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Device modelling of tin based perovskite solar cell with distinct hole transport layer material

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The present study describes the computational analysis and optimization of lead-free build perovskite solar cells (PSC) using different hole transport layer materials (HTLM). The proposed new design explores the environmentally friendly tin based perovskite structure *i.e.*, Glass/FTO/PCBM/$CH_3NH_3SnI_3$/HTL/Au. The focus of this paper is to boost the efficacy of lead-free PSC by implementation of distinct HTLM. In addition, the efficiency of the photovoltaic cell has been exacerbated with the optimization of thickness of the absorber film, the defect concentration, interface defect concentration, the acceptor density of the perovskite film and the quantum efficiency. The results have shown that with the use of Cu_2O as a HTLM showed a remarkable efficiency of 28.57% compared to other hole transport layer materials. Finally, the results obtained make Cu_2O as a potential candidate for the Tin based PSC.

Keywords: Perovskite solar cell (PSC), Hole transport layer material (HTLM), Efficiency, Thickness

1 Introduction

In the last decade, Perovskite solar cells (PSC) have become increasingly popular due to their ability to absorb light, optimum bandgap[1], good diffusion length[2] and low-cost manufacturing[3] compared to Si-based Solar Cells. Efficiency of lead-based PSC increased significantly from 3.8% to 25.2% in the last few years[4]. Even though the lead-based PSC are highly efficient solar cells, they suffer from high toxicity, which prevents them from being commercialised. This is due to the lead element present in the perovskite structure which is harmful to the environment and may cause environmental problems. Therefore, great efforts should be made to remove the toxicity of PSC by introducing a non-toxic element in the perovskite structure[5]. Fortunately, there are earth-friendly metal cations that can be used, including Tin, Bismuth, Antimony and Germanium, which have been shown to replace lead in the PSC.

The toxicity of PSC-based lead can be avoided by using $CH_3NH_3SnI_3$ as an absorbance layer[6] and efficiency of perovskite photovoltaic cells can be increased, since the PSC-based tin has a direct bandgap of 1.30 eV and has a good optical absorbing property[7], making it a suitable candidate for optoelectrical applications. Tin build perovskite photovoltaic cells have a flat heterostructure design[8] and a small bandgap that allows a large amount of visible light to be absorbed. The major obstacle to this Tin PSC device is the oxidation of Sn^{+2} ion to Sn^{+4} ion when exposed to air. However, extensive research has increased the stability of tin PSC by adding tin fluoride (SnF_2) to the perovskite structure, which reduces the oxidation of Sn-based perovskite photovoltaic cells [9,10]. In addition, high doping has been done in this structure so that the movement of the charge particle can be done easily[11,12].

Although the tin-driven perovskite structure has improved rapidly, the efficiency of the tin-driven device is still low. The reason behind this is the interface properties between the absorbance film and Hole Transport Layer Material (HTLM), the defect of the perovskite structure. In this work, different HTLMs such as Cu_2O, CuI, Spiro-OMeTAD, PEDOT: PSS are used to analyse the behaviour of a tin based PSC device to increase the efficacy of the photovoltaic cell. For electron transport layer material (ETLM), PCBM ([6,6]-phenyl-C61-butyric acid methyl ester) is considered as a pivotal substance to minimise trap states between ETLM and perovskite absorbance layers in order to minimise ion migration[13,14]. The objective of this manuscript is to

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examine the design of the Glass/FTO/PCBM/ $CH_3NH_3SnI_3$/ HTLM/Au solar cell and to investigate different parameters such as thickness, defect, quantum efficiency of the solar cell to achieve better performance by optimising these layers through numerical simulation software. SCAPS-1D is used as a numerical simulation software to study the design and different parameters of the perovskite-based tin solar cell.

2 Materials and Methods

2.1 Novelty of the research

- Device Modelling of Tin based PSC heterojunction has been performed extensively.
- To enhance the efficacy of the tin based perovskite solar cell, four different HTLM are used in the structure of the cell to study its effects on the architecture of the photovoltaic cell.
- Optimization of perovskite/Cu_2O case solar cell gives the best result compared to other HTLM cases. The efficiency of the cell is 6% higher compared to the unoptimized solar cell for the Cu_2O case.
- According to the findings, the quantum efficiency (QE) of the Cu_2O case PSC device is higher than that of the other cases.

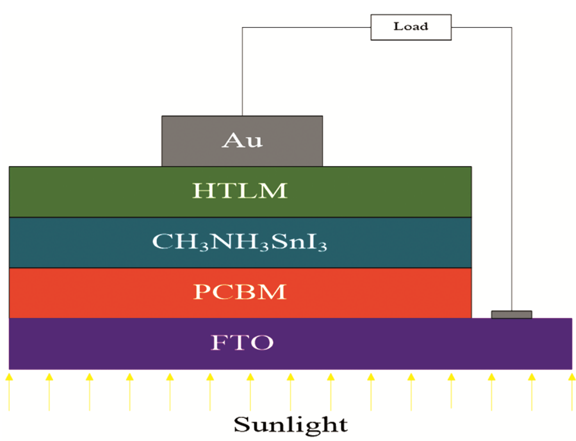

Fig. 1 — Configuration of perovskite photovoltaic cell.

2.2 Device configuration and simulation parameter

The basic structure of the perovskite-based n-i-p tin heterojunction solar cell is shown in the Fig. 1. In this architecture Cu_2O, CuI, Spiro-OMeTAD, PEDOT: PSS is considered to be the HTLM (say, p-type layer) for the perovskite solar cells. $CH_3NH_3SnI_3$ (say i-type layer) is the main absorbing layer of the solar cell; PCBM (say n-type layer) acts as an ETLM in the cell. Whereas FTO acts as the first layer to receive sunlight, and then this light passes through all subsequent layers to absorb solar energy. Gold is the back contact of the metal in this device.

Table 1 illustrates the basic configuration of each layer used in the perovskite solar cell. All parameters illustrated in Table 1 and Table 2 have been taken from past literature[15-17]. Here the R_a (Radiative Recombination) parameter is also considered in such a way that the effect of band-to-band recombination in the absorber layer could be studied and correlated with practical perovskite solar cells. Table 2 shows interface defects between the absorber film and the HTLM & absorber film and ETLM layer. In this solar cell, the type of defect is neutral, the electron and hole cross sections, denoted by C_e and C_h, E_v is denoted as energy with relative to reference level[18]. The numerical simulation was performed in the SCAPS 1D software to study the electrical characteristics of the PSC by different parameters of each film of photovoltaic cell material. SCAPS 1D is a one-dimensional programming software build on three paired differential equations, *i.e.*, Poisson equation, Continuity of electrons and holes[19,20]. With this software it can easily model seven layers of thin film

Table 1 — Basic configuration of perovskite photovoltaic cell

	$CH_3NH_3SnI_3$	CuI	Cu_2O	Spiro-OMeTAD	PEDOT:PSS	PCBM	FTO
Thickness (nm)	300	30	30	30	30	85	500
E_g (eV)	1.3	3.1	2.17	3.06	1.5	2	3.6
□	4.17	2.1	3.2	2.05	3.6	4.2	4
N_c (cm^{-3})	1×10^{19}	2.8×10^{19}	2.02×10^{17}	2.8×10^{19}	1×10^{21}	2.5×10^{21}	2.2×10^{18}
N_v (cm^{-3})	1×10^{18}	1×10^{19}	1×10^{19}	1×10^{19}	1×10^{21}	1×10^{21}	1.8×10^{19}
μ_e ($cm^2v^{-1}s^{-1}$)	1.6	100	200	1×10^{-4}	1	0.20	20
μ_h ($cm^2v^{-1}s^{-1}$)	1.6					0.20	10
P_d (cm^{-3})	-	-	-	-	-	2.93×10^{17}	1×10^{19}
P_a (cm^{-3})	3×10^{17}	1×10^{18}	1×10^{18}	1×10^{18}	1×10^{18}	-	-
ε_r (eV)	10	6.5	7.11	3	10	3.9	9
N_t ($1/cm^3$)	2×10^{15}	2×10^{14}	2×10^{14}	2×10^{14}	2×10^{14}	2×10^{14}	-
R_a (cm^3/s)	2×10^{-12}	-	-	-	-	-	-

Table 2 — Interface defect parameters of perovskite solar cell

Parameters	HTLM/$CH_3NH_3SnI_3$ Interface	$CH_3NH_3SnI_3$/ETLM Interface
Type of Defect	Neutral	Neutral
C_e (cm^2)	1×10^{-19}	1×10^{-19}
C_h (cm^2)	1×10^{-19}	1×10^{-19}
E_v	Above the highest E_v	Above the highest E_v
Energy with respect to reference (eV)	0.06	0.06
Total density (1/cm^2)	1×10^{10}	1×10^{10}

Table 3 — Simulation result of PSC device with different HTLM

HTLM	V_{oc} (V)	J_{sc} (mA/cm^2)	FF (%)	Efficiency (%)
Cu_2O	0.992	26.583	85.55	22.57
CuI	0.988	24.967	84.79	20.92
PEDOT:PSS	0.895	22.268	79.84	15.91
Spiro-OMeTAD	0.979	23.912	83.66	19.60

solar cells, consider different models of recombination, tunneling effect, different types of defect and interface defect and can also measure various AC and DC evaluations, Capacity-Conductance values, solar cell quantum efficiency and so on[21]. Various solar cell models, such as CdTe, CIGS, PSC, etc., have been modelled with this software[21-23]. This model has an operating temperature of 300 K and the perovskite solar cell device is modelled under AM. 1.5 light range with a light power of 1000 (W/m^2).

Table 3 shows the simulation result of tin based PSC with different HTLM. This result is been obtained by considering the parameters of Table 1 and Table 2.

The next section of the paper examines the contribution of various parameters, such as analysis of the thickness variation of the absorbance layer, defect concentration of the absorber film, the interface defect of the perovskite photovoltaic cell, the acceptor density and the QE of the photovoltaic cell. Various HTLMs have also been examined with this structure in order to obtain a better electrical performance. Optimization of all these layers has also been done to improve the efficacy of the photovoltaic cell.

3 Results and Discussion

3.1 Impact of thickness variation of $CH_3NH_3SnI_3$ PSC with different hole transport layer materials

The Tin-based perovskite absorber layer is a crucial component of the PSC device because it plays a big part in cell behaviour. It is important to optimise the thickness of the absorber layer by balancing the charges generated by photo generation and recombination in the solar device. Figure 2 illustrates the effect of varying the thickness of the absorber film from 0.3μm to 1μm. First, the thickness of the absorber layer has been varied with different HTLMs considered. Figure 2 (a) depicts the J_{sc} of the photovoltaic device and is affected by the thickness of the absorber film. For all cases of different HTLM, J_{sc} reaches about 27.7 mA/cm^2 at a thickness of 1μm. This means that the thicker the absorbing material, the more holes and electrons can be generated by longer wavelength absorption. Figure 2 (b) shows the V_{oc} of the PSC device which decreases slightly as the width of the absorber film increases. In PEDOT: PSS case only V_{oc} increases. The decrease in V_{oc} is due to the increase in I_o at a higher value, giving carriers more opportunities for recombination. This can be explained[15] with given Eq. (1).

$$V_{oc} = \frac{PkT}{c}\log\left(\frac{Jsc}{I_0} + 1\right) \quad \dots (1)$$

Here p represents a factor, J_{sc} represents current density, $\frac{PkT}{c}$ represents thermal voltage and I_o represents dark saturation current. I_o reply on the recombination of the photovoltaic device. Therefore, V_{oc} is an indication of amalgamation of holes and electrons in the photovoltaic cell. Fill Factor corresponds to the series resistance & shunt conductance of the photovoltaic cell. As shown in Fig. 2 (c) there is almost a slight decrement in fill factor of the device with respect to thickness. This mean that there is a slight increment in series resistance of the photovoltaic cell when thickness is increased. Figure 2 (d) depicts the efficiency of the PSC device when thickness is varied. For the case of Cu_2O, efficiency reaches to 23.49% from 22.57% at 0.5μm. Beyond that efficiency decreases to 23.21% at 1μm. While for other HTLM there is a relatively high

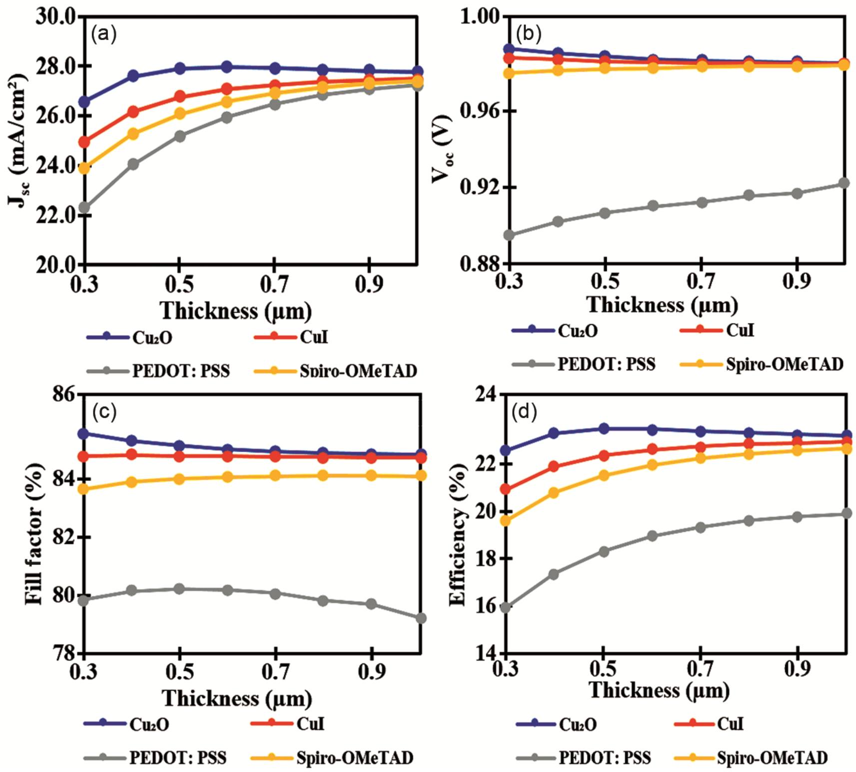

Fig. 2 — Impact of thickness variation on perovskite solar cell (a) J_{sc}, (b) V_{oc}, (c) Fill factor and (d) Efficiency of the photovoltaic cell.

increment in the efficacy of the photovoltaic cell with reference to thickness. From the efficiency graph it can be concluded the optimized thickness of the absorber film for the various HTLM cases. Table 4 shows the optimised thickness of the absorber film for different HTLMs.

Table 4 — Optimized thickness of absorber film with various HTLM

HTLM	$CH_3NH_3SnI_3$ thickness (μm)
Cu_2O	0.5
CuI	1
PEDOT:PSS	1
Spiro-OMeTAD	1

3.2 Impact of defect concentration on PSC device

The working condition of the perovskite-based tin photovoltaic cell may be limited due to very high level of defect in the perovskite absorber film. Defects in the absorber layer can cause carrier recombination, which reduces cell efficiency and cell life. Figure 3 shows the impact of defect density on the perovskite absorber layer by varying defect from 2×10^{14} cm^{-3} to 2×10^{17} cm^{-3}. With increase in the concentration of the defect, the electrical characteristics of the photovoltaic cell decrease rapidly as illustrated in Fig. 3 (a-d) for each HTLM case. Value of efficiency for Cu_2O, Spiro-OMeTAD, CuI reaches to about 9.56% at 2×10^{17} cm^{-3} defect density. Whereas for PEDOT: PSS material efficiency is 8.40%. The rapid drop in the electrical characteristics of all parameters is mainly due to the trapping condition in the defective areas, which causes electron and hole recombination faster than photon generation. Thus further, a minimum defect size of 2×10^{14} cm^{-3} is required for a perovskite solar cell to operate at a high efficiency.

3.3 Impact of interface defect concentration on $CH_3NH_3SnI_3$/HTLM layer

Numerical simulation analysis has been carried out at the interface defect concentration of absorber layer and HTLM. Figure 4 illustrates the impact of interface defect concentration on PSC device from 1×10^{10} cm^{-3} to 1×10^{15} cm^{-3}. The result of the simulation shows the variation in efficacy of the photovoltaic cell as illustrated in Fig. 4 (a). Best efficiency is only retained by the Cu_2O material *i.e.*, 17.23% at 1×10^{15} cm^{-3} defect value. While for CuI and Spiro-OMeTAD case efficiency comes out to be 16.71% and 16.45% respectively. For V_{oc} (Fig. 4 (b)) effect of interface defect concentration is very small. The major change is in the J_{sc} and FF of the device as

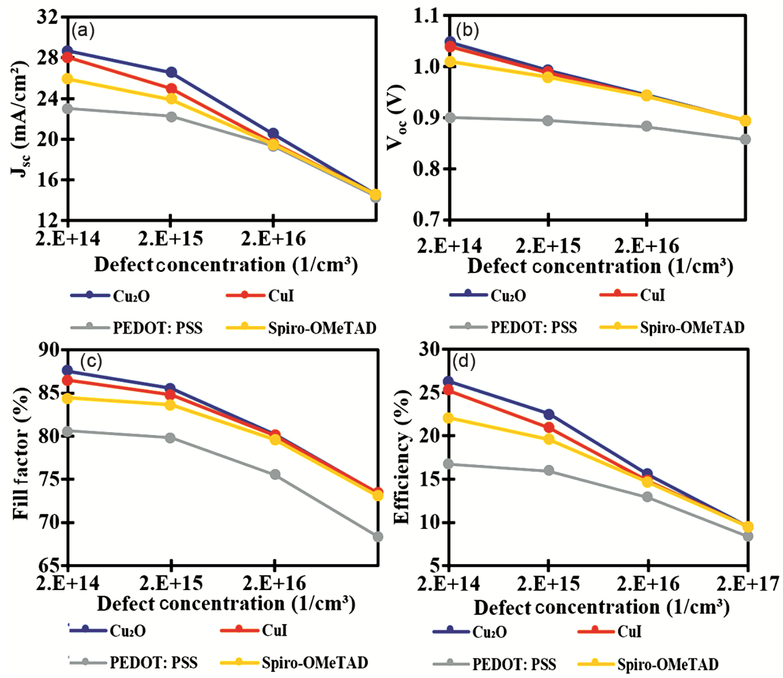

Fig. 3 — Impact of defect density on perovskite solar cell illustrating (a) J_{sc}, (b) V_{oc}, (c) fill factor, and (d) efficiency of the photovoltaic cell.

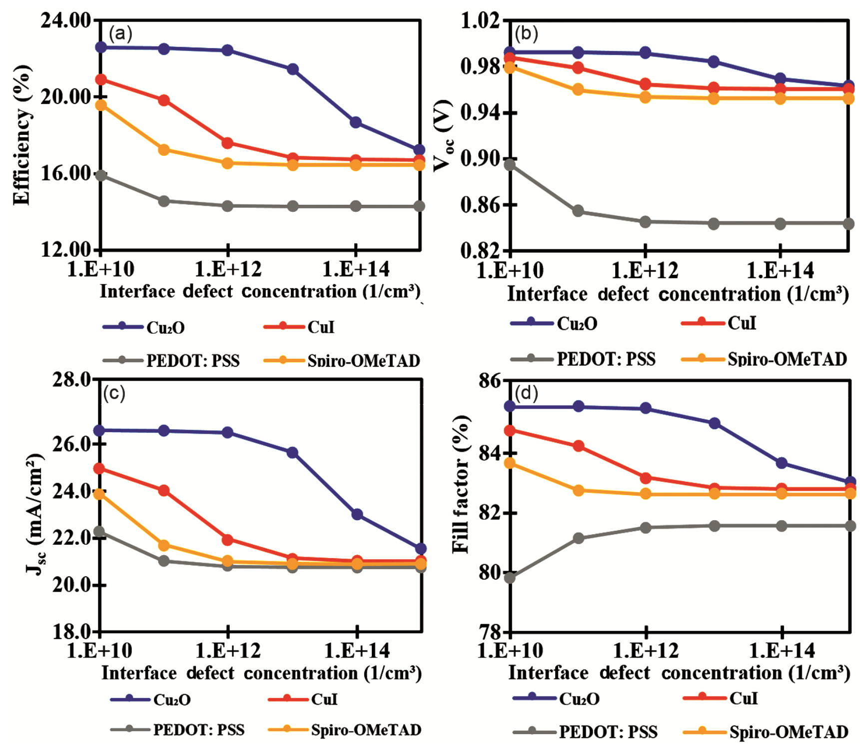

Fig. 4 — Impact of interface defect on PSC device graph showing (a) J_{sc}, (b) V_{oc}, (c) fill factor, and (d) efficiency of the photovoltaic cell .

depicted in Fig. 4 (c & d) respectively when the interface defect concentration is varied. The decrease in current density is due to the diffusion of holes and electrons at the interface of the absorber film and HTLM. As a result, optimum value of interface defect concentration of 1×10^{10} cm^{-3} should be maintained.

3.4 Impact of acceptor density of perovskite layer

A very high doping concentration is very important in tin based perovskite structure. With high acceptor

Table 5 — Optimised design of PSC device

HTLM	V_{oc} (V)	J_{sc} (mA/cm^2)	FF (%)	Efficiency (%)
Cu_2O	1.072	30.087	88.57	28.57
CuI	1.061	29.288	88.35	27.46
PEDOT:PSS	1.022	27.847	86.45	24.62
Spiro-OMeTAD	1.056	28.268	88.20	26.34

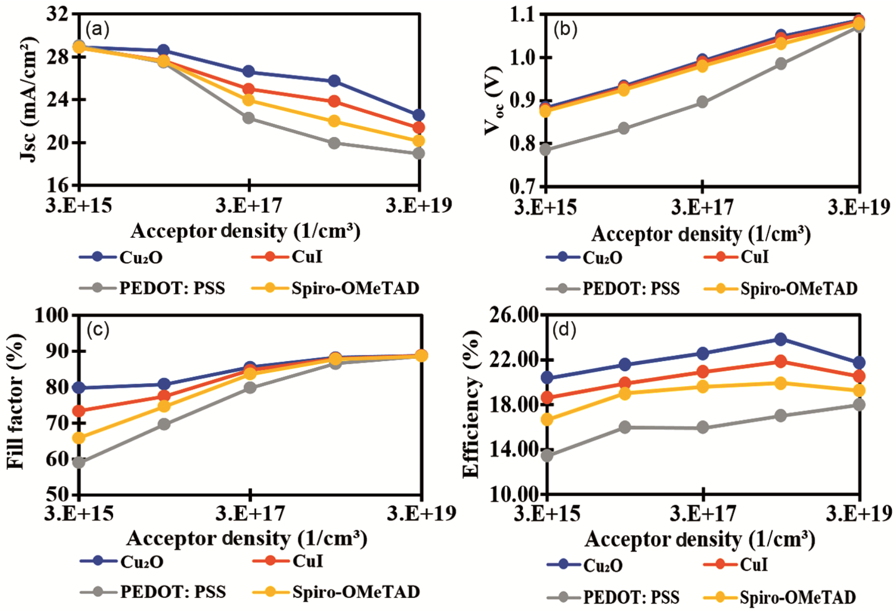

Fig. 5 — Impact of acceptor density on perovskite layer (a) J_{sc}, (b) V_{oc}, (c) fill factor, and (d) efficiency of the photovoltaic cell.

concentration, movement of charge particles is very easy to their respective contacts. Also, high doping directly effects the electrical performance of the photovoltaic cell. Therefore, its analysis is very crucial in designing efficient PSC device. In this acceptor density is changed from 3×10^{15} cm^{-3} to 3×10^{19} cm^{-3}. Simulation results reveals that there is a gradual fall in J_{sc} of the photovoltaic cell as illustrated in Fig. 5 (a). Although V_{oc} and FF increases constantly with respect to acceptor concentration variation as depicted in Fig. 5 (b & c). But the analysis of the efficiency of the perovskite photovoltaic cell beyond 3×10^{18} cm^{-3} acceptor concentration, there is a decrease in efficacy of the photovoltaic cell because incrementing the doping level can promote the movement of charge particles but beyond a limit a too high acceptor concentration reduces the mobility of carriers and increases carrier recombination [23,24], which can easily be seen in Fig. 5 (d). Therefore, it is significant to maintain the acceptor concentration at the value of 3×10^{18} cm^{-3}.

3.5 Quantum efficiency of tin based perovskite solar cell

Quantum efficiency is the measure of the collected carriers by the photovoltaic cell to the incident photons[25]. It is expressed in wavelength. Figure 6 illustrates the quantum efficiency of PSC device with distinct HTLM. From the graph it is reveal that quantum efficiency of Cu_2O PSC device is greater than all other HTLM PSC device. This mean that the photon absorption capacity is high in Cu_2O case and generation of carriers is also high with respect to others. While lowest is in the case of PEDOT: PSS. As a consequence, the efficiency of the Cu_2O case is also large in comparison to others as shown in Table 5.

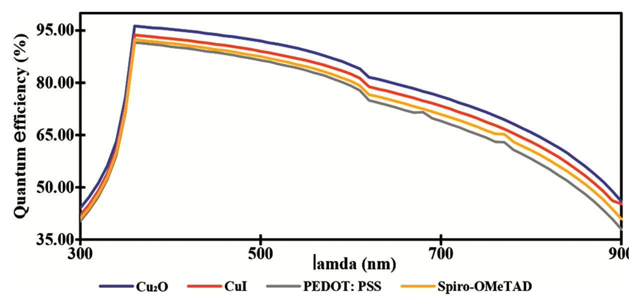

Fig. 6 — Quantum efficiency of tin based perovskite solar cell.

After examination of optimized width of perovskite absorber layer, defect concentration, interface defect density and acceptor density of tin based perovskite solar cell with considering different HTLM. Table 5 illustrates the electrical characteristics of the optimized PSC device. The performance of PSC device with Cu_2O HTLM is the highest among other hole transport layer material. The efficiency obtained with optimized $CH_3NH_3SnI_3/Cu_2O$ design is 28.57% whereas for CuI is 27.46%, Spiro-OMeTAD is 26.34% and for PEDOT: PSS is 24.62%. With optimization of layers of perovskite solar cell, there is a huge increase in efficiency of the solar cell in case of Cu_2O case. About 6% of efficiency is increased on comparison with the result with unoptimized Cu_2O case PSC device.

4 Conclusion

A computational analysis of tin build perovskite solar cells with different HTLMs has been performed using SCAPS simulation software. First, the analysis of perovskite photovoltaic cells with distinct material for transporting holes has been simulated. The results show that the efficiency of the PSC-based tin conversion device is low. The impact of thickness variation, interface defect density, defect density and acceptor density were further investigated. The electrical characteristics of the PSC are greatly improved by optimising these parameters. The results show that for Cu_2O HTLM, efficiency is 28.57 per cent, J_{sc} =30.087 mA/cm^2, V_{oc} =1.072 V and Fill Factor =88.57%. While for CuI, PEDOT: PSS, Spiro-OMeTAD case, efficiency is good but lower than for Cu_2O. When the quantum efficiency of different PSC are compared, it is observed that the optical absorption capacity of the Cu_2O PSC device is high compared to other HTLM PSC devices. Therefore, with optimization of layers the better results can be achieved in tin based perovskite solar cell in respect of power conversion value.

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