

Numerical Simulation of $\text{Ch}_3\text{Nh}_3\text{PbI}_{3-x}\text{Cl}_x$ Perovskite solar cell using SCAPS-1D

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ABSTRACT: In this article, the performance of mixed halide perovskite layer ($\text{Ch}_3\text{Nh}_3\text{PbI}_{3-x}\text{Cl}_x$) is investigated using a computer based software known as solar cell capacitance simulator (SCAPS-1D). Solar cell capacitance simulator was developed by Marc Burgelman at the University of Gent. SCAPS is used to analyses the micro and poly crystalline and photonic structure. SCAPS measure various parameters of a solar cell like open circuit voltage, Fill Factor, Short circuit current density, PCE. SCAPS and runs using the governing equations which includes continuity equations, Poisson equation, of electron and hole. The solar cell structure is based on the mixed perovskite compound as an absorber layer and Pedot:Pss is used as a HTM; PCBM is used as an ETM. The contact materials are FTO coated glass (Front contact) and Al (back contact) is used. The total cell structure Al/PCBM/ $\text{Ch}_3\text{Nh}_3\text{PbI}_{3-x}\text{Cl}_x$ /Pedot:Pss/FTO coated glass, represents the inverted planar hetero junction architecture. We study the influence of absorber layer thickness, defect density on the performance of the device. Effect of working temperature on the efficiency of solar cell is clearly explained. The thickness of absorber layer is increased from 300nm to the 900nm and observed that moderate thickness is necessary for achieving good efficiency and the quality of the absorber layer is understand by the defect density. The defect density is varied from 10^{14} cm^{-3} to 10^{16} cm^{-3} . Studying the influence of defect density on the PCE is very important to understand the material properties. By varying the temperature from 300K to 450K, we can understand the influence of temperature on power conversion efficiency. The optimization was done by taking the thickness of absorber layer as 450nm and the defect density as 10^{14} cm^{-3} and the operating temperature is 300K, with these parameters the efficiency greater than 26% is predicted. Simulation results will give good results for feasibly fabricating high efficiency mixed halide perovskite solar cell. Validation of simulation model was done by comparing with an experiment.

Keywords: $\text{Ch}_3\text{Nh}_3\text{PbI}_{3-x}\text{Cl}_x$, SCAPS-1D, Planar hetero junction, Simulation, Solar cell.

I. INTRODUCTION

From past seven years, the perovskite solar cell efficiency has been increasing enormously from 3.8% (2009) to 22.1% (2016) [1-4]. Excellent Opto-electronic properties of perovskite materials such as long diffusion length for carrier transport and broad absorption spectrum that covers the maximum visible region [5-6], encouraging to use the perovskite material to use as absorber materials in solar cells. Inorganic-organic hybrid perovskite bring down the cost of large scale solar cells. The performance of a total device and the film quality strongly depends upon the various deposition and processing conditions. There are various deposition techniques are currently using to develop the methyl ammonium lead halide perovskite solar cells which includes, one step deposition or two step solution processed, vapour deposition, vapour assisted process [7-20]. Doping the $\text{Ch}_3\text{Nh}_3\text{PbI}_3$, with chlorine results a new mixed halide perovskite material, having long diffusion length compatible with different architectures [21-22]. Mixed halide perovskite material will be formed by co-evaporating MAI and PbCl_2 onto the substrate. Chlorine doping, improves the uniformity of the film with that there is a considerable increase in the diffusion length up to 1 μm . Recent reports showed that the chlorine presence improves the carrier transport at the interfaces of the architecture [23]. However stability issue of the perovskite solar cells has to be resolved.

II. METHODOLOGY

To understand the physical mechanism of the device simulated model is necessary. A very few simulations were reported in past. In this work we used the computer based simulation software known as solar cell capacitance simulator (SCAPS). SCAPS was developed by Burgelman, at the university of Gent, Belgium and allow the researchers to make access free. SCAPS runs based semi-conductor equations those are continuity, Poisson, semi-conductor equations. SCAPS measures FF, Voc, Jsc, efficiency of a simulated model. By simulating the defined profiles model, using SCAPS we can understand the various profiles such as band gap profiles, recombination profiles etc and every measurement can be done in light and dark conditions.

The basic equations of SCAPS programme are as follows:

The continuity equation electrons and holes are:

$$\frac{dJ_n}{dx} = G-R \quad (1)$$

$$\frac{dJ_p}{dx} = G-R \quad (2)$$

The Poisson equation is

$$\frac{d^2\phi(x)}{dx^2} = \frac{e}{\epsilon_0 \epsilon_r} (\rho(x) - n(x) + N_D - N_A + \rho_p - \rho_n) \quad (3)$$

The Drift and Diffusion Equations are:

$$J_n = D_n \frac{dn}{dx} + \mu_n n \frac{d\phi}{dx} \quad (4)$$

$$J_p = D_p \frac{dp}{dx} + \mu_p p \frac{d\phi}{dx} \quad (5)$$

Where J_n = Electron Current Density.

J_p =Hole Current Density.

R = Recombination Rate

G= Generation Rate

ϕ = Electrostatic potential

e = Electric Charge

ϵ_0 =Vacuum Permittivity

ϵ_r =Relative Permittivity

p and n are hole and electron concentration

N_D =Charged impurities of donor

N_A =Charged impurities of acceptor

ρ_p and ρ_n are holes and electron distribution.

III. DEVICE ARCHITECTURE

The $CH_3NH_3PbI_{3-x}Cl_x$ based solar cell adopts the inverted planar architecture with Poly(3,4-ethylenedioxy thiophene)polystyrene sulfonate(PEDOT:PSS), a polymer material is used as a HTM material and Phenyl C-61 Butyric acid methyl ester (PCBM) as an electron transport material, in between the HTM and ETM, an absorber layer is inserted and the total architecture is completed with the suitable contact materials those are FTO coated glass(front contact) and Al(back contact).

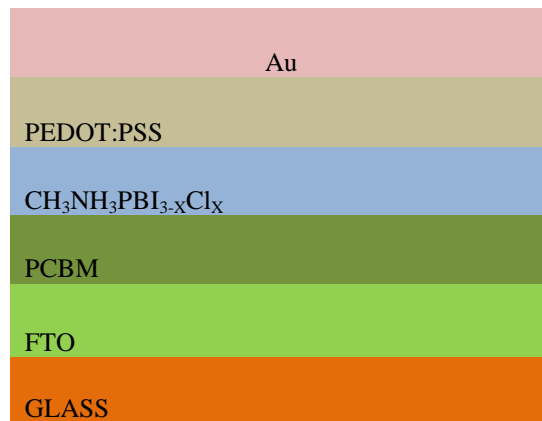


Fig: 1 Schematic representation perovskite solar cell

IV. SIMULATION PARAMETERS

The parameters used for the simulation are taken from the experimental procedures and numerical analysis was done by using different tools and programme.

Table 1. The parameters set for $CH_3NH_3PbI_{3-x}Cl_x$ based solar cell at 300K and at A.M. 1.5G

Parameters	PEDOT:PSS	$CH_3NH_3PbI_{3-x}Cl_x$	PCBM
Thickness(μm)	40	0.450	0.050
Band gap(eV)	3.6	1.730	1.300
Electron affinity(eV)	1.57	3.8	3.75
Dielectric permittivity(relative)	3.0	6.5	9.000
CB effective density of states($1/cm^3$)	$2.200E+17$	$2.200E+17$	$1.500E+18$
VB effective density of states($1/cm^3$)	$1.800E+19$	$1.800E+19$	$1.000E+19$
Electron thermal velocity(cm/S)	$1.00E+7$	$1.00E+7$	$1.00E+7$
Hole thermal velocity(cm/S)	$1.00E+7$	$1.00E+7$	$1.00E+7$
Electron mobility($cm^2/V.S.$)	$1.000E+1$	$2.000E-1$	$2.000E-3$
Hole mobility($cm^2/V.S.$)	$4.000E+2$	$2.000E-1$	$2.000E-4$

V. RESULTS

Effect of absorber thickness on the efficiency:

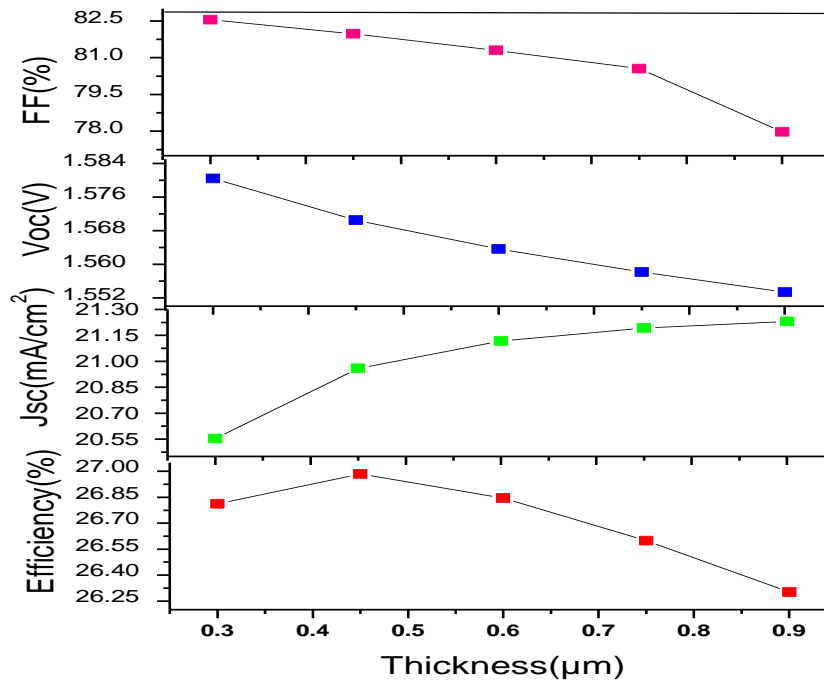


Fig:2 Graph representing the variation of PV Parameters by varying the thickness

The thickness of perovskite shows the effect on the effect on exciton generation and extraction of charge carriers. Recent experimental studies providing the information that the thickness of $CH_3NH_3PbI_{3-x}Cl_x$ is in between the 400nm-800nm[24-26] in both the planar and inverted architectures. The range of thickness of absorber layer is in between the 400nm-800nm having the diffusion length(1000nm) which is more than $CH_3NH_3PbI_3$ perovskite material.

In this simulation work we vary the thickness of perovskite layer from 300nm-900nm, to optimize the thickness and to get the high efficiency. From the above graph(thickness versus efficiency) it is showing that as the thickness is changing from 300nm, the efficiency slowly increases up to 450 nm and later slowly decreases. Increase of efficiency with increasing thickness representing the production of new charge carriers and thickness increases more than 500nm, the efficiency slowly decreases representing the increases of recombination and less extraction rate of electron and hole pairs. The main reason for the increase of efficiency with the increase of thickness is the increase of optical density. As the thickness exceeds more than,400nm then there is a mismatch between the carrier diffusion length and absorption depth of absorber layer, due to this the charges will recombine before reaching to the electrodes. It is mandatory for optimizing the thickness to achieve good efficiency. If we observe the J_{sc} versus thickness graph as the thickness increases J_{sc} also increases and reaches to the $21.30mA/cm^2$ and it saturates in between the 800nm to 900nm. The short circuit current density mainly

depends upon the generation of electron-hole pairs. Increase of short circuit current density representing the generation of electron-hole pairs. Increased resistances and recombination are the reason for the slight decrease in of FF and Voc. When the doping profiles of the absorber layer of the conduction band and the valence band are in the order of 10^{14} cm^{-3} , and the thickness of the layer is set to be 850nm, then the PCE of the device is 5.15%, which is comparable with the experimental result[27] assuring that the simulation model is valid.

Influence of defect density of absorber : To optimize the functioning of absorber layer, there is necessary of understanding the effect of defect density on the performance of a device. Practically there are point defects are observed in $CH_3NH_3PbI_{3-x}Cl_x$ layer. From the below graph Increase of defects in the absorber layer, leads to be decreased all the solar cell characteristics such as FF, Voc, Jsc, efficiency. Presence of defects are the main responsible for the recombination of charge carriers. The defect energy levels of an absorber layer is explained by the Gaussian-Distribution model. The recombination centres appears at deep energy levels are known as Schokely-Red Hall non-radiative centre. SRH model clearly explains the defect density of absorber layer. SRH model equation is as follows:

$$R = \frac{np - n_i^2}{\tau_p \left(n + N_C e^{\frac{(E_g - E_i)}{KT}} \right) + \tau_n \left(p + N_V e^{\frac{E_i}{KT}} \right)} \quad (6)$$

Here ‘n’ and ‘p’ are the concentration of electrons and holes.

If $qV > KT$; then n_i^2 will be neglected.

τ_n, τ_p are the life time of electron and hole.

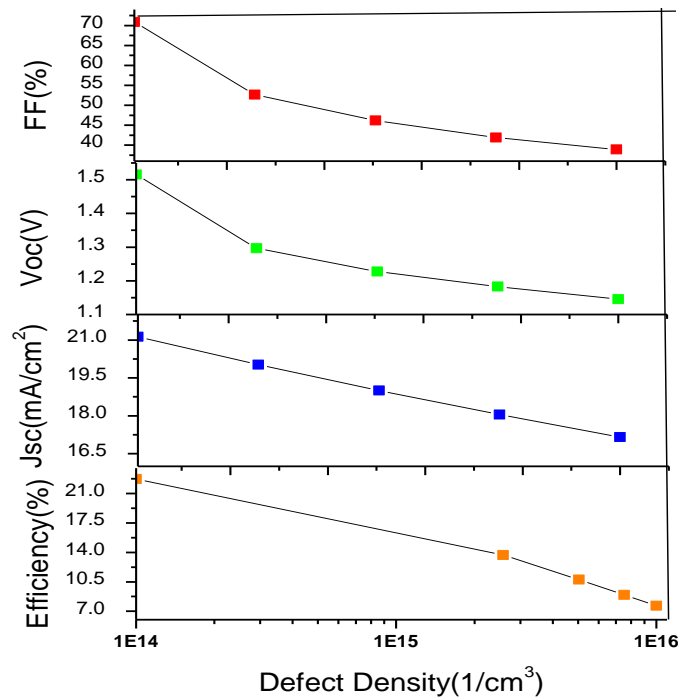


Fig:3 Graph representing the variation of PV Parameters by varying the defect density of absorber layer

In the simulation process, we can remove the total defects in the absorber layer, but practically it is not possible. To identify the effects of total defects on the performance of a device, few defects are added in the absorber layer and the defect density is increased from 10^{14} cm^{-3} to 10^{16} cm^{-3} . Increase of defect density leads to the decrease of recombination resistance. By increasing the defect density, the number of charge carriers may not generated, and may not totally collected by the collectors. Increase of defect density, mainly effects the charge transport process and the collection process of the device. By the increase of defect density, the solar cell parameters such as efficiency, FF, Voc, Jsc, decreases. When the defect density of absorber layer reaches to the 10^{16} cm^{-3} , then the efficiency drops to the 7%, due to the increase of resistance and at this level of defects Jsc drops to 16.5 mA/cm^2 and $Voc=1.1 \text{ V}$ $FF=40\%$. To achieve the good efficiency, there is necessary of increase of quality of the absorber layer. The optimized defect density of absorber layer is 10^{14} cm^{-3} .

Influence of Temperature on the device performance:

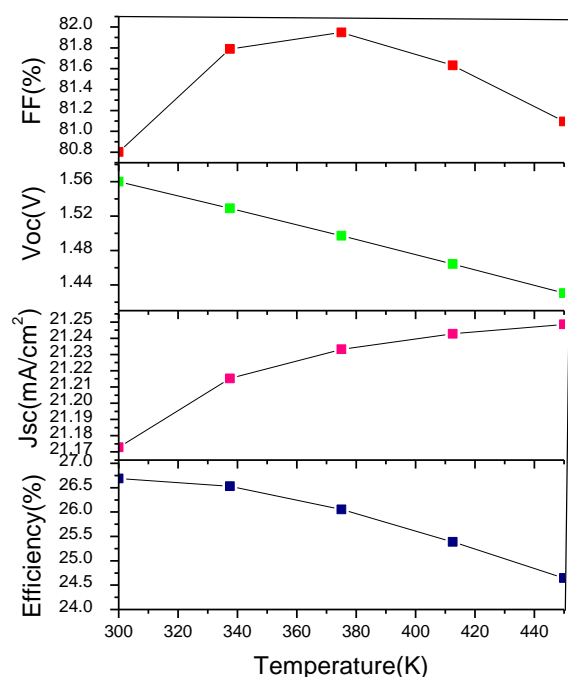


Fig:4 Graph representing the variation of PV Parameters by varying the Temperature(K)

Temperature also influences the performance of a solar cell device. To understand the effect of temperature on the electrical performance of a solar cell, the temperature of the simulated model is changed from 300K to 450K, then the considerable changes are observed. From the above graph, we can say that as the temperature increases, there is a drastic decrease in the performance of a device. This is attributed due to the increase in the series resistance leads to the decrease in the carrier diffusion length. As the temperature increases, the recombination rate also increases. Due to this at higher temperatures, the efficiency and fill factor drops very rapidly. As their temperature increases due to the thermal generation of carriers, there is a slight increase in the short circuit current density, but the rate of decrease of open circuit voltage is larger than the rate of increase of short circuit density and finally the efficiency decreases. To achieve good efficiency the optimum temperature of the simulated model is set to be 300K.

VI. METHODOLOGY

All the material parameters are given as input parameters and the optimized parameters are given in the architecture. The results obtained from the simulated mode are shown in the below figure and the efficiency reaches to the nearly 27%.

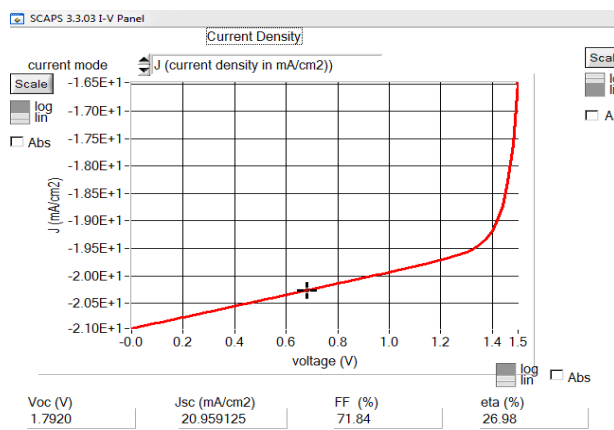


Fig:5 Simulated J-V graph using SCAPS-1D

VII. CONCLUSION

In summary, we developed a simulated model, having the architecture (Al/PCBM/ $Ch_3Nh_3PbI_{3-x}Cl_x$ /Pedot:Pss/FTO coated glass) contains planar hetero junction device. In this we studied the effect of thickness of absorber on the efficiency of device and as the thickness is more than 450nm, then the efficiency drops rapidly. At the optimum thickness of 450nm, (Al/PCBM/ $Ch_3Nh_3PbI_{3-x}Cl_x$ /Pedot:Pss/FTO coated glass) the devices were found to have power conversion efficiency up to 27%. In the same way, the effect of defect densities on the efficiency of a device was found. When the defect density is in the order of 10^{14} cm^{-3} , then the achieved good efficiency of 27%. The effect of temperature also studied and at the optimum temperature, used in the simulation process is 300K.

REFERENCES

- [1] S. Kazim, M. K. Nazeeruddin, M. Grätzel and S. Ahmad, *Angew. Chem., Int. Ed.*, 2014, 53, 2812–2824.
- [2] H. J. Snaith, *J. Phys. Chem. Lett.*, 2013, 4, 3623–3630.
- [3] N.-G. Park, *J. Phys. Chem. Lett.*, 2013, 4, 2423–2429.
- [4] P. Gao, M. Grätzel and M. K. Nazeeruddin, *Energy Environ. Sci.*, 2014, 7, 2448–2463.
- [5] D. B. Mitzi, in *Progress in Inorganic Chemistry*, John Wiley & Sons, Inc., 2007, pp. 1–121.
- [6] T. C. Sum and N. Mathews, *Energy Environ. Sci.*, 2014, 7, 2518–2534.
- [7] J.-H. Im, C.-R. Lee, J.-W. Lee, S.-W. Park and N.-G. Park, *Nanoscale*, 2011, 3, 4088–4093.
- [8] H.-S. Kim, C.-R. Lee, J.-H. Im, K.-B. Lee, T. Moehl, A. Marchioro, S.-J. Moon, R. Humphry-Baker, J.-H. Yum, J. E. Moser, M. Grätzel and N.-G. Park, *Sci. Rep.*, 2012, 2, 591.
- [9] M. M. Lee, J. Teuscher, T. Miyasaka, T. N. Murakami and H. J. Snaith, *Science*, 2012, 338, 643–647.
- [10] Z. Ku, Y. Rong, M. Xu, T. Liu and H. Han, *Sci. Rep.*, 2013, 3, 3132.
- [11] W. A. Laban and L. Etgar, *Energy Environ. Sci.*, 2013, 6, 3249–3253.
- [12] J. Shi, J. Dong, S. Lv, Y. Xu, L. Zhu, J. Xiao, X. Xu, H. Wu, D. Li, Y. Luo and Q. Meng, *Appl. Phys. Lett.*, 2014, 104, 063901.
- [13] D. Bi, S.-J. Moon, L. Haggman, G. Boschloo, L. Yang, E. M. J. Johansson, M. K. Nazeeruddin, M. Grätzel and A. Hagfeldt, *RSC Adv.*, 2013, 3, 18762–18766.
- [14] J. H. Heo, S. H. Im, J. H. Noh, T. N. Mandal, C.-S. Lim, J. A. Chang, Y. H. Lee, H.-j. Kim, A. Sarkar, M. K. Nazeeruddin, M. Grätzel and S. I. Seok, *Nat. Photonics*, 2013, 7, 486–491.
- [15] J. H. Noh, S. H. Im, J. H. Heo, T. N. Mandal and S. I. Seok, *Nano Lett.*, 2013, 13, 1764–1769.
- [16] J. M. Ball, M. M. Lee, A. Hey and H. J. Snaith, *Energy Environ. Sci.*, 2013, 6, 1739–1743.
- [17] B. Cai, Y. Xing, Z. Yang, W.-H. Zhang and J. Qiu, *Energy Environ. Sci.*, 2013, 6, 1480–1485.
- [18] E. Edri, S. Kirmayer, D. Cahen and G. Hodes, *J. Phys. Chem. Lett.*, 2013, 4, 897–902.
- [19] N. Pellet, P. Gao, G. Gregori, T.-Y. Yang, M. K. Nazeeruddin, J. Maier and M. Grätzel, *Angew. Chem., Int. Ed.*, 2014, 53, 3151–3157.
- [20] Y. Ogomi, A. Morita, S. Tsukamoto, T. Saitho, N. Fujikawa, Q. Shen, T. Toyoda, K. Yoshino, S. S. Pandey, T. Ma and S. Hayase, *J. Phys. Chem. Lett.*, 2014, 5, 1004–1011.
- [21] J. T.-W. Wang, J. M. Ball, E. M. Barea, A. Abate, J. A. Alexander-Webber, J. Huang, M. Saliba, I. Mora-Sero, J. Bisquert, H. J. Snaith and R. J. Nicholas, *Nano Lett.*, 2013, 14, 724–730.
- [22] K. Wojciechowski, M. Saliba, T. Leijtens, A. Abate and H. J. Snaith, *Energy Environ. Sci.*, 2014, 7, 1142–1147.
- [23] Shiqiang Luo and Walid A. Daoud, *Crystal Structure Formation of $CH_3NH_3PbI_{3-x}Cl_x$ Perovskite Materials* 2016, 9, 123; doi:10.3390/ma9030123.
- [24] S. D. Stranks, G. E. Eperon, G. Grancini, C. Menelaou, M. J. P. Alcocer, T. Leijtens, L. M. Herz, A. Petrozza and H. J. Snaith, *Science*, 2013, 342, 341–344.
- [25] Y. Zhao and K. Zhu, *J. Phys. Chem. Lett.*, 2013, 4, 2880–2884.
- [26] E. Edri, S. Kirmayer, D. Cahen and G. Hodes, *J. Phys. Chem. Lett.*, 2013, 4, 897–902.
- [27] Fatemeh Zabihi, Mohammad-Reza Ahmadian-Yazdi and Morteza Eslamian, *Fundamental Study on the Fabrication of Inverted Planar Perovskite Solar Cells Using Two-Step Sequential Substrate Vibration-Assisted Spray Coating (2S-SVASC)* Nano scale Research Letters - December 2016 DOI: 10.1186/s11671-016-1259-2