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# SIMULATION OF CZTS/ZnO/FTO HETERO-JUNCTION SOLAR CELL

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A R T I C L E I N F O

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## Abstract

*The abundance of Copper, Zinc, Tin and Sulphur is the reason that CZTS is a probable material for large-scale power generation. The environmentally friendly nature of CZTS when paired with either Zinc Oxide (ZnO) or Fluorine doped Tin Oxide (FTO), which is also abundant and non-toxic has made it choice material for investigation that could produce a p-n hetero-junction desired in changing solar energy into electricity. Solar cell Capacitance simulator (SCAPS 1-D), developed by Dr. Marc Burgelman and his research group at University of Gents, Belgium, is the simulator tool employed to model the desired p-n hetero-junction solar cell. SCAPS-1D was used to solve the Poisson, hole and electron continuity equations so that information concerning the device properties of the CZTS/ZnO/FTO based solar cells could be obtained. The Solar cell data were then processed to obtain I-V measurements. The values of band offsets* $\Delta E_c$ *and* $\Delta E_v$ *at the ZnO/FTO interface were found to be 0.135 eV and 0.384 eV and* $\Delta E_c$ *and* $\Delta E_v$ *at CZTS/ZnO were 0.226 eV and 2.008 eV respectively. It had been shown from the results thata solar cell with CZTS/ZnO/FTO hetero-junction layer with efficiency of 24.23 % is realistic andit is of the order of the most efficient thin film solar cell produced with* $Cu(In,Ga)Se_2$ *(CIGS) and Cadmium Sulfide (CdS) based ones. This implies that CZTS can favourably compete as an efficient absorber layer. The planar configuration proposed in this work was to enable the simulation with SCAPS.*

## 1.0 Introduction

Materials such as amorphous silicon (a-Si), Copper-Indium-Gallium-di-Selenide/Sulfide (CIGS) and Cadmium Telluride (CdTe) have been the dominated absorbing thin-film materials in the production of solar cells [1]. Though, Cadmium Sulfide (CdS) is the most

used thin-film material for buffer /window/ schottky barrier for industrially produced solar cell [2].The study of these thin-films materials show that, Cd and Ga are toxic but In and Te are rare and expensive. However, the departure from non-renewable energy source is necessary due to effect of $CO_2$ in causing global warming [3]. With these in mind,it is pertinent to search for materials that will pose no harm to the environment for usage in Solar cells either for the absorbing/window layers with a comparably highconversion efficiency. $Cu_2ZnSnS_4$(CZTS) is a keterite (a sulfide mineral) and it's a quaternary semiconductor which is sufficiently abundant and none of its constituent elements is harmful even in their combinations to the environment [4]. ZnO is also a very abundant and as well poses no harm to the environment. This study looks into the combination of ZnO and CZTS (ZnO/CZTS)as window/absorber hetero-junctionrespectively. There are so many softwares used to simulate thin-film solar cells and they are not limited to; Solar cells Capacitance Simulator (SCAPS), Analysis of Microelectronics and photonic Structure (AMPS), Sentarius and Silvaco-TCAD. For this study, SCAPS is used in the simulation of ZnO/CZTS hetero-junction. When compare SCAPS simulation software with other simulation softwares, SCAPS exhibits the largest number of AC and DC electrical measurements which include short circuit current density (*Jsc*), fill factor (*FF*), open circuit voltage (*Voc*), conversion efficiency (*Eff*), quantum efficiency (*QE*), spectral response, generation and recombination profile, which is based on the hole and electron continuity equations together with Poisson equation. All these physical quantities can be calculated in light and dark condition and also at different illuminations and temperatures.

**1.1 Theoretical background to the study**

Solutions to some three equations namely, Poisson's equation, continuity equation for holes and electrons are embedded in SCAPS for the physics of device transport. Poisson equation is given as [4];

$$\frac{d}{dx}\left(\varepsilon(x)\frac{d\varphi}{dx}\right) = q.[p(x) - n(x) + N_D^+(x) - N_A^-(x) + p_t(x) - n_t(x)] \quad (1)$$

(Continuity equations for holes

$$\left(\frac{1}{p}\right)\frac{dj_n}{dx} = -G_{op}(x) + R(x) \quad (2)$$

and electrons;

$$\left(\frac{1}{q}\right)\frac{dj_p}{dx} = G_{op}(x) - R(x) \quad (3)$$

The parameters in equations (1) to (3) are defined as; **ε** is the permittivity, **q** is the magnitude of the charge of an electron, **n** for free electron, p for free hole, $n_t$is the trapped electron, $p_t$is the trapped hole,$N_D^+$is the ionized donor-like doping concentration, $N_A^-$ is the ionized acceptor-like doping concentration, $J_n$ is the electron current density, $J_p$ is the hole current density, **R** is the net recombination rate resulting from band-band (direct) recombination and Shockley-Read-Hall (SRH) (indirect) recombination traffic through gap states, and $G_{op}$ is the optical generation rate due to externally imposed illumination. In transport theory, where the electron population may be degenerated or the material properties varies with position, the electron current density, $J_n$ and the hole current density $J_p$can be expressed as [4];

$$J_n(x) = q\mu_n n\left(\frac{dE_{fn}}{dx}\right) \quad (4)$$

and

$$J_p(x) = q\mu_p n\left(\frac{dE_{fp}}{dx}\right) \quad (5)$$

where $\mu_n$ and $\mu_p$ are electron mobility and hole mobility respectively. It is essential to remember that equations (4) and (5) are general formulations that include diffusion, drift and motion of electrons and holes due to effective fields arising from band gap, electron affinity, and densities of states gradients.

The three main equations (1), (2) and (3) must hold at every position in the model and the solution to these non-linear equations involves the determining the state variables Ψ(x), $E_{fn}(x)$ and $E_{fp}(x)$ which completely defines the system at every point x. These three equations cannot be solved analytically because they are coupled and non-linear (due to recombination factor in the continuity equations for hole and electron respectively), hence numerical methods must be utilized. Equations (4) to (6) are the necessary boundary conditions that the solutions of equations (1) to (3) must satisfy [4].

$$\Psi(0) = \Psi_0 - V \quad (6)$$

$$\Psi(L) = 0 \quad (7)$$

$$J_p(0) = -qS_{po}[p_0(0) - p(0)] \quad (8)$$

$$J_p(L) = -qS_{pL}[p(L) - p_0(L)] \quad (9)$$

$$J_n(0) = -qS_{no}[n(0) - n_0(0)] \quad (10)$$

$$J_n(L) = -qS_{nL}[n_0(L) - n(L)] \quad (11)$$

## 2.0 Methodology

The simulation procedure follows closely with the parameters defined in Table 1 which were used as input parameters in the SCAPS-1D simulator. They are all cited from experimental study from literature with reasonable estimates in some cases [5].The cell structureused in the simulation is p-CZTS/n-ZnO/n-FTO and is shown in Fig. 1. This cell structure consists of Fluorine doped Tin Oxide, an ultra-thin window layer, namely, a highly conductive n-type Al-doped ZnO (n-ZnO) and a $Cu_2ZnSnS_4$ (CZTS) which is a p-type quaternary semiconductor. In this simulation, the influence and the contributions of the shunt resistance and series resistance are not considered. Also, the structure is not voltage biased, and the working point temperature is set at 300K. The absorption coefficient of the materials used was determined by the simulator based on the input parameters (Table 1) and the arrangement of the model as allowed by the SCAPS-1D simulator.

**Table 1:** Opto-electronic properties of the materials used in the simulation [5].

| Parameters | p- CZTS | n-ZnO | n-FTO |
|---|---|---|---|
| Band Gap $(eV)$ | 1.56 | 3.35 | 3.60 |
| Density of States – Conduction band $N_c(cm^{-3})$ | $2.2\ X\ 10^{18}$ | | |
| Density of states – Valence band | | | |
| Electron affinity | 4.21 | 4.35 | 4.50 |
| Electron mobility | 100 | 25 | 20 |
| Hole mobility | 20 | 100 | 100 |
| Free carrier Concentration | | 0 | 0 |
| Free carrier Concentration | 0 | | |

| | | | |
|---|---|---|---|
| Relative permittivity | 10 | 9 | 10 |
| Thickness (µm) | (0.05 – 2.00) | 0.02 | 0.0125 |

Figure 2 is the description of how the simulation took place, step 2 to step 4 can be interchanged and doesn't follow any particular order, while steps 1, 5 and 6 must retain their position to get the best out of SCAPS-1D simulator. The absorber layer is varied along side the transparent conductive oxide (FTO) (Table 1). Various efficiencies were generated based on the thickness variation described in Table 1. The consitutents of the solar cell thickness with highest efficiency was noted. This cell was then subjected to re-simulation with previous working conditions but with varied temperature between 280 K and 500 K with step height of 20 K.

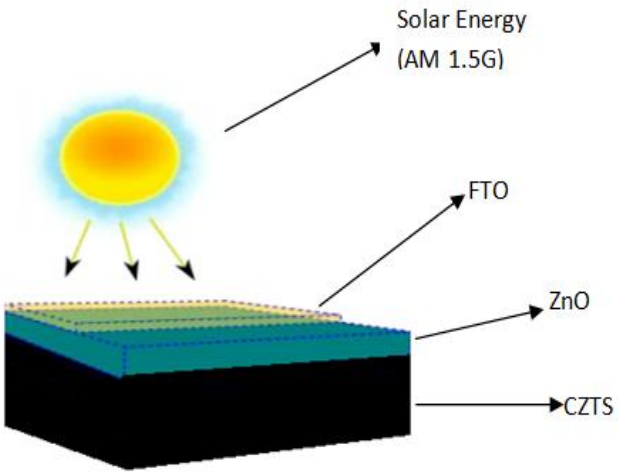


Figure1. The structure of CZTS based solar cell used in the simulation[2].

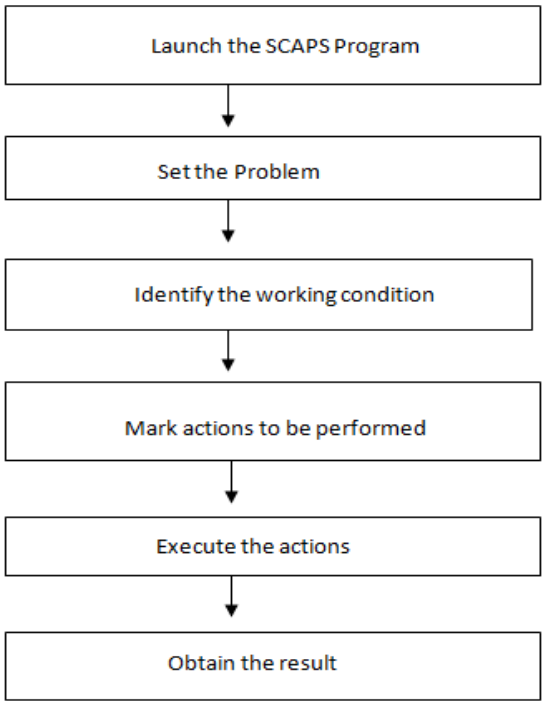


**Figure 2.** The Simulation procedure

## 3.0 Results and Discussion

Energy band diagram and I-V characteristicsof the simulated solar cellSCAPS-1D simulation of FTO/ZnO/CZTS Solar cell have been investigated using I-V measurements and CV measurements at temperature 300K. Fig. 3shows the band gap line up model of n-FTO/n-ZnO/p-CZTS hetero-junction which was constructed from the data obtained from the simulation gave a Type II (staggered) band alignments at both interfaces [7]. The valuesof band offsets $\Delta E_c$ and $\Delta E_v$ at the ZnO/FTO interface are found to be 0.135 eV and 0.384 eV and$\Delta E_c$ and $\Delta E_v$ at CZTS/ZnO are 0.226 eV and 2.008 eV respectively. The simulated thickness of the CZTS layer was varied from 0.05µm to 2µm to analyze the effect of absorber layer thickness in the cell performance, while other materials thicknesses were kept constant. It was

observed that the open circuit Voltage ($V_{oc}$) increased from 1.0034 V to 1.0861 V, the short circuit current density ($J_{sc}$) increased from 7.7988 mA/cm$^2$to 25.5098 mA/cm$^2$, Fill factor (FF) decreased from 88.25 % to 87.46 % and efficiency increased from 6.91 % to 24.59 %. The reason been that the thicker the absorber layer, the more of photons with longer wavelengths will be absorbed, which thus make a contribution to the generation of electron-hole pairs [6].

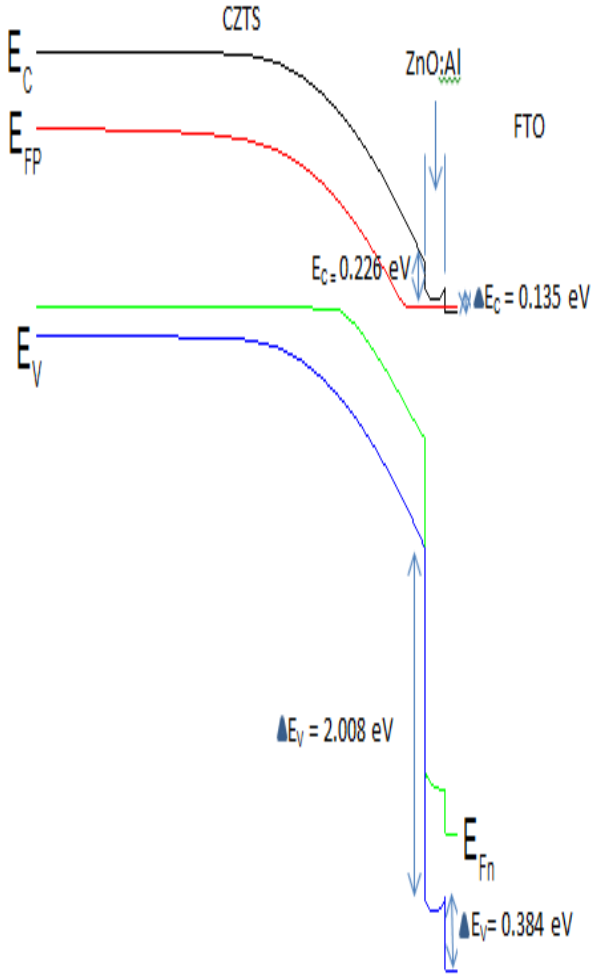


Figure 3: The band alignment showing the band offsets of the hetero-junctions layer

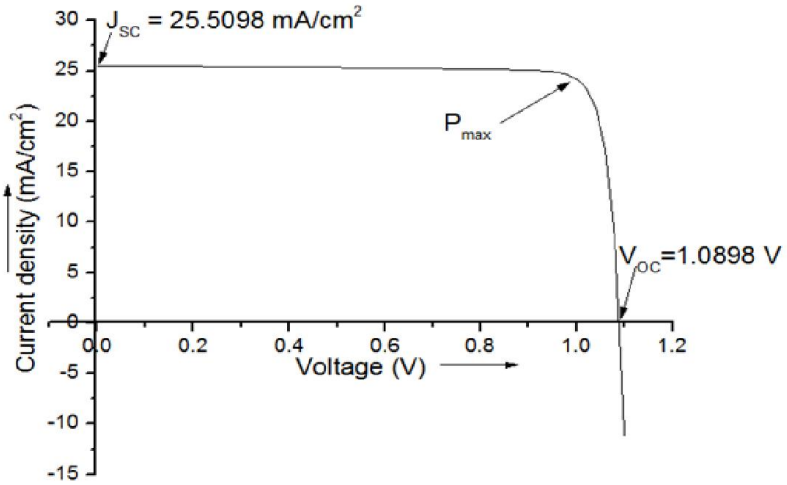


Figure 4: J-V characteristics of CZTS/ZnO/FTO solar cell.

### 3.1 The dependence of cell performance on the thickness of CZTS layer

At the beginning of the simulation, the absorber layer thickness was varied from 0.05 µm to 2 µm to check the contribution of the layer to the cell performance, while other material parameters of different layers are kept constant. Figures 5-8 show the cell performance evaluation of CZTS thickness on the performance of the simulated solar cell. These figures showed that the current voltage characteristics of the solar cell increased based on the increment in the thickness of the absorber layer. This is due to the magnitude of carrier density which enhances the recombination process and thus reduces the probability of the collection of the photo-generated electron-hole pair [6]. The magnitude of the wavelength of the photons is a function of how these photons are absorbed by the CZTS layer which defines the collected efficiency of the electron-hole pair.

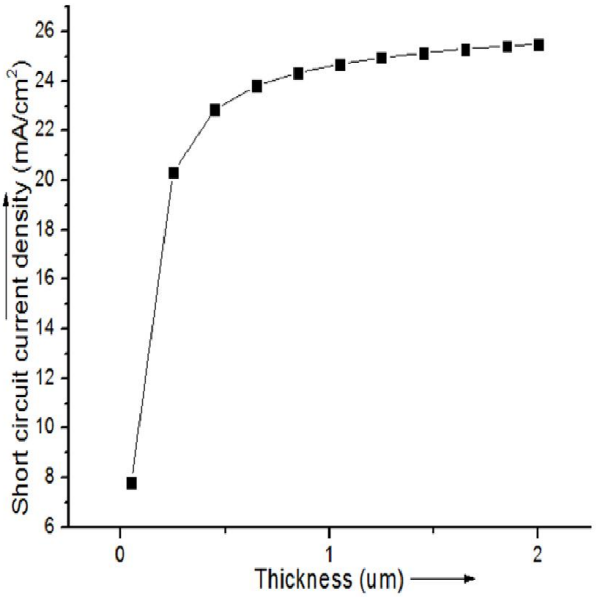


Figure 5: Performance evaluation of thickness of CZTS as a function of short circuit current density.

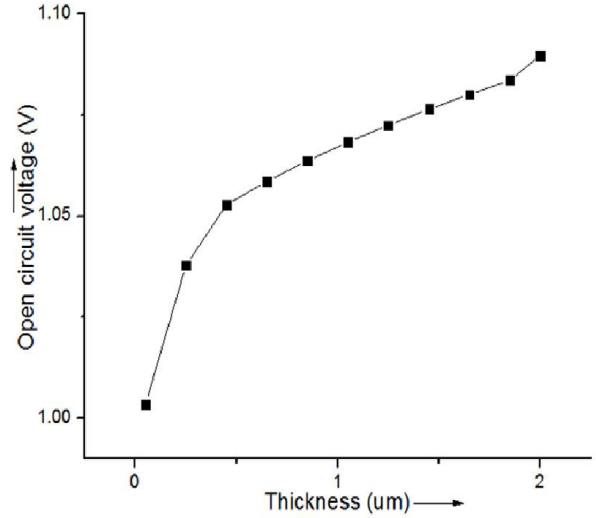


Figure 6: Performance evaluation of thickness of CZTS as a function of short open circuit voltage.

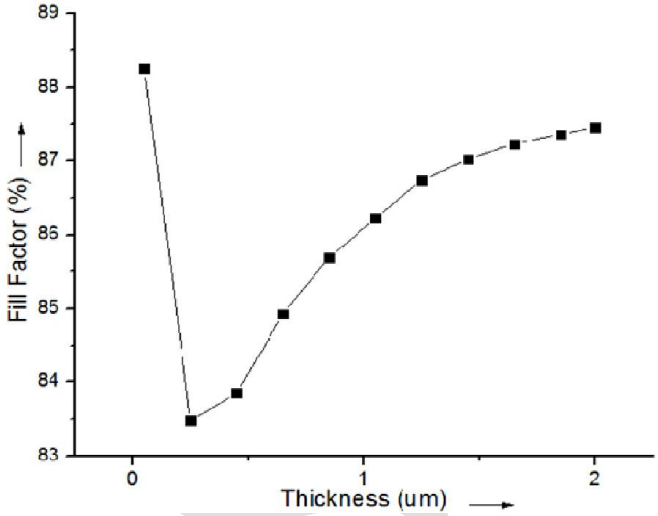


Figure 7: Performance evaluation of thickness of CZTS as a function of fill factor.

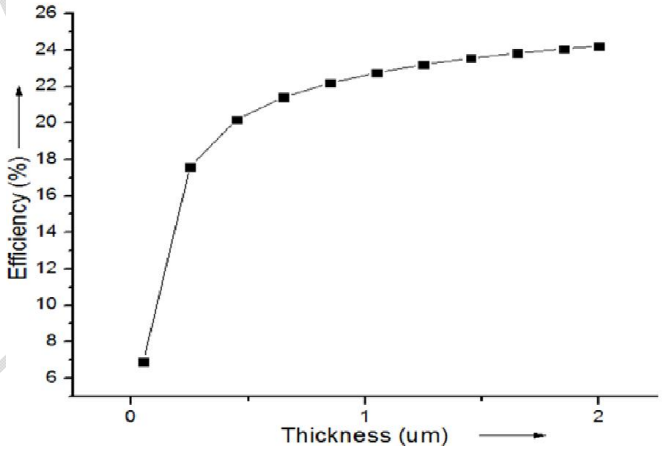


Figure 8: Performance evaluation of thickness of CZTS as a function of efficiency.

### 3.2 Effect of environmentaltemperature on the solar cell

The environmental temperature plays a significant role in the working operations of the solar cell. This may be due to the fact that the outdoor temperature is the working temperature at which the solar cell works. The effect of the temperature on the solar cell had been investigated with different environmental temperature in the range of 280 K to 500 K with

step height of 20 K. The results of the simulation are reported in Figures 9-12. There was convergence issue at 280 K. The results showed that all electrical parameters except short circuit current density decreases as the environmental temperature is increased. The reverse saturation current is increasing with increased environmental temperature and the increase in saturation current decreases the open circuit voltage [6]. The effect of temperature increment on the efficiency of the solar cell was found to be 0.042 %/K. This showed that for every unit rise in environmental temperature, the efficiency of the solar cell will drop by 0.042 %.

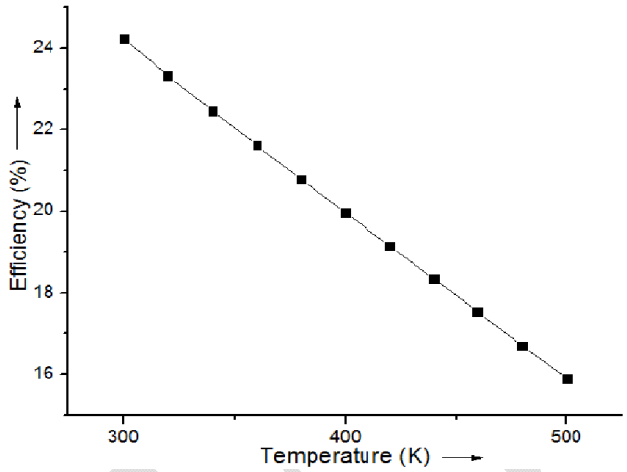


Figure 9: Performance evaluation of environmental temperature as a function of efficiency.

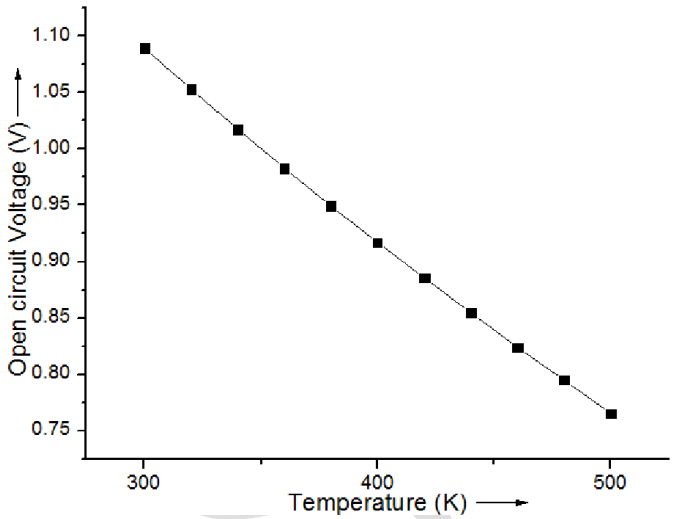


Figure 10: Performance evaluation of environmental temperature as a function of open circuit voltage.

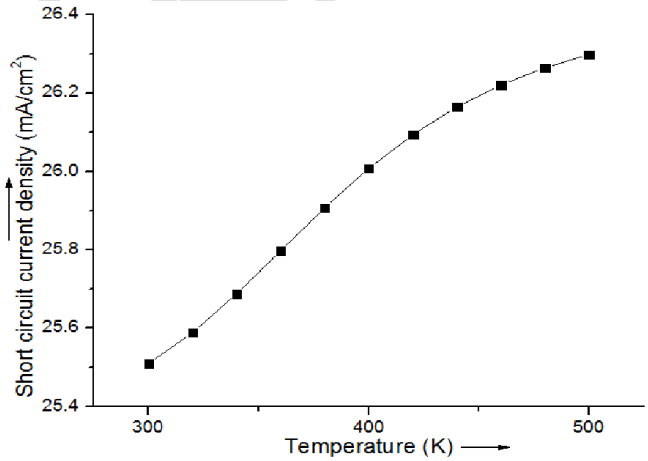


Figure 11: Performance evaluation of environmental temperature as a function of short circuit current density.

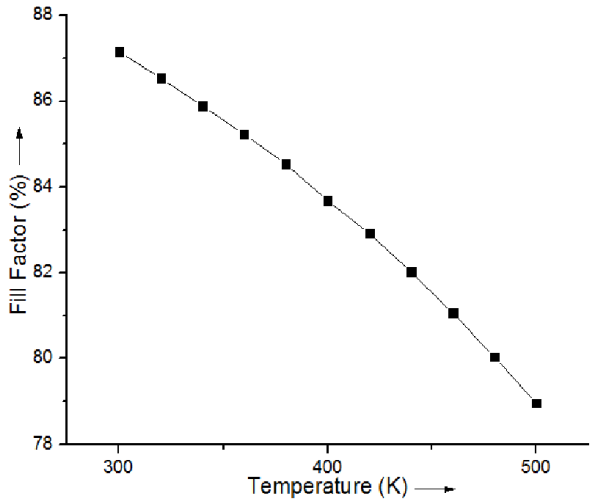


Figure 12: Performance evaluation of environmental temperature as a function of fill factor.

## 4.0 Conclusion

In conclusion, it has been observed from the results discussed that CZTS based solar cell with oxides-binary semiconductor can perform excellently well like CIGS based solar cells. An efficiency of > 24 % was achieved with this solar cell and it is of the order of the most efficient thin film solar cell produced with $Cu(In,Ga)Se_2$ (CIGS) and Cadmium Sulfide (CdS) based ones. The effect of temperature incrementon efficiency of the solar cell was found to 0.042 %/K. The planar configuration proposed in this work was to enable the simulation with SCAPS. The obtained results will be helpful in the fabrication of a CZTS based solar cells.

**Acknowledgement**

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