A simulation study of perovskite based solar cells using CZTS as HTM with different electron transporting materials

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In this manuscript, we have performed the device modeling on perovskite based solar cells (PSC,s) to investigate the potential of different hole transport materials (HTM's) in combination with electron transport materials (ETM) using SCAPS 3.3 software package. Our simulated results depict that in the case of PSCs with CZTS, various parameters such as Voc, FF and PCE have demonstrated their maximum values at HTM thickness 700nm. It is further observed that the increase thickness of absorber layer resulted in the significant improvement of different performance parameters at specific limit then become constant. Moreover, studies of metal contact exposed that by increasing the work function of front contact of PSC efficiency decline to 7.34%. Optimized value of FTO front contact and Ni back contact metal work function were found to be 4.4 and 5.35 eV respectively. But at higher value of defect density in the PSCs, the performance of the cell is independent of thickness. At the carrier concentration of ETM is 10^{18} cm^{-3}, ZnO and TiO_2 have PCE 12.52 and 12.69 % respectively.

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1. Introduction

Perovskite based solar cells (PSCs) are supposed to be next generation solar cells due to their configuration for superb optoelectronics response due to low cost fabrication and unrivalled gain of power conversion efficiency. Therefore, first Perovskite material was reported as a good absorbent material in 1979 and since then gained the interest of research community with the passage of every day [1]. It is fundamental fact absorber layer play crucial role in the fabrication of high efficiency solar cells [2]. Other important parameters such as carriers mobility, dopant concentration, morphology and band alignment of hole and electron transporting material (HTM, (ETM) as absorber are important for conduction of carriers to the front and back contacts [3].

Previously Spiro-OMeTAD is being used as HTM in PSCs in the literature but due to high cost and instability posing a barrier in the way of commercialization of PSCs [4,5]. Therefore, it is need of time to search new configuration of PSCs. In this search, some other materials such as CuI, NiO, Cu_2O and CuSCN [6,7] have been extensively used as HTM in PSCs due to their higher carrier mobility, suitable inherent properties, apt energy band position and imperious chemical stability [8]. But adequate power conversion efficiency as compared to their organic equivalent is still lacking. On the other hand, Perovskite has the structural similarity with inorganic materials. Interestingly both perovskite and inorganic materials have same exciton type i.e. Wannier type [9] and deal with similar photoexcited, therefore can be better option. But the point defects at the HTM/perovskite interface and band level alignment might be basic aspects limiting the detected efficiencies in PSCs. In this perspective, Cu_2ZnSnS_4 (CZTS) is supposed to be an ideal candidate

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due to its favorable properties including a direct band gap (1.4-1.5 eV), high absorption coefficient ($>10^4 cm^{-1}$), non-toxic, earth abundance and low cost [10].

There are few reports about this structure in the literature such as Q.Wu fabricated the PSC with CZTSas a stable and cheap HTM and Au TCO with 12.75% efficiency as compared to the Spiro-OMeTAD centered devices [11]. Inverted p-i-n PSCs are another good candidates because they exhibited the efficiency upto 15.4% with admirable fill factor 81% [12]. Later Li et al., has described the the solar cell efficiency about 13.75% [13] of inverted PSCs with CZTS as HTM, which is grown by spin-coating technique. But research work is still needed to optimize the properties of each component in the structure to enhance the efficiency of a cell.

This study demonstrated the application of CZTS as HTM in PSCs through Device modeling package. SCAPS used to simulate the PSCs and the effect of material properties on the different performance parameters of cell [14-16]. Various transparent conducting oxides such as ZnO and TiO_2 are tested as ETMs in the presence of CZTS and their impact on the PCE are judiciously studied

2. Details of Simulation Procedure

This simulation was performed using SCAPS 1D (3.307) software which was developed by the Department of Electronics and Information Systems (ELIS), University of Gent [17]. The basic structure of Perovskite based solar cells is shown in Fig. 1. This structure consisted of n-type ZnO and TiO_2 which are used as electron transporting layer (ETM), low p-type doped $MAPbI_3$ perovskite as absorber layer, inorganic CZTS as Hole transporting layer (HTM), FTO is used as metal electrode/front contact and Ni as back contact. Furthermore; we have introduced two intrinsic defects layers (IDLs) between ETM/$MAPbI_3$ (IDL1) and HTM/$MAPbI_3$ (IDL2) respectively. Both defect layers have total trap density of $1.0x10^9$ cm-3 but all other parameters are similar to perovskite (table 1) [18, 19]. After the basic bulk parameters some interface trap parameters are supported to make device functional in table 2. Pre-factor A_α is used as 10^5 to adjust absorption coefficient.

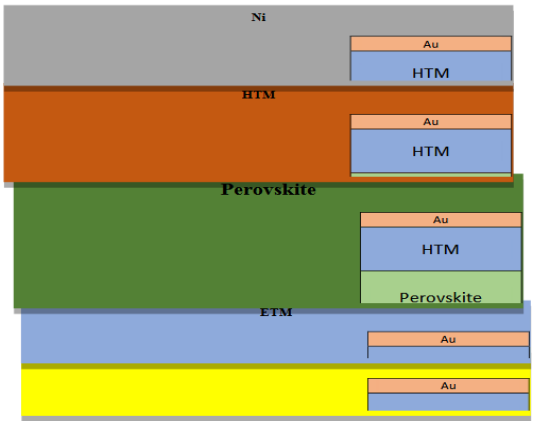

Fig. 1. Schematic device structure of perovskite based thin film solar cell.

Table 1, List of various parameters used in this simulation study

Parameters	**(ETM)**		**IDL1**	**Perovskite**	**IDL2**	**HTM**
	ZnO	**TiO_2**		**($CH_3NH_3PbI_3$)**		**CZTS**
Dielectric Constant [.]	9	10	6.5	6.5	6.5	10
Electron affinity[eV]	4	4	3.9	3.9	3.9	4.5
Band gap[eV]	3.3	3.2	1.55	1.55	1.55	1.5
Effective CB density(N_c)[cm^{-3}]	3.7 E+18	2E17	2.2 E+18	2.2 E+18	2.2 E+18	2.2 E+18
Effective VB density(N_v)[cm^{-3}]	1.8 E+19	6E17	1.8 E+19	1.8 E+19	1.8 E+19	1.8 E+19
Effective electron mobility μ_n[cm^2/Vs]	100	100	2	2	2	100
Effective hole mobility μ_p[cm^2/Vs]	25	25	2	2	2	25
Doping concentration acceptor N_a[cm^{-3}]	0	0	0	0	0	2E16
Doping concentration donor N_d [cm^{-3}]	1E+18	2E19	1E+13	1E+13	1E+13	10
Electron thermal velocity ve [cm/s]	1E7	1E7	1E+7	1E+7	1E+7	1E+7
hole thermal velocity vh [cm/s]	1E+7	1E+7	1E+7	1E+7	1E+7	1E+7
Thickness [nm]	50	50	1	450	1	350

Table 2.Defect layer properties and interface defect parameters of CZTS/perovskite based thin film solar cells.

Defect layer properties	**ZnO**	**TiO_2**	**$MAPbI_3$**	**CZTS**
capture cross section of electron/holes (cm^2)	1E-12 1E-15	1E-15 1E-17	1E-15 1E-16	3.900E-13 1.000E-15
Defect type	neutral	Donor	neutral	acceptor
Energy level w.r.t ref (eV)	1.1	0.6	1.2	0.024
Characteristic energy(eV)	0.1	0.1	0.1	0.1
Density of states N_t(cm^{-3})	1E17	1E14	2.5E13	1E14
Energetic distribution	Gaussian	Single	uniform	uniform
Interface trap defects	**ZnO-$MAPbI_3$**	**$MAPbI_3$-CZTS**	**TiO_2-$MAPbI_3$**	
Acceptor like state density (cm^{-2})	1.0E9	1.0E9	1.0E9	
capture cross section of electron/holes (cm^2)	1.0E-18 1.0E-17	1.0E-18 1.0E-19	1.0E-19 1.0E-18	
Energy level w.r.t ref (eV)	0.07	0.32	0.07	

3. Result and discussion

3.1. Effect of front and back contact work function

Work function of transport conducting oxide (TCO) has significant importance for the effective collection of charge carriers. Fig 2(a, b) shows the impact of front and back contact work function with different ETMs on CZTS based perovskite solar cell PV constraints respectively. Fig. 2 (a) demonstrated that value of Jsc has negligible effect while the values of PCE, FF and Voc have decreasing trend with the work function greater than conduction band minimum of ETMs. On the contrary, high work function creates electrostatic barrier for electrons in CZTS and Ohmic contact for holes. Fig 2 (b) illustrated the Voc and efficiency of different faces of back metals contact. Each face of metal has different work function. Au (100) gives maximum efficiency but it is too expensive. On the other hand Ni (111) showed moderate efficiency with some advantages of earth abundant therefore it may help to reduce the cost of the device.

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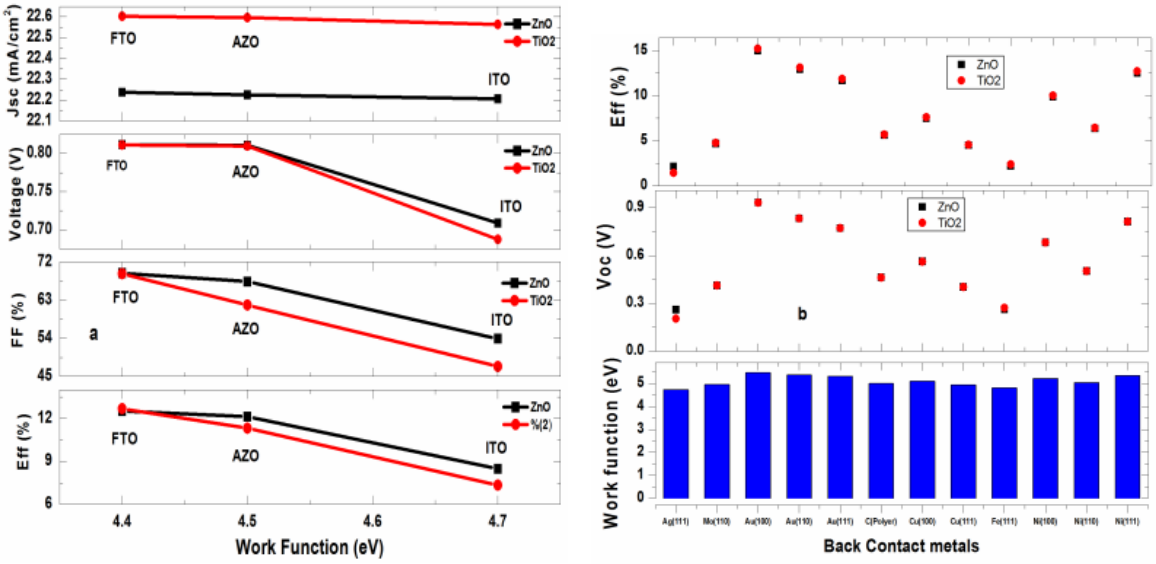

Fig. 2. (a)Variation of PVC parameters vs. front contact work function (b) Open-circuit voltage and efficiency of PSCs with Au, Ni, Cu, C, Mo, Fe and Ag different faces as back contact metals.

3.2. Effect of thickness of CZTS

The impact of HTM thickness variation on the PV device performance is shown in fig 3. The solar cell parameters, especially V_{oc} and FF values are raised sharply up to 300 nm thickness but rate decreased beyond thickness 400 nm. Efficiency is increasing gradually with the thickness and optimal value is found to be at thickness 350 nm for both samples. This result showed that 350 nm thickness of inorganic CZTS gives intrinsically high stability, high hole mobility so it become the key candidate as HTM in PSCs related to a lower recombination. While Jsc has shows no influence of HTM thickness for both cases.

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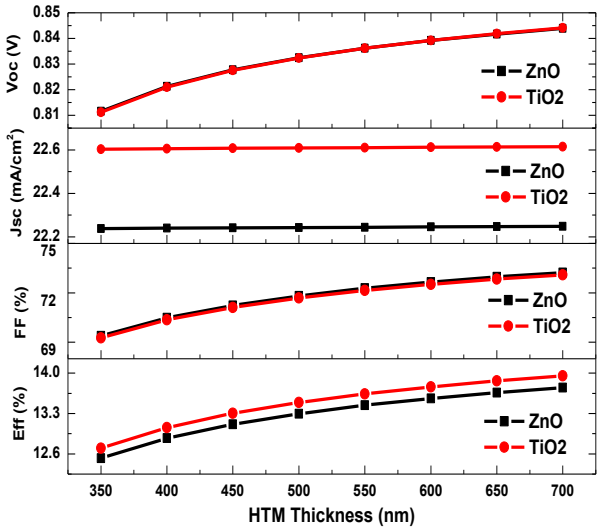

Fig. 3. Effect of CZTS thicknesses on various parameters of PVC parameters.

3.3. Effect of Perovskite thickness

The influence of the variation of absorber layer thickness is shown in fig 4. Efficiency and Jsc are found to be increased gradually with the thickness, and the optimal value was obtained at thickness 450 nm for both ZnO and TiO_2 cases. This optimal value of thickness is satisfactory for the diffusion of charge therefore cause a minimum resistance in the way of carriers. Above 350 nm thickness series resistance is increased which resulted in the PV performance increased. TiO_2 is found to be more advantage over ZnO because at active layer thickness of ETM, calculated parameters such as Voc, Jsc, FF and Eff has values 0.811V, 22.62142mA/cm^2, 69.26% and 12.699% respectively which are very close to experimental result reported in the literature [26].

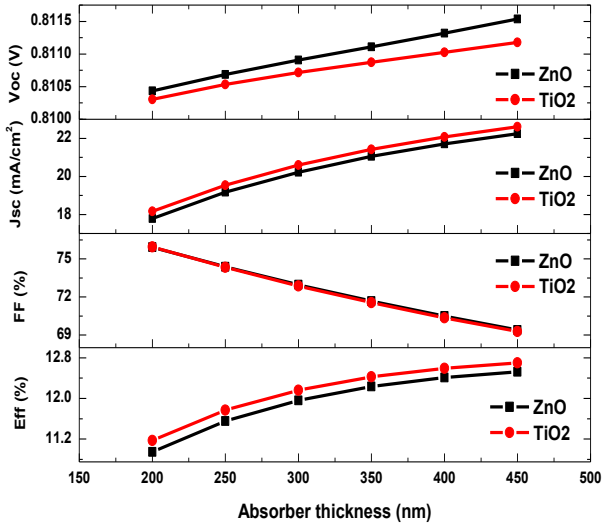

Fig. 4.The graph demonstrated the effect of absorber layer thickness on the different parameters of PVC such as Eff, FF, Joc and voltage.

3.4. Effect of ETMs thickness

Fig. 5 demonstrated the relationship of various solar cell parameters such as PCE, FF, jsc and Voc with the thickness of the ETMs (ZnO, TiO_2). In the case of TiO_2, all parameters decline slightly due to change in series resistance. It has high reflectance and absorption coefficient and

less transmittance as compare to ZnO. While in the case of ZnO PCE and Jsc and Voc are decreasing slowly with FF increase gently.

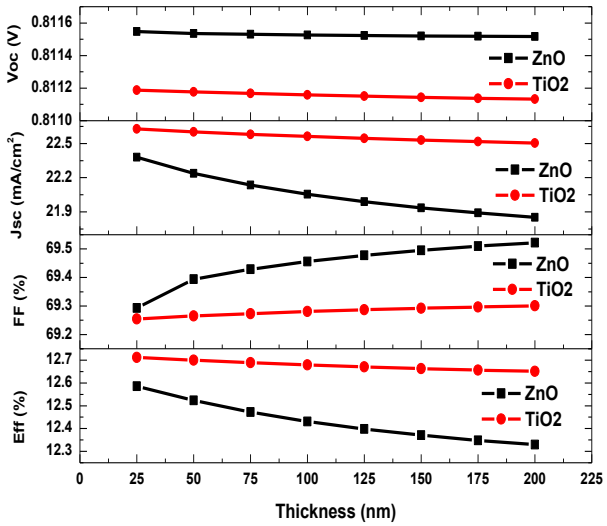

Fig. 5.Graph between thickness of ETMs and efficiency parameters of PVC.

3.5. Effect of dopant concentration of ETMs

Fig. 6 is evident that dopant concentration of ETMs changed from 10^{15} to 10^{21} cm^{-3} and plotted the PV cell parameters against dopant concentration. PCE and FF are affected in similar manner in both cases up to dopant concentration 10^{18} cm^{-1} but beyond this value there is no specific change in all parameters. Jsc first slightly decrease for both ZnO and TiO_2 than become constant while Voc of TiO_2 has abruptly falls as N_D increased which may be due to small conductivity of electrons.

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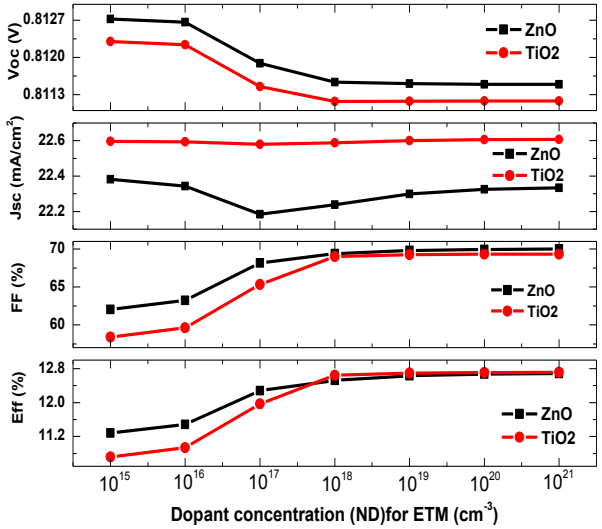

Fig. 6.Relationship of dopant concentration of ZnO and TiO_2 with various parameters of device structure.

Fig. 7 (a) shows the simulated I-V curve at the interface of perovskite and ZnO, TiO2 as ETMs with CZTS as HTM. With TiO2 ETM and CZTS HTM perovskite solar cell demonstrates a PCE= 12.70%, FF = 69.23%, Jsc=22.62 mA/cm^2 and Voc=0.811 V. Our simulated results have slightly values when compared with results obtained from Spiro-OMeTAD based solar cell [26].

Our simulation showed that TiO_2 as ETM with CZTS as HTM exhibit satisfactory efficiency, but these parameters have still less values to that of Spiro-OMeTAD as HTM, which is due to the misalignment of CZTS/Perovskite. The total rate of generation and recombination of perovskite solar cells with different ETMs shows in fig. 7(b). The 450 nm thickness of perovskite material ensures that most of the light is absorbed and small section can be transmitted, this transmitted light may have impact on the rate of generation and recombination of carriers. A large generation of carriers occurred in perovskite layer in the presence of ZnO as compared to TiO_2 because it generated the electrons (minority carrier). Thus, the total recombination rate is also high in ZnO due to its large band gap [27]. The recombination of TiO_2 is lower than other ZnO is fortunate in CZTS as HTM, which promotes the highest Eff and FF in CZTS based reliable PSCs.

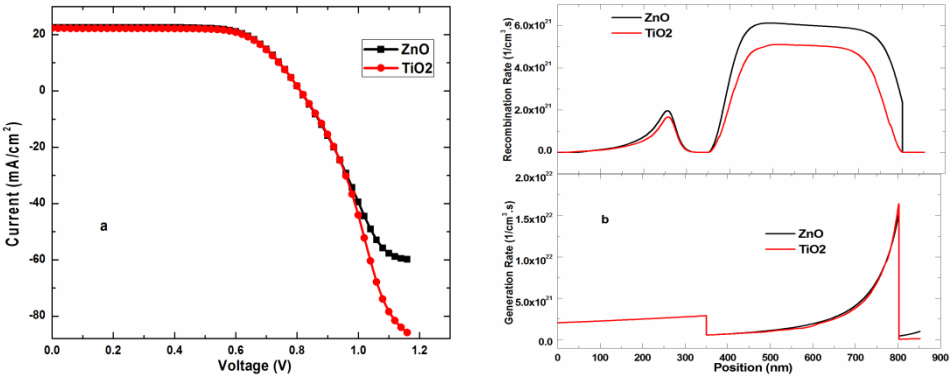

Fig. 7. (a) I-V Characteristic at interface (b) Carrier's generation and recombination rate.

3.6. Temperature effect

Fig. 8 shows the performance of device by varying the temperature 300 to 400K. At operating temperature less than room temperature, the PSCs with CZTS HTM show no convergence as temperature approach to 300K cell show sufficient result up to 320 K. Higher temperature has detrimental on performance due to mobility of carrier's resistivity increased the in the way of carriers.

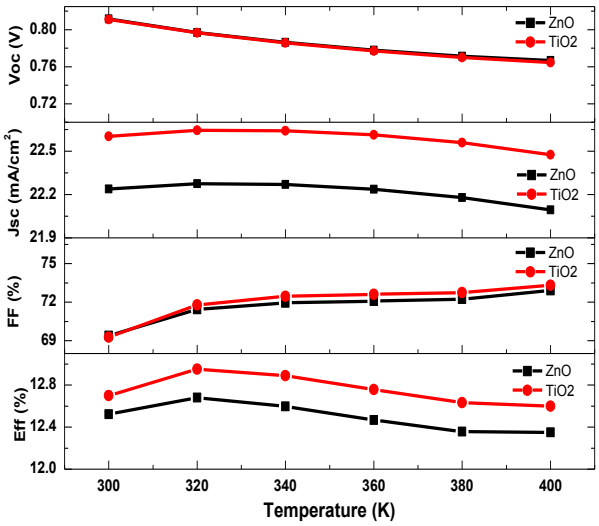

Fig. 8. Variation of PV parameters with temperature.

4. Conclusion

This manuscript deals with the simulation study on organo-metal halide perovskite based solar cells in which CZTS used as potential HTM with two different ETMs (ZnO and TiO_2). CZTS was used as HTM instead of Spiro-OMeTAD in order to reduce toxicity and the cost of Perovskite solar cells. Influence of all layer's thickness, effect of front and back contact work function, dopant concentration of ETMs with interface characteristics and rate of carrier generation and recombination were studied. Optimal values of all these parameters were calculated to achieve high efficiency. The data showed that TiO_2 as ETM give outstanding performance with power conversion efficiency of 12.69% and other performance parameters with CZTS HTM as compared to ZnO.

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