Influence of defect density and layer thickness of absorption layer on the performance of tin based perovskite solar cell

Priyanka Roy, Numeshwar Kumar Sinha, Sanjay Tiwari and Ayush Khare*

National Institute of Technology, Raipur

*Corresponding author’s e-mail address: proy.phd2018.phy@nitrr.ac.in

Abstract. The tremendous progress exhibited by Perovskite solar cells (PSCs) within the decade has made PSCs the fastest growing PV cell to date. The PSCs has exhibited increment in power conversion efficiency (PCE) from 3.2% to 25.2% within a decade. In PSCs, usually MAPbX₃ (X being Cl, Br and I) layer is used as an absorber layer. The incorporation of toxic Lead (Pb) is a matter of concern by some of the researchers. In order to deal with this Tin (Sn) is being used as an alternative of Pb. However, the performance of Sn based PSC still lags behind Pb based PSC. In this work, we demonstrate an efficient Sn based PSC with Jₘ of 32.6398 mA/cm², Vₘ of 0.8946V, FF of 80% and PCE of 23.4%. The results exhibits the potential of Sn based PSCs which is not only efficient but also is environmental friendly. We study the impact of defect density and layer thickness of absorber layer over the performance of Sn based PSC. An analysis on the effect of doping in Electron Transport Layer (ETL) and Hole Transport Layer (HTL) over the performance of Sn based PSC is also conducted.

Key Words: Perovskite solar cell, Tin based perovskite solar cell, SCAPS-1D, Defect Density, Absorber layer thickness;

1. Introduction
The PSCs have exhibited their enormous potential by rapid advancement in performance within a decade. The PSCs have shown increment from 3.2% to 25.2% in PCE within a decade [1]. However, although these cells exhibit appreciable performance but still the incorporation of toxic Lead (Pb) is the matter of concern [2]. It is a well-known fact that toxicity due to lead can cause severe health risks and also has a deplorable impact on our ecosystem. This is one of the factors which is creating a negative impact over users and avoiding its market acceptance of the final product. MAPbX₃ (where X is Cl, Br or I) is the widely adopted absorber layer in the PSCs. Tin (Sn) have been used by several researchers as an alternative of Pb which is nontoxic. Unfortunately, Sn based PSCs suffers from drawbacks: (i) efficiency as high as Pb based PSCs are not yet achieved, (ii) instability in ambient conditions, (iii) degrades easily due to oxidation of Sn²⁺ into Sn⁴⁺. All such demerits tend to restrict the development of Sn based PSCs. Till date the most efficient tin based PSC has attained PCE of 9.6%[3].It is seen that Tin based perovskite when deposited over TiO₂ has exhibited poor surface coverage [4]. Moreover, the issue of ion immigration takes place when TiO₂ is used as ETL. In order to deal with this here we use ZnO-NR as ETL. In this work, we demonstrate an efficient Sn based PSCs, and efficiency as high as 23.4% has been achieved. This work suggests the fact that tin based
PSC also has the ability to exhibit performance comparable to lead based PSC. An optimum range of absorber layer thickness, absorber defect density and doping level of ETL & HTL is also investigated.

2. Simulation Setup

SCAPS-1D (Solar Cell Capacitance Simulator) version 3.3.07 has been used to simulate the PSC. This software was specifically developed for CdTe and CuInSe2 family. The several extensions improved its capabilities enabling the analysis of other types of solar cell. As compared to other softwares, SCAPS-1D has in-built operation window and differentiated models for defects, recombination and grating. This software is based upon general semiconductor physics, like poisons equation, drift diffusion equation and continuity equation. The basic equations are generally elucidated in 1D in a steady state condition. SCAPS analyses the physics behind the model and examines the electric field distribution, recombination profiles, individual current densities and carrier transport mechanism. This software enables to add upto 7 semiconducting layer with various material and defect properties[5].

2.1 Device Structure

![Figure 1. Schematic of device architecture of simulated Sn based PSCs: (a) Au/Spiro-OmeTAD/ MASnI3/ZnO-NR/FTO](image)

We adopted planar architecture structure the schematic shown in Figure 1. The simulated PSC has five layers: (i) Gold (Au) as metal based cathode (ii) Hole transport layer (HTL) as p-type 2,2,7,7’-tetrakis-(N,N-dimethoxyphenyl-amine)-9,9’-spirobifluorene (Spiro-OmeTAD) (iii) absorber layer as Methylammonium lead trihalide (MASnI3) (iv) ETL as Zinc oxide nanorod (Zno-NR) (v) Transparent Conductive Oxide(TCO) as Flourine doped Tin Oxide (FTO). The material perovskite as an absorber layer exhibits ambipolar behaviour with high mobility for both electron and hole. Its function is to absorb the incident radiation leading to the creation of the charge carriers. The function of ETL is to extract and transfer electron and block hole. Whereas, the function of HTL is to extract and transfer holes and block electrons.

2.2 Parameters

The parameters selected for simulation are taken from literature. Table-1 summarizes all the parameters used during simulation and Table-2 enclosed the data for front and back contact. The MASnI3 based solar cell is simulated at AM1.5G at 300K. The absorber layer, HTL and ETL defect density was taken as $10^{14}$ cm$^{-3}$, $10^{15}$ cm$^{-3}$ and $10^{15}$ cm$^{-3}$ respectively. The parameter values of various layers are extracted from research work carefully [6][7][8].
### Table 1 The parameters used for simulation

| Parameters                        | Spiro-omeTAD | MASnI3  | ZnO-NR       | SnO2: F |
|-----------------------------------|--------------|---------|--------------|---------|
| Thickness (µm)                    | 0.5          | 0.6     | 0.5          | 0.25    |
| Band gap (eV)                     | 3.17         | 1.2     | 3.27         | 3.5     |
| Electron affinity (eV)            | 2.1          | 4.17    | 4.3          | 4.4     |
| Dielectric Permittivity           |              |         |              |         |
| CB effective density of states (1/cm³) | 2.5E+18     | 2.1E+18 | 2E+18        | 2.2E+18 |
| VB effective density of states (1/cm³) | 1.8E+19     | 1.9E+19 | 1.8E+20      | 1.8E+19 |
| Electron thermal velocity (cm/S)  | 1E+7         | 3E+7    | 1E+7         | 1E+7    |
| Hole thermal velocity (cm/S)      | 1E+7         | 3E+7    | 1E+7         | 1E+7    |
| Electron mobility (cm²/V/S)       | 2E-4         | 1.6E+0  | 1E+2         | 2E+3    |
| Hole mobility (cm²/V/S)           | 2E-4         | 2E-1    | 2.5E+1       | 1E+2    |
| Shallow uniform donor density ND (1/cm³) | 0           | 0       | 1E+18        | 2E+19   |
| Shallow uniform acceptor density NA (1/cm³) | 1E+20       | 6E+18   | 0            | 0       |

### Table 2 Parameters for Back and Front contact

| Parameters                        | Back Contact | Front Contact |
|-----------------------------------|--------------|---------------|
| Surface recombination velocity of electrons (cm/s) | 1.00E+7     | 1.00E+5      |
| Surface recombination velocity of holes (cm/s)       | 1.000E+5    | 1.000E+7     |
| Metal work function (eV)             | 5.1444       | 4.43          |
| Majority carrier barrier height relative to Ef (eV)  | -0.0444      | -0.0600       |
| Majority carrier barrier height relative to Ev (eV)  | -0.0000      | -0.0028       |
3. Result and Discussion
The best performance is attained at thickness of 0.4µm with, PCE=23.4%, $J_{sc}=32.6398$ mA/cm², $V_{oc}=0.8946$V and FF = 80%. The J-V curve of the simulated Sn based PSC is shown in Figure 2.

![J-V curve of simulated Sn based PSC.](image)

### 3.1 Impact of Defect Density and Thickness of Absorber Layer on the Performance
In order to obtain better PV performance the absorber layer plays a crucial role. The generation of photo excited charge carriers usually occurs at the absorber layer. The film quality and morphology of this layer has a direct impact over the PV performance of the PSC. The performance parameters of the PSC are highly dependent over the absorption layer thickness and defect density. In this work, we vary the absorber defect density ($N_t$) from range 1E12 to 1E16. It is seen that the performance parameters reduces to a great extend as the $N_t$ increases as shown in Figure 3. At $N_t=1E^{12}$, the performance parameters are: PCE= 30.17%, $V_{oc}=1.357$V, $J_{sc}=39.9123$ mA/cm², FF= 55.7% and when $N_t=1E^{16}$ the performance parameters are: PCE= 2.56%, $V_{oc}=0.6796$V, $J_{sc}=5.0988$ mA/cm², FF= 73.84%. It is seen that PCE, $J_{sc}$ and $V_{oc}$ decreases with increases in $N_t$. Whereas the FF initially increases till 1E14 reaches to a maximum value and then decreases. The decrement in the performance with increase in defect density is basically due to the enhancement in the recombination process which leads to annihilation of the charge carriers. At low defect density, the carrier diffusion length is high and recombination process is low thereby contributing to better PV performance.
The performance of PSC depends upon the thickness of the absorber layer to a great extent as the photo excited charge carrier generation occurs at this layer. The absorber layer thickness has direct influence on the PV performance of the device as it affects the diffusion lengths of the charge carriers. If the absorber layer is too thick, then the charge carriers might recombine before reaching the charge collecting electrodes and too thin absorber layer will not be able to absorb the incident radiation properly, thereby reducing the overall performance of the device. In this study we vary the absorber layer thickness at range 0.1-1μm, keeping the thickness of ETL and HTL fixed. The result can be seen from Figure 4 that performance parameters are highly thickness dependent. The $V_{OC}$ decreases with increase in thickness of the absorber layer. The $J_{SC}$ and PCE increases initially and reaches maximum at $t=0.4\mu m$, and then slightly decreases.
Figure 4. Variation of performance parameters of Sn based PSC with change in absorber layer thickness: a) Variation of $V_{oc}$, b) variation of $J_{sc}$, c) variation of FF and d) variation of Efficiency as function of absorber’s thickness.

3.2 Impact of Doping Level in HTL and ETL

The PV performance of solar cell is highly affected by the electrical behavior of the layer, which can be altered by addition of a dopant. The doping of HTL and ETL improves the PV performance by raising the interface electric field. In order to understand the impact of doping effect over HTL and ETL, we vary the acceptor carrier density ($N_A$) and donor carrier density ($N_D$) from $1 \times 10^{14}$ to $1 \times 10^{19}$ cm$^{-3}$.

Firstly, analysing the doping effect on HTL, we vary the acceptor carrier density ($N_A$). The variation in performance parameters with carrier concentration is shown in Figure 5. It is seen that, $V_{oc}$ is constant till $1 \times 10^{16}$, and the increases after $1 \times 10^{16}$. Similarly $J_{sc}$, FF and PCE increases abruptly from $1 \times 10^{16}$ and value gets constant after $1 \times 10^{18}$ signifying the optimum range to be $1 \times 10^{16}$ to $1 \times 10^{18}$. 
Figure 5. Variation of performance parameters of Sn based PSC with change in acceptor carrier concentration (N_A): Variation of performance parameters of Sn based PSC with change in absorber acceptor carrier concentration: a) Variation of Voc, b) variation of Jsc, c) variation of FF and d) variation of Efficiency as function of absorber’s acceptor carrier concentration.

It is seen that the Voc doesn’t depends upon N_D whereas J_sc and PCE increases from 1E16 to 1E18 and then gets constant. The optimum range for carrier concentration is 1E16 to 1E18. The impact of donor carrier concentration (N_D) over the performance of Sn based PSC is shown in Figure 6 [6].
Figure 6. Variation of performance parameters of Sn based PSC with change in donor carrier concentration (ND): Variation of performance parameters of Sn based PSC with change in absorber donor carrier concentration: a) Variation of Voc, b) variation of Jsc, c) variation of FF and d) variation of Efficiency as function of absorber’s donor carrier concentration.

4. Conclusions

Table 3 Optimized values for Sn based PSC.

| Optimized Parameters | ETL | MASnI$_3$ | HTL |
|----------------------|-----|-----------|-----|
| N$_d$(cm$^{-3}$)      |     | 1E$^{12}$ |     |
| N$_A$(cm$^{-3}$)      |     |           | 1E$^{16}$-1E$^{18}$ |
| N$_D$(cm$^{-3}$)      | 1E$^{16}$-1E$^{18}$ |     |
| Absorber thickness (µm) |     | 0.4µm    |

In this work, we demonstrated the potential of Sn based PSC with a performance being comparable to
Pb based PSC by attaining a high PCE of 23.4%. The impact of defect density and thickness of absorber layer is studied. It is seen that defect density of absorber layer must be as low as possible and optimum layer thickness should be 0.4µm to attain high performance. The optimum doping concentration of ETL and HTL required for better PV performance was studied. The obtained results are summarized in Table-3. However, practically the device suffers from issue like poor device stability due to easy oxidation from Sn²⁺ to Sn⁴⁺. This issue can be solved by improving the fabricating process which can deposit high quality defect free films and using proper device encapsulation.

Acknowledgement
The authors would like to thank Professor Marc Burgelman, Department of Electronics and Information Systems, University of Gent for the development of the SCAPS software package and allowing its use.

References
[1] NREL 2019 PV Research Cell Record Efficiency Chart
[2] Lyu M, Yun J H, Chen P, Hao M and Wang L 2017 Adv. Energy Mater. 7 1602512
[3] Shao S, Liu J, Portale G, Fang H H, Blake G R, ten Brink G H, Koster L J A and Loi M A 2018 Adv. Energy Mater. 8 1702019
[4] Hao F, Stoumpos C C, Guo P, Zhou N, Marks T J, Chang R P H and Kanatzidis M G 2015 J. Am. Chem. Soc. 137 11445–52
[5] Marc Burgelman, Koen Decock, Alex Niemegeers, Johan Verschraefen S D 2018 SCAPS manual
[6] Du H J, Wang W C and Zhu J Z 2016 Chinese Phys. B 25 108802
[7] Mandadapu U, Vedanayakam S V and Thyagarajan K 2017 Simulation and Analysis of Lead based Perovskite Solar Cell using SCAPS-1D Indian J. Sci. Technol. 10 1–8
[8] Anwar F, Mahbub R, Satter S S and Ullah S M 2017 Int. J. Photoenergy 2017 1