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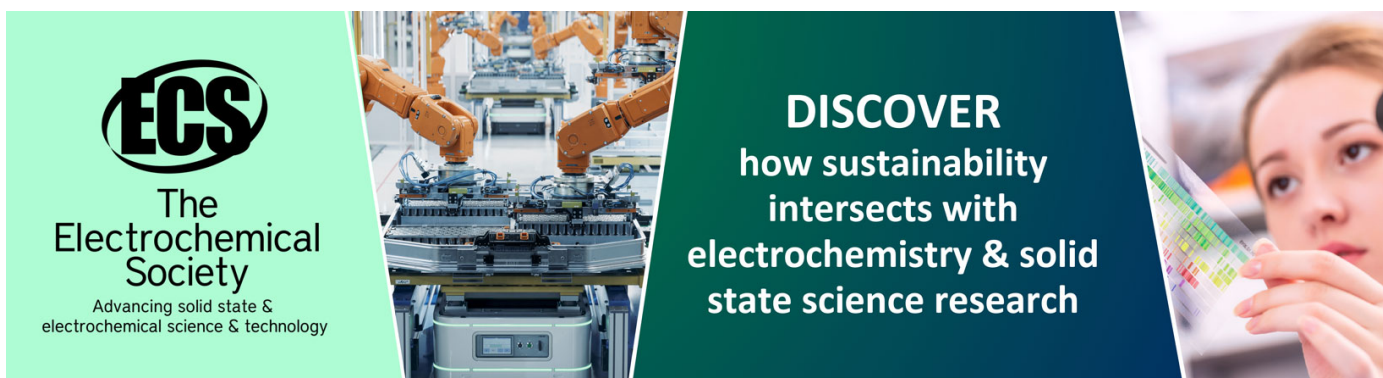
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# Impact of hole transport layer on the performance of all-inorganic tin (Sn) based perovskite solar cells

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**Abstract.** The power conversion efficiency (PCE) of perovskite solar cells (PSCs) has shown vast increment from 3.81% to 25.5% within a decade. Despite the fast progress and many advantages, these cells are facing an issue of toxicity and poor device stability. In this work, we deal with the issue of toxicity by using Tin (Sn) instead of Lead (Pb). The PSCs are simulated using Solar Simulator Capacitor (SCAPS-1D version 3.3.07) software. We used all-inorganic, lead free material, Cesium Tin–Germanium Tri-iodide ( $\text{CsSn}_{0.5}\text{Ge}_{0.5}\text{I}_3$ ) as an absorber material. We further investigate the influence of hole transport layer (HTL) on the performance of Sn based PSCs. Simulation and analysis of following  $\text{CsSn}_{0.5}\text{Ge}_{0.5}\text{I}_3$  based PSC devices have been done: using (i) HTL free configuration (ii) inorganic HTL and (iii) organic HTL. The simulated cells are in planar n-i-p architecture. This work depicts the fact that Sn based PSCs have a potential to serve as high performance solar cells. The results signifies the impact of HTL on the performance of PSCs, in this study, we also suggest alternatives to the widely used HTM (Spiro-OMeTAD) that not only produce comparable photovoltaic performance but also are cost effective. We also analyse the influence of using various metal cathodes on the simulated cell. The result suggests that presence and type of HTM is having an impact on the contact selection criteria. The influence of HTL thickness variation on the performance of the PSCs are also studied.

## 1. Introduction

The Perovskite Solar Cells (PSCs) have revealed their potential by showing rapid growth in performance (3.81%-25.5%) within a shorter span of time [1]. This has made PSCs the fastest growing PSCs to date. However, the incorporation of toxic Lead (Pb) is still the matter of concern for researchers [2]. It is a well-known fact that toxicity due to lead causes harmful impact on our ecosystem and also causes severe health risks. This factor is creating hindrance in the market acceptance of the final product [3]. Generally,  $\text{MAPbX}_3$  (where X is Cl, Br or I) is widely adopted absorber layer in the PSCs. In order to replace Pb, Tin (Sn) have been used by several researchers which is nontoxic. Unfortunately, Sn based PSCs suffers from drawbacks: (i) instability in ambient conditions, (ii) degrades easily due to oxidation of  $\text{Sn}^{2+}$  into  $\text{Sn}^{4+}$ , (iii) efficiency as high as Pb based PSCs are not yet achieved. All such issues are restricting the



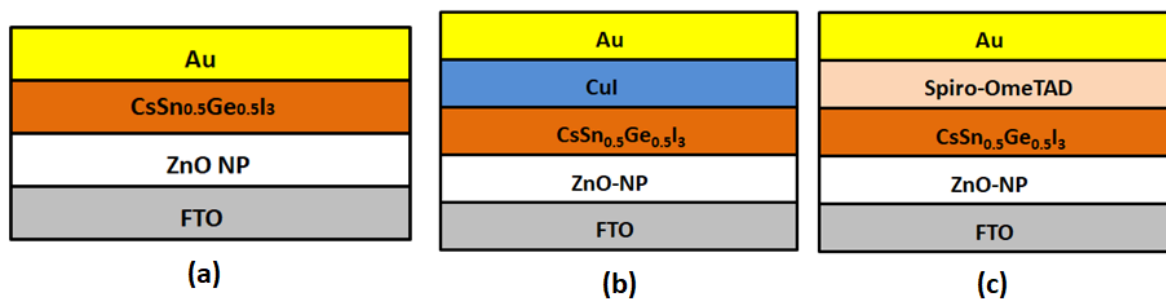
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development of Sn based PSCs. To date the highest efficient Sn based PSC has attained PCE of 9.6%[4]. In this work, we demonstrate an all-inorganic type of PSC using  $\text{CsSn}_{0.5}\text{Ge}_{0.5}\text{I}_3$  (Caesium germanium tin triiodide) as light harvester layer. Min cheng et al. [5] demonstrated  $\text{CsSn}_{0.5}\text{Ge}_{0.5}\text{I}_3$  based PSC using Spiro OmeTAD and PCBM as hole transport and electron transport material respectively. The device fabricated by them attained PCE of 7.11%. Moreover, the device exhibited excellent stability by working efficiently with decrement in performance by less than 10% for more than 500 hours under one sun illumination condition and nitrogenous atmosphere. Here, we present a  $\text{CsSn}_{0.5}\text{Ge}_{0.5}\text{I}_3$  based PSC in (a) HTL free configuration (b) using inorganic HTL and (iii) using organic HTL. The motive of using different aspect of hole transport layer (HTL) is to investigate its impact on the performance of PSCs. We also discuss the influence of HTM on the performance of PSC and suggest alternatives to the conventional HTM Spiro-OMeTAD. The existing research suggests that Spiro-OMeTAD participates and accelerates the process of degradation rendering poor lifetime of the cell. It has been observed that Sn based perovskite while deposited over  $\text{TiO}_2$  exhibits non uniform surface coverage [6]. The problem of ion immigration occurs when Titania ( $\text{TiO}_2$ ) is used as ETL. In order to deal with it, here we use Zn-nanoparticles (NP) as ETL. An efficiency of 24.5% has been attained in this work.

## 2. Simulation Setup

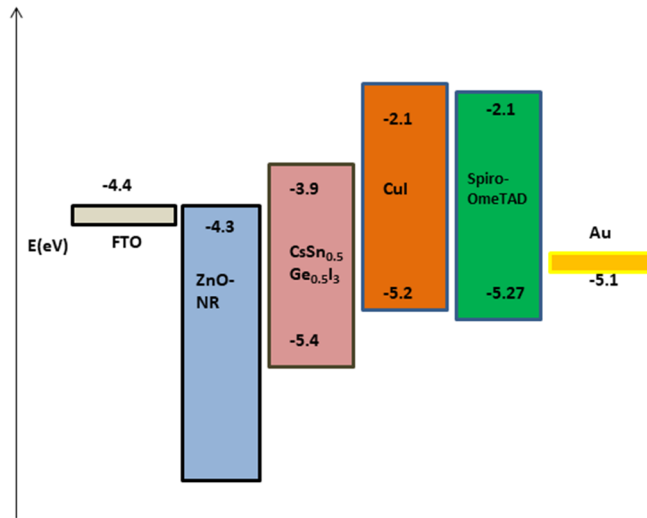
We use SCAPS-1D (version-3.3.07) to simulate and analyze the PSCs [7]. This software is an open source solar cell simulating software which is highly user friendly. It is basically built to study inorganic solar cells comprising heterogeneous structure like CdTe, CIGs, CZTs etc. PSCs incorporate the material perovskite as an absorber layer which is hybrid combination of both organic and inorganic solar cells. The fact that this material has Wannier type exciton, and the cell has planar heterogeneous structure similar to inorganic cells enables the analysis of this cell using SCAPS-1D [7].

### 2.1 Device Structure



**Figure 1.** Schematic of device architecture of simulated Sn based PSCs.

The simulated cells have planar architecture structure, the schematic shown in Figure 1. The energy band diagram of the simulated cells is shown in Figure 2. The simulated PSCs have following layers: **(i)** Metal cathode (Au) **(ii)** Hole transport layer (HTL) [p-type 2,2,7,7'-tetrakis-(N,N-dimethoxyphenylamine)-9,9'-spirobifluorene (Spiro-OMeTAD) and copper Iodide (CuI) **(iii)** absorber layer as Caesium Tin–Germanium Tri-iodide ( $\text{CsSn}_{0.5}\text{Ge}_{0.5}\text{I}_3$ ) **(iv)** Electron transport layer (ETL) as Zinc oxide nanorod (Zno-NR) **(v)** Fluorine doped Tin Oxide (FTO) as Transparent Conductive Oxide (TCO). We simulate three different PSCs, in (a) HTL free configuration (b) using inorganic HTM (CuI) (c) using organic HTM (Spiro-OMeTAD) shown in Fig. 1.



**Figure 2.** Energy-band diagram of the simulated cell.

## 2.2 Parameters

The electrical parameters adapted for simulation are selected from existing literature. Table-1 summarizes all the parameters used during simulation. The based solar cell is simulated at AM1.5G at 300K. The ETL, HTL and absorber layer defect density was taken as  $10^{15} \text{ cm}^{-3}$ ,  $10^{15} \text{ cm}^{-3}$  and  $10^{14} \text{ cm}^{-3}$  respectively [8–12].

**Table 1.** The parameters used for simulation.

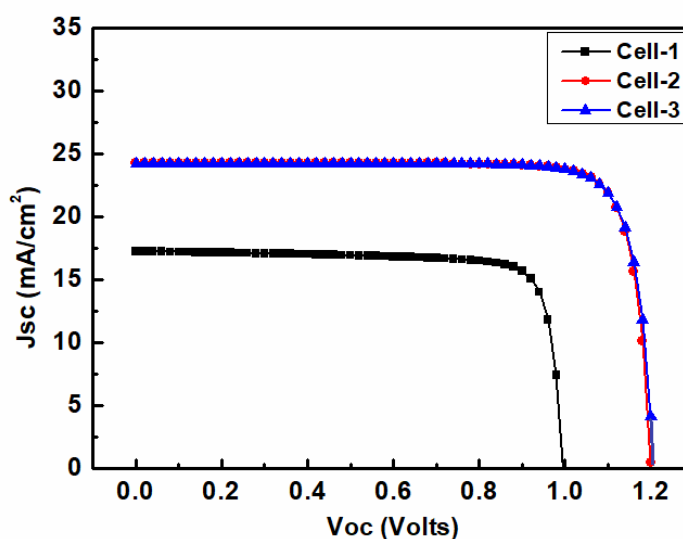
| Parameters                                              | Spiro-OMeTAD | CuI     | CsSn <sub>0.5</sub> Ge <sub>0.5</sub> I <sub>3</sub> [13] | ZnO- NR | SnO <sub>2</sub> : F |
|---------------------------------------------------------|--------------|---------|-----------------------------------------------------------|---------|----------------------|
| Thickness (μm)                                          | 0.5          | 0.5     | 0.4                                                       | 0.5     | 0.25                 |
| Band gap(eV)                                            | 3.17         | 3.1     | 1.5                                                       | 3.27    | 3.5                  |
| Electron affinity(eV)                                   | 2.1          | 2.1     | 3.9                                                       | 4.3     | 4.4                  |
| Dielectric Permittivity                                 | 3            | 6.5     | 28                                                        | 9       | 9                    |
| CB effective density of states (1/cm <sup>3</sup> )     | 2.5E+18      | 2.2E+19 | 3.1E+18                                                   | 2E+18   | 2.2E+18              |
| VB effective density of states (1/cm <sup>3</sup> )     | 1.8E+19      | 1.8E+19 | 3.1E+18                                                   | 1.8E+20 | 1.8E+19              |
| Electron thermal velocity(cm/S)                         | 1E+7         | 1E+7    | 9.74E+2                                                   | 1E+7    | 1E+7                 |
| Hole thermal velocity(cm/S)                             | 1E+7         | 1E+7    | 2.13E+2                                                   | 1E+7    | 1E+7                 |
| Electron mobility(cm <sup>2</sup> /VS)                  | 2E-4         | 4.39E+1 | 0                                                         | 1E+2    | 2E+3                 |
| Hole mobility(cm <sup>2</sup> /VS)                      | 2E-4         | 2E+2    | 1E+18                                                     | 2.5E+1  | 1E+2                 |
| Shallow uniform donor density ND (1/cm <sup>3</sup> )   | 0            | 0       |                                                           | 1E+18   | 2E+19                |
| Shallow uniform acceptor density NA(1/cm <sup>3</sup> ) | 1E+18        | 1E+18   |                                                           | 0       | 0                    |

## 3. Result and Discussion

### 3.1 Performance

Apart from the carrier generating absorber layer, the other two transport layers, electron transport layer (ETL) and hole transport layer (HTL) renders a performance deciding factor as they are responsible for the charge extraction of the cell [14]. The current research is going on to find out an efficient perovskite

absorber layer exhibiting good photovoltaic performance along with stable behavior. An effort is also being made to come up with a HTM being capable of improving the photovoltaic performance and also should be capable of maintaining stability by getting rid of the hygroscopic behavior. The role to hole transport material (HTM) is to extract the holes from the absorber layer and efficiently transfer it towards cathode. To date, the most widely used HTM is Spiro-OMeTAD, PTAA, PEDOT:PSS and P3HT [15–18]. These organic HTM based cells gave high efficiency and  $V_{oc}$  but still its commercialization is not yet developed due to its unstable nature in presence of moisture, temperature, light and also its high cost. Therefore, in this work we simulate three configurations of non-toxic PSCs, (i) Cell-1, HTL free PSC, a PSC in which HTL is omitted is termed as HTL free PSC. The removal of HTL from PSC fabrication not only simplifies the fabrication process but also it reduces the cost to a great extent. The simulated cell has configuration of Au/  $CsSn_{0.5}Ge_{0.5}I_3$ /ZnO-Np/FTO. (ii) Cell-2 using inorganic HTL (CuI), the inorganic materials tend to have higher conductivity and carrier mobility and also exhibit stability. The device configuration is Au/ CuI/ $CsSn_{0.5}Ge_{0.5}I_3$ /ZnO-Np/FTO. (iii) Cell-3 using widely used Spiro-OMeTAD. The device configuration is Au/ Spiro-OMeTAD/ $CsSn_{0.5}Ge_{0.5}I_3$ /ZnO-Np/FTO. The role of electron transport material (ETM) is to extract electrons from the absorber layer and transfer it towards anode for collection [19,20]. We further use ZnO NP as ETM, which has high electron mobility, carrier concentration also requires low temperature processing condition. The simulated cell attains performance enclosed in Table-2. The JV curve of the simulated cell is shown in Figure 3. The results shows the fact that HTL free PSCs will poses lower efficiency as compared to PSC with HTL. The theoretically simulated cells showed the difference of 10% in PCE. The conventionally used HTM (Spiro-OMeTAD) is widely used on PSCs due to its ability to attain high performance parameters. However, studies suggest that it actively participates within the process of degradation also it is expensive. The Cell-2 has CuI as HTM and device exhibited the best performance by attaining highest performance parameters among all. This work shows that the widely used Spiro-OMeTAD can be replaced using inorganic HTM such as CuI. This will not only help attaining high performance parameters but also will reduce the overall cost of the device.



**Figure 3.** JV curve of the simulated cell.

**Table 2.** The attained performance parameters by the simulated cells.

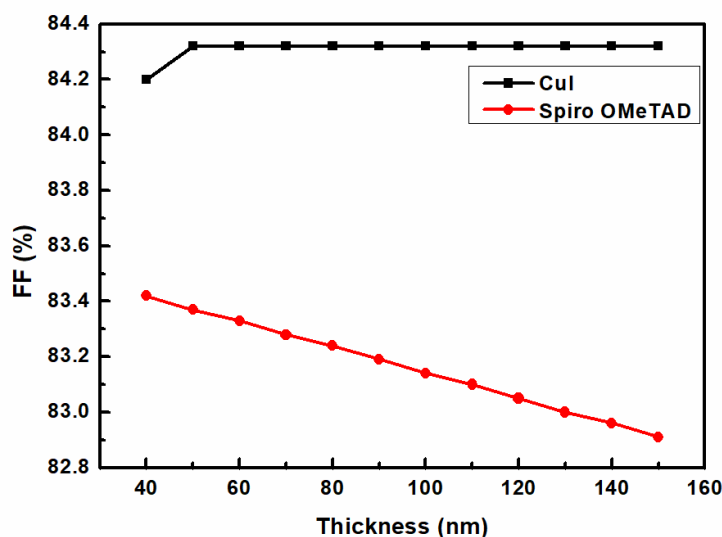
| Cell No.      | Voc(V) | Jsc(mA/cm <sup>2</sup> ) | FF(%) | PCE(%) |
|---------------|--------|--------------------------|-------|--------|
| <b>Cell-1</b> | 0.9968 | 17.2450                  | 82.14 | 14.12  |
| <b>Cell-2</b> | 1.2011 | 24.2167                  | 84.2  | 24.5   |
| <b>Cell-3</b> | 1.2107 | 24.2176                  | 83.42 | 24.46  |

### 3.2 Performance analysis by varying HTL thickness

The cell performance is influenced by HTL's thickness and material type. In this section, we study the influence of the HTL thickness variation from 50-150nm using organic (Spiro OMeTAD) and inorganic (CuI) HTMs. The thickness of HTLs not only affects the cell performance but also acts as a capping layer to avoid contact between cathode and absorber layer. Figure 4 shows the impact of HTL layer thickness (40-150nm) on the Fill factor (FF) of the simulated PSCs. It can be observed that, the Fill factor (FF) is not much affected for cell-2 (where CuI is being used as an HTM). However, Spiro OMeTAD based cell has exhibited a decrement in FF with increase in thickness of HTL. The organic material poses lower charge carrier mobility and conductivity as compared to the inorganic materials. As a result, when thickness of the organic HTM (Spiro OMeTAD) layer increases, the layer resistance increases which further lowers the performance of the cell. In case of inorganic HTL (CuI) the FF is not much affected by HTL thickness variation due to comparatively higher charge carrier mobility.

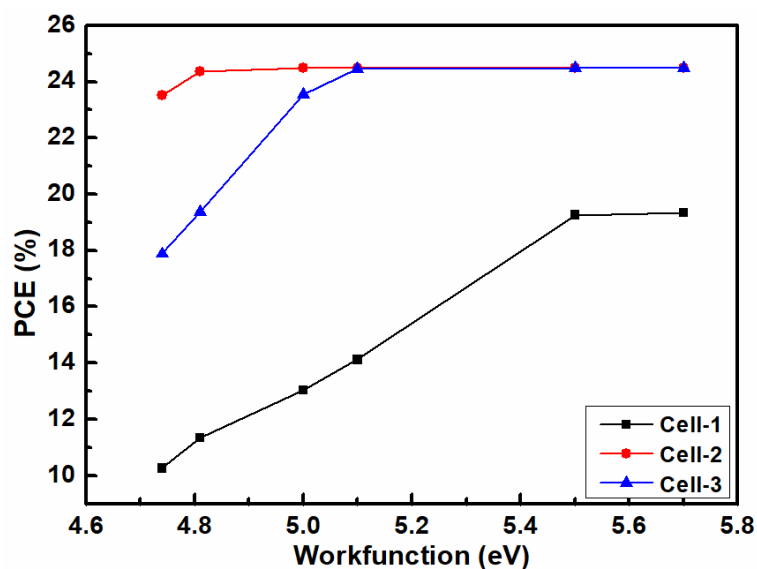
### 3.3 Performance analysis using various contacts

In this section, we simulate Sn-PSCs with and without HTM using different back contacts. The simulated device has configuration of FTO/ ZnO NP / CsSn<sub>0.5</sub>Ge<sub>0.5</sub>I<sub>3</sub>/(Spiro-OMeTAD or CuI) /Back contacts. The different back contacts used are Pt (5.7eV), Ni(5.5eV), Au(5.1eV), C(5.0eV), Fe(4.81eV), Ag(4.74eV).

**Figure 4.** Impact of HTL layer thickness (40-150nm) on the Fillfactor (FF) of the simulated PSCs.

This analysis is carried out to understand the influence of different back contacts of Sn-PSCs performance using various HTLs. Figure 5 shows the variation of performance parameters with different back contacts on the Sn-PSC's performance with ZnO-NPs as ETM and various HTMs.

As the work function of the back contact tends to be higher than that of HTM's, it ensures proper hole collection and electron blocking. It can be said that, using a back contact with high work function will transfer holes efficiently leading to higher performance. It is observed that with increase in the contact work function the PCE initially increases and later gets saturated (Higher the value of bandgap of HTM earlier is the saturation point reached). The performance of Cell-1 (HTL free) seemed to be most dependent on the metal cathode. Cell-1 exhibited increment in performance with increase in contact work function till 5.4eV and later gets saturated. Cell-3 (using Spiro-OMeTAD) exhibited increment with increase in contact work function till 5.2 eV and later gets saturated. Cell-2 (using CuI) exhibited least metal cathode dependent behaviour by attaining the saturation point quiet early, around 4.84eV. It is because of the high charge carrier mobility of the used HTM (CuI). Therefore, it can be said that, in case of high charge carrier mobility metal contact with even lower function like Ag is capable of rendering good performance.



**Figure 5.** Energy-band diagram of the simulated cell.

#### 4. Conclusions

In this work, we studied a heterojunction  $\text{CsSn}_{0.5}\text{Ge}_{0.5}\text{I}_3$  based PSCs with planar architecture using ZnO nanoparticles (NP) as an ETM. We use various perspectives of HTL and simulate HTL free, organic and inorganic HTMs to study its usage with  $\text{CsSn}_{0.5}\text{Ge}_{0.5}\text{I}_3$  based PSCs. It was seen that, PSC with configuration: FTO/ZnO/  $\text{CsSn}_{0.5}\text{Ge}_{0.5}\text{I}_3$  /CuI/Au attained maximum performance with 24.5% PCE, 1.2011V  $V_{oc}$ , 82.4% fill factor and 24.2  $\text{mA}/\text{cm}^2$   $J_{sc}$ . If CuI is used instead of the conventional Spiro-OMeTAD as HTM one can obtain good performance parameters along with reduction in overall device cost. Impact of HTL thickness variation on the performance of PSCs is also studied. The result signifies that HTMs carrier mobility and conductivity have influence on the HTL thickness selection. An analysis was conducted to study the performance using various metals as back contacts. It was observed that, presence and type of HTL has an impact on the metal cathode selection. This work also provides an alternative to use other cathode metal than widely used Au, thereby reducing the cost of the PSCs.

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