_4/CdTe/In solar cell has a wider depletion region compared to the glass/İTO/ Cu_2ZnSnS_4/CdTe/İn 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_2ZnSnS_4/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 ~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_2ZnSnS_4/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_2ZnSnS_4 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.

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