An Efficient CZTS Solar Cell from Numerical Analysis

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***Abstract*—The Copper Zinc Tin Sulfide (CZTS) is considered as one of the promising semiconductor materials in Kesterite family for potential solar cells absorber material. This work focuses on the numerical model and simulation of efficient CZTS based thin-film solar cell. Popular thin-film solar cell simulator wxAMPS was used for simulation of (Al:ZnO/i-ZnO/CdS/CZTS/Mo)structured solar cell and the effects of different layer properties on cell performance parameters were analyzed. An optimized cell with 15.84% (%FF=72.86, *Voc*=0.78Volt and *Jsc*=27.98 mA/cm^2) energy conversion efficiency has proposed. The temperature coefficient (TC) of 0.02%/°C had shown the higher stability of the proposed cell. All of the simulated results had encouraged towards fabrication of high performance thin-film CZTS solar cells.**

Keywords*— *Thin-film solar cell, CZTS, Numerical Simulation, wxAMPS, Conversion efficiency

I. Introduction

The world is approaching towards big crisis of energy as most of the conventional energy resources are going to be depleted. In this situation, solar photovoltaic is one of the most effective ways for the direct power generation from the sunlight. In recent years, photovoltaic keeps on being one of the quickest developing ventures with development rates beyond 40% per year [1].

Among the photovoltaic technologies, Thin-film Solar Cells (TFSCs) have gained popularity for its material usage in a lower scale. Popular TFSCs are Chalcopyrite based polycrystalline binary semiconductor material CdTe (Cadmium Telluride) and quaternary semiconductor material $Cu_2In_xGa_{1-x}Se_2$ (CIGS) is commercially successful. However, there are some restrictions on the usage of limited material Indium (In) and Tellurium (Te) which are raised problems about restriction on generation limit of Photovoltaic (PV) cells.

For solving the issues, Cu_2ZnSnS_4 (CZTS), a quaternary semiconductor material consists of earth abundant material Zn and Sn is one of the hot candidates for PV technology. Abundance of Sn and Zn in earth is very much higher than In (45 times and 1500 times correspondingly) and the price of Indium is almost in the order of twice higher than Sn and Zn [2]. Bandgap energy of CZTS is in the range of 1.4eV to 1.5eV which is suitable for photovoltaic conversion [3]. Furthermore high absorbance capability (absorption coefficient, α is more than 10^6/m) ensures the good possibility of photovoltaic conversion.

Multiphase defects or impurities like ternary and quaternary compounds are more easily formed than CZTS formation. So, pure CZTS crystal formation is a very challenging task and it is formed in a narrow region [2-3].

Highest conversion efficiency of CZTS based photovoltaic solar cell is 10% (confirmed) and 11% (notable exceptions) were fabricated by UNSW [4], Australia whereas William Shockley and S. J. Queisser gives the limiting value of conversion efficiency of single junction solar cell is 30% [5-6]. So there is a huge scope to explore the performance of CZTS based photovoltaic solar cells.

In this research paper, Numerical simulation of CZTS based solar cells has been done with solar device simulator wxAMPS. The cells are simulated by varying the properties of different layers and the important performance parameters were analyzed.

II. Device Structure and Materials

A. Basic Format of CZTS solar Photovoltaic Cell

The photovoltaic effect in heterodiode consists of transparent conducting oxide: Cadmium Tin Oxide (CTO) and CZTS thin film is first reported by Ito and Nakezawa [7]. P-CZTS material is the main absorber layer in CZTS solar cell. The general structure of CZTS based solar cell (Aluminum doped ZnO/intrinsic-ZnO/CdS/CZTS/Mo/Glass substrate) is shown in Fig.1.

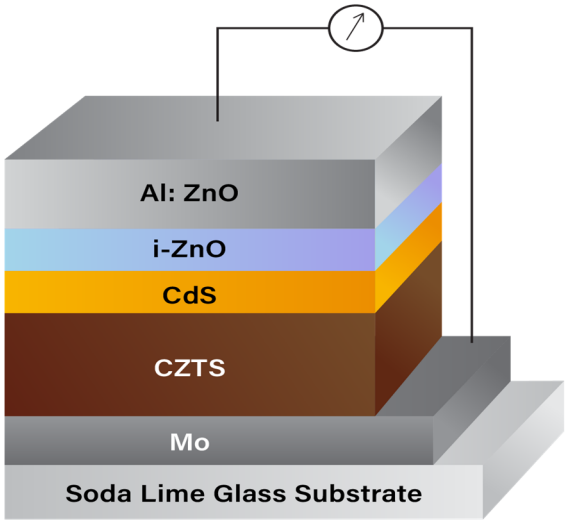

Fig.1. CZTS solar cell structure (thickness is not scaled)

CdS and CZTS are the buffer and absorber layer respectively form the p-n junction and constitute the key part of the device. Aluminum doped ZnO is transparent conducting oxide which creates an n-n+ junction before metal semiconductor contact junction, ensures a low resistive contact for electron transport. The whole structure should be grown layer by layer into a substrate to form a stable structure, because the layer thickness is in the order of nm to µm scale, the cell has no rigidity or mechanical strength of

its own. Usually cell deposited on glass substrate for mechanical strength.

B. Device Modeling and Simulation

Before any type of expensive fabrication, the performance of a cell can be estimated by numerical simulation. For simulation, electrical modeling of layers is needed. Popular solar cell simulator wxAMPS (Analysis of Microelectronic and Photonic Structures with wxWidgets) was used in this work. The wxAMPS is a refresh variant of well-known simulator AMPS (Analysis of Microelectronic and Photonic Structures) created by S. Fonash and refreshed by Angus Rockett [8]. Calculation of wxAMPS is altered by consolidating Newton and Gummel techniques and is a decent apparatus to break down various sorts of solar photovoltaic cells, for example, CdTe and CIGS thin films and different materials. Intra band tunneling model in wxAMPS works extremely well for solar cells of low deformity, for example, CIGS and CdTe Solar cells [9].

In this paper we consider a basic structure of CZTS absorber material based TFSCs consists of CdS heteropartner as described in Fig.1. Material properties utilized in this simulation, which depended on literature, experiments [10-13] and in some case, based on reasonable estimations. Electrical properties of different layers are shown in TABLE I.

TABLE I: OPTIMIZED ELECTRICAL PROPERTIES OF DIFFERENT LAYERS OF CZTS PV CELL

	Layers			
Layer Properties	Al:ZnO	i-ZnO	CdS	CZTS
Thickness (μm)	0.1	0.06	0.06	1.8
Energy Bandgap, E_g (eV)	3.3	3.3	2.4	1.5
Electron Affinity, χ (eV)	4.4	4.4	4.2	4.3
Relative Permittivity, ε_r	9	9	10	7
Density of states in CB, N_c (cm^{-3})	2.22×10^{18}	2.22×10^{18}	2.22×10^{18}	2.22×10^{18}
Density of states in VB, N_v (cm^{-3})	1.78×10^{19}	1.78×10^{19}	1.78×10^{19}	1.78×10^{19}
Electron and Hole Mobility, μ_n and μ_p ($cm^2/v/s$)	100 and 25	100 and 25	100 and 25	100 and 25
Doping Density, N_a or N_d (cm^{-3})	10^{20} (D)	10^{18} (D)	10^{18} (D)	10^{16} (A)

The symbol D means donor and A means acceptor in TABLE I.

The simulation works are done by indicating the device structure and electrical and optical parameters of materials as input contentions of the test system. At that point determined the energy band diagram, recombination profile and transport properties are determined based on the Poisson equation just as continuity conditions. Recombination in profound mass dimensions and their occupation are portrayed by Shockley-Read-Hall (SRH) recombination concept.

III. RESULT AND DISCUSSIONS

Simulations were done in wxAMPS environment to examine the effect of different layer properties on cell performance. Further the results were analyzed to fit an optimized result.

A. Effect of thickness of Al:ZnO(AZO)

To investigate the effect of Aluminum doped ZnO (AZO) layer thickness on the performance parameters of the cell, simulations were done in wxAMPS for different thickness of AZO varying from 50 nm to 500 nm while all other properties of different layers of the cell were kept constant. The simulation results are shown in Fig.2.

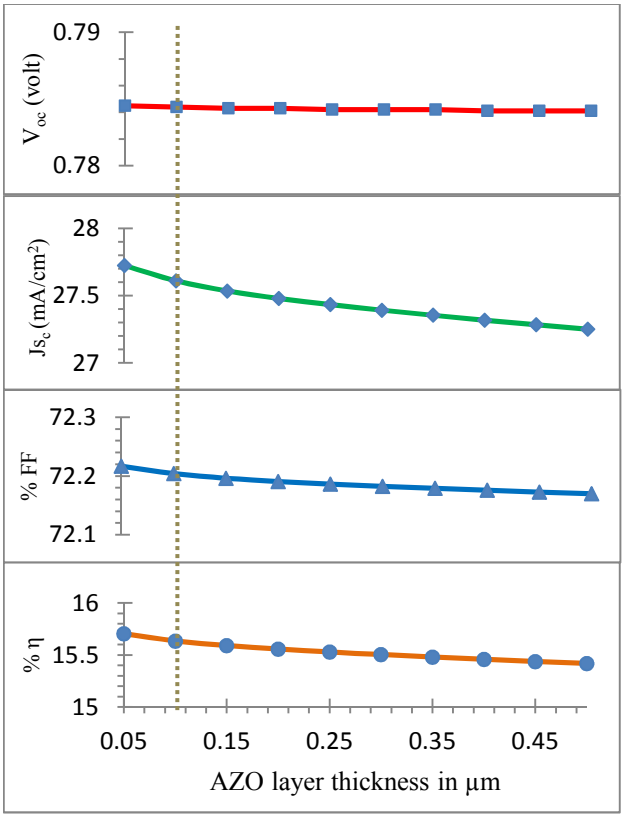

Fig.2. Performance parameters versus AZO layer thickness

The simulation result shows that V_{oc}, J_{sc} and FF are shrinked with the growth of AZO due to the higher absorption of light in the low wavelength region of sun spectrum. So the AZO thickness has been chosen in the lower value (100 nm) which can be easily deposited by popular deposition technique sputtering.

B. Effect of thickness of CdS layer

Cadmium Sulfide (CdS) having a bandgap energy of around 2.42eV, guarantee most of the incident light assorted towards junction. Hypothetically, n-layer thickness ought to be minimal to recoil the series resistance of the device. In the meantime a decreased thickness of CdS allows low absorption in the blue region of the sun spectrum as well as improved short circuit current density, J_{sc}.

Simulations were done by varying the thickness of CdS from 50 nm to 200 nm and the effects in performance parameters were observed. Obtained simulated results are shown in Fig.3.

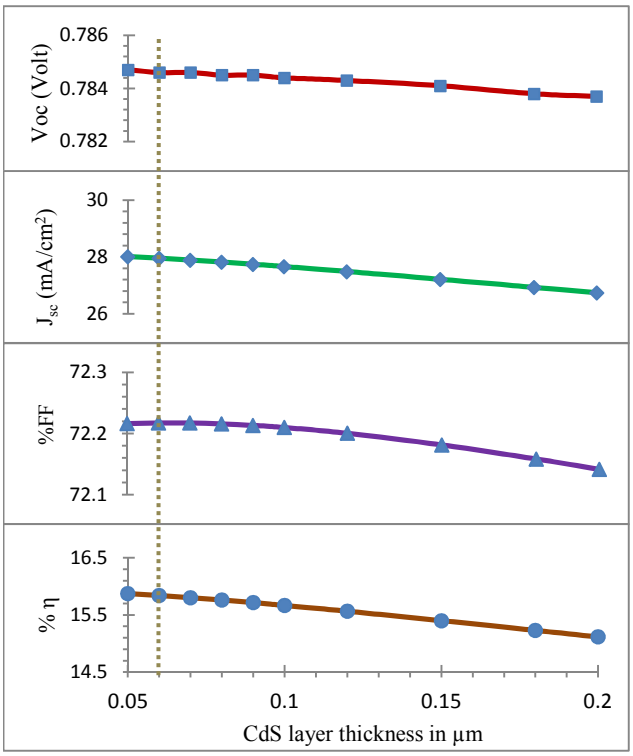

Fig.3. Effect of CdS layer thickenss on cell performance

The simulation results shows that V_{oc}, J_{sc} and FF are shrinked with the growth of CdS as described in the previous paragraph. So the CdS thickness has been chosen in the lower value (60 nm) which can be easily deposited by very popular and cheap deposition technique named Chemical Bath Deposition (CBD).

C. *Effect of absorber layer (CZTS) thickness*

To get acceptable photo conversion efficiency with thin absorber layer is one of the main challenges of thin-film PV cells. The reliance of performance of CZTS solar PV cell on the absorber thickness is considered by changing the CZTS layer thickness differs from 0.1µm to 3 µm while other parameters of the layer as well as other layers are kept unaltered. The results are shown in Fig.4.

It is noted that the V_{oc} and J_{sc} increased with absorber layer thickness due to the large amount of absorption in the longer wavelength region of the sun spectrum and more electron-hole pair generation. Due to the increment of both V_{oc} and J_{sc}, efficiency has been also improved with increasing thickness of the absorber layer. For CZTS thickness greater than 1.8µm, efficiency has shown a decreasing trend due to the bulk recombination and then the decreasing trend of fill factor dominates for thicker absorber layer. Bulk use of materials means more costly device, then the cost of device plays an important factor and a trade of between efficiency and cost should be considered in design.

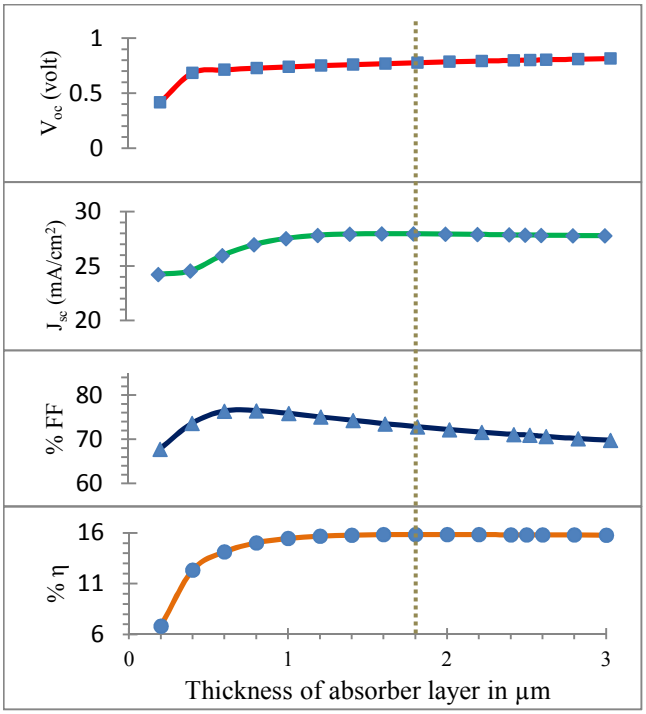

Fig.4. Dependency of Performance parameters on absorber layer thickness

D. *CZTS doping density*

Further simulations were done in wxAMPS to investigate the effect of absorber layer doping profile from 10^{14} cm^{-3} to 10^{17} cm^{-3} in the performance parameters while all other properties of CZTS as well as other layers were kept unchanged. The results are shown in Fig.5.

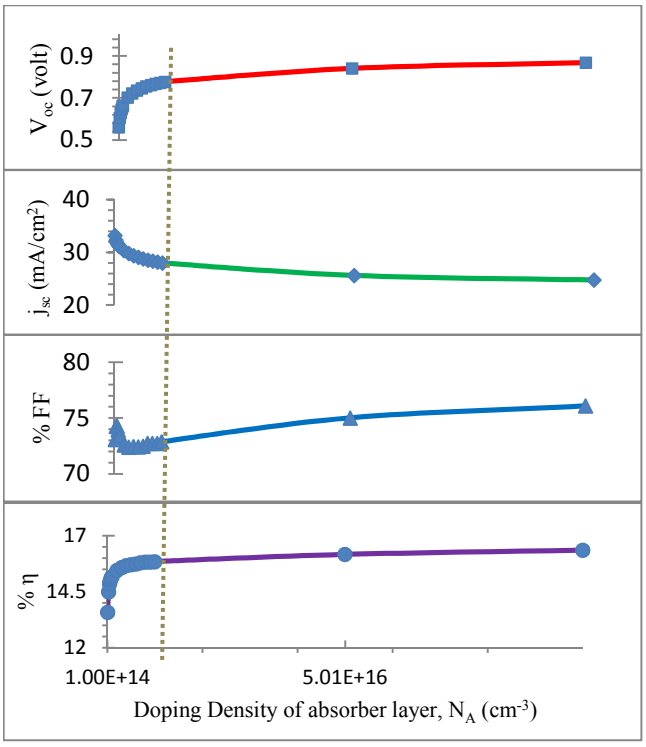

Fig.5. Performance parameters versus absorber layer doping profile

Fig.5. illustrates that the open circuit voltage has increased while the short circuit current density has decreased with the doping profile of CZTS. Fig.6. is an alternative representation of the dependency of V_{oc} and J_{sc} with doping profile of absorber layer. A series of J-V curves are illustrated in a same plot for different doping profile of CZTS absorber.

Dependency of V_{oc} with absorber doping (N_A) can be analyzed as in (1), where I_L is photo generated current and I_o is diode saturation current which is inversely proportional to doping concentration, N_A.

$$v_{oc} = \frac{KT}{q} \ln\left(\frac{I_L}{I_o} + 1\right) \quad (1)$$

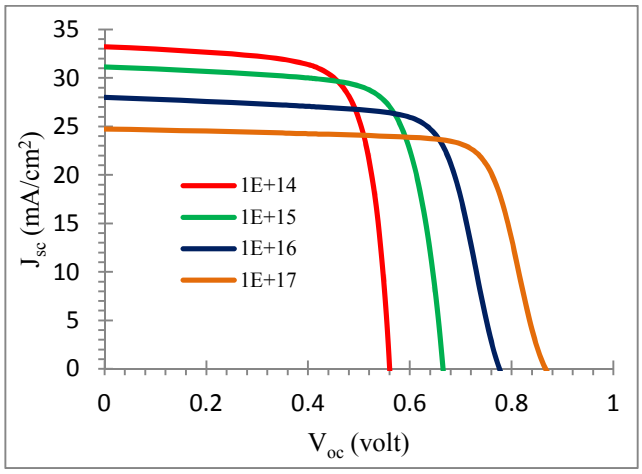

Fig.6.Representation of J-V curves for different doping profile of CZTS absorber layer

It is clear from Fig.6 that I_o is decreased with larger doping profile of the absorber layer and further reduction in I_o causes higher V_{oc} for higher N_A according to the equation 1 as well as simulation results show the same trend of V_{oc} as shown in Fig.5. and Fig.6. Short circuit current density, J_{sc} is decreased with increasing doping density due to the enhanced recombination probability. This will create an obstacle in the path of electron transport and hence reduces the J_{sc}. Disturbance in carrier transport as well as recombination also reduces the external quantum efficiency. The value of N_A had set at 10^{16} cm^{-3} because fabrication of CZTS with heavy doping is very tough.

E. Effect of absorber layer defect density in cell performance

There are so many studies in literature demonstrated that the donor type imperfections were formed strongly than the acceptor type in CZTS material [10]. So the single acceptor type defect is introduced to analyze the defect state of CZTS absorber. The effect of defect density of CZTS in performance is presented in Fig.7.

It is observed that the V_{oc} and J_{sc} are not affected strongly in low level defect but for the defect level 10^{14} and higher, the V_{oc} and J_{sc} were abruptly affected by the defect states as well as the cell performance was strongly diminished. The possible reason is a large no of trap states which further causes huge recombination of photo-generated carrier as well as reduction in J_{sc}, V_{oc} and finally the conversion efficiency.

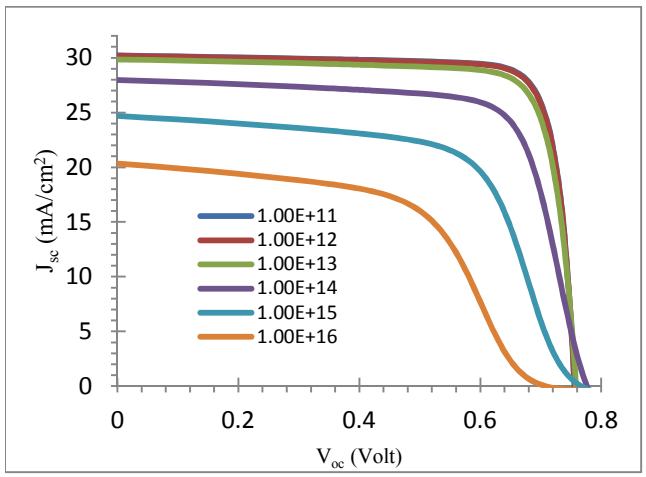

Fig.7. A series of J-V curves with variety of CZTS defect density

F. Effect of absorber layer thickness on Quantum Efficiency

Fig.8. shows a series of external quantum efficiency curves for different thickness of CIGS absorber layer. Visible change in quantum efficiency has occurred up to 1.5µm thickness of CZTS absorber. Variation in CZTS layer thickness affects the external quantum efficiency because higher absorber layer thickness results in more photon generated carrier which offers good possibility to get more carriers in the external circuit.

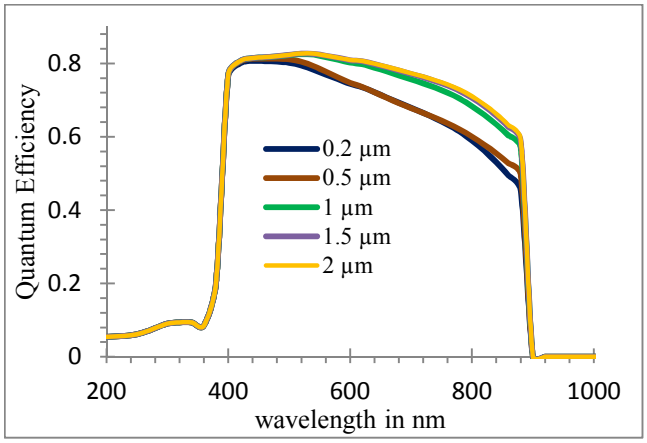

Fig.8. External Quantum Efficiency of CZTS solar cell for different thickness of CZTS

But no visible change has been observed in the quantum efficiency curve for CZTS thickness of more than 1.5µm due to the dominating bulk recombination than the photon generated carrier.

G. Thermal stability of the proposed cell

So as to investigate the stability of the optimized CZTS solar photovoltaic cell with increasing operating temperature, simulations were done in wxAMPS by varying the operating temperature of the cell from 25°C to 125°C and the result is shown in Fig.9.

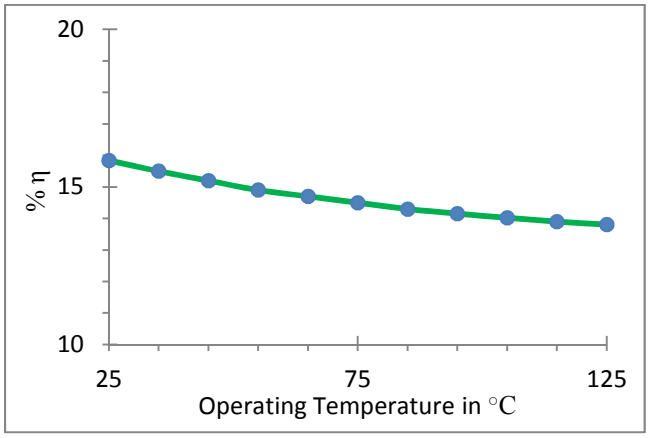

Fig.9. Thermal stability analysis of the optimized CZTS cell

The simulation result points that the optimized CZTS solar photovoltaic cell shows very superior stability with higher operating temperature. The temperature coefficient was calculated as 0.02%/°C from the numerical simulation.

H. Energy band structure of the simulated cell

Energy band structure of the simulated cell as illustrated in Fig.1. is shown in Fig.10.

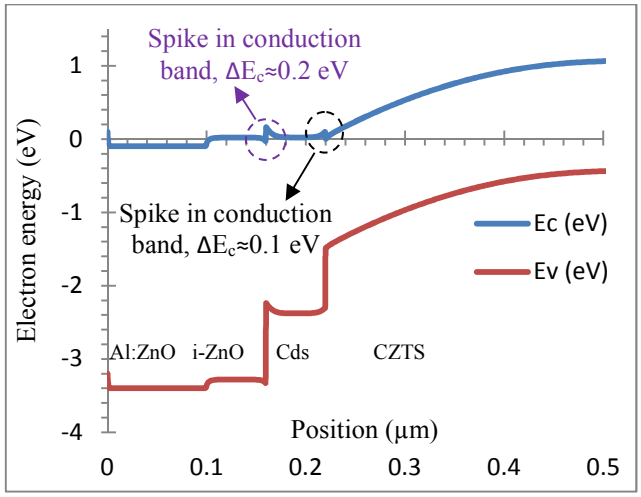

Fig.10. Energy band structure of CZTS solar cell as shown in Fig.1

Positive conduction band discontinuity ($\Delta E_c = \chi_1 - \chi_2$, where χ_1 and χ_2 are electron affinities of CZTS and CdS layer correspondingly) creates a spike in the conduction band in the CdS-CZTS heterointerface and also in CdS-i:ZnO heterointerface as shown in Fig.10. A cliff in the conduction band near absorber layer enhances interface recombination in chalcopyrite based solar photovoltaic cell consists of wide bandgap material [14]. As ΔE_c is 0.1 eV and 0.2eV here and the spike energy more than 0.3 eV is not good for carrier transport, so it doesn't create any obstracle in carrier transport and additionally it creates an electric field which further accelerates carrier transport in the heterointerface.

IV. Conclusion

Basic structure of thin-film CZTS solar cell with CdS buffer layer was modeled and simulated by varying different layer properties. The impact of different layer thickness on conversion efficiency and othe performance parameters were investigated. The dependancy of doping concentration and defect dencity of CZTS absorber layer were also investigated and analyzed. Simulation shows that 15.84 % (*FF*=72.86%, J_{sc}=27.98 mA/cm^2, *and* V_{oc}=0.78 Volt) conversion efficiency has been achieved for the optimized cell. The simulated cell with optimized layer properties presents a better conversion efficiency of 15.84% as compared to the counterparts [4] and the layers as well as the device can be fabricated by different popular deposition techniques like sputtering and chemical bath deposition.

Acknowledgment

The authors might want to recognize Department of EEE and Renewable Energy Laboratory (REL) of Chittagong University of Engineering and Technology (CUET), Chattogram-4349, Bangladesh for supporting this work.

References

[1] Alessio Bosio and Alessandro Romeo, "Thin Film Solar Cells: Current Status and Future Trends",Nova Science Publishers, Inc. New York, ISBN:978-1-53611-363-1.

[2] Hongxia Wang, "Progress in Thin Film Solar Cells Based on Cu_2ZnSnS_4", International Journal of Photoenergy, Volume 2011, Article ID 801292, doi:10.1155/2011/801292

[3] H. Katagiri, K. Saitoh, T. Washio, H. Shinohara, T. Kurumadani, and S. Miyajima, "Development of thin fim solar cell based on Cu_2ZnSnS_4 thin fims," Solar Energy Materials and Solar Cells, vol. 65, no. 1–4, pp. 141–148, 2001.

[4] Martin A. Green, Yoshihiro Hishikawa, Ewan D. Dunlop, Dean H. Levi, Jochen Hohl-Ebinger, Masahiro Yoshita, Anita W.Y. Ho-Baillie, "Solar cell efficiency tables (Version 53)", Prog Photovolt Res Appl. 2019;pp.27:3–12.

[5] William Shockley, Hans J. Queisser, "Detailed Balance Limit of Efficiency of p‐n Junction Solar Cells" Journal of Applied Physics, vol. 32, pp. 510-519,1961

[6] Sven Ruhle, "Tabulated values of the Shockley–Queisser limit for single junction solar cells," Solar Energy 130, pp. 139-147, 2016.

[7] Kentaro Ito and Tatsuo Nakazawa "Electrical and Optical Properties of Stannite-Type Quaternary Semiconductor Thin Films", Japanese Journal of Applied Physics, Volume 27, Part 1, Number 11

[8] Y Y. Liu, Y. Sun, and A. Rockett, "An improved algorithm for solving equations for intra-band tunneling current in heterojunction solar cells," *Thin Solid Films*, vol. 520, no. 15, pp. 4947–4950, 2012.

[9] Y. Liu, D. Heinzel and A. Rockett, "A new solar cell simulator: WxAMPS," Photovoltaic Specialists Conference (PVSC), 2011 37thIEEE, Seattle, WA, pp. 002753-002756,2011.

[10] M. Djinkwi Wanda, S. Ouédraogo, F. Tchoffo, F. Zougmoré and J. M. B. Ndjaka, "Numerical Investigations and Analysis of Cu_2ZnSnS_4 Based Solar Cells by SCAPS-1D," International Journal of Photoenergy Volume 2016, Article ID 2152018, 9 pages.

[11] M.T. Ferdaous, S.A. Shahahmadi, P. Chelvanathan, Md. Akhtaruzzaman, F.H. Alharbi, K. Sopian, S.K. Tiong, N. Amin, "Elucidating the role of interfacial MoS_2 layer in Cu_2ZnSnS_4 thin film solar cells by numerical analysis",Solar Energy 178 (2019), p.p.162–172

[12] W. Zhao, W. Zhou and X. Miao, "Numerical simulation of CZTS thin film solar cell," 2012 7th IEEE International Conference on Nano/Micro Engineered and Molecular Systems (NEMS), Kyoto, 2012, pp. 502-505. doi: 10.1109/NEMS.2012.6196826

[13] Xiaolei Liu, Xiaojing Hao, Shujuan Huang, Gavin Conibeer,"Numerical Modeling of CZTS Solar Cells", 39thIEEE Photovoltaic Specialists Conference, 2013.

[14] K.Wang, O. Gunawan, T. Todorov et al., "Thermally evaporatedCu_2ZnSnS_4 solar cells," *Applied Physics Letters*, vol. 97, no. 14, Article ID: 143508, 2010.