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Prospects of alternate buffer layers for CZTS based thin films solar cells from Numerical Analysis – A Review

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Abstract

Numerical simulation is essential to study the complex heterogeneous absorber/buffer interface in CZTS thin films. In this work, the authors provide a comprehensive report on the numerical simulation of CZTS thin film solar cells with alternate nontoxic buffers in comparison to the toxic CdS buffer modeled through more asserted solar cell capacitance simulator (SCAPS). An analysis is made on the cause for the change in cell performance using different buffers which paves a way to experimentally fabricate completely nontoxic and cost effective high efficiency solar cell.

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Keywords: Buffer layer, CZTS solar cells, SCAPS, Simulation, Thin film solar cells.

Reviewed by* **ICETSET'16 *organizing committee*

1. Introduction

Research on CdTe and $Cu(In,Ga)Se_2$ (CIGS) based cells had dominated for the last several decades due to the efficiency. The environmental impact of the toxic cadmium and the scarcity of indium in these compounds lead to the search for an alternate. Copper Zinc Tin Sulphide (CZTS) fits to be a promising substitute with a suitable band gap in the range of 1.4 to 1.5 ev and high absorption coefficient of $10^4 cm^{-1}$ in the visible spectral region [1] with natural abundance in earth crust and environmentally benign constituents. CZTS occurs in two primary crystal structures known as stannite-type (space group I42m) and kesterite-type (space group I4) with different arrangement of Cu and Zn atoms. Among the two phases kesterite phase is more thermodynamically stable [2].

Several vacuum and non-vacuum based techniques have been utilized for preparing CZTS absorber thin films. The development of CZTS based technology concerns the absorber-buffer layer interface. The more common buffer layer material used is CdS which is found to give the best performances devices both in CIGS and CZTS. The toxicity and narrow band gap energy of CdS which leads to absorption in the blue region urges the search for other buffer layers with wider band gap energy and nontoxic nature.

Numerical models on polycrystalline thin-film solar cells is an important to test the feasibility of anticipated explanations and to predict the effects of various parameters such as defects on the efficiency of the solar cell. Simulation based theoretical investigation on photovoltaic (PV) device helps to obtain an optimum value for the parameters for a proposed model. Modeling is used to understand the underlying processes behind the working of a solar cell and helps to improve their performance in real time.

II.SCAPS

SCAPS is a one dimensional solar cell simulation program developed by Alex Niemegeers, Marc Burgelman, Koen Decock, Johan Verschraegen, Stefaan Degrave at the department of Electronics and Information Systems (ELIS) of University of Gent, Belgium [3-8]. SCAPS is a one dimensional windows-oriented program, developed with LabWindows/CVI for cell structures of the CIGS, CuInSe2 and the CdTe family. Several modifications in this software however improved its capabilities to work with Si and GaAs family solar cells and amorphous cells (a-Si and micro amorphous Si). It has the largest number of measuring parameters based on continuity equation together with Poisson equation. Several alternate buffers for CZTS absorber have been studied using SCAPS.

III.ALTERNATE BUFFER LAYERS

A. In_2S_3 buffer

The Mo/CZTS/CdS/ZnO/Al structure with CdS buffer enabled the record efficiency of 12.6% [9]. CdS having a band gap of 2.53 ev is used as a prominent buffer due to its improved interface with the absorber CZTS and higher transmission in the blue wavelength region. varied the thickness of CZTS from 1µm to 2.2µm [10] and optimized the thickness as 2.2µm which yielded a Nowshad Amin et al maximum efficiency of 7.55% (Fig.1) owing to the fact that increasing thickness of the absorber leads to capture of more number of photons. Figure 2 gives a comparison between CdS and In_2S_3 buffers.

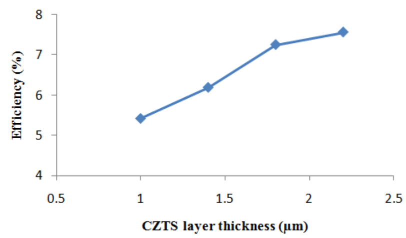

Fig. 1. Efficiency vs thickness of absorber

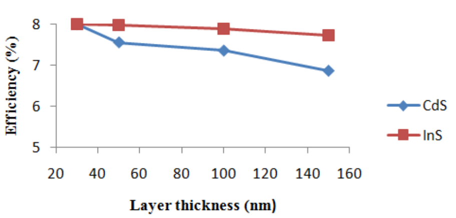

Fig. 2. Efficiency vs thickness of buffer

The thickness of CdS was kept as 0.5µm to avoid absorption of photons in the buffer layer. The alternate buffer In_2S_3 having a band gap (2.84 ev) higher than that of CdS (2.4 ev) helps in avoiding the lower energy photons. The band gap and thickness of In_2S_3 was varied and Nowshad Amin *et al.* found that 2.9 ev and 50 nm thick layer resulted in a higher efficiency of 7.9% which is greater than that for CdS. (Fig.3)

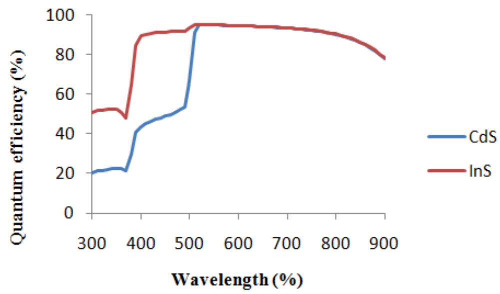

Fig. 3. Spectral response of CdS and In_2S

The experimentally reported value with In_2S_3 buffer by G.Rajeshmon *et al.* [11] is only 1.85%. Nowshad Amin *et al.* thus proved that In_2S_3 is a better alternative to CdS for CZTS solar cells and more experimental research is needed to understand the influence of basic factors such as defect and recombination on the cell performance. The input parameters used are given in Table I.

Table I

MATERIAL PARAMETERS USED IN SIMULATION.

Parameters	**p-CZTS**	**n- In_2S_3**	**n - ZnO**
Thickness(µm)	2.20	0.050	0.20
Band gap(eV)	1.50	2.80	3.30
Electron affinity (eV)	4.50	4.70	4.60
Dielectric permittivity (relative)	10.00	13.50	9.00
CB density of state (cm^{-3})	2.2E+18	1.8E+19	2.2E+18
VB density of state (cm^{-3})	1.8E+19	4.0E+13	1.8E+19
μ_n (cm^2 /Vs)	1.0E+2	4.0E+2	1.0E+2
μ_p (cm^2/Vs)	2.5E+1	2.1E+2	2.5E+1
Donor density ND (cm^{-3})	1.0E+1	1.0E+18	1.0E+18
Acceptor density(NA)	2.0E+14	1.0E+1	0
Shunt Resistance	370 Ω		
Series Resistance	4.25 Ω		

An investigation on the effect of In_2S_3 buffer layer thickness and its carrier density on the performance of CZTS cell are made by Peijie Lin *et al.* [12]. The device structure used is n-ZnO:Al/i-ZnO/n-In_2S_3/p-CZTS with two window layers. The operating temperature is set to 300K, no consideration on series and shunt resistance and only one type of single compensating defect located near the mid gap is taken into account.

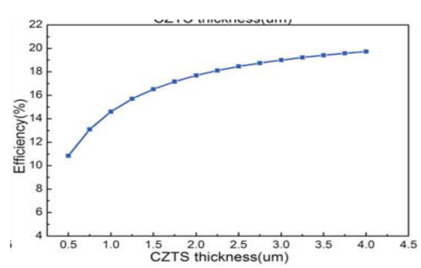

Fig. 4. Efficiency vs thickness of absorber

Thickness of the CZTS is changed from 500 nm to 4000 nm. It is seenfrom the figure 4 that the increasing rate of efficiency slows down as the thickness of the CZTS is increased above 2500 nm which is little bit more when compared with Nowshad Amin *et al.* (2.2 µm).

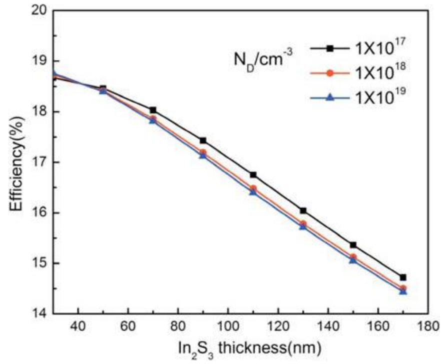

Fig. 5. Efficiency vs thickness of buffer

Too thin buffer layer results in leakage current and too thick layer leads to photon loss in buffer layer. Hence the thickness of In_2S_3 is maintained to be in the range of 20 nm to 30 nm (Fig. 5). The Gaussian type defects are introduced with density ranging from $1X10^9cm^{-3}$ to $1X10^{17}$ cm^{-3} and found that the defect density above $1X10^{13}cm^{-3}$ deteriorates the performance of the cell completely (Fig.6). So the process conditions should be altered so as to control the defects below $1X10^{13}cm^{-3}$.

The carrier density is altered from $1X10^{17}cm^{-3}$ to $1X10^{19}$ cm^{-3} and the minimum value suits due to the reason that higher carrier concentration leads to reduction in the width of space charge region. With these optimized values, an efficiency of 19.28% is reached which is much greater than the experimentally achieved result. The physical parameters used in the simulation are given in Table II.

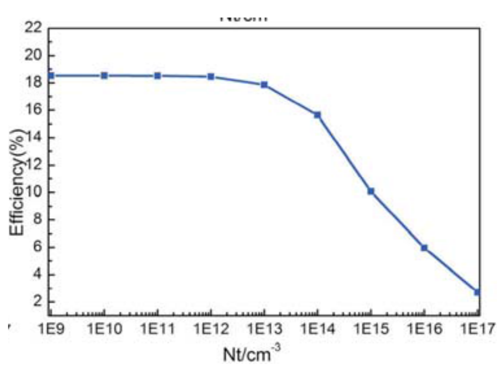

Fig. 6. Cell performance with different defect density

Table II

SEMICONDUCTOR PARAMETERS

Parameters	p-CZTS	n- In_2S_3	i - ZnO	n-ZnO:Al
Thickness(µm)	2.50	0.050	0.05	0.20
Band gap(eV)	1.50	2.80	3.30	3.30
Electron affinity (eV)	4.50	4.70	4.60	4.60
Dielectric Permitivity	10.00	13.50	9.00	9.00
Nc (cm^{-3})	2.2E+18	1.8E+19	2.2E+18	2.2E+18
Nv (cm^{-3})	1.8E+19	4.0E+13	1.8E+19	1.8E+19
μ_n (cm^2 /Vs)	1.0E+2	4.0E+2	1.0E+2	1.0E+2
μ_p (cm^2/Vs)	2.5E+1	2.1E+2	2.5E+1	2.5E+1
Donor density ND (cm^{-3})	0	1.0E+17	1.0E+5	1.0E+18
Acceptor density(NA)	1.0E+17	1.0E+1	0	0
Gaussian Defect Density (cm^{-3})	1.0E+12	1.0E+18	1.0E+18	1.0E+18

B. ZnS buffer

M.L.Hossain et al. [13] reported an efficiency of 9.8% for the structure ZnS/CZTS. The thickness of the CZTS absorber is varied from 1 µm to 2.5 µm and ZnS thickness is changed from 0.2 µm 1.0 µm and optimized the values to 2.5µm and 0.2µm (Fig.7). The high band gap of ZnS (3.5 ev) results in less absorption of low wavelength photons and a better interface with CZTS creating a potential barrier to dissociate the excitons.

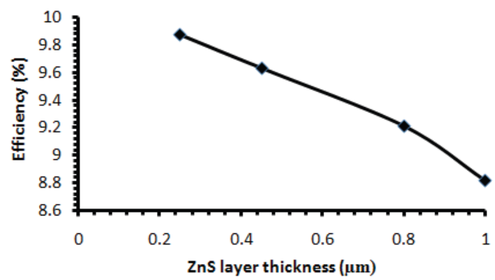

Fig. 7. Efficiency vs thickness of buffer

C. SnS_2 buffer

An analysis on SnS_2 buffer layer with SnS back surface layer for CZTS solar cells is made by Atul Kumar *et al* [14]. The modified cell structure MO/p-SnS/p-CZTS/n-SnS_2/ZnO is considered. SnS_2 has band gap value similar to CdS and can be synthesized by wet chemical methods [15]. The simulation parameters is given in Table III.

Table III

SIMULATION PARAMETERS

Parameters	p-CZTS	n- SnS_2	n - SnS	i - ZnO
Thickness(µm)	2.68	0.10	0.02	0.10
Band gap(eV)	1.50	2.24	1.25	3.30
Electron affinity (ev)	4.50	4.24	4.20	4.60
μ_n (cm^2 /Vs)	1.0E+2	5.0E+1	2.5E+1	1.0E+2
Donor density ND (cm^{-3})	1.0E+1	1.0E+17	1.0E+1	1.0E+18
Acceptor density (NA)	1.0E+17	1.0E+1	3.0E+19	1.0E+1
Absorption coefficient (cm^{-1})	2.0E+4	5.0E+13	1.0E+5	Scaps value
Series Resistance	4.25 Ω cm^2			
Shunt Resistance	400 Ω cm^2			

The thickness of the absorber layer is taken as 2.68 µm. From the simulation curves (Fig.8) it is seen that the absorber thickness should be within 2.5 µm to 3.0 µm.

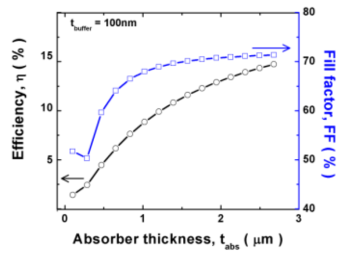

Fig. 8. Efficiency vs thickness of absorber

The SnS_2 thickness is varied from 0.05 µm to 0.25 µm and 100 nm (Fig.9) gives maximum efficiency of 14.25%.

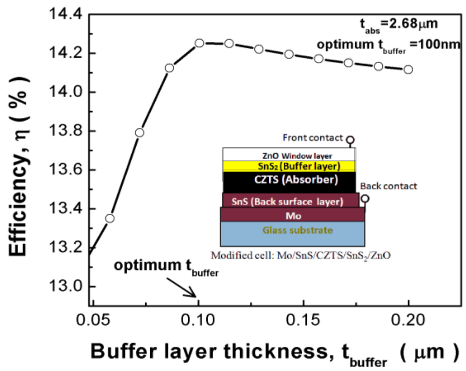

Fig. 9. Efficiency vs thickness of buffer

SnS back surface layer in between CZTS and MO provides an effective path for the passage of holes and acts as a barrier for electrons thus reducing the hole density in the absorber leading to low recombination current (Fig.10).

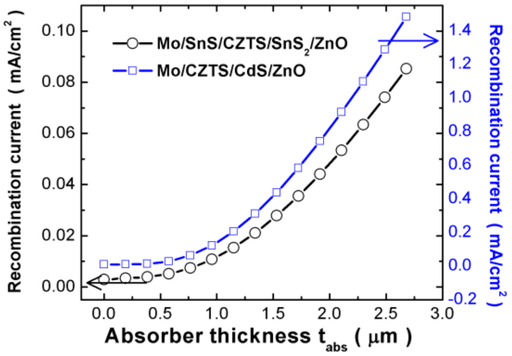

Fig. 10. Dependence of Efficiency and fill factor on CZTS thickness

D. TiO_2 buffer

M.Houshmand *et al.* [16] considered the usage of TiO_2 nano buffer layer and an ultra-thin CZTS absorber and studied the carrier generation, charge collection and I – V characteristics including their degradation. The parameters used are given in Table IV.

Table IV

BASELINE PARAMETERS USED IN SCAPS

Parameters	p-CZTS	n- TiO_2
Thickness(μm)	1.00	0.05
Band gap(eV)	0.90	3.50
μ_n (cm^2 /Vs)	80-100	20
μ_p (cm^2 /Vs)	20-50	10
Donor density ND (cm^{-3})	1.000E+1	1.000E+16
Acceptor density(NA)	5.000E+17	1.000E+1
Electron thermal velocity (cm/s)	1.000E+7	1.000E+7
Hole thermal velocity (cm/s)	1.000E+7	1.000E+7

The cell structure is assumed to be an abrupt surface barrier structure with the depletion region at the CZTS side. The temperature dependence of the I–V curves shows that the thermionic emission is not a dominant process. The open-circuit voltage increases in the first steps of defect increment due to narrower depletion width for the higher density of defect and it reduces by further increase in defect because of higher recombination loss [16].

E. ZnSe buffer

ZnSe with its band gap 2.90 is made as an alternative to CdS buffer and the cell performance is reported by M.A.olopade *et al*. [17]. The standard cell structure is considered. The input parameters are given in Table V.

For an absorber thickness of 2.50 μm and a buffer thickness of 0.08 μm the efficiency attained a maximum of 6.76%. The J-V characteristics are also studied.

Table V

INPUT PARAMETERS USED FOR MODELING

Parameters	CZTS	ZnSe	n - ZnO
Thickness(μm)	2.50	0.08	0.08
Band gap(eV)	1.45	2.90	3.30
Electron affinity (eV)	4.50	4.09	4.60
Dielectric permittivity (relative)	10.00	10.00	9.00
CB density of state (cm^{-3})	2.2E+18	1.5E+18	2.2E+18
VB density of state (cm^{-3})	2.0E+18	1.8E+19	1.8E+19
μ_n (cm^2 /Vs)	5.0E+1	5.0E+1	1.0E+2
μ_p (cm^2/Vs)	5.0E+1	2.0E+1	2.5E+1
Donor density ND (cm^{-3})	0	0	1.0E+17
Acceptor density(NA)	2.0E+15	5.5E+7	0

IV. CONCLUSION

The summary shows that several potential buffers can be used in CZTS solar cells in place of toxic CdS. Apart from the above, many buffers like Zno, ZnS, ZnMgO, $InZnSe_x$, SnO_2 can be taken into consideration. Generally, the investigation of hetero junctions is more complicated compared with homo junctions because of the effect of interface states, which cannot be avoided in the majority of hetero junctions. The efficiency can be improved by means of a doping, band gap grading, tailoring the thickness of absorber and buffer layer, surface modification and also by inter layer introduction. A new challenge to fabricate CZTS family solar cells with nontoxic buffers has been opened up with the feasibility of achieving higher efficiency. The device modeling leads to better understanding of the physical processes that governs the experimental study.

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