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# Numerical Simulations on Perovskite Photovoltaic Devices

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#### Abstract

Organometal halide perovskites have recently attracted tremendous attention due to their potential for photovoltaic applications, and they are also considered as promising materials in light emitting devices. In particular, in the last years promising photovoltaic devices with efficiencies above 20% have already been prepared using organometal halide perovskites as absorbent materials.

A planar heterojunction perovskite-based solar cell is made of three main layers sandwiched between the two conducting electrodes. The standard design for a planar heterojunction perovskite-based solar cell is: Back electrode/ Hole Transport Material (HTM)/ Perovskite absorber / Electron Transport Material (ETM) / Transparent electrode. For planar heterojunction-based solar cells, recent efforts have revealed that increasing conductivity of the hole transport materials by doping and optimizing charge collection by adjusting the absorber thickness could bring a positive impact on the efficiency. Electron transporting materials are also a crucial component in perovskite-based solar cells. The effect of different electron transporting materials in the final behaviour of the PV device can also be numerically simulated. Several PV parameters such as thicknesses of the absorber, HTM and ETM, respectively can be optimized by simulation methods and subsequently implemented by experimentalists. The hole mobility and acceptor concentration of the HTM, interface trap density and work-function of back contact metal have shown significant influence on the device performance. Even with these strong merits, enhancement of hole mobility and conductivity of HTM, stability of perovskite and TiO<sub>2</sub> and replacement of toxic lead are still crucial. Through suitable processing/synthesizing of the perovskite absorbers, best engineering the selective contact, and increasing conductivity of HTM and ETM will boost the stability as well as performance of the device.

This chapter presents a review of the evolution of perovskite materials from their discovery to their present significance as the main constituent of a new class of photovoltaic devices. We also evaluate the use of numerical simulation methods for determining the optimal configuration of perovskite-based solar cells and analyzing their optoelectronic behavior. The outcome of a simulation study on organometal halide perovskite focusing on the role of the different components of the solar cell using Solar Cell Capacitance Simulator as a simulation tool are discussed. A photoconversion efficiency of 22.7%,  $V_{OC}$  =



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1.12 V,  $J_{SC}$  = 24.66 mA/cm<sup>2</sup> and FF = 82.1% has been found after optimizing the different parameters involved. These results still are slightly higher than the experimental ones but the confluence between both are expected in the short time.

**Keywords:** Organometal halide perovskites, CH<sub>3</sub>N<sub>3</sub>PbI<sub>3</sub>, Hole Transport Materials, Electron Transport Materials, photovoltaic solar cell, photocurrent, photoconversion efficiency

## 1. Introduction

The world is highly mechanized, competitive, depends almost upon machinery, life style is being improving day by day consequently energy consumption rate is increasing unexpectedly. To fulfill the current energy demand, the world depends, to date, upon fossil fuel based (coal, natural gas, and petroleum products) energy resource. At the mean time, its reservoirs are limited and getting depleted gradually, cost is highly influencing by socio-economic and political situations, and its use creates an adverse effect to the environment as well as to the human health. Thus, everyone should think its best alternative before it comes to an end. So, it is the high time to look at and develop the unexhausted, environment friendly green/clean energy and associated technologies. As a source of energy solar energy is free, unlimited, and available everywhere in this world. The best option, hereby, might be solar energy and solar cell technology which is the main purpose of this paper and discussed briefly below. However, to date the relatively low efficiency to cost ratio of photovoltaic solar cells limiting its use. Thus, increasing efficiency and decreasing cost of solar cell is the major challenge to the researchers, academicians and industrialists.

### 1.1. Solar cells

In every step and activity in our life, such as: cooking a food, lighting a home and a street, opening a college and a hospital, running a vehicle and a factory etc we need energy. Thus energy is extremely crucial factor for better quality of life for one and all, employment creation and industrial as well as economic development in a country. Global population, their living style/standard, industries and hence the energy demand is increasing day by day where world energy generation capacity is nearly 18 TW [1] and otherwise almost remaining the same. The main resource of energy, worldwide, is fossil fuel based energy. Actually it is untenable and also contributes substantially to climate change and global warning. World nuclear energy report 2014 highlighted the fact that "the nuclear share in the world's power generation declined steadily from a historic peak of 17.6% in 1996 to 10.8% in 2013". In the world, 31 countries with 388 reactors are currently generating 333 GW. 67 reactors are under construction since July 2014 with a total capacity of 64 GW [2]. Nuclear energy data indicates that it would not meet the current energy demand and it is quite hazardous to the mankind too. The renewable resources; hydroelectricity, geothermal, wind, bio-fuels are limited. On the other hand solar energy is inexhaustible, accessible, nonhazardous and environment friendly too which can directly be changed into heat and electricity. In facts feasible capacity of generation of electricity from the sun light is 1000 times higher than the current world energy demand [1]. Moreover, production of photo-electricity on one day is sufficient for one year by using even a less efficient photovoltaic solar cell. So, it would be the best option to resolve the world future energy demand and crisis.

Solar cell is usually called photovoltaic which literary means the conversion of light or photon into electricity. Edmund Becquerel discovered photovoltaic effect in 1839 by illuminating silver chloride in an acidic solution and measuring the current whereas this effect was observed in 1876 by W. G. Adams and R. E. Day for the first time in a solid: selenium [3, 4].

In 1883, Charles Fritts demonstrated thin film selenium cell and he had realized enormous potential of photovoltaic devices [3]. Albert Einstein discovered the photoelectric effect in1905, and awarded by the Nobel Prize in Physics 1921 for this theoretical work [5]. The next significant step forward came 34 years later, after Fritts, where the work was carried out with the copper-cuprous oxide by Grondahl in 1927 [6] and he described the outcome of the work as development of a rectifier and a photovoltaic cell.

Almost at the same time, silicon had drawn the attention of researchers as it was emerging for use as point contact rectifier. Russel S. Ohl, Bell laboratory engineer, developed a "diode" in 1939 by doping one side of silicon with electron donor and other side with acceptor material. After one year he had observed an electric voltage across the ends of the so formed "p-n junction diode" when light shone it. It was the first invention of the photovoltaic device based on silicon semiconductor thus; Ohl got a patent for his work and this effect. This fact revealed after their paper published in 1952 [7]. In the same laboratory in 1954 D. M. Chapin, C. S. Fuller, and G. L. Pearson announced the first "modern photovoltaic silicon cell" with the efficiency of 6% [8]. Vanguard I was the first satellite to use solar power launched by USA in 1958. After that Explorer III, Vanguard II and Sputnik-3 were launched with PV-powered system on board.

In order to design a solar cell and realize the role of different components we must understand basic steps or processes they are undertaken in the solar cell layers. Following are the processes that undergo to convert electromagnetic energy into electrical energy in a photovoltaic [9] where this phenomenon is known as photovoltaic action:

- absorption of incident light by an absorber i.e., interaction between the photon and an absorber to generate either electron-hole pairs or excitons so, the absorber jumps to the excited state i.e., an electron from valence band to conduction band,
- the separation of charge carrier of opposite types and to move in opposite directions i.e., toward contact the electrodes (anode and cathode),
- the separate extraction of these carriers to an external circuit via contacts where energetic electron leaves an electrode, does something useful at an electrical load, hereby loose energy, and finally returns back to initial position through another electrode to complete one round trip,
- at the end of the round trip, the electron recombine with a hole so that the absorber returns back to the ground state and ready to absorb another photon for next trip.



Source: [10, 11]

Figure 1. Global PV market by Technology



### Source: [10, 11]

Figure 2. Worldwide growth of Photovoltaics

Since that time different solar cell technologies have been developed and achieved different efficiencies. Now NREL divided the solar cell technologies into 5 categories they are: Crystalline silicon cells, single junction GaAs, multijunction cells, thin film technologies and emerging PV. Gradual development of solar cells and their best efficiency is illustrated in Figure 3 [12]. Leonid A. Kosyachenko categorized the solar cell technologies as so called first, second and third generation photovoltaics. Based on Kosyachenko classification, all types of silicon wafer based and GaAs solar cells are represented as the first generation photovoltaics. Amorphous silicon (a-Si) and non silicon based thin film such as CIGS, CdTe based solar cells are so-called second generation photovoltaics, relatively younger dye-sensitized solar cells (DSSCs), organic and quantum dots solar cells are the third generation photovoltaics [1], whereas hybrid solar cells are considered as fourth generation solar cells. There is always more space in third and fourth generation photovoltaic technology to identify and develop further new materials and solar cell devices to achieve a low cost and high efficiency.



Figure 3. Best research cell efficiencies [12]

Silicon is indirect band gap (BG) material even though its BG is 1.1eV thus, silicon based solar cell consumes a huge material and energy, as a consequence, a low productivity, high labor cost and hence a very low efficiency to cost ratio even for mass production with feasible efficiency of 16-17% and 13-15% in case of single- and polycrystalline materials respectively [13]. Even with such demerits, since the date of first comercial manufacture of PV solar cells around in 60's decade of 20<sup>th</sup> century to date the silicon based solar cells have been extremly dominating the photovoltaic technology. However, in the last decade new generation of

materials and devices (eg; dye sensitized, cadmium telluride and copper indium gallium selenide based solar cells) has spread the photovoltaics region.

It is illustrated by Figure 1. Figure 2, 3 and 4, inspiring gestures, show the worldwide orientation towards the solar cell technologies; hopefully it would be the first in near future. Organic sensitizers in dye sensitized solar cells (DSSCs) have low absorption coefficients and narrow absorption bands which limit the photovoltaic performance [15]. Liquid organic electrolyte in DSSCs is volatile and can easily be degraded by ultravoilet radiation, so stability is the another major issue in this technology [1].



Figure 4. Projected global growth of PV. [14] (Source: Growth of photovoltaics)

Cadmium, tellurium, indium and galium are rare elements and almost they are expensive too furthermore, Cd and Te are toxic as well as scattered elements [1, 16]. These facts about existing materials always look for the low cost, easy processability, low consumption of material, reproducible, environment friendly, non toxic and easy abundant absorbing material for the solar cell industries.

### 1.2. Perovskites

The main concern in designing a photovoltaic solar cell is to maximize the efficiency to cost ratio i.e., to reduce the total cost, increase the efficiency and life time of PV module [17]. There are various factors they affect the efficiency of a solar cell. The first and foremost factor is the percentage of electromagnetic energy reaching the absorber which the solar cell converts into electricity. Secondly, the types of materials since different materials have different absorption coefficients and band gap and hence different maximum theoretical efficiency [18]. Third factor

is the structure of the material or semiconductor used in the cell. Higher performance of solar cell is expected and usually observed in perfect crystalline structure with suitable dopants. Fourth is thickness of the absorbing material. Too thin and too thick; both are not suitable for good photovoltaic action. In the former one the thickness may not sufficient for diffusion of charge carriers whereas latter case increases the cost and reduces efficiency. Fifth factor is the amount of light reaching the absorbing material i.e., reflectance, transmittance and absorbance of the material. Sixth factor affecting the efficiency is the temperature since different materials have different response to temperature higher than room temperature.

### 1.2.1. Structure of perovskites

In 1839, Gustav Rose discovered the mineral calcium titanate (CaTiO<sub>3</sub>) in Ural Mountain, Russia and gave the name Perovskite to honor the Russian mineralogist L. A. Perovski [19]. Any material that resembles the crystal structure of mineral CaTiO<sub>3</sub> is termed as perovskite structure or simply perovskite. It is generally represented by the formula ABX<sub>3</sub> where A is a big-sized cation (either organic or inorganic), B is divalent small metallic cation (Cu<sup>2+</sup>, Mg<sup>2+</sup>, Ge<sup>2+</sup>, Sn<sup>2+</sup>, Pb<sup>2+</sup>, Eu<sup>2+</sup>, Yb<sup>2+</sup>, etc), and X is halide ion (Cl<sup>-</sup>, Br<sup>-</sup> and I<sup>-</sup>) which binds to both cations [20]. The perovskites can be divided into two main categories: alkali halide perovskite and organo-metal halide perovskite.

Perovskites possess different astonishing optoelectronic behaviors which make the perovskite as promising candidate of photovoltaic absorber. Ferroelectric behavior, discovered half a century ago, is one of the characteristics among them.

In 1979, Salau reported the potassium lead iodide as a direct band gap material with the value 1.4 to 2.2 eV, which suits the solar spectrum [21, 22]. Capability of halide perovskite to convert light to electricity was discovered in 1990s and fabricated for LED.

 $\alpha$ ,  $\beta$ ,  $\gamma$ , &  $\delta$  are four possible phases of perovskite where  $\alpha$  is high temperature phase T > 327 K and has cubic structure (eg CsSnI<sub>3</sub>). This structure allows only one formula unit per unit cell, so CH<sub>3</sub>NH<sub>3</sub><sup>+</sup> cannot obtain cubic structure. For a temperature T < 327 K perovskite changes from  $\alpha$  to  $\beta$  phase usually found in tetragonal structure with lattice parameters a = 8.855 Å and c = 12.659 Å where exact values depend on molecular orientation [23].

Generally, ABX<sub>3</sub> has cubic structure and  $\alpha$  phase where B has 6 nearest neighbor X ions (octahedral) and A has twelve fold coordination sites as shown in Figure 5.

One crucial parameter to maintain the cubic structure of perovskite is the tolerance factor,  $t = (R_A+R_X)/\sqrt{2}$  ( $R_B+R_X$ ). It should be close to one to obtain in the cubic structure where, R is radius of the ions and suffixes A, B and X are as defined above. Hendon et al. mentioned that stable perovskite is found in the range 0.7< T < 1 [24], which guides cation A must be larger than B in this regard, CH<sub>3</sub>NH<sub>3</sub> ion is one of the best options. Smaller t could be lead to lower symmetry tetragonal  $\beta$  phase or orthorhombic  $\gamma$  phase. For MAPbI<sub>3</sub> perovskite, transition from  $\alpha$  to  $\beta$  to  $\gamma$  occurs at 327 and 160° K respectively. The transition of perovskite is depending on the tilting and rotation of the BX<sub>6</sub> polyhedra in the lattice. Whereas the fourth phase  $\delta$  is non perovskite phase [23, 24, 25, 26, 27].



Source: Perovskite http://www.surrey.ac.uk/chemistry/perovskite/what/history/index.htm

Figure 5. Cubic structure of MAPbI<sub>3</sub> perovskite

### 1.2.2. Electronic Behavior

Pb has an occupied 6s orbital, which is below the top of valence bands of the perovskite. This lone pair of s electrons often gives rise to unusual behaviors in perovskite [28]. Unlike GaAs and CdTe, in the first principle study carried out by Walsh et al., 2011 density of states (DOS) and partial charge density plots of halides perovskite showed the coupling between Pb s and I p (anti-bonding state) contribute to VBM but CBM is derived almost from the Pb p state [28, 29]. And perovskite gets ionic and covalent, dual nature in electronic structures. Thus organic part/ion does not play a direct role to determine electronic behaviors but takes part in stabilizing perovskite structure and changing the lattice constants.

Experimental/research works and DFT-PBE calculations show the different values of band gap for perovskites. Band gap of perovskite depends on synthesizing process and the size of organic/inorganic cation, metallic ion and very less in halide ion. Band gap of CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>, CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub>, CH<sub>3</sub>NH<sub>3</sub>PbCl<sub>3</sub>, CH<sub>3</sub>NH<sub>3</sub>Pb<sub>3-x</sub>Cl<sub>x</sub> are 1.49-1.61, 1.95 eV, 2.46 eV and 1.59 eV respectively [20, 30] whereas mostly used band gap for CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> is 1.5 eV [27].

### 1.2.3. Ambipolar conductivity

The electronic structure of MAPbI<sub>3</sub> perovskite is different compared to conventional semiconductor. A cation Pb p orbital has a much higher energy level than anion p orbital as in p-s semiconductor and hence CBM of MAPbI<sub>3</sub> is more dispersive. At the meantime VBM is also dispersive due to strong s-p coupling. Based upon the formula  $m^* = h^2 \left[\frac{\partial^2 \varepsilon(k)}{\partial^2 k}\right]^{-1}$  [31] effective mass of electron is balanced by that of hole in MAPbI, perovskites which finally results into

mass of electron is balanced by that of hole in  $MAPbI_3$  perovskites which finally results into an ambipolar charge transport behavior in perovskite based solar cells.

### 1.2.4. Optical properties

Absorber is the key player in photovoltaic solar cells to achieve good performance. In this context, optical absorption strength and range are the crucial factor of the materials. The edge transition for MAPbI<sub>3</sub> perovskite comes from mixed s-p coupling and Pb p orbital so that transition probability from Pb s to Pb p is high [27]. Moreover, perovskite is direct band gap material and hence it has high optical absorption strength and wider range to absorb sufficient solar energy to achieve high value of power conversion efficiency. Figure 6 shows the absorbance spectra for three MAPbX<sub>3</sub> perovskites with different halide components; X=I, Br and Cl. Notice that the band gap changes with the selection of halide whereas MAPBI<sub>3</sub> has the best band gap for photovoltaic applications.



Figure 6. Absorbance for different organometal halide perovskites MAPbI<sub>3</sub>, MAPbBr<sub>3</sub> and MAPbCl<sub>3</sub>.

The performance of the photovoltaic solar cells mainly depends upon absorption value, and thickness of the absorption layer. Plot in Figure 7 shows the variation of performance of the solar cell with thickness of the perovskite. Usually performance of solar cell increases with increase in thickness of the perovskite. Furthermore, the plot shows that thin layer of MAP- $bI_3$  layer yields high fill factor (FF).

### 1.2.5. Defects in perovskites: intrinsic/point defect

Efficiency of a solar cell is highly affected by defects such as point/intrinsic and grain boundaries, crystalline structure and amount of doping of an absorbing material when processed via low-cost method. Electron and hole diffusion length and open circuit voltage ( $V_{OC}$ ) of a solar cell is greatly influenced by the point (Schottky and Frenkel) defects [27]. The defect densities of perovskite depend on the formation energy and hence chemical potential, it corresponds to precursors, partial pressure and temperature. The defects with low formation



Figure 7. Variation of FF and PCE with thickness of perovskite

energy create only shallow level which results the long electron-hole diffusion length and high  $V_{OC}$ . On the other hand defects with deep levels have high formation energy it results into unpleasant effect on electron-hole diffusion length and  $V_{OC}$ . Experimental and simulation results of the long electron-hole diffusion length and high  $V_{OC}$  conforms the unusual shallow defect levels [27].

In CIGS and CdTe, p-type doping is easier in equilibrium and n-type doping is rather difficult due to self-compensation. But in MAPbI<sub>3</sub> the formation energy of methylammonium (MA) interstitial defect (donor like) and iodine vacancy defect (acceptor like) have similar values that make both; p-type and n-type doping possible. Unlike other researchers, Agiorgousis et al. and Baumann et al. suggested and pointed out the strong covalent bonds and deep level defects by using first principles calculations [32, 33]. Despite that the presence of defects and traps in perovskite and particulars of their impact are so far under discussion and investigation.

### 1.2.6. Progress in perovskite solar cells

In 2009, Miyasaka et al. opened up first perovskite solar cell based on mesoporous  $TiO_2$  photoanode and observed the power conversion efficiency (PCE) 3.81% and 3.13% for MAPbI<sub>3</sub> and MAPbBr<sub>3</sub> respectively along with their poor cell stability [15].

In 2012, Kanatzidis and his coworkers synthesized alkali metal perovskite (floride doped CsSnI<sub>3</sub>) as p-type Hole Transporting Material (HTM) in dye sensitized solar cells where 10.2% PCE was reported. At the mean time, Michael Gratzel & coworkers with N. G. Park used MAPbI<sub>3</sub> as light absorber with SpiroMETAD on mesoporous TiO<sub>2</sub> where measured efficiency was 9.7%. Snaith in collaboration with Miyasaka boosted PCE and V<sub>OC</sub> to 10.9 % and 1.13 V respectively by replacing the n type mesoporous titanium oxide by an inert Al<sub>2</sub>O<sub>3</sub> scaffold [34] in the consequence of faster diffusion of electron through the perovskite.

Liu and Snaith et al. in 2013 further boosted the efficiency to 15.4% via architecturing the vapor deposition heterojunction solar cell without electron conduction scaffold [35]. Since that time

to about end of 2014, in reference [36 - 40] reported 15.6%, 15.9%, 16.7%, 19.3% and 20.1% PCE respectively. Astonishingly it is a great improvement in the efficiency for perovskite based solar cells, as shown in Figure 3, also makes the perovskite as a premising candidate for immediate future PV solar cells. The main aim of photovoltaic design is to optimize efficiency to cost ratio. In this context, among the perovskite family, MAPbI<sub>3</sub> is one who proved itself as a best and champaign material due to its favorable opto-electric behavior, long lifetime, low temperature solution processability, ferroelectricity and hence a superb photovoltaic performance. There are lots of space to further improve the efficiency and deep insight into excellent optoelectronic behavior, thermodynamic stability of the perovskite absorber and the formation mechanism of the dominant intrinsic defects.

## 2. Numerical Simulations

Simulation is a crucial technique to realize deep insight into the physical operation, viability of proposed physical explanation and effect of physical changes on performance of the solar cell devices. There are various simulation models (SCAPS, AMPS, SCAP, etc) for solar cells simulation. SCAPS (Solar Cell Capacitance Simulator) is one-dimensional simulation program with seven semiconductor input layers developed by a goup of solar cell researcher at the department of Electronics and Information System, University of Gent, Belgium [41]. It is impractical as well as wastage of time and money to design a solar cell without simulation works. It minimizes not only the risk, time and money rather analyzes layers properties and role to optimize the solar cell performance. In order to simulation a device all the basic input parameters should be well defined so that it behaves as a real counterpart. The perovskite-based solar cells have employed a similar structure with inorganic semiconductor solar cells, such as CIGS, and Wannier-type exciton in the perovskite is found. Thus SCAPS like 1D simulator can be employed to simulate the perovskite based solar cells [42].

The main features of the latest version of SCAPS, to address the basic parameters, are as follows [41]:

- up to 7 semiconductor input layers can be defined as shown in Figure 8 and 9,
- almost all parameters can be graded: band gap (Eg), electron affinity ( $\chi$ ), dielectric constant ( $\varepsilon$ ), valence and conduction band density of states ( $N_V$  and  $N_C$ ), charge carriers mobility ( $\mu_n$  and  $\mu_p$ ), accetor and donor dopant concentration ( $N_A$ ,  $N_D$ ), thermal velocity of charge carriers ( $V_{thn}$  and  $V_{thp}$ ), working temperature (T) and absorption constant ( $\alpha$  m<sup>-1</sup>) all traps (defects)  $N_t$  are to be defined,
- recombination mechanisms: band-to-band (direct), Auger, SRH-type,
- defect levels: in bulk or at interface; their charge state and recombination is accounted for,
- defect levels, charge type: no charge (idealization), monovalent (single donor, acceptor), divalent (double donor, double acceptor, amphoteric), multivalent (user defined),

	Sen	PS 5.5.00 Solar Cell Dell	nition Panel		
Layers left contact (back)	Interfaces	illuminated from :	apply voltage V to : left contact right contact	current reference as consumer generator	a
add layer					***
right contact (front)					
Info on graded parameters only available a	after a calculation				
Problem file new problem set up on: 19-6-2015 at 12:38:29	after a calculation				
Problem file new problem set up on: 19-6-2015 at 12:38:29 Remarks (edit here)	after a calculation				

Figure 8. SCAPS-Solar cell definition panel.



Figure 9. SCAPS-Solar cell definition panel with simulation

- defect levels, energetic distributions: single level, uniform, Gauss, tail, or combinations are available as shown in Figure 10,
- defect levels, optical property: direct excitation with light possible (impurity photovoltaic effect, IPV),

AYER 2	2 p-MAPbl3		p-MAPbI3	Recombination model			
thickness (μm)		0.400		Band to band recombination			
		uniform pure A (v	-0) -	Radiative recombination coefficient (cm³/s) 0.000E+0			
The layer is pure A: y	= 0, uniform	0.000		Auger electron capture coefficient (cm^6/s) 0.000E+0			
Semiconductor Prope	rty P of the pure material	pure A (y = 0)		Auger hole capture coefficient (cm^6/s) 0.000E+0			
				Recombination at defects: Summary			
bandgap (eV) 1.500			Defect 1				
electron affinity (eV)		3.930	Defect 1				
dielectric permittivity (relative)         30.0           CB effective density of states (1/cm^3)         2.5           VB effective density of states (1/cm^3)         2.5           electron thermal velocity (cm/s)         1.00           hole thermal velocity (cm/s)         1.00           hole nobility (cm?/s)         5.00           hole mobility (cm?/s)         5.00		30.000		charge type : neutral total density (1/cm3): Uniform 1.500e+12 grading Nt(y): uniform energydistribution: CB tail; Et = 0.70 eV above EV; Ekar = 0.01 eV			
		2.500E+20 2.500E+20					
			1.000E+7				
		1.000E+7 5.000E+1	inis detectioniy, if active: Lh = 9.3e+01 µm, Lp = 2.9e+02 µm				
		5.000E+1	000E+1				
		Allow Tunneling effective mass of electrons effective mass of holes	1.000E+0		Defect2 T		
effective mass of holes	1.000E+0			Defect 2			
no ND grading (uniform	m)		-	total density (1/cm3): Uniform 1.500e+12			
shallow uniform donor density ND (1/cm3) 2.140E+14			grading Nt(y): uniform energydistribution: VB tail; Et=0.70 eV above EV; Ekar = 0.01 eV this defect only, if active: tau_n = 6.7e+05 ns, tau_p = 6.7e+04 ns this defect only, if active: Ln = 2.9e+02 μm, Lp = 9.3e+01 μm				
no NA grading (uniform)							
shallow uniform acceptor density NA (1/cm3) 2.140E+17							
Absorption model							
		alpha (y=0) from mo from file	del	Edit         Edit         Edit         Add a           Defect 1         Defect 2         Defect 3         Defect 4         Defect 5			
absorption constan	tA (1/cm eV^(1/2)) 1.	.000E+5		Remove Remove Remove			
absorption constant B (eV^(1/g/cm) 0.000E+0							
	30	0\absorption\MAP	bl3.txt	(no metastable configuration possible)			
1	1	abaanding fin fam.					

Figure 10. SCAPS-Solar cell simulations with sample data and defects.

- meta-stable defects: transitions between acceptor and donor configurations for known metastable defects in CIGS: the V\_Se and the In\_Cu defect; also custom set meta-stable transitions implemented,
- contacts: work function or flat-band; optical property (reflection of transmission filter) filter,
- tunneling: intra-band tunneling (within a conduction band or within a valence band); tunneling to and from interface states,
- generation: either from internal calculation or from user supplied *G*(*x*) file,
- illumination: a variety of standard and other spectra included (AM0, AM1.5D, AM1.5G, AM1.5G edition2, monochromatic, white, etc),
- illumination: from either the *p*-side or the *n*-side; spectrum cut-off and attenuation,
- working point for calculations: voltage, frequency, temperature can be chosen by user,
- the program calculates energy bands, concentrations and currents at a given working point, *J-V* characteristics, ac characteristics (*C* and *G* as function of *V* and/or *f*), spectral response (also with bias light or voltage),

- batch calculations possible; presentation of results and settings as a function of batch parameters,
- loading and saving of all settings; startup of SCAPS in a personalized configuration; a script language including a free user function,
- very intuitive user interface,
- a script language facility to run SCAPS from a "script file"; all internal variables can be accessed and plotted via the script,
- a built-in curve fitting facility,
- a panel for the interpretation of admittance measurements.

In this study, perovskite based solar cell is simulated with three input layers; where two layers are p-type one is Hole Transporting Material and Electron Blocked Layer (say HTM), another low doped organic lead halide perovskite is used as active/absobing layer. N-type transparent conducting oxide can be used as the Electron Transporting Material (ETM) which blocks the holes. Thicknesses of HTM/MAPbI<sub>3</sub>/ETM layers are 400/450/90 nm, respectively, if not stated there. Furthermore, front and back contact are used to collect and transport the charge carriers effectively to the external circuit. The simulations were carried out under 1 Sun using differnt material to optimize the solar cell devices and to realize the role of individual layer.

### 3. Solar cells physics

The basic physical principles [9, 41, 43] of a solar cell device are given below:

### 3.1. Absorbance and absorption coefficient

When an absorbing material of thickness d is being illuminated by an electromagnetic energy (usually light) of wavelength  $\lambda$  and intensity I ( $\lambda$ ), some of light is reflected (R), some is absorbed (A) and remaining is transmitted (T) through the material. Now absorbance [A<sub>abs</sub> ( $\lambda$ )] and absorption coefficient [ $\alpha$  ( $\lambda$ )] can be defined as

$$A_{abs}(\lambda) = -\log_{10}\left[\frac{T(\lambda)}{I(\lambda) - R(\lambda)}\right]$$
(1)

$$\alpha(\lambda) = \frac{A_{abs}(\lambda)}{d}$$
(2)

### 3.2. Density of States

The valence band  $(N_v)$  and conduction band  $(N_c)$  effective densities of states are temperature dependent material properties which are given by formulae

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$$N_{V} = \frac{(m_{p}^{*})^{\frac{3}{2}}\sqrt{2}}{\pi^{2}\hbar^{3}}\sqrt{(E - E_{V})}$$
(3)

$$N_{C} = \frac{(m_{n}^{*})^{\frac{3}{2}}\sqrt{2}}{\pi^{2}\hbar^{3}}\sqrt{(E - E_{C})}$$
(4)

where  $m_p^*$  and  $m_n^*$  are effective mass of hole and electron, E, E<sub>V</sub> and E<sub>C</sub> are energy levels at steady state, valence band edge and conduction band edge respectively.

#### 3.3. Carrier concentration

In thermal equilibrium, number of free electrons and holes charge densities; n and p respectively are given by

$$n = N_C \exp(\frac{E_F - E_C}{kT_n}) = N_C \exp(\frac{V_n}{kT_n})$$
(5)

$$p = N_v \exp(\frac{E_v - E_F}{kT_p}) = N_c \exp(\frac{V_p}{kT_p})$$
(6)

Where  $E_F$  if Fermi level and V is built in potential, k Boltzmann constant and T is spatially varying electron and hole temperature.

#### 3.4. Poisson's equation

Poisson's equation defines the electric field (E) that is modified as a result of the current flowing and the charge in the delocalized states, traps and recombination centers in the device as given below

$$\frac{\partial}{\partial x}\left(\varepsilon\frac{\partial\Psi}{\partial x}\right) = -q[p-n+N_{D}^{+}-N_{A}^{-}+\frac{\rho_{def}}{q}]$$
(7)

where,  $\psi$  is electrostatic potential,  $\varepsilon$  is dielectric constant and q is electronic charge.

The first two terms in right side are free charge carriers per volume, third and fourth are ionized donor and acceptor-like dopants i.e,. localized states and  $\varrho_{def}$  is defect charge density.

### 3.5. Formula for p-n junctions diode

Solar cell behaves as a p-n junction diode. The voltage and current in ideal diode are given by formulae as below:



where n<sub>i</sub> is intrinsic carriers concentrations.

$$I = I_0[\exp(\frac{qT}{kT}) - 1] \tag{9}$$

where  $I_0$  is saturation current.

#### 3.6. Solar Cell Formulae

$$V_{OC} = \frac{nkT}{q} \ln(\frac{I_{SC}}{I_0} + 1)$$
(10)

$$J = J_0[\exp(\frac{qT}{nkT}) - 1] - J_{SC}$$
<sup>(11)</sup>

where,  $V_{OC}$ ,  $J_{SC}$  and  $J_0$  are open circuit voltage, short circuit current and saturation current density respectively.

### 3.7. Electron and hole Diffusion lengths

Collection length, a distance over which light absorption caused excitaions can be transported, is limited by diffusion, drift, or combination of the two. The electron and hole diffusion length are given by

$$L_{n}^{Diff} = \left[D_{n}\tau_{n}\right]^{\frac{1}{2}}$$
(12)

elecron diffusion length.

$$L_{p}^{Diff} = \left[D_{p}\tau_{p}\right]^{\frac{1}{2}}$$
(13)

hole diffusion length.

where  $D_n = kT_n\mu_n$  is electron diffusion coefficient,  $D_p = kT_p\mu_p$  hole diffusion coefficient,  $\tau$  s life time and  $\mu$ s mobility of electron and hole.

#### 3.8. Transport equation

Mobility of free electrons, holes, variation of carrier concentrations and hence quasi Fermi level with position result electron and hole currents. Thus, in thermal equilibrium

$$J_n = -\frac{\mu_n n}{q} \frac{\partial E_{Fn}}{\partial x} \tag{14}$$

$$J_p = +\frac{\mu_p p}{q} \frac{\partial E_{Fp}}{\partial x}$$
(15)

where  $\mu_n$  and  $\mu_p$  are electron and hole mobilities, and n and p are free electrons and holes density,  $E_{Fn}$  and  $E_{Fp}$  are electron and hole quasi-Fermi level respectively.

#### 3.9. Continuity equations

In the absence of illumination and recombinations, in steady state, the free electron current density at any point in a solar cell device must be equal to that at some other piont. Same is valid for holes too. In a device generation and recombinations both are undertaken. Thus, the conservation of free electrons and free holes in the device is expressed as continuty equations



where Gs are photo generation rates and  $\Re$  s are recombination rates in the device.

#### 3.10. Recombination

Shockley-Read-Hall (SRH), Radiative and Auger recombinations are the possible recombination mechanisms in solar cells, they are given as

$$\mathfrak{R}^{L} = \frac{\upsilon \sigma_{n} \sigma_{p} N_{T} [np - n_{i}^{2}]}{\sigma_{p} [p + p_{1}] + \sigma_{n} [n + n_{1}]}$$
(18)



Radiative recombination

$$\mathfrak{R}_{n}^{A} = \left[\frac{n-n_{0}}{\tau_{n}^{A}}\right] \tag{20}$$

$$\mathfrak{R}_{p}^{A} = \left[\frac{p - p_{0}}{\tau_{p}^{A}}\right] \tag{21}$$

#### (Eqs. 20 and 21 are Auger recombinations)

where  $\sigma s$  are capture cross-sections for electrons and holes, v electron thermal velocity,  $N_T$  number of gap states per volume,  $n_i$  intrinsic number density,  $g_{th}{}^R$  gives the number of electrons in conduction band and holes in valence band generated per unit time per unit volume and  $\tau_n{}^A \& \tau_p{}^A$  are electron and hole lifetimes.

#### **3.11.** Power conversion efficiency

The fraction of incident power converted into usefull electricity by the solar cells is termed as Power conversion efficiency ( $\eta$ ). It is given as below:

$$\eta = \frac{P_{out}}{P_{in}} = \frac{FF \times V_{OC} J_{SC}}{P_{in}}$$
(22)

Fill Factor 
$$FF = \frac{V_{mp}J_{mp}}{V_{OC}J_{SC}}$$
 (23)

where  $V_{\mbox{\scriptsize mp}}$  and  $J_{\mbox{\scriptsize mp}}$  are voltage and current at maximum power point respectively.

### 3.12. Work function of contacts

In most of the cases work function of the front and back contacts are well defined. Otherwise, in flat band case the work function of contact (s) is calculated as follows:

$$\Phi_{m} = \chi + k_{B}T \ln(\frac{N_{C}}{N_{D} - N_{A}})$$
(24)
when contact is n-type
$$\Phi_{m} = \chi + E_{g} - k_{B}T \ln(\frac{N_{C}}{N_{A} - N_{D}})$$
(25)

when contact is p-type

$$\Phi_m = \chi + k_B T \ln(\frac{N_C}{n_i})$$
(26)

when contact is intrinsic.

where  $\Phi_m$  is workfunction of metal/material,  $\chi$  is electron affinity,  $k_B$  is Boltzmann constant, T is operating temperature,  $N_C$  is conduction band effective density of states, and  $N_A$  and  $N_D$  are shallow acceptor and donor dopant concentrations respectively.

### 4. Results and Discussions

Figure 11 is the absorptance plots where the absorption coefficient,  $\alpha$  (1/m) of titanium oxide is derived from reference [44], Zinc oxide is from SCAPS abs. file and that of MAPbI<sub>3</sub> is based on [45, 46]. The absorption coefficient for MAPbI<sub>3</sub> perovskite displayed in the Figure is very similar to that measured for perovskite synthesized in UPV laboratory, Valencia, Spain. The energy band diagram for the solar cell used in the simulation is shown in Figure 12.

From Figure 11, it is clear that the cutoff wavelength of perovskite lays around 825 nm so, the band gap  $\approx$  1.5 eV, which is the closer value required for ultimate theoretical limit according to W. Shockley and H. J. Queisser [18]. The band gap of perovskite depends on size of organic/ inorganic (larger cation), metal (small cation), and halide (anion) components chosen during the processing and preparation. Increase in size of the cations and anion changes the covalent character between the cation (s) and anion and size of ionic radius which ultimately yields blue shift and red-shift respectively of the band gap [22, 47]. The band gap of the absorbing material is a crucial parameter for photovoltaic action as the absorber is the key material in a solar cell device [9]. Thus, suitable combination of the cationic components and anionic component in

perovskite results into an extremely suitable absorber to yield the solar cells of better performance.



Figure 11. Absorbance of ZnO, TiO<sub>2</sub> and MAPbI<sub>3</sub>



Figure 12. Energy band allignment

The **absorber layer**, **charge transporting layers**, front and back contacts, defects, interface and surface property are the major components and properties they have effect on the performance of the solar cell systems. **Operating temperature** of the solar cells plays a vital role in the performance of the PV devices. Considering these facts the simulation works are undertaken to find out role of individual layer and their associated properties which are briefly discussed below.

### 4.1. Role of absorber

As absorber is the key component in the solar cell devices the deep knowledge and understanding about this matter is crucial to design and fabricate a solar cell. Here our study has focused on realization of role of absorber to make more practical and optimization of the performance of the PV devices. For compensation ( $N_A/N_D$ ) ratio and Gaussian energy distribution we have chosen two ETMs; TiO<sub>2</sub> and ZnO. Simulation with different aspects of the absorbing material is discussed below.

### 4.1.1. Variation of thickness of the absorber

### 4.1.1.1. Without considering interface trap density of states

Performance of the cell depends mainly on optoelectronic characteristics and thichness of the absorber layer. Thus simulations are carried out to examine the device parameters with thickness of the absorber from 50 nm to 700 nm under 1 Sun (AM1.5G) illumination. First of all simulations were carried out without considering interface trap density of states neither shallow minority carrier concentration. But inputs value of band tail density of states, and Gaussian acceptor/donor states of MAPbI<sub>3</sub> were  $10 \times 10^{14} \, \text{eV}^{-1} \text{cm}^{-3}$  and  $10 \times 10^{14} \, \text{cm}^{-3}$  respectively. The short circuit current and PCE both are found to be increased sharply with increase in thickness up to 500 nm as shown in Figure 13. After this, increment is very slow and reaches to almost optimal efficiency 25.22%, V<sub>oc</sub> 1.2 V, J<sub>sc</sub> 25.49 mA/cm<sup>2</sup> and FF 82.56% at 700 nm which is closed to the detailed bance limit [18]. At the 700 nm thickness MAPbI3 absorbs almost incident photons to create the electron-hole pairs and the photo generated almost carriers are separated and transproted to the HTM and ETM by the built in field with minimum recombination thus, it can be consider as the length of optimal photovoltaic action.

### 4.1.1.2. Considering interface trap density of states

Dark current and current under illumination in PV solar cells are illustrated in Figure 14. In dark, solar cell behaves as a large flat diode and produces a very small current due to the minority charge carriers in the device structure which resembles to J-V characteristics of a pn junction diode. Device without trap defect is not possible so, to make more practical solar cell we introduce the total trap density =  $1.0 \times 10^9$  cm<sup>-2</sup> in the interfaces and added shallow level donor and acceptor density N<sub>D</sub> = 10% of N<sub>A</sub> and N<sub>A</sub> = 10% of N<sub>D</sub> in HTM and ETM respectively. Simulation results shown in Figures 7 is quite interesting and suggested to more rational. State of affairs here is somewhat different than the former case. It reveals that: i) the device parameters are found to be decreasing with introduction of interface traps due to change in shunt



Figure 13.  $J_{SC}$  and PCE vs thickness



Figure 14. J-V curve as a function of illuminations

resistance, ii) parameters are increasing more or less steeply up to 350 nm and very slowly beyound 450 nm, iii) fill factor is observed maximum value of 82.24% for 100 nmthickness where other parameters also have significant values. The results show that 450 nm thickness is also sufficient for good photovoltaic action. Furthermore, 700 nm is sufficient for optimal photovoltaic performance where  $V_{OC}$ ,  $J_{SC}$ , FF and PCE are observed 1.12 V, 25.49 mA/cm<sup>2</sup>, 82.29% and 23.48% respectively. Beyond this thickness there might increase in resistance that

results in insignificant increment in PCE. The rate of the photogeneration of charge carriers depends on the amount of light reaching, absorption range and thickness of the absorber, here MAPbI<sub>3</sub> perovskite since it is the key component of the solar cell. Figure 15 is the quantum efficiency curves as a function of wavelength of incident light for different thickness of the absorber also verifies the above mentioned upshot. Besides, our results for an absorber thickness of 400 nm is similar but expected to improve to move towards the practicality than reported by [45].



Figure 15. Variation of quantum efficiency with thickness of absorber.

### 4.1.2. Band tail density of states of perovskite

The input parameters for band tail density has varied from  $1.0 \times 10^{12}$  eV<sup>-1</sup>.cm<sup>-3</sup> to  $1.0 \times 10^{17}$  eV<sup>-1</sup>.cm<sup>-3</sup>. J-V curves as a function of band tail defect is shown in Figure 16, which shows the defects in the absorber has greatly influenced the V<sub>OC</sub>, and finally to the performance of the device. Infact, band tail density of states are the intra-band gap states which may act as recombination centers for charge carriers and are also called defects in layer (s) of the solar cell. Simulation studies have envisaged that similar nature is not observed for HTM and ETM as reported by [45] too, since photogeneration of the charge carriers is taken place in the absorber say active layer. The Figure 16 tells that defects do not significantly influence the J<sub>SC</sub> since amount of incident photon and thickness are remaing unchanged. Relatively higher value of V<sub>OC</sub> is observed which is similar to [45, 48, 49]. It is also observed that V<sub>OC</sub> and J<sub>SC</sub> are almost same from  $1.0 \times 10^{12}$  to  $1.0 \times 10^{14}$  eV<sup>-1</sup> cm<sup>-3</sup>. These are the consequences of the larger absorption rang, high crystalinity, low pinhole, shallow level defect densities and a prolonged

electron-hole lifetime in perovskite which are characteritics of materials and also created unintentionally/purposefully during the deposition/coating/processing the layer (s). Similar result is reported by L. M. Herz et. al. [49].



Figure 16. JV curve as a function of band tail density of states

### 4.1.3. Role of interface trap density

Research process always endeavor towards the perfect by realizing and optimizing the overall behaviours of the material. So, simulations were carried out with setting the interface trap densities from  $1.0 \times 10^8$  cm<sup>-2</sup> to  $1.0 \times 10^{14}$  cm<sup>-2</sup> and studied the results. Figure 17 shows that V<sub>OC</sub> and PCE are decreasing with increase in interface trap density upto  $1.0 \times 10^{13}$  cm<sup>-2</sup> and remaining almost same beyond this. Figure 18 shows that QE is considerably small when trap density is above  $1.0 \times 10^{11}$  cm<sup>-2</sup>. The plots show the crucial role of interface trap density in efficiency of the solar cells since interface traps at high level are also the recombination centers and hence change in shunt resistance. Optimizing doping of the HTM and ETM, and formation of homogeneous, smooth, and flat surface will significantly reduce the interface trap density.

### 4.1.4. Compensation ratio $(N_A/N_D)$ of the absorber

For this study, simulation works have been carried out with two different ETMs;  $TiO_2$  and ZnO. Figure 19 shows the effect of compensation ratio in MAPbI<sub>3</sub> perovskite. In this case, simulation works have been carried out with variation of compensation ratio from 0 to 20%. Increase in compensation ratio of perovskite, an absorber, and results into slightly decreased in the performance of the PV devices in both cases suggested to increase in recombination/loss within it. The similar effect which has been observed in both ETMs increases the aptness of substituting  $TiO_2$  by ZnO.



Figure 17.  $V_{\text{OC}}$  and PC vs interface traps



Figure 18. QE as a function of interface traps

### 4.1.5. Gaussian Energy Distribution in Perovskite

Figures 20 and 21 are the JV curves as the function of the Gaussian energy distribution (defect) of MAPbI3 perovskite. Simulations have been carried out with varying the defect values from  $10^{12}$  to  $10^{19}$  cm<sup>-3</sup>. It is found that V<sub>OC</sub> and hence PCE of PV devices have been decreasing with increase in Gaussian defect for both ETMs. Beyond  $10^{17}$  cm<sup>-3</sup> i.e., at high defect levels performance of the device goes significantly decreasing due to more recombination, loss and change in resistance.



Figure 19. PVC Parameters vs Compensation ratio  $(N_{\text{A}}/N_{\text{D}})$  of  $MAPbI_{3}$ 



Figure 20. Gaussian Defects of Perovskite with TiO<sub>2</sub>

#### 4.2. Role of Electron Transporting Materials

Two usual conducting oxides; titanium oxide and zinc oxide have been used to analyze the role of electron transporting layer in the heterojunction thin film solar cells. The band gap and



Figure 21. Gaussian Defects of Perovskite with ZnO

electron affinity of the materials should be such that it conducts the free electrons and creates barrier to the holes. Here simulation works are carried out with varying layer properties of two transparent conducting oxides as ETMs. They are briefly discussed below.

### 4.2.1. Thickness of the ETMs

Figure 22 is the plot of solar cell parameters;  $V_{OC}$ ,  $J_{SC}$ , FF and PCE versus thickness of the ETMs; TiO<sub>2</sub> and ZnO. In both cases  $V_{OC}$ ,  $J_{SC}$  and PCE are gradually decreasing due to fractional absorption of incident light by the ETMs layer, the bulk recombination and surface recombination at the interface and change in series resistance. Thickness of ETMs has been varied from 50 nm to 450 nm to make the practical devices. Observation showed that TiO<sub>2</sub> is more sensitive than that of ZnO due to its high absorption coefficient and reflectance and less transmittance than ZnO. It is obvious that the increase in thickness of the ETM lessen the performance of the solar cells due to increase in partial absorption of photons and resistance of the device.

Moreover, we have carried out simulation works with practically viable thickness of  $TiO_2$  - ETM as shown in Figure 23 which is the plot of FF and PCE as a function of thickness of  $TiO_2$ . FF and PCE are gradually decreasing due to fractional absorption of incident light by the  $TiO_2$  layer, the bulk recombination and surface recombination at the interface [22]. But fill factor in this case is found to be slightly increasing with increase in thickness suggested the higher conductivity of the  $TiO_2$  than MAPbI<sub>3</sub> and SpiroMeOTAD and partial absorption of the light.

### 4.2.2. Band tail density of states of perovskite

Figure 24 and 25 are the J-V curves as a function of band tail defect varies from  $10^{12}$  to  $10^{17}$  eV<sup>-1</sup>.cm<sup>-3</sup>. The plots show that the defects in the absorber has influenced the V<sub>OC</sub>, and finally to the performance of the device due to the change in shunt resistance. Band tail density of states



Figure 22. Variation of PV cells parameters with thickness of ETMs



are particularly intra-band gap recombination centers are also called defects. Both the Figures tell that defects do not significantly influence the  $J_{sC}$  since amount of incident photon and thickness of system are remaing unchanged. Relatively higher value of  $V_{OC}$  is observed as [48, 49]. It is also observed that  $V_{OC}$  and  $J_{sC}$  are almost same from  $1.0 \times 10^{12}$  to  $1.0 \times 10^{14}$  eV<sup>-1</sup> cm<sup>-3</sup>.

These are the consequences of the larger absorption rang, high crystalinity, low pinhole, shallow level defect densities and a prolonged electron-hole lifetime in perovskite which are characteritics of materials and also created unporposefully/purposefully during the coating/ processing/fabrication of the layer (s). This is similar result as reported by [49]. Furthermore,  $TiO_2$  has found relatively less sensitive than in ZnO due to small electron mobility and higher doping concentration than ZnO.



Figure 24. Band Tail of Perovskite with TiO<sub>2</sub> as ETM



Figure 25. Band Tail of Perovskite with ZnO as ETM

### 4.2.3. Interface trap density of states

Figures 26 and 27 are the JV curves as a function of interface trap density varied from  $1.0 \times 10^8$  to  $1.0 \times 10^{15}$  cm<sup>-2</sup>. It is quite clear from the plots that V<sub>OC</sub> and PCE are decreasing with increase in interface trap density upto  $1.0 \times 10^{14}$  cm<sup>-2</sup>. It shows that interface trap increases the recombination centers and hence change in shunt resistance. There is decrease in J<sub>SC</sub> with the interface trap beyond  $1.0 \times 10^{12}$  cm<sup>-2</sup> suggested to increase in series resistance. Relatively more

sensitiveness of ZnO than  $TiO_2$  towards interface trap indicates the relatively small defect and small electron mobility of  $TiO_2$ . Optimizing doping of the ETM, and formation of homogeneous, smooth, and flat surface will significantly reduce the interface trap density and hence increase the performance.



Figure 26. Interface Trap of Perovskite with TiO<sub>2</sub>



Figure 27. Interface Trap of Perovskite with ZnO

### 4.2.4. Role of Dopant Concentrations of ETMs.

The plot of PV cell parameters as a function of dopant concentration ( $N_D$ ) of both ETMs TiO<sub>2</sub> and ZnO is shown in Figure 28. The study has been carried out from 10<sup>15</sup> to 10<sup>21</sup> cm<sup>-3</sup> values. Both ETMs have exhibited the similar performance here too.  $V_{ocr}$  FF and PCE have been increasing with increase in dopant concentration of TiO<sub>2</sub> and ZnO up to around 10<sup>18</sup> cm<sup>-3</sup> due to the increase in conductivity of ETM. Although dopant concentrations have been increasing beyond this value PV parameters remain unchanged due to Moss-Burstein effect [50].Variation of dopant concentration of TiO<sub>2</sub> is found to be little bit more sensitive than that of ZnO up to around 10<sup>18</sup> cm<sup>-3</sup> due to smaller value of electron mobility and hence small conductivity of TiO<sub>2</sub>.



4.2.5. Interface Trap Electron/Hole Capture Cross-Section.

Figure 29 shows the effect of interface trap electron/hole capture cross-section for both interfaces on performance of the device where the value varies. The electron/hole capture cross-sections have been varied from  $10^{-14}/10^{-15}$  and  $10^{-15}/10^{-14}$  to  $10^{-20}/10^{-21}$  and  $10^{-21}/10^{-20}$  cm<sup>2</sup> for first and second interfaces respectively. Plots show that V<sub>OC</sub> and PCE both are decreasing with increase in cross-section of TiO<sub>2</sub> and ZnO due to increase in recombination/loss and change in shunt resistance. ZnO is observed more sensitive than that of TiO<sub>2</sub> toward the higher values of interface trap electron/hole capture cross-sections. It is suggested that ZnO has such more defects than TiO<sub>2</sub> and hence less efficient in real practice.



Figure 29.  $V_{OC}$  and PCE vs Interface Trap Electron/Hole Capture Cross-section.

#### 4.3. Role of HTM

#### 4.3.1. Role of thickness of the HTM

Figures 30 is the plot of FF and PCE versus practically viable thickness of the



Figure 30. Variation of FF and PCE with thickness of HTM.

HTM (Spiro-MeOTAD). In the case of HTM, fill factor and PCE both are decreasing with increase in thickness suggested the increase in recombination and resistance. Thus, a superb junction diode like contact between the absorbar and HTM is necessary to increase the fill

factor and hence to improve the efficiency of the device. It is obvious that the decrease in thickness of the HTM improves the performance of the solar cells due to decrease in recombination and resistance of the device.

### 4.3.2. Role of hole mobility and acceptor concentration of the HTM

Figures 31 and 32 show the effect of hole mobolity and acceptor contrantration of HTM respectively on the device performance. The Spiro-MeOTAD has relatively low hole mobility value. Note that different researcher [34, 45, 51] have reported different values of hole mobility of SpiroMeOTAD but  $2.0 \times 10^4$  cm<sup>2</sup>/V s has been used in this study. Due to small value of hole mobility and acceptor concentration low value of FF and hence the low PCE are observed. The value goes on increasing with increase in hole mobility and acceptor concentration. Properties such as hole mobility and dopant concentration (N<sub>A</sub>), are responsible for resistance/conductance of the HTM, here Spiro-MeOTAD, they highly influence the performance of the device. Although Spiro-MeOTAD has merits either enhencement of conductivity and dopant concentration of this material or replacement of it by suitable HTM is highly appreciable for better performance of the device.



Figure 31. J-V curve as a function of hole mobolity.

#### 4.4. Role of front and back contacts

#### 4.4.1. Role of workfunction of the back contact metal

In this case, simulations were carried out at thicknesses 400/400/90 nm of the device layers so as to compare the outcome with references [45, 46]. Figure 33 is the plot of fill factor and PCE versus workfunction of the counter electrode. It is found that fill factor and PCE both are



Figure 32. J-V curve as a function of dopant concentrations (N<sub>A</sub>).

decreasing with decrease in workfunction of the back contact metal. Back contact is the counter electrode connected to the HTM to collects the holes or to enter the almost relaxed electrons into the device from the external circuit. Figure 12 shows the energy band alignment between different layers of the device.



Figure 33. FF and PCE vs workfunction of back contact.



Figure 34. PV all parameters vs workfunction of front contact.

An ohmic contact between them is necessary to transport the holes efficiently to the back contact. As workfunction of back contact is 5.0 eV or above than the HTM i.e., workfunction of the back contact is nearly equal to or slightly greater than that of HTM then holes transport effectively and there would be barrier for electrons. Below 5.0 eV a dipole oriented positive in the metal and negative in the HTM results an electrostatic barrier to the holes or Schottky barrier [9] and hence difficultly arise in holes transportation at contact. This indicates the requirement of gold (workfunction = 5.1 eV) like higher workfunction material to develop ohmic contact to conduct the hole to the electrode [44, 45, 47]. Moreover, it is quite clear from the Figure 33 that, at workfunction 4.64 eV i.e., of Ag [52], PCE is decreased to about 18 % with  $V_{OC}$  = 1.12 V<sub>JSC</sub> = 24.32 mA/cm<sup>2</sup> and FF = 69 %. This result has close agreement with the experimentally determined value 15. 4% PCE, 1.07 V V<sub>OC</sub>, 21.5 mA/cm<sup>2</sup> J<sub>SC</sub> and 67% FF for MAPbI<sub>3</sub> perovskite based planner solar cell with the Ag as counter electrode [46]. Thus, our result claims the realism in performance of device than reported by [45]. Consequently, it always opens the pathway to replace the Au-counter electrode if someone is focused on the cost. Besides, there are other options too with favorable high value workfunction material to replace the counter electrode [53].

#### 4.4.2. Role of workfunction of the front contact

For the sake of convenient and to make real solar cells simulations were carried out at thicknesses 400/400/90 nm of the device layers. Figure 34 is the the PV all parameters versus workfunction of the electrode/front contact. It is found that fill factor and PCE both are increasing with decrease in workfunction of the front contact material. Front contact is the electrode connected to the ETM to collects the energetic electrons to go round the external circuit to do some useful work over there and at the mean time it allows the light to reach the

absorber. Figure 12 shows the energy band alignment between different layers of the device. An ohmic contact between them is necessary to transport the electrons efficiently to the front contact. As workfunction of front contact is slightly smaller than or nearly equal to the workfunction of the ETM, there is ohmic contact for the electrons and barriers for the holes. Thus, a comparatively low workfunction and transparent material is suitable to use as front contact material.

### 4.5. Role of temperature

Usually in simulation studies and fabrications 300K is chosen as the operating temperature where it is regarding as the room temperature. In actual practice the operating temperature varies with latitude, altitude, day of the year and time of the day of the place concerned. Moreover, performance of a solar cell is affected by the operating temperature as well. In this context we have varied the temperature from 277K to 410K to realize actual behavior of the perovskite based solar cells.



Figure 35. Variation of PV parameters with temperature (K)

Figure 35 shows the variation of PV parameters with variation of operating temperature of the solar cells where performance of the solar cells is influenced by operating temperature. At temperature lower than room temperature the solar cells have exhibited higher performance and at room temperature all PV parameters have moderate value. The temperatures above room temperature have detrimental to the overall performance. At higher temperature the carrier concentrations, mobility of the charge carries, resistance and band gap of the materials would be greatly affected that would ultimately alter PV parameters. Figure 36, JV curve as a function of temperature, conforms the variation of  $V_{OC}$ , FF and hence resistance in the solar cell devices.



Figure 36. JV curve as a function of temperature

### 4.6. Concentrator solar cells and multi-Sun

Figure 37 is the solar irradiance at air mass zero (AM0, i.e., extraterrestrial irradiance) and air mass 1.5 global (AM1.5G, terrestrial irradiance). When sunlight enters the Earth's atmosphere then there is absorption, transmission, reflection, and scattering the light by ozone, oxygen, water in different phases, carbon dioxide and atmospheric contents. As a consequence the extraterrestrial radiation greatly modifies into global (direct plus diffuse) radiation on the Earth's surface. Extraterrestrial radiation is concerned mainly to the PV devices in space where as global is significant to the terrestrial activities including PV solar cell devices.



**Figure 37.** Solar irradiance vs wavelength for different air mass.



Figure 38. PV parameters vs Air Mass.

Figure 38 shows the variation of all PV parameters with solar spectrum in different air mass for perovskite as absorber. Efficiency is maximum at AM1.5G. Fill factor is went regularly decreasing from AM1.5D to AM0. Intense light would be changed the temperature, carrier concentrations, band gap, mobility of the charge carriers and resistance they would ultimately change the performance of the PV devices.



Figure 39. Solar spectrums at different Suns.

Variation of solar irradiance for different 'Sun' is illustrated in figure 39. An array of mirrors or lenses have been employed in order to focus onto a small sized absorber which is thereby subjected to intense sunlight for the generation of energy in one form to another [54] this is so called 'multi-sun' which enhances efficiency and reduce the size of the solar cell devices and the PV device is called concentrator solar cells.



Figure 40. PV parameters vs Suns.

Figure 40 shows the effect of 'multi-sun' on the performance of the solar cell devices. Observations found that this is effective from 2 'Sun' to around 30 'Suns' and maximum values are found at around 5 Suns for the perovskite solar cells. After 30 'Suns' they produce detrimental effect to the performance which would be due to change in carrier concentrations, mobility of the charge carries, resistance and band gap of the materials.

# 5. Conclusions

In this paper we have discussed the outcome of a simulation study on organometal halide perovskite focusing on the role of the different layers of the solar cell using SCAPS as a simulation tool. An interestingly high performance; PCE 22.72%,  $V_{OC} = 1.12 \text{ V}$ ,  $J_{SC} = 24.66 \text{ mA/} \text{ cm}^2$ , and FF = 82.12% have been observed for 450 nm thickness of absorber. Increase in thickness of the absorber has increased the PCE. In the case of HTM and ETM performance has been decreasing with increase in thickness. The higher values of  $J_{SC}$ ,  $V_{OC}$ , FF, and quantum efficiency plots have proved the low pinholes and shallow defect density, outstanding absorption range and strength. The hole mobility and acceptor/donor concentration of the HTM and ETM, Band tail of perovskite, interface trap density and workfunction of back and front contacts (electrode

and counter electrode) have shown significant influence on the device performance. Even with these strong merits of HTM and ETM, enhancement of hole mobility and conductivity of HTM and ETM, stability of perovskite and  $TiO_2$  and replacement of toxic lead are still crucial. Through suitable processing/synthesizing of the perovskite absorbers, best engineering the selective contact, and increasing conductivity of HTM and ETM will boost the stability as well as performance of the device.

This paper has also been focused on the study of two Electron Transporting Materials on organometal halide perovskite based solar cells. An interestingly high PCE, in both cases, have been found for 400 nm thickness of absorber. ZnO as ETM has been found slightly more efficient than  $TiO_2$  by using similar baseline parameters. In the case of increase in thickness of the ETMs PCE have found significant influence but the effect in  $TiO_2$  is more prominent than in ZnO due to low hole mobility and somewhat more absorption as well as less transmission of light through  $TiO_2$ . Furthermore, dopant concentrations of ETMs and compensation ratio  $(N_D/N_A)$  of perovskite have also changed the performance of the devices due to increase in conductivity and recombination/loss respectively. This study has pointed out two things - first, ZnO is found slightly more defective than  $TiO_2$  as practical solar cell with ZnO is less efficient. Although simulations have shown ZnO to be more efficient than  $TiO_2$  in real practice it is less efficient since ZnO possessed relatively more band tail and interface traps. Second, ZnO is a good alternative of  $TiO_2$  for highly efficient solar cells to reduce the cost and enhance the electron mobility.

Change in temperature and illumination have affected the performance of the solar cells due to change in carrier concentrations, mobility of the charge carries, resistance and band gap of the materials.

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