Effect of different inorganic Hole Transport Material Layers on the performance of Tin Halide Perovskite Solar Cells

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***Abstract*—** Perovskite Solar Cell based on lead causes damage to the health of all the living organisms due to its toxic behaviour. So, Tin based Perovskite Solar Cell are preferred, simulated and analysed. This paper represents the effect of different parameters on Tin Halide Perovskite Solar Cells output parameters when different inorganic Hole Transport Material Layers viz. Cu_2O, CuSCN and CuI are used. Based on the simulations done using one dimensional device simulator, it has been observed that optimised doping concentration, thickness, Total Density of the interfaces, Defect density, Electron affinity of Absorber, Electron Transport Material and Hole Transport Material results in enhanced output parameters like Fill factor, Output Voltage, Current Density and Power Conversion Efficiency. It has been analysed that for the proposed efficient design of Tin Halide Perovskite Solar Cells Power Conversion Efficiency of 23.93 percent, Current Density of 34.34 mA per sq. cm, Fill Factor of 87.1 percent and Output Voltage 0.8V have been achieved using Cu_2O as Hole Transport Material Layer where as the results obtained using CuSCN with Power Conversion Efficiency of 23.92 percent, Current Density of 34.33 mA per sq. cm, Fill Factor of 87.85 percent and Output Voltage 0.79V are also competent enough to be used as Hole Transport Material with lead free Perovskite material.

Keywords-*Pollution, Current Density, Thickness, Band Gap*

I. INTRODUCTION

The conventional sources of energy like fossil fuels, coal, Natural Gas and petroleum cannot fulfil our growing energy requirements and moreover these non renewable sources of energy cause pollution and can be depleted easily with the current pace of growing energy consumption but recovery of fossil fuels take large number of years. So, renewable sources are required nowadays which are available in abundance that can not only be renewed but are also pollution free. Harvesting solar energy with the help of Solar cells is a renewable source of energy [1]. These are non conventional sources of energy which can be produced from different types of sources like sun, wind, rain, water and tides. Generation of electric energy from solar energy is a topic of great interest nowadays. Minimum Power uitilistion is desirable so there is a need to enhance Power Conversion Efficiency (PCE) [2]. The third generation solar cells, Perovskite Solar Cells (PSC) has caused significant enhancement of PCE from 3.8% in 2009 [3] to 22.1% in 2016 [4]. The study of power generation from PSC is valuable.

II. SOLAR CELLS

For generation of electric energy solar cells are very beneficial [5]. Devices that transform Solar Energy directly into electricity through photovoltaic effect are called Solar Cells [5]. Based on photovoltaic technology First Solar Cells were developed in 1888 [6]. Solar cell panels are the Solar Cell Modules which consists of assemblies of Solar Cells to harness Sunlight generate Solar Energy [5]. Solar Cells embedded in the Solar panel absorb sunlight in the form of photons [5]. When the band gap of Solar Cell material matches with the energy of photons which means photons are absorbed to generate free electrons which leads to the formation of electron hole pair [5]. On n-type side electrons are generated which move to p-type semiconductor-metal contact where the electrons recombine with holes to generate electron-hole pair [5]. There is a special formation of solar cells in which electrons are permitted to move only in single direction to generate Direct Current [5]. Satellites, remote site water pumping, lighthouses, calculators, watches, cameras, light meters and outback telecommunications stations are the applications of Solar Cells. Based on the generation of solar Cells Perovskite solar cells which is third generation solar cells are analysed and simulated using one dimensional device simulator because of their potential of generating high efficiency at low production costs, easy handling and tuning capability.

A. *Perovskite Solar Cells (PSC) as Third generation Solar cell*

PSC is the Technology i.e. emerging at extremely high pace due to its efficiency enhancing capability from 3.8% in 2009 [3] to 22.1% in 2016 [4]. Perovskite Solar Cells contain Perovskite Structured Compound which is made up of lead or tin halide based material. This is used because of its accessibility in production, its low cost in production and high PCE. PSC is a good light harvester due to its significant features such as ideal band gap, broad absorption spectrum, and good carrier transport mechanism, ease of fabrication on the flexible substrate and tunable band gap and long diffusion length [7]-[12]. PSC ancillary perceives enthralling applications in photo-detectors, water photolysis and radiation detection [13]. Photovoltaic innovation to generate materials based PV operation and devices can be acquired using PSC [13]. Absorption coefficient of PSC is high which results in increase in the amount of light absorbed by the solar cell is also increased that leads to increase in the amount of charge carriers generated by the photons which results in reduction in energy loss and increase in the number of carriers in the electrodes [14]. Absorption coefficient of PSC is quit high that results in absorption of complete visible solar spectrum by the ultra thin films around 500nm [15]. Inclusion of Perovskite material, which can be generated in laboratories, into solar cells was first outlined in 2009 [16]. In 2015 PSC with 21% efficiency where as in 2016 efficiency of PSC have reached up to 22.1% [16].

B. Lead free PSC based on Tin Halide

PSC based on lead are injurious to all living organisms due to toxic nature lead, which dissolves in water bodies and spread its toxicity. This leads to harmful effects not only to the aquatics but also the plants which grow on the toxic soil resulted from mixture of toxic water consisting of lead. This toxic water when consumed by humans causes various health related issues such as increased blood pressure, abnormal functioning of kidney and decrease in haemoglobin level. Tin Halide based PSC are harmless and more sustainable as compared to lead halide based PSC because Sn^{2+} gets oxidised to Sn^{4+} metal oxides which are toxicologically inactive [17].

C. Tin Halide based proposed Design Structure

Fig 3 shows layered architecture for Tin Halide PSC for the proposed design i.e. Glass Substrate/TCO/TiO2 (buffer) (ETM)/ $CH_3NH_3SnI_3$ (Absorber)/(Cu_2O/ CuSCN/ CuI) (HTM)/Metal back contact and Fig 4 shows the structure generated for the proposed design using one dimensional device simulator. Sun light or Photons are allowed to strike the Glass Substrate Material on the right contact which is the Front side and these photons are passed through the transparent conductive oxide (TCO). Electron Transport Material (ETM) Layer, placed after TCO is made from Titanium Oxide i.e. n-type of Perovskite material and consists of electrons for conduction. Absorption Layer made up of $CH_3NH_3SnI_3$ i.e. intrinsic type of Perovskite material is placed after ETM. Hole Transport Material (HTM) Layer, placed after Absorption Layer is made from Copper Oxide material and consists of holes for conduction. Metal back contact is used at the last on the left side which is connected to the voltage supply. Interfacing layers ETM/Absorber and HTM/Absorber are also added to get enhanced output parameters.

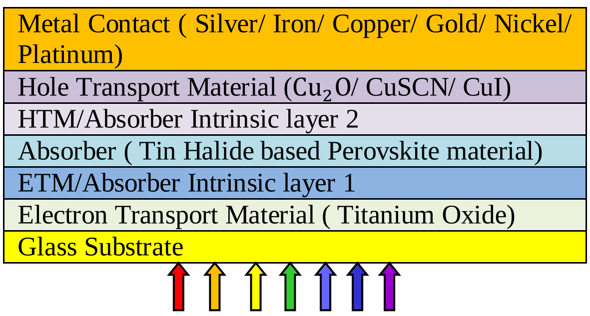


Fig 1. Layered architecture of Tin Halide based PSC

III. PROPOSED DESIGN PARAMETERS AND SIMULATION

Doping concentration, thickness, Total Density of the interfaces, Defect density, and Electron affinity of Absorber, Electron Transport Material and Hole Transport Material are the parameters which are focused to analyse best optimised output parameters using control variable method. Table 1 shows initial parameters for the proposed design. Based on these initial parameters Current Density – Voltage (J-V) characteristics of PSC in Fig 1 and 2 are analysed. Initially Power Conversion Efficiency of 13.52%, Current Density of 21.319 mA per sq. cm, Fill Factor of 79.28% and Output Voltage 0.8V are the acquired output parameters when Cu_2O is used as HTM .

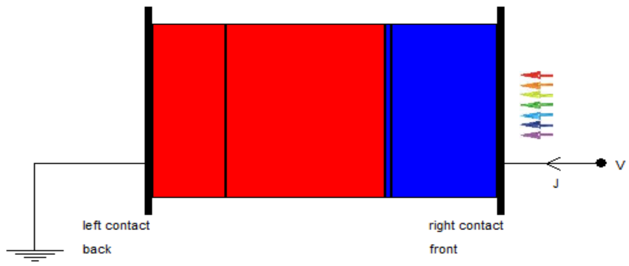


Fig 2. Pictorial representation of Proposed Structure

IV. Results and Discussions

A. Effect on Band Diagrams

Fig 3 shows the band diagrams generated for the proposed design using different HTMs among which Band gap of Cu_2O < Band gap of CuI < Band gap of CuSCN. Larger will be the Band Gap more will be the requirement of photonic energy to excite the electrons from Valence Band (VB) to the Conduction Band (CB) and vice-versa. As a result for the HTM with smaller Band gap electrons can easily cross the barrier potential to reach the CB even for small photonic energy. Energy of photons should be more than the Band gap energy of the material for the excitation of electron from VB to CB. But if the Band Gap is too much narrow more electrons will cross the barrier potential resulting in increment in the recombination rate will leads to degradation in the performance in terms of output parameters. On the band diagram graph the defect level energy of the defects persisting and the transition energy of meta-stable defects are depicted. Energy E_t is evaluated in case the defect has an energy distribution (e.g. Gauβ or CB tail). Defect level occupation is depicted on the occupation probability graph. The 'occupation with electrons' represents the fraction of defects in the acceptor configuration for a meta-stable defect transition and the 'occupation with holes' the fraction of defects in the donor configuration. The occupation of several (typically 7) sublevels in this distribution is depicted when the defect has an energy distribution (uniform, Gauß, tail).

B. Effect of thickness of absorber layer

Thickness of the Absorber Layer affects solar spectrum response on which efficiency depends. Performance of solar cell is affected by thickness of absorber layer. Thickness of absorber layer is varied and it is observed that the optimum thickness of Absorber layer i.e. 750nm in which efficient results are obtained with high PCE for Tin Halide PSCs because in the presence of light absorber layer charge recombination behaviours will become dominant because of large defect density.

TABLE1. Different HTMs and the proposed design parameters

Parameters	TCO [19]	TiO2 (buffer) [19]	$CH_3NH_3SnI_3$ (Absorber) [19]	Cu_2O [HTM] [18]	CuSCN [HTM] [18]	CuI [HTM] [20]
Thickness (nm)	500	30	350 (variable)	350	350	350
Band gap (eV)	3.5	3.2	1.3	2.17	3.4	3.1
Electron affinity χ (eV)	4	4.26	4.17	3.2	2.1	2.1
Relative permittivity ε_r	9	9	8.2	7.1	10	6.5
Effective conduction Band Density N_c (cm^{-3})	2.20e+18	2e+18	1e+18	2.5e+18	2.5e+18	2.5e+18
Effective valence band density N_v (cm^{-3})	1.8e+19	1.8e+19	1e+18	1.8e+19	1.8e+19	1.8e+19
Electron mobility μ_n ($cm^2/V\cdot s$)	20	20	1.6	2e+2	2e-4	44
Hole mobility μ_P ($cm^2/V\cdot s$)	10	10	1.6	8e+2	100e-2	44
Shallow uniform acceptor density, N_A ($1/cm^3$)	0	0	3.2e+15	9e+21	1e+18	3e+18
Shallow uniform donor density N_D ($1/cm^3$)	2e+19	1e+16	0	0	0	0
Defect density N_t (cm^{-3})	1e+15	1e+15	4.5e+17	1e+14	1e+14	1e+14

Current density increases with increasing thickness but thicker absorber layer will absorb more photons that results in more electron-hole pair creation. Chances of recombination increase as longer distance is travelled by the charges for diffusion with thicker absorber layer. There is decrease in efficiency with increase in thickness at certain point. Recombination rate enhances with increasing thickness which leads to reduction in output voltage hence there is reduction in efficiency. Absorber layer thickness should be selected such that its thickness is less than diffusion length of excess charge carriers. Up to certain absorber thickness output voltage remains high after that there is reduction in fill factor with increasing absorber thickness leading to internal power consumption.

TABLE2. Parameters for interface defect and the defect in the absorber and HTM

Parameters and units	Absorber [19]	HTM [18]	ETM/Absorber interface [19]	HTM/Absorber interface [19]
Defect type	neutral	neutral	neutral	Neutral
Capture cross section for Electrons (cm^2)	2e-14	1e-15	1e-15	1e-15
Capture cross section holes (cm^2)	2e-14	1e-15	1e-15	1e-15
Energetic distribution	Gaussian	single	single	Single
Energy level with respect to E_v (above E_v , eV)	0.65	.1	0.6	0.6
Characteristic energy (eV)	0.1	-	-	-
Total Density ($1/cm^3$) uniform	1e+14	1e+14	1e+17	1e+17

Table 2 shows initial parameters for defects in the Absorber, HTM and the two interfaces as depicted in Fig 3. Tin halide based PSC has narrower band gap as compared to lead halide based PSC which leads to red shift in Quantum Efficiency (QE) to 950nm in Tin halide based PSC which results in increased absorption in at infrared wavelengths.

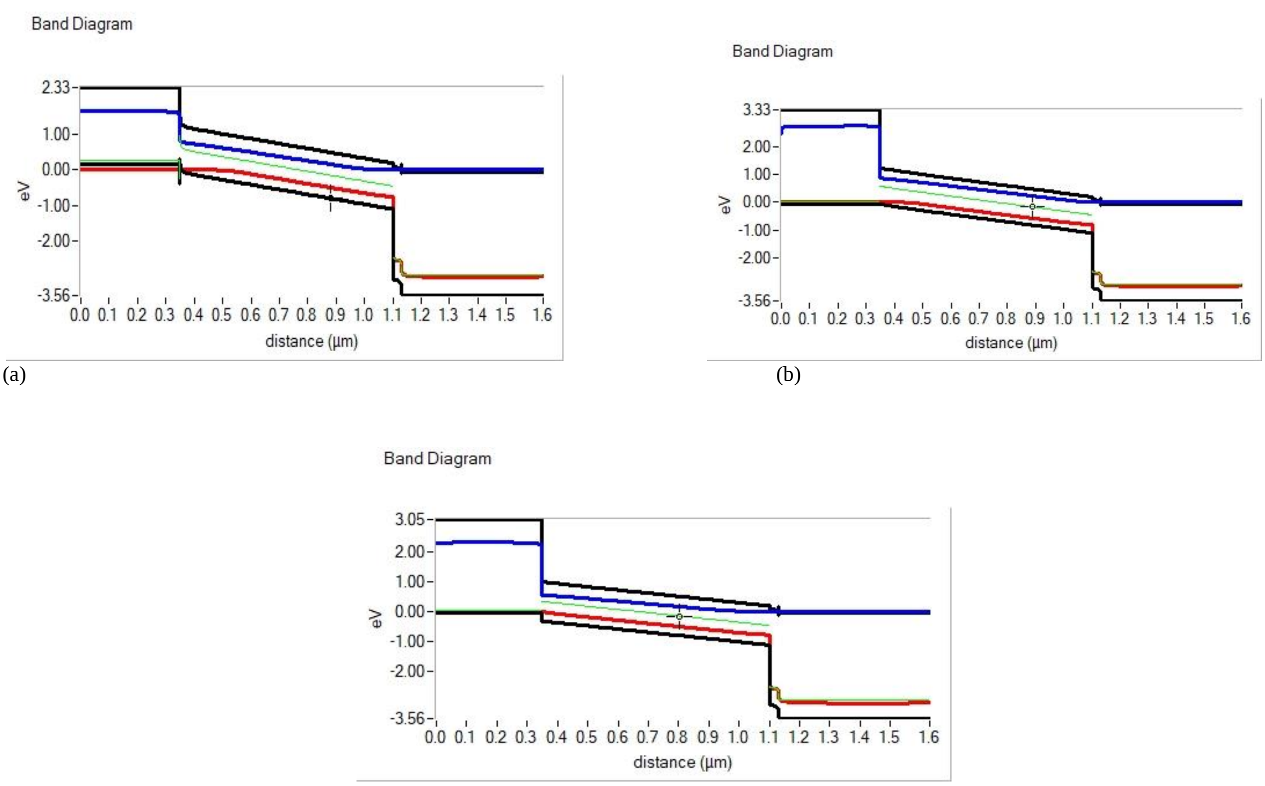
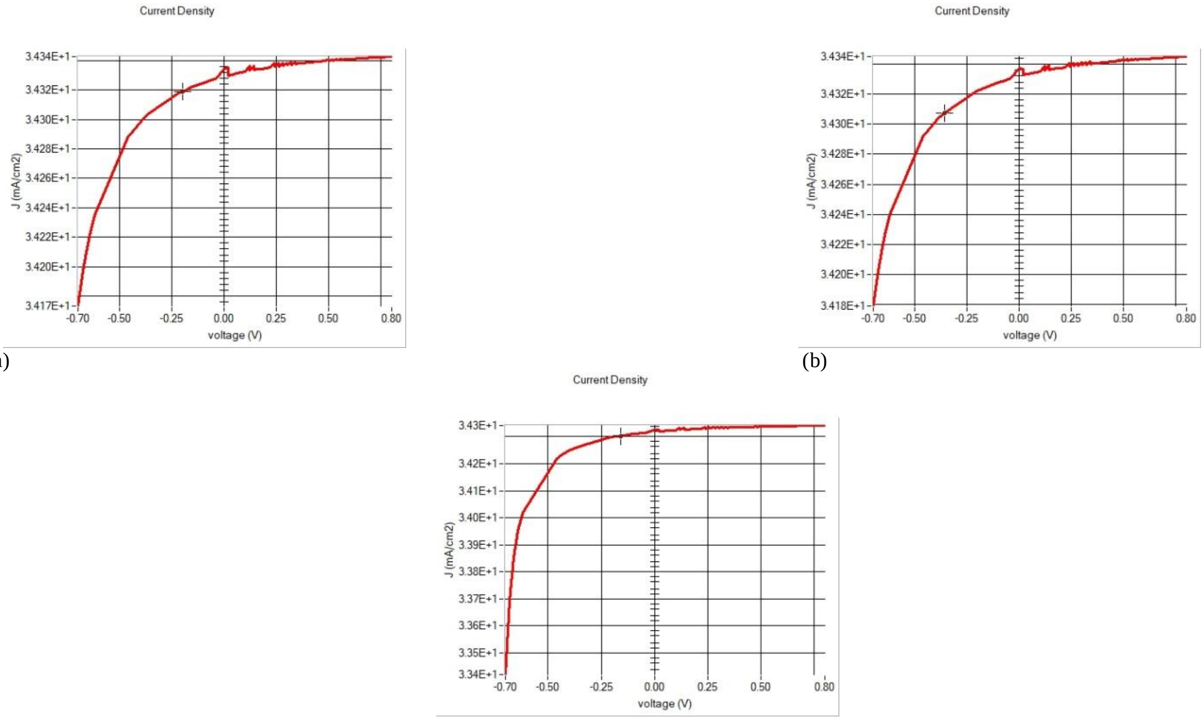


Fig 3. Band Diagrams generated for the proposed design when different HTMs (a) Cu_2O (b) CuSCN (c) CuI are used

Fig 4 shows Current density Vs Voltage (J-V) Curve for the proposed design when different HTMs (a) Cu_2O (b) CuSCN (c) CuI are used for the best optimised design. Maximum Current density is achieved for the proposed design when Cu_2O is used as HTM which is 0.087% better than the referred design [19]. Current density obtained when CuSCN and CuI are used as HTM are also competing with Cu_2O as HTM with minor differences as shown in Table 3. For CuI there is sharp increase for the initial voltages in Current density as shown in Fig 4 (c) as compared to other two HTMs in which gradual changes are depicted for initial voltages.

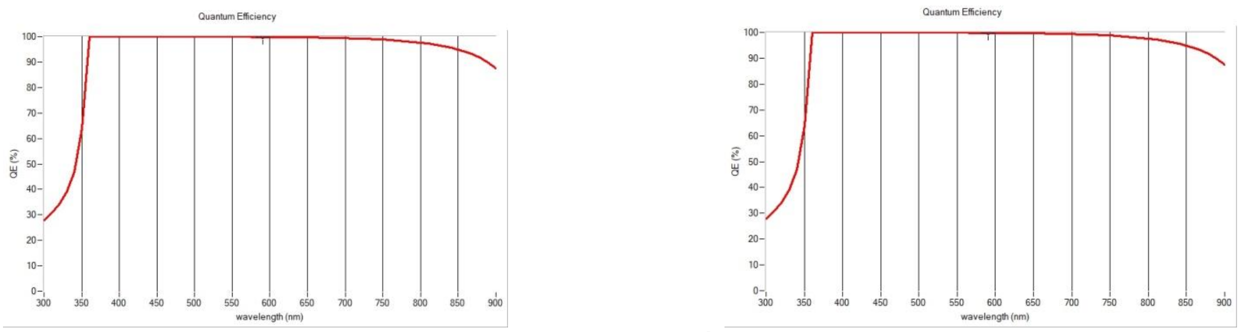


(a) (b) (c)

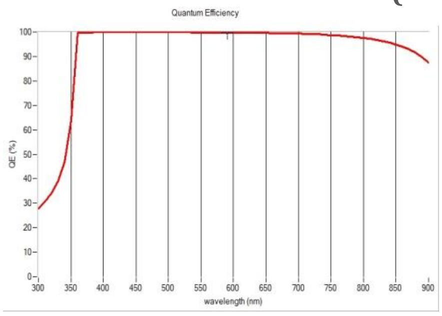
Fig 4. J-V Curve for the proposed design when different HTMs (a) Cu_2O (b) CuSCN (c) CuI are used

C. Effect of defect density on the Interfaces and absorber

It has been observed that there is negligible effect on efficiency till the defect density is below 1e+12 per cubic centimetre. There is decrease in efficiency when defect density exceeds above 1e+12 per cubic centimetre. Recombination rate increases with increasing defect density. The optimised value of the defect density of the interfaces achieved is 1e+10 per cubic cm. Possibility of taking part in reverse saturation current increases with increase in number of holes in the absorber layer. Hence there is decline in open circuit voltage this leads to low electric conversion efficiency.



(a) (b)



(c)

Fig 5. QE Curve for the proposed design when different HTMs (a) Cu_2O (b) CuSCN (c) CuI are used

Fig 5 shows Quantum Efficiency (QE) Curve for the proposed design when different HTMs (a) Cu_2O in which best results are obtained for wavelength range 360-660nm (b) CuSCN in which best results are obtained for wavelength range 360-660nm (c) CuI in which best results are obtained for wavelength range 360-650nm are used for the best optimised design.

TABLE3. Comparison Table

Output parameters	Referred design model [19]	Proposed design model for Cu_2O [HTM]	Proposed design model for CuSCN [HTM]	Proposed design model for CuI [HTM]
Fill Factor	79%	87.1%	87.85%	85.11%
Output Voltage	0.92V	0.8V	0.793	0.8008
Current Density in mA per sq. cm	31.59	34.34	34.33	34.326
PCE	23.36%	23.93%	23.92%	23.39%

Table 3 shows Best Output optimised Parameters obtained for the proposed design model when different inorganic HTMs are used when compared with Referred design model [19]. Simulations are done using SCAPS-1D [21].

V. CONCLUSION

In this paper theoretical Simulation and Analysis of Tin halide Perovskite Solar Cells (PSC) different inorganic Hole Transport Material (HTM) viz. Cu_2O, CuSCN and CuI is done using one dimensional device simulator. The study reveals that Cu_2O as HTM achieves highest PCE, but FF is less as compared to CuSCN as HTM for the proposed design whose efficiency is nearly comparable to Cu_2O for CuI as HTM, output voltage is enhanced but other output parameters are degraded as compared to other 2 HTM materials for the proposed design. Quantum efficiency reaches to its maximum value for wavelength range 360nm-660nm when Cu2O or CuSCN are used as HTM whereas when CuI is used as HTM, wavelength range is 360nm to 650nm. This is theoretical data gathered using simulation which can be used experimentally to design highly efficient Tin Halide based PSC which will be more sustainable to the environment as compared to Lead Halide based PSC.

VI. REFERENCES

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