

Performance Study of CZTS Solar Cell by Optimizing Buffer Layer Materials (ZnS and SnS) using AMPS-1D Simulation

Md. Samiul Islam Sadek^{1*}

¹Department of Electrical and Electronic Engineering
Southeast University, Dhaka, Bangladesh,

Abstract

The characteristics performance of the kieserite based $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) based solar cell is investigated using a simulation program called Analysis of Microelectronic and Photonic Structures (AMPS). The cell structure is based on a p-type $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) compound semiconductor as the absorber layer and ZnO is used as the transparent conductive oxide (TCO) layer, which serves as the front contact of the cell as well. ZnS is used as the starting material for the n-type heterojunction partner of the p-CZTS layer, which is replaced by SnS to evaluate the performance of the cell for different buffer layers. The influence of the operating temperature, doping concentration, thickness of both ZnS and SnS are changed one after another and the simulator provides the basic solar cell parameters like open-circuit voltage (V_{oc}), short circuit current (J_{sc}), Fill Factor (FF), and efficiency as output. The parameters of the other two layers namely TCO and absorber layer are kept constant at their optimal values respectively. The results depict that SnS is a better option to form the basic PN junction of CZTS based solar cell as its' obtained efficiency is about 15% whereas, the efficiency of ZnS based cell is only about 11%. All these simulation results will give some important guides for feasibly fabricating higher efficiency CZTS solar cells.

Keywords: CZTS, ZnS, SnS, Solar Cell, Efficiency, TCO, AMPS-1D Simulation

I. Introduction

The quaternary compound $\text{Cu}_2\text{ZnSnS}_4$ (CZTS)—and its related alloys $\text{Cu}_2\text{ZnSnSe}_4$ (CZTSe) is emerging as a promising active-layer semiconductor for low-cost thin-film solar cell application due to its suitable optical properties, elemental availability, and nontoxicity of its constituents (Ito and Nakazawa, 1988), (Tanaka, *et al.*, 2007). In the literature, CZTS refers widely to the selenide, sulfide, or sulfide-selenide form of the compound. CZTS is a p-type semiconductor with a direct bandgap of about 1.0 eV for selenide (CZTSe) (Grossberg, Krustok, Timmo, & Altosaar, 2009) and about 1.5 eV for sulfide (CZTS) (Tanaka, *et al.*, 2007). It possesses an absorption coefficient of more than 10^4 cm^{-1} , and the bandgap can be further tuned between 1.0 and 1.5 eV by varying the ratio of selenium to sulfur in the CZTS compound.

Although CZTS is relatively a new material, there have been numerous published works reporting different approaches for fabricating

CZTS, including vacuum and non-vacuum methods. The record efficiency for a CZTS device, whose absorbing active layer was fabricated by a solution-based method, is 12.6% (Wang, *et al.*, 2014). An efficiency of 6.7% was reported in 2008 by the Japanese group headed by Katagiri (Katagiri, *et al.*, 2008), using a $\text{Cu}_2\text{ZnSnS}_4$ thin film deposited by co-sputtering technique.

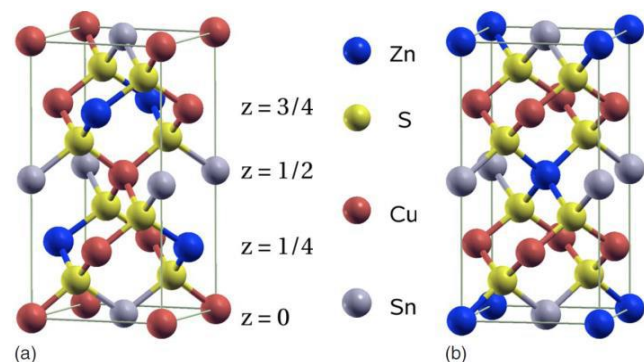


Figure 1: Schematic representations of the Kesterite (a) and Stannite (b) structures

* **Corresponding Author:** Md. Samiul Islam Sadek, Senior Lecturer, Department of Electrical and Electronic Engineering, Southeast University, 251/1 & 252 Tejgaon I/A, Dhaka 1208, Bangladesh untry; Email: msisadek@seu.edu.bd

A rapid improvement was then demonstrated: in 2011 the IBM group (Shin, *et al.*, 2013) reported an 8.4% efficiency solar cell obtained from co-evaporated CZTS; vacuum-deposition based CZTS submodules (about 5×5 cm²-sized) with efficiency increasing from 6.2 (Hiroi, *et al.*, 2011) to 8.6% (Hiroi, *et al.*, 2011) have been reported by Solar Frontier between 2011 and 2012 and very recently an efficiency of 9.2% has been achieved (Kato, *et al.*, 2012). Despite this rapid improvement, performances of CZTS based solar cells remain still far from their theoretical limit of about 30% (Shockley & Queisser, 1961).

II. Methodology

A simulation is an imitation of the operation of a real-world process or system. The act of simulating something first requires that a model be developed; this model represents the key characteristics, behaviors, and functions of the selected physical or abstract system or process. For working material at following the three steps. At first, we considered the simulation process then the laboratory experiment, and the final step is physical setup. In this simulator ZnO, ZnS, CZTS of operating temperatures are varying 300k to 360k. At this stage into the layer info value of ZnO and CZTS materials have different optoelectronic properties like as (Relative permittivity, Electron mobility, Hole mobility, Doping concentration, Bandgap, Electron affinity) are fixed. On the contrary, only for ZnS materials are varying the different optoelectronic properties. At this time, the light is ON in the Illumination condition and I-V Curve is shown. Changing the value of spectrum parameters are following through the material.

Due to this condition reflectivity increased or decreased Back contact and Front contact. Now, these data parameters are saved on simulation software AMPS and finally run this for getting simulation results then we can get the value of Efficiency, Open circuit voltage, and Fill factor. Here SnS material is also the same simulation process as ZnS material. My research materials were also simulation-based. Here consider this simulation for ideal basis material. The solar cell structure is based on ZnS and SnS materials. The structure of the solar cell is a three-layer model device. Materials of ZnS and SnS solar cell structure are as shown in Figure.2.

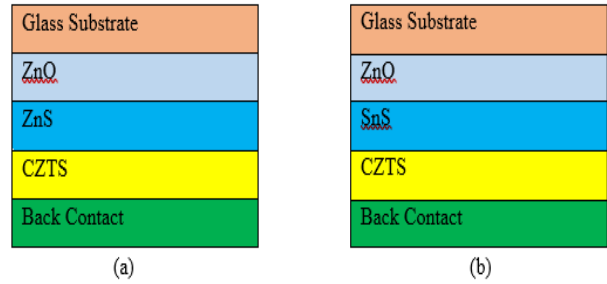


Figure 2: Simulated Structure of the proposed solar cell (a) ZnS as buffer layer (b) SnS as a buffer layer

As contact is immensely vital for a charge collection in solar cells, the numerical values used in AMPS-1D simulation for these two buffer layers (ZnS and SnS) both for front and back contacts are tabulated below shown in Table 2 and these parameters are the boundary condition of AMPS-1D simulation software.

Table 1: Front and back contact values for both cells

| Front contact | Back contact |
|--------------------------------|--------------------------------|
| PHIBO = 0.30 eV | PHIBL = 1.50 eV |
| SNO = 1.0×10^7 cm/sec | SNL = 1.0×10^7 cm/sec |
| SPO = 1.0×10^7 cm/sec | SPL = 1.0×10^7 cm/sec |
| RF = 0.00 | RB = 1.00 |

The material parameters of different constituent layers are carefully taken from different literature which is tabulated below.

Table 2: Front and back contact values for both cells

| Parameters | ZnO (TCO) | ZnS (Buffer) | SnS (Buffer) | CZTS (Absorber) |
|------------------------------------|-----------|--------------|--------------|-----------------|
| Thickness (nm) | 100-450 | 100-170 | 100-450 | 1000 |
| ϵ | 9 | 10 | 12.5 | 10 |
| Eg (eV) | 3.35 | 3.64 | 1.25 | 1.56 |
| X (eV) | 4.35 | 3.5 | 4.2 | 4.21 |
| μ_n (cm ² /Vs) | 25 | 50 | 25 | 100 |
| μ_p (cm ² /Vs) | 100 | 20 | 100 | 20 |
| n, p (/cm ³) | 1e18(n) | 1e17(n) | 7.4e16(n) | 4e16 |
| N _c (/cm ³) | 2.2e18 | 1.5e18 | 1e19 | 2.2e18 |
| N _v (/cm ³) | 1.8e19 | 1.8e18 | 4.13e19 | 1.8e19 |

III. Results and Discussions

III.A: Result Analysis for ZnS as a buffer layer

Zinc sulfide is an inorganic compound with the chemical formula of ZnS. This is the main form of zinc found in nature, where it mainly occurs as the mineral sphalerite. Although this mineral is usually black because of various impurities, the pure material is white, and it is widely used as a pigment. In its dense synthetic form, zinc sulfide can be transparent, and it is used as a window for visible optics and infrared optics

In this simulation, ITO is used as the front contact which is used as the transparent conductive oxide (TCO) layer of the cell. The earth-abundant and non-toxic $\text{Cu}_2\text{ZnSn}(\text{SSe})_4$ shortly known as CZTS is used as the main absorber layer. The two most important materials namely ZnS and SnS are used as the buffer layers to form the n-type heterojunction partner underneath the p-CZTS layer. Different parameters like thickness, carrier concentration, temperature, Reflectivity have been changed for ZnS and SnS to find the highest efficiency of the cell.

III.A.1: Effects of thicknesses of ZnS layer on efficiency

It has been observed that the efficiency increases up to 130 nm and then it decreases for higher values of thickness of the ZnS layer. The increase of efficiency at lower thickness is due to more light gets transmitted through the buffer layer and absorbed by the absorber CZTS layer.

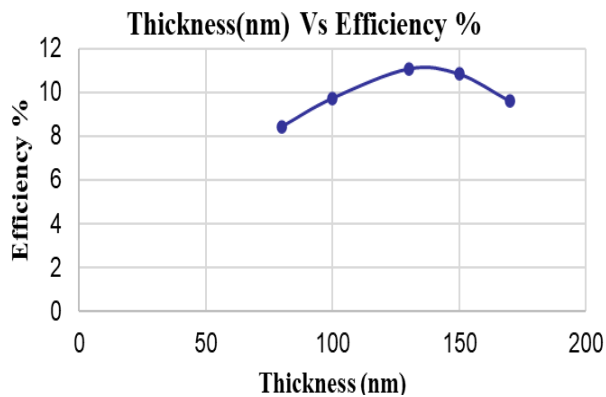


Figure 3: Effect of ZnS layer thicknesses on the overall efficiencies of the proposed solar cell

However, at higher values of thickness, the incoming light is restricted into the buffer layer and less amount of light will be transmitted to the absorber. Therefore, the number of carriers will be reduced.

III.A.2: Effects of doping concentrations of ZnS layer on efficiency

The doping concentration of ZnS is varied over a wide range of (1×10^{12} to $1 \times 10^{17} \text{ cm}^{-3}$) values. It has been observed the efficiency reaches a peak value of 1×10^{16} , which is 9.92, and then it decreases drastically at higher concentrations. This is because, higher doping means, a high number of electrons and holes which in turn increase the overall current of the device and hence the output power. However, at higher doping, efficiency decreases due to structural defects (heavy doping effect).

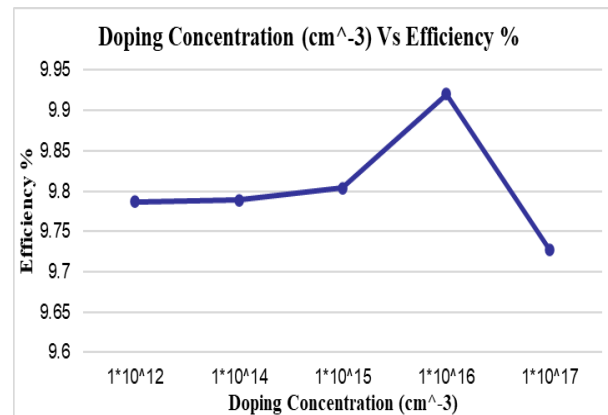


Figure 4: Effect of doping concentrations of the ZnS layer on the overall efficiencies of the proposed solar cell

III.A.3: Effects of temperature on overall optimized solar cell structure

The effect of operating temperature has been investigated in this work for the temperatures ranging from 300 K to 360 K. The efficiency and other output parameters degrade drastically with the increase in the operating temperature. With higher temperatures, additional thermal energy is gained by the electrons. This extensive energy gained by the electrons creates an unstable situation and causes them to recombine with the holes before they could reach the depletion region and get collected.

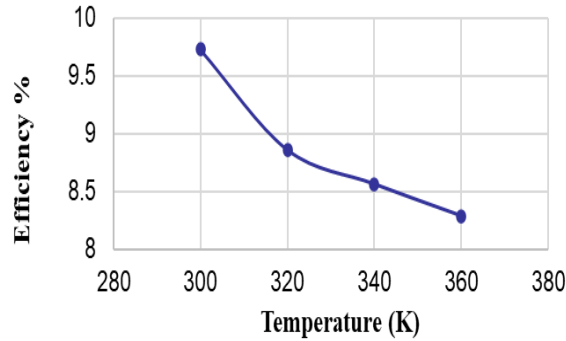


Figure 5: Effects of temperature on overall optimized solar cell structure

III.A.4: Effects of front contact reflectivity on overall optimized solar cell structure

It has been observed that the efficiency of the solar cell decreases if the value of the reflection coefficient increases. This is very much accepted, because if the reflection coefficient increases, more and more light will be reflected from the front surface of the solar cell, and absorption of light decreases. A maximum value of efficiency of about 9% is obtained at the front contact reflectivity of 0.1.

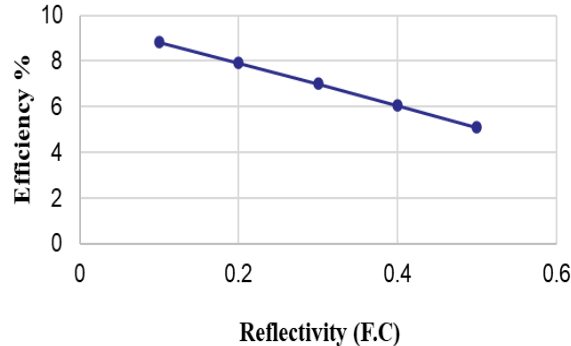


Figure 6: Effects of front contact reflectivity on overall optimized solar cell structure

III.A.5: Effects of back contact reflectivity on overall optimized solar cell structure

It has been observed that the efficiency of the solar cell increases if the value of the reflection coefficient increases. This is very natural because, if the reflection coefficient increases, more and more light will be reflected back and forth and maximum light will be trapped inside the structure. A maximum value of efficiency of about 9.62 % is obtained at back contact reflectivity of 0.9.

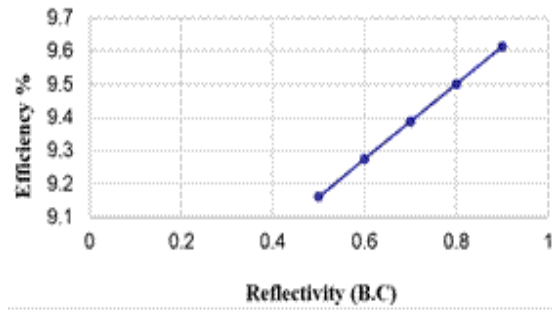


Figure 7: Effects of back contact reflectivity on overall optimized solar cell structure

III.B: Result Analysis for SnS as buffer material

Tin sulfide is a chemical compound of tin and sulfur. The chemical formula is SnS. Its natural occurrence concerns herzenbergite (α -SnS), a rare mineral. At elevated temperatures above 905K, SnS undergoes a second-order phase transition to β -SnS. In recent years, it has become evident that a new polymorph of SnS exists based upon the cubic crystal system.

III.B.1: Effects of thicknesses of SnS layer on efficiency

It has been observed that the efficiency increases up to 400 nm and then it decreases for higher values of thickness of the SnS layer. The increase of efficiency at lower thickness is due to more light gets transmitted through the buffer layer and absorbed by the absorber CZTS layer. However, at higher values of thickness, the incoming light is restricted into the buffer layer and less amount of light will be transmitted to the absorber. Therefore, the number of carriers will be reduced.

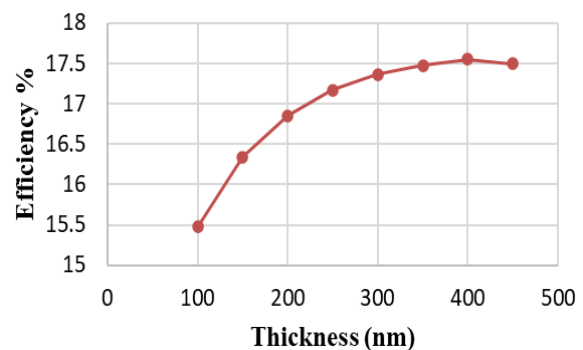


Figure 8: Effect of SnS layer thicknesses on the overall efficiencies of the proposed solar cell

III.B.2: *Effects of doping concentrations of ZnS layer on efficiency*

The doping concentration of SnS is varied over a wide range of (7.4×10^{12} to $7.4 \times 10^{20} \text{ cm}^{-3}$) values. It has been observed the efficiency reaches a peak value of $7.4 \times 10^{20} \text{ cm}^{-3}$, which is 15.477, and then it decreases drastically at higher concentrations. This is because, that, higher doping means, a high number of electrons and holes which in turn increase the overall current of the device and hence the output power. However, at higher doping, efficiency decreases due to structural defects (heavy doping effect).

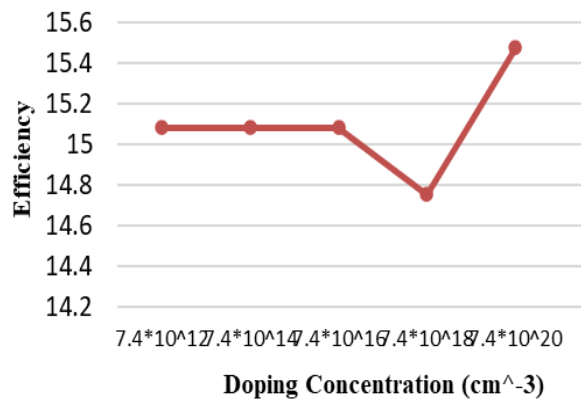


Figure 9: Effect of doping concentrations of SnS layer on the overall efficiencies of the proposed solar cell

III.B.3: *Effects of temperature on overall optimized solar cell structure*

The effect of operating temperature has been investigated in this work for temperatures ranging from 300 K to 360 K.

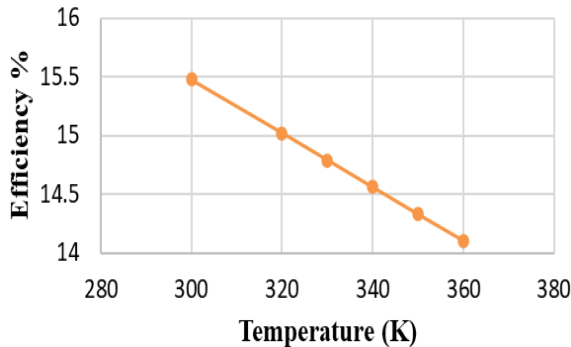


Figure 10: Effects of temperature on overall optimized solar cell structure

The efficiency and other output parameters degrade drastically with the increase in the operating temperature. With higher temperatures, additional thermal energy is gained by the electrons. This extensive energy gained by the electrons creates an unstable situation and causes them to recombine with the holes before they could reach the depletion region and get collected.

III.B.4: *Effects of front contact reflectivity on overall optimized solar cell structure*

It has been observed that the efficiency of the solar cell decreases if the value of the reflection coefficient increases. This is very much accepted, because if the reflection coefficient increases, more and more light will be reflected from the front surface of the solar cell, and absorption of light decreases. A maximum value of efficiency of about 14.025% is obtained at the front contact reflectivity of 0.1.

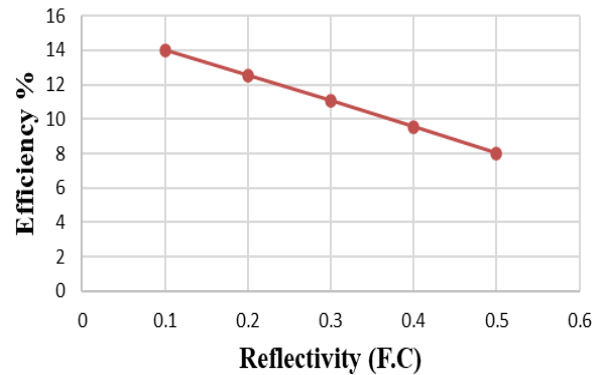


Figure 11: Effects of front contact reflectivity on overall optimized solar cell structure

III.B.5: *Effects of back contact reflectivity on overall optimized solar cell structure*

It has been observed that the efficiency of the solar cell increases if the value of the reflection coefficient increases. This is very natural because, if the reflection coefficient increases, more and more light will be reflected back and forth and maximum light will be trapped inside the structure. A maximum value of efficiency of about 15.34% is obtained at back contact reflectivity of 0.9.

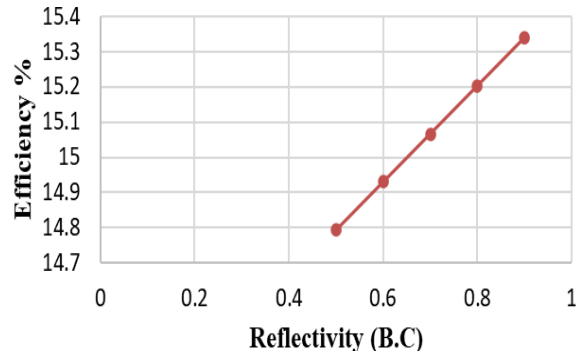


Figure 12: Effects of back contact reflectivity on overall optimized solar cell structure

IV. Conclusion

The simulation has been done with the AMPS-1D simulation program. Also, the simulated results clearly show that SnS is better than ZnS in terms of efficiency. The efficiency of ZnS is 9.727% whereas the efficiency of SnS is 15.477%. The lattice constant of ZnS is $a = 3.82\text{\AA}$, whereas the lattice constant of CZTS is $a = 5.475\text{\AA}$, so, there is a considerable amount of lattice mismatching between ZnS and CZTS, which eventually creates a trap state for outgoing electrons, so the efficiency will be reduced. However, in the case of SnS, the lattice constant is $a = 4.33\text{\AA}$, so the little mismatch is present in this case, so no dangling bond will be created and hence the efficiency will be better. Moreover, the bandgap mismatching between ZnS ($E_g = 3.64\text{ eV}$) and CZTS ($E_g = 1.56\text{ eV}$) is more than the SnS ($E_g = 1.25\text{ eV}$) and CZTS.

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