

Investigating the Effect of ZnSe (ETM) and Cu₂O (HTM) on Absorber Layer on the Performance of Perovskite Solar Cell Using SCAPS-1D

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Abstract: Tin perovskite (CH₃NH₃SnI₃) have attracted a lot of attention and could be a viable alternative material to replace lead perovskite in thin film solar cells. A detailed understanding on the effects of each component of a solar cell on its output performance is needed to further develop the technology. In this work, a numerical simulation of a planar hetero-junction tin based perovskite solar cell using Solar Cell Capacitance Simulator (SCAPS) to study some parameters that can influence the performance of tin PSC with Cu₂O as HTL and ZnSe as ETL performed. The thickness of absorber material, ETL and HTL, the bandgap of absorber material and ETL was investigated. Results revealed that the thickness and bandgap of the absorber material and ETL of ZnSe strongly influence the PCE of the device. The performance of the cell increases with reduction in thickness of ZnSe. ZnSe is found to be a replacement for TiO₂ which is expensive. Cuprous oxide of HTL in tin based PSC is efficient and better than the expensive spiro-MeOTAD which is easily degradable. Furthermore, results of simulation and optimization of various thicknesses indicates that ZnSe has a PCE of 21.11%, FF of 68.33%, J_{SC} of 33.51mA/cm² and V_{OC} of 0.92V. These values slightly increase after optimization of parameters to PCE of 22.28%, FF of 70.94%, J_{SC} of 31.01mA/cm² and V_{OC} of 1.01V.

Keywords: Solar Cell, Perovskite, Device Simulation, SCAPS, Efficiency

1. Introduction

During the past years, organic-inorganic metal halide perovskites have gained tremendous attention for their application in high-performance solar cells because of its peculiar features like high conversion efficiency and low cost processing. Research for alternative absorber materials for synthesis of low cost, stable and highly efficient solar cells are in great demand which is a better replacement for energy generation from fossil fuel such as coal, petroleum and natural gas which people use today that causes environmental pollution and it is not renewable.

Organic-inorganic hybrid perovskite solar cells have attracted great attention in the photovoltaic research community due to its ease of processing low cost of

production and relatively high efficiency which make it more preferable over other existing solar cell materials. Within a limited period of time, organic-inorganic halide of tin based perovskite solar cell has proved its potential for increasing its efficiency rapidly from 6.4% to 19.3% in 2014. Perovskite solar cells is a kind of solar cell device which use perovskite based material as the light absorbing layer. Methyl ammonium tin tri-iodide (CH₃NH₃SnI₃) perovskite [1] has an appropriate optical property that are highly desirable as photovoltaic material because of its excellent characteristics like direct bandgap (1.3eV), a high absorption coefficient and long diffusion length. Since the demand for energy is increasing due to the rapid improvement of technology [40]. Solar cell converts the energy of light directly into electricity by the photovoltaic effect due to its physical and chemical

phenomenon. [2]. Researchers have developed solar cell based on tin perovskite and a PCE exceeding 6% [1]. Despite the tremendous progress made in tin based perovskite, there are few issues that need to be addressed: resistance to degradation and replacement of expensive hole transport material. HTM plays an essential role in a photovoltaic device for determining its stability and PCE. An HTM needs high carrier mobility and should form a defect free interface with the absorbing layer to minimize carrier recombination.

It is of great importance to improve the performance and material properties of the architecture solar cell. Our intention in this work is to examine the performance of optimized zinc selenide (ZnSe) as electron transporting material (ETM), cuprous oxide (Cu_2O) as hole transporting material (HTM), tin based halide perovskite solar cells and fluorine doped tin oxide (FTO) as transparent conducting oxide (TCO) using a software package known as solar cell capacitance simulator in one dimension (SCAPS-1D). A series of studies on the parameters of the cell are carried out according to the thickness of the absorbing layer, ETL and HTL, band gap of the absorber layer and ETL and hole mobility of the HTL. Of recent, the search for alternative absorber materials, synthesis of low-cost and highly efficient solar cells became prominent and the most viable substitution for lead is tin which is a member of the group 14 elements and period 5 in the periodic table. Tin based perovskite is a non-toxic material, potential environmentally

friendly and causes no harm to human health and also stands as a replacement to lead for commercial purposes because of its toxicity.

2. Modeling and Simulation of the Device

The working mechanism of solar cells can generate electricity from sunlight using a photovoltaic effect, which is the physical and chemical phenomenon. When a solar cell is exposed to light, a portion of the photon with the energy larger than the bandgap is absorbed by the semiconductor. The absorbed photons with sufficient excitation energy can cause the transport of electrons and holes; electrons in the conduction band and holes in the valence band move in different directions. The basis setting is determined by light or dark illumination. The photovoltaic parameters used to describe the performance of a photovoltaic device are short circuit current density (J_{SC}), open circuit voltage (V_{OC}), fill factor (FF) and conversion efficiency (η). SCAPS-1D is one-dimensional simulation software developed by Burgelman *et al.* from the University of Gent, Belgium. SCAPS can be determined by variety of properties related with solar cells such as energy bands, concentrations, currents, I-V characteristics, C-V, C-f, and QE.

The flow chart below shows procedures in running a simulation with SCAPS and its action panel



Figure 1. SCAPS flow chart and action panel [3].

The flow chart of SCAPS working procedure describes how SCAPS is lunch by opening the action panel. Set problem by inputting the layers of the perovskite structure to give input parameters. Specify the working condition which includes temperature, voltage, frequency and number of points. Specify actions to be measured are I-V, C-V, C-F and QE and finally run SCAPS to display the simulated plots of the solar cell parameters such as output circuit voltage, short circuit current density, fill factor and efficiency.

Most state of the art perovskites are based on TCO/ETL/perovskite/HTL/metal structure, where TCO, ETL and HTL refer to transparent conducting oxide, electron transport layer, hole transport layer respectively and the perovskite material (absorber layer) is the heart of the solar cell. The cell model is based on $\text{FTO}/\text{ZnSe}/\text{CH}_3\text{NH}_3\text{SnI}_3/\text{Cu}_2\text{O}/\text{Ag}$ and the energy bandgap used for this simulation is shown in Figure 2.

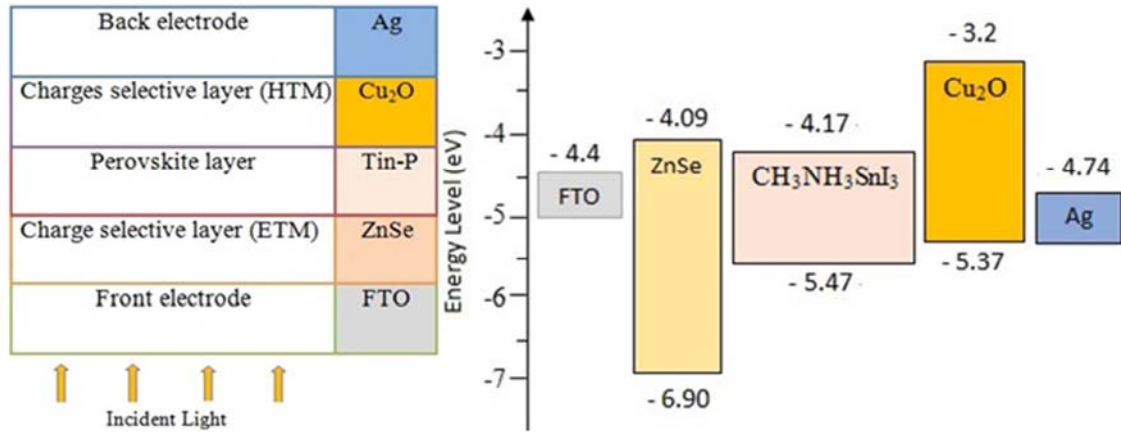


Figure 2. Model of sandwiched simulation structure and energy levels diagram of different ETM with perovskite solar cell.

The two defect interfaces ZnSe/CH₃NH₃SnI₃ and CH₃NH₃SnI₃/Cu₂O was inserted for carrier recombination, the energy levels diagram as shown in figure 2 indicates the conduction band offset is -0.08eV at ZnSe/CH₃NH₃SnI₃ interface. -0.08eV signifies that the position of zinc selenide (ETL) layer is lower than that of the perovskite layer makes

the device to achieve a good performance because of an enhanced built in electric field to the electrons. The valence band offset is +0.1eV at CH₃NH₃SnI₃/Cu₂O interface, signifies that as the position of the perovskite layer is higher than that of cuprous oxide (HTL) layer, which will enable high device performance and the rate of energy loss will be reduced.

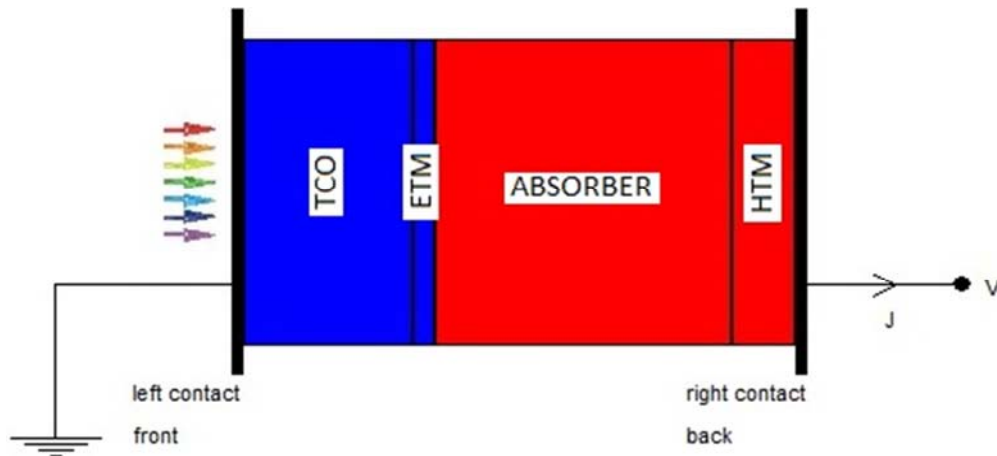


Figure 3. The structure of perovskite solar cell in the simulation.

The parameters for different layers in the simulation are chosen on the basis of theoretical considerations, experimental data and existing literature or in some cases, reasonable estimation [4, 5, 6 & 7]. Thermal velocities of the electron and hole are both set to be equal to 10^7 cm/s but for the perovskite layer are set to be 10^6 cm/s. The absorber is a *p*-type semiconductor doped with a carrier density of 3.2×10^{19} cm⁻³. The defects in the absorption layer are set to be neutral, Gaussian energetic distribution with a characteristic energy of 0.1eV, with a defect density of 10^{15} cm⁻³ but absorber layer is 10^{14} cm⁻³. The work function of FTO and metal back contact for hole transport are considered to be 5.10eV and 4.74eV [8] respectively. All the simulations operate under the scanning voltage from 0V to 1.1V. All simulations in this work were performed under ambient temperature (300 K). The electrical parameters are V_{OC} , J_{SC} , FF and efficiency generated by SCAPS-1D were then used to determine the optimum bandgap of the absorber layer in the

configuration. The current density voltage (J-V) curves and quantum efficiency (QE) of the best solar cells from the simulation were then determined.

3. Results and Discussions

3.1. Effect of ZnSe as ETL and Cu₂O as HTL on the J-V and QE Curves of PSC

Figure 4 shows simulated J-V curves for a CH₃NH₃SnI₃ based device in the planar electron-absorber-hole (n-i-p) configuration with Cu₂O as HTL and ZnSe as ETL. Cu₂O/ZnSe cell has high power conversion efficiency (PCE) of 19.65% with a high open circuit voltage (V_{OC}) of 0.89V, short circuit current density (J_{SC}) of 32.44 mA/cm² and highest fill factor (FF) of 67.77% respectively. This simulation result provide evidence to prove that ZnSe is a probable material to be used as electron transport material on like TiO₂ which is expensive and the simulated device performance is consistent with the experimental results of tin based PSCs [9].

Cuprous oxide has very high hole mobility, the hole mobility enhances the efficiency of ZnSe. Figure 5 shows the quantum efficiency (QE) of the cell featured with a high platform between 300nm and 900nm with the maximum of 96% at 700nm. In SCAPS, QE is the external quantum efficiency (EQE) or IPCE is the internal power conversion efficiency.

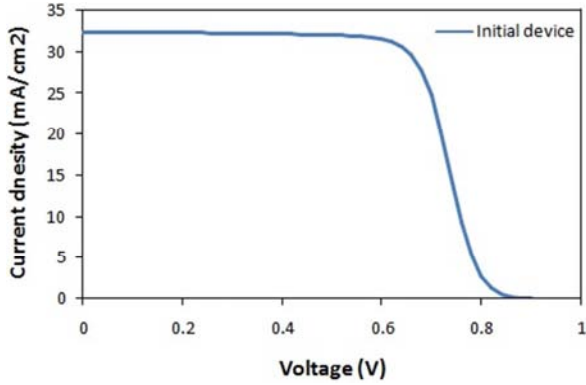


Figure 4. J-V curves of PSC with initial device parameters.

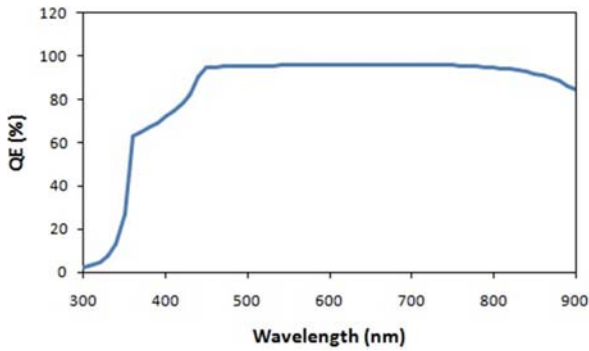


Figure 5. QE curves of PSC with initial parameter.

3.2. Effect of the Thickness of Absorbing Layer

Absorber layer thickness plays a major role in determining the efficiency of the device. To confirm the optimum absorber thickness, simulation has been carried out in the range of 0.03 to 1.5 μm while other parameters are kept constant. Absorber layer thickness variation affects the diffusion length of carriers because if the absorber layer thickness is too low (lower than 0.03 μm), absorption rate decreases, ultimately efficiency also decreases. Similarly, if the absorber layer thickness is too high (higher than 1.2 μm), then the charge carriers may not travel up to the charge collection layers which result to decrease in the efficiency as shown in table 1. Table 1 shows that an increase in thickness of absorber layer means we are increasing the light absorbed which could result in the increase in PCE and J_{SC} but FF decreases resulting to increase in charge carriers and increase in J_{SC} which could improves the PCE gradually while V_{OC} increases gradually but remains invariable at 0.89V from the thickness of 0.5 μm since more charge carriers will not be far away from the surface which is a recombination site. The simulated parameters such as PCE, FF, J_{SC} , V_{OC} of the $\text{CH}_3\text{NH}_3\text{SnI}_3$ solar cells, with varying perovskite thickness as shown in Figure 6. The maximum PCE of 19.82%, with J_{SC}

of 32.91 mA/cm^2 , FF of 67.44%, V_{OC} of 0.89V is achieved when the thickness reaches 0.9 μm .

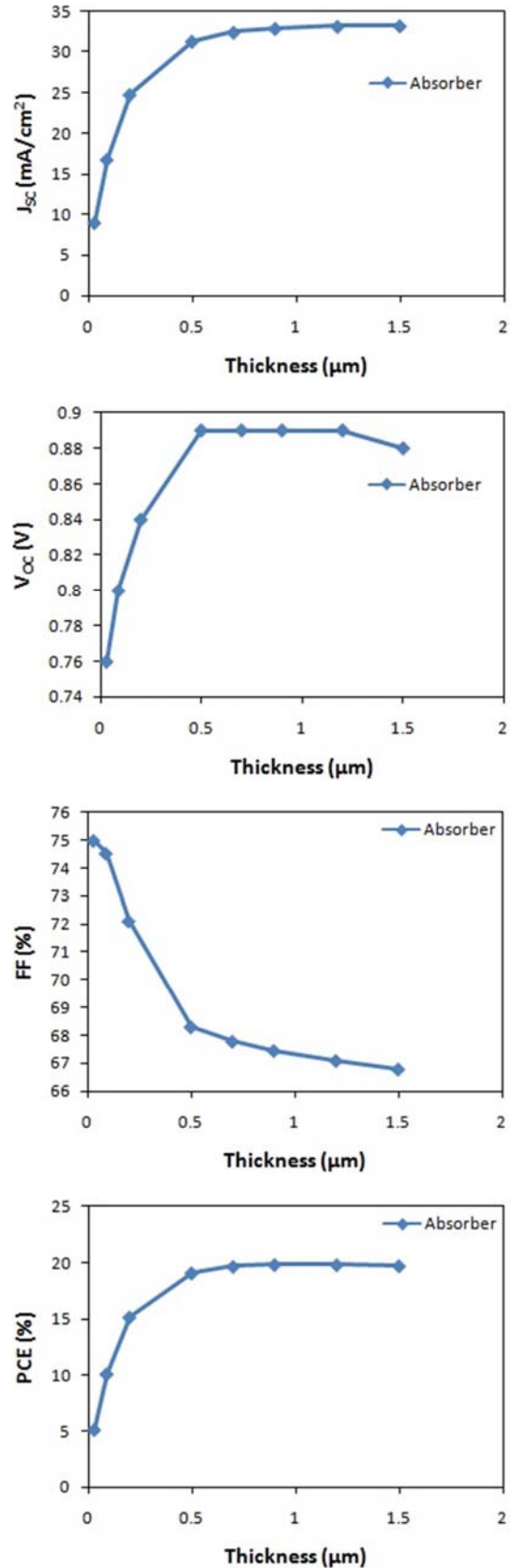


Figure 6. Variation in performance parameters of PSC with thickness of Absorber.

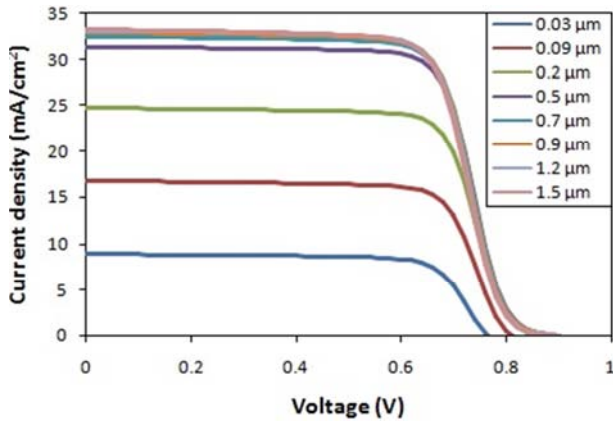


Figure 7. J-V curves of PSC with different values of Absorber thickness.

Table 1. Dependence of solar cell performance on absorber layer.

Absorber thickness (μm)	J _{sc} (mA/cm ²)	V _{oc} (V)	FF (%)	PCE (%)
0.03	8.87	0.76	74.99	5.08
0.09	16.76	0.80	74.53	10.11
0.2	24.73	0.84	72.11	15.15
0.5	31.32	0.89	68.29	19.08
0.7	32.44	0.89	67.77	19.65
1.9	32.91	0.89	67.44	19.82
1.2	33.16	0.89	67.08	19.81
1.5	33.23	0.88	66.77	19.71

3.3. Effect of the Thickness of ETL

The effect of the thickness of zinc selenide (ETL) on the performance parameters of the cell ranging from 0.0050 to 0.0800 μm obtained in figure 8. Table 2 shows that when there is an increase in the thickness of electron transporting material it results in decrease in J_{sc}, FF and efficiency of the device while V_{oc} decreases but remain invariable from 0.89V at the thickness of 0.0100 μm. This signifies that when the material is thicker, it provides a longer diffusion path for the electron to reach the electrode which limit (the solar cell parameters) the charge collection efficiency and transmitting of incident photon decreases with increasing thickness. High performance was obtained, when the thickness of ETL was 0.0050 μm with J_{sc} of 33.13 mA/cm², V_{oc} of 0.90V, FF of 68.16% and high PCE of 20.44%.

Table 2. Dependence of solar cell performance of the thickness of ZnSe (ETL).

ZnSe thickness (μm)	J _{sc} (mA/cm ²)	V _{oc} (V)	FF (%)	PCE (%)
0.0050	33.13	0.90	68.16	20.44
0.0100	32.91	0.89	67.76	20.03
0.0150	32.81	0.89	67.75	19.90
0.0300	32.63	0.89	67.75	19.77
0.0350	32.58	0.89	67.75	19.74
0.0450	32.49	0.89	67.76	19.68
0.0500	32.44	0.89	67.77	19.65
0.0800	32.18	0.89	67.79	19.50

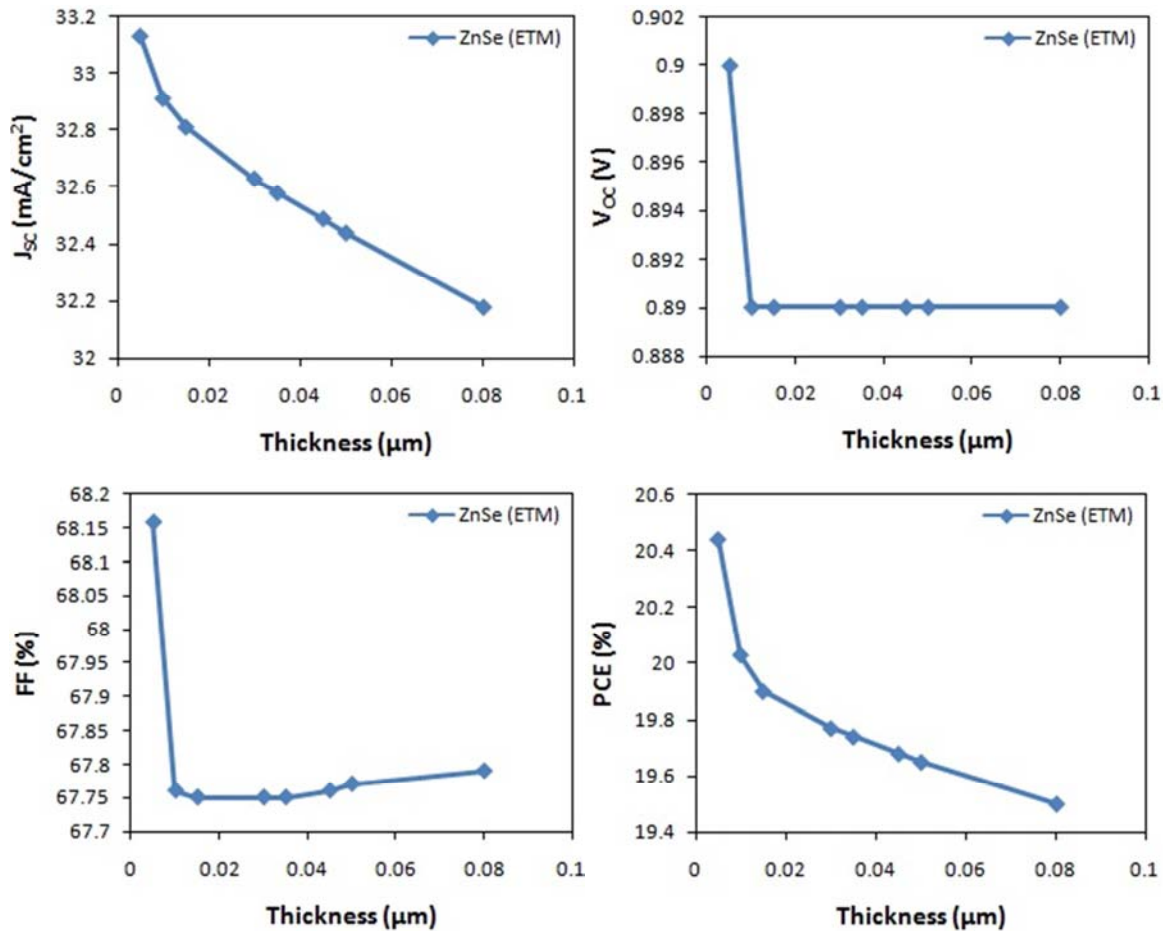


Figure 8. Variation in performance parameters of PSC with thickness of ZnSe (ETL).

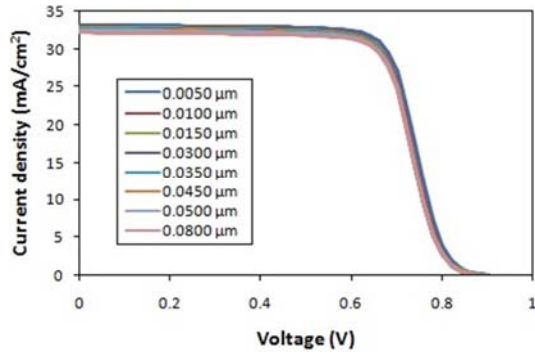


Figure 9. J-V curves of PSC with different values of ZnSe (ETL) thickness.

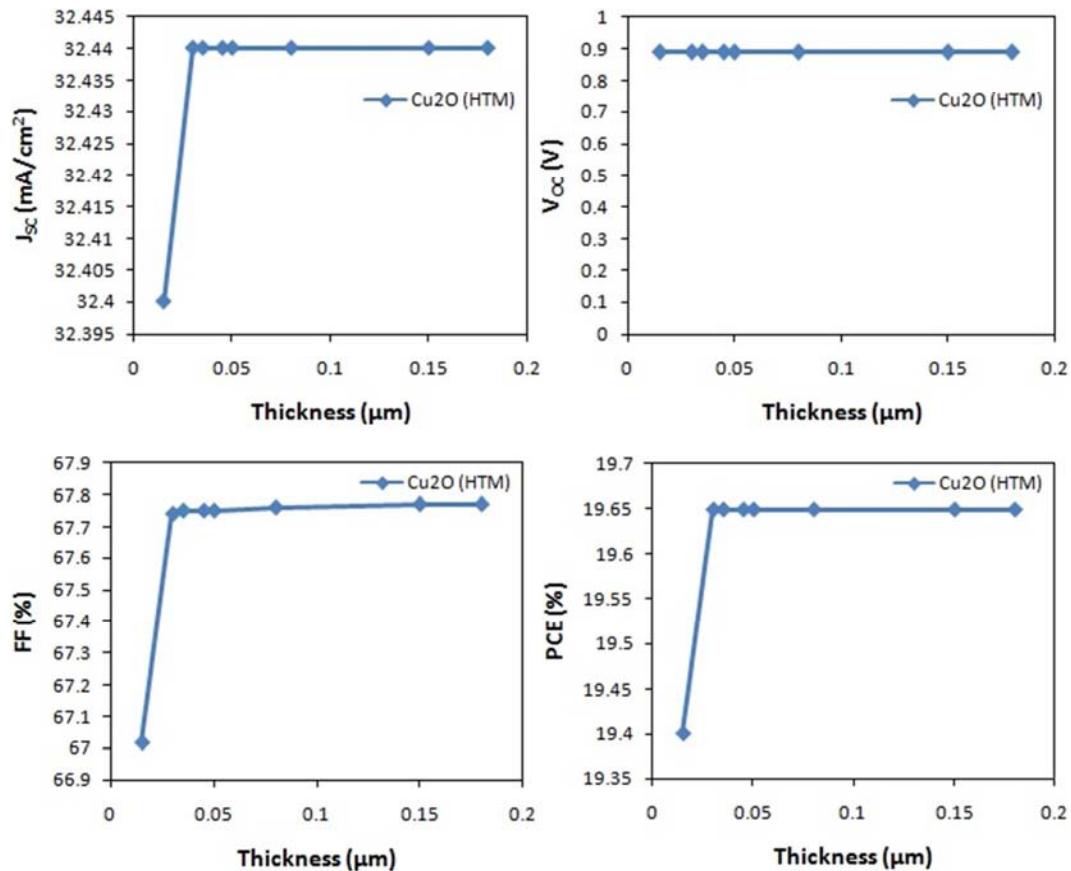


Figure 10. Variation in performance parameters of PSC with thickness of Cu₂O (HTL).

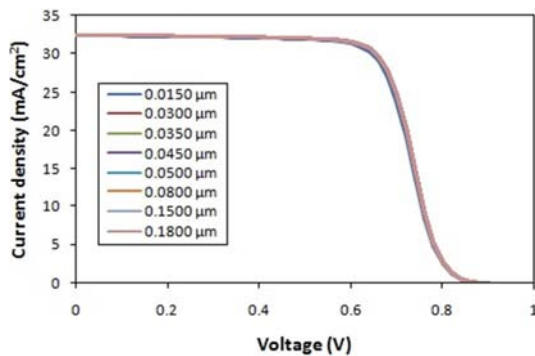


Figure 11. J-V curves of PSC with different values of Cu₂O (HTL) thickness.

It was observed that after varying the thickness of cuprous oxide as shown in table 3, it results to an increase in J_{sc} , FF and PCE at 19.65% remains invariable from the thickness of 0.0300 μm while V_{oc} remains invariable all through due to partial conversion of light and high conductivity. Similarly, from what was obtained from above that an increase in the thickness of ETL could result to decrease in the efficiency; reverse is the case when an increase in the thickness of HTL could result to increase in the efficiency of the device. The effect of the thickness of cuprous oxide on the performance parameters of the cell ranging from 0.0150 μm to 0.1800 μm was shown in figure 11. A maximum performance was obtained on J_{sc} of 32.44 mA/cm^2 , V_{oc} of 0.89V, FF of 67.77% and PCE of 19.65%.

Table 3. Dependence of solar cell performance on Cu₂O (HTL).

Cu ₂ O thickness (μm)	J_{sc} (mA/cm^2)	V_{oc} (V)	FF (%)	PCE (%)
0.0150	32.40	0.89	67.02	19.40
0.0300	32.44	0.89	67.74	19.65
0.0350	32.44	0.89	67.75	19.65
0.0450	32.44	0.89	67.75	19.65
0.0500	32.44	0.89	67.75	19.65
0.0800	32.44	0.89	67.76	19.65
0.1500	32.44	0.89	67.77	19.65
0.1800	32.44	0.89	67.77	19.65

3.4. Effect of the Bandgap of Absorber Layer

It was observed that the J-V curve shown in Figure 13 after varying the bandgap ranging from 0.8 to 1.4eV of the absorber layer, there is a decrease in short circuit current density (J_{sc}) at 29.48mA/cm² but increases in open circuit voltage (V_{oc}) at 0.99V, FF at 70.47% and PCE at 20.57% which are the optimized parameters for the bandgap due to increase of photoconductivity and photosensitivity as plotted in Figure 12. Furthermore, at 1.5eV, J_{sc} at 25.77mA/cm² and PCE at 20.01% decrease due to the increase of V_{oc} at 1.08V and FF at 71.66% because of the decrease of

photoconductivity and photosensitivity.

3.5. Effect of the Bandgap of ETL

Moreover, the J-V curve in figure 15, was observed that when the bandgap was varied it results to increase in J_{sc} at 32.97mA/cm² and PCE at 19.97%, decrease in FF at 67.72% and V_{oc} at 0.89V is stable (invariable) throughout without considering reduction of light absorption because the quantity of electron hole pairs is increased which increases the efficiency of the solar cell as shown in Table 5.

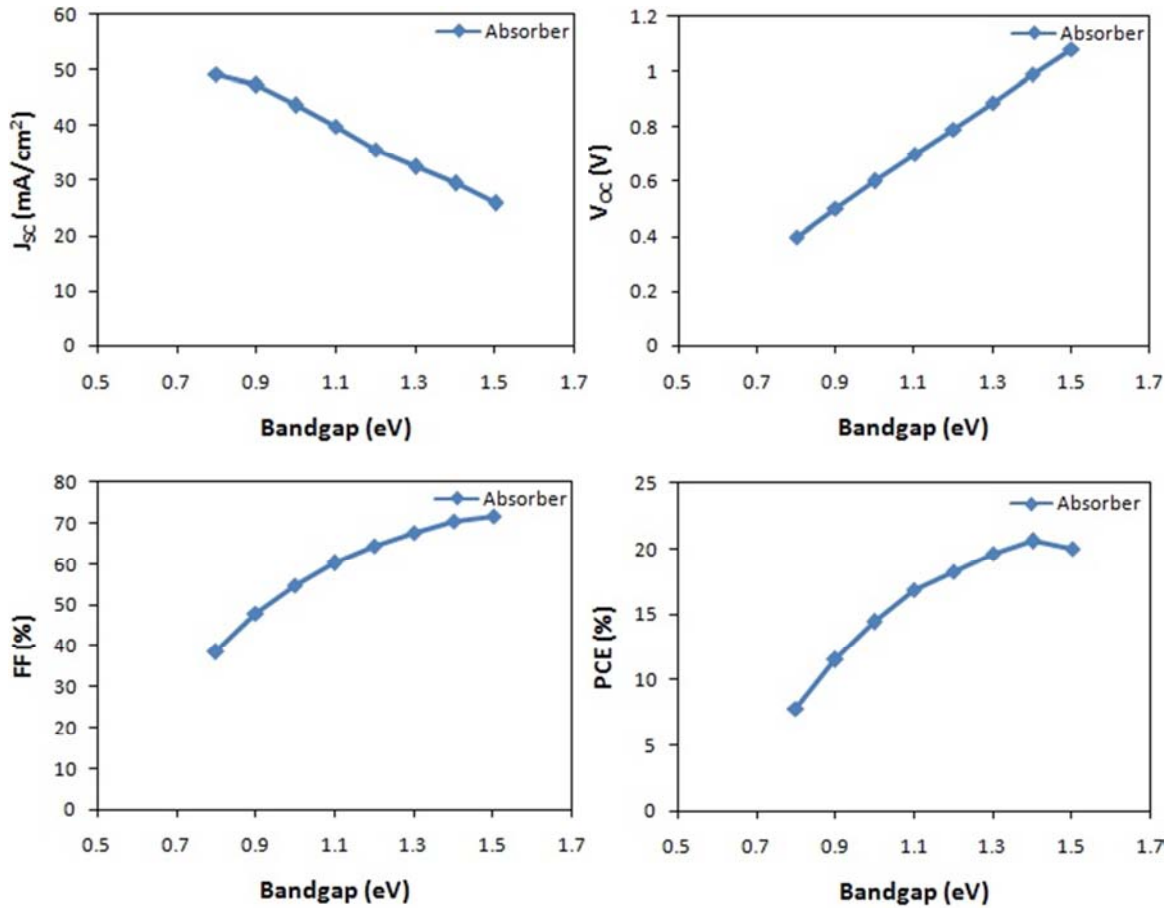


Figure 12. Variation in performance parameters of PSC with bandgap of Absorber layer.

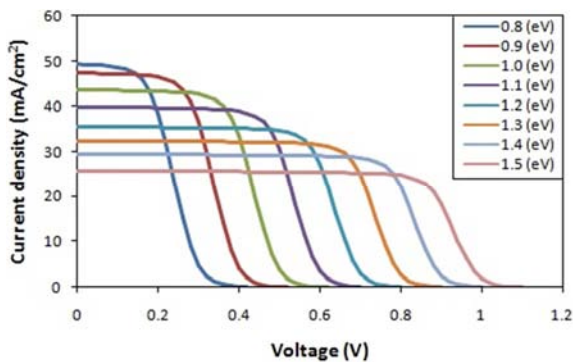


Figure 13. J-V curves of PSC with different values of Absorber layer bandgap.

Table 4. Dependence of solar cell performance on Absorber layer.

Absorber bandgap (eV)	J_{sc} (mA/cm ²)	V_{oc} (V)	FF (%)	PCE (%)
0.8	49.26	0.40	38.48	7.76
0.9	47.32	0.50	48.00	11.50
1.0	43.62	0.60	54.82	14.43
1.1	39.90	0.70	60.18	16.84
1.2	35.54	0.79	64.36	18.24
1.3	32.44	0.89	67.77	19.65
1.4	29.48	0.99	70.47	20.57
1.5	25.77	1.08	71.66	20.01

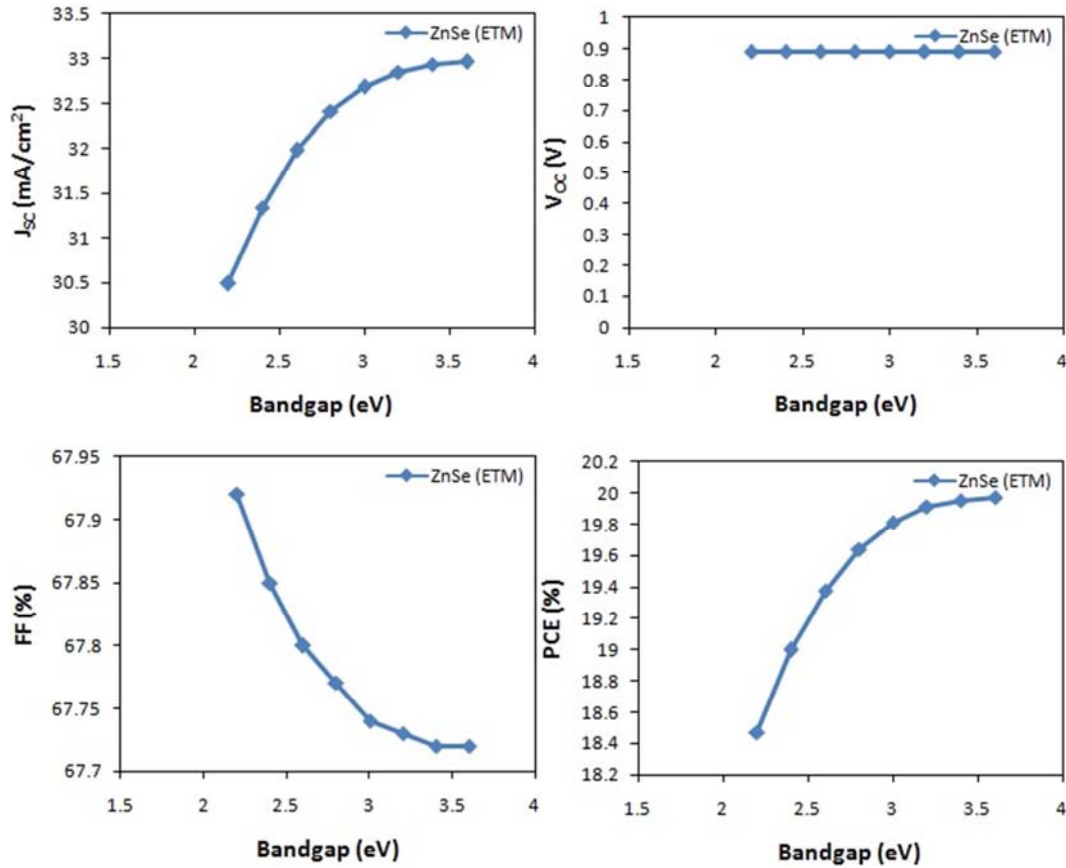


Figure 14. Variation in performance parameters of PSC with bandgap of ZnSe (ETM).

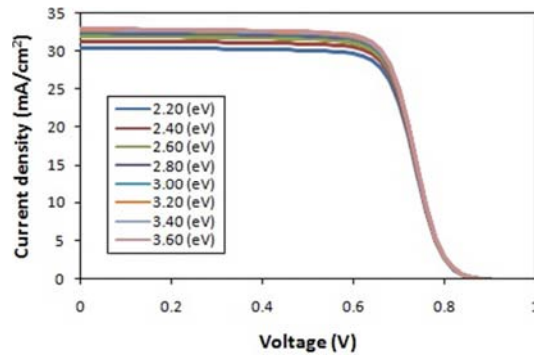


Figure 15. J-V curves of PSC with different values of ZnSe (ETL) bandgap.

Table 5. Dependence of solar cell performance on ZnSe (ETL).

ZnSe bandgap (eV)	J_{sc} (mA/cm ²)	V_{oc} (V)	FF (%)	PCE (%)
2.20	30.48	0.89	67.92	18.47
2.40	31.34	0.89	67.85	19.00
2.60	31.98	0.89	67.80	19.38
2.80	32.42	0.89	67.77	19.64
3.00	32.69	0.89	67.74	19.81
3.20	32.86	0.89	67.73	19.91
3.40	32.94	0.89	67.72	19.95
3.60	32.97	0.89	67.72	19.97

3.6. Effect of the Hole Mobility of HTL

On the other hand, in Figure 16, the hole mobility has an appreciable effect on the performance of the PSCs because the basic role of this layer is to extract the holes from the

excitons reaching the interface between the perovskite and the HTL while rejecting the electrons backward to the ETL. Cuprous oxide (Cu₂O) is a good option for hole transporting material which serves as a replacement to spiro-OMeTAD which is expensive and is easily degraded. The hole mobility

of cuprous oxide (Cu₂O) in this work is high, which is good for the device performance and this is the reason why p-type doping to enhance hole mobility in the HTL layer is

necessary because it is important for materials with large hole mobility should be considered for the selection of hole transport material.

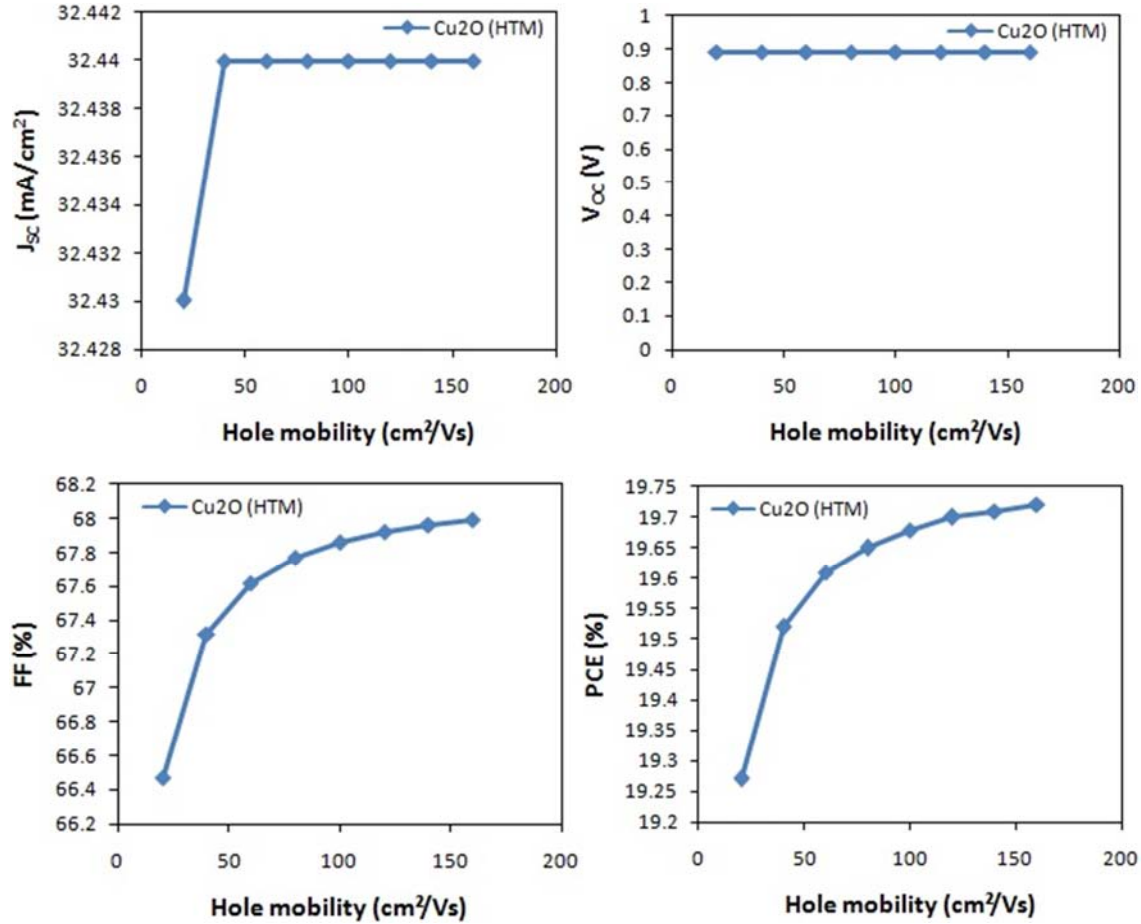


Figure 16. Variation in performance parameters of PSC with hole mobility of Cu₂O (HTL).

When the hole mobility of Cu₂O is varied, J_{sc} decreases gradually and remains invariable, V_{oc} is invariable, the FF decreases and increases, PCE increases gradually because of the carriers diffusion length which is longer than the thickness of the HTL. The optimum performance with J_{sc} of 32.44 mA/cm², V_{oc} of 0.89 V, FF of 67.99% and PCE of 19.72% is obtained under 160 cm²/Vs as shown in Table 6.

Table 6. Dependence of solar cell performance on Cu₂O (HTL).

Cu ₂ O hole mobility (cm ² /Vs)	J _{sc} (mA/cm ²)	V _{oc} (V)	FF (%)	PCE (%)
20	32.43	0.89	66.47	19.27
40	32.44	0.89	67.32	19.52
60	32.44	0.89	67.62	19.61
80	32.44	0.89	67.77	19.65
100	32.44	0.89	67.86	19.68
120	32.44	0.89	67.92	19.70
140	32.44	0.89	67.96	19.71
160	32.44	0.89	67.99	19.72

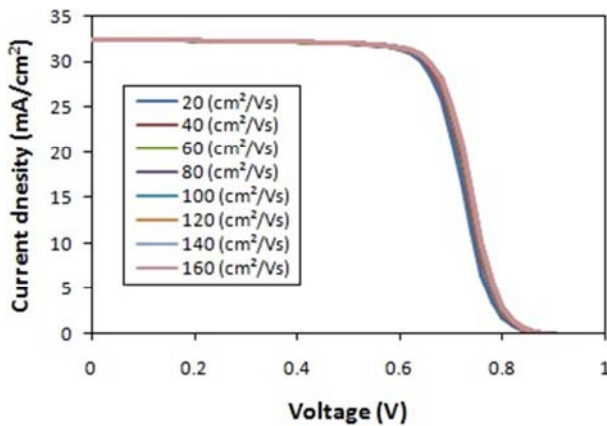


Figure 17. J-V curves of PSC with different values of Cu₂O (HTL) hole mobility.

3.7. Performance of Optimized Parameters

The thickness, bandgap and hole mobility was considered as the following factors by which we obtain J_{sc} of 30.73 mA/cm², V_{oc} of 0.99 V, FF of 70.51% and PCE of 21.66%. The final optimized parameters and optimized J-V curve are shown in table 7 and figure 18 respectively. We compared our simulated results with the experiment work published by other researchers and the related data is summarized in table 8. The best power conversion efficiency of 6.09% has been achieved for PSCs with spiro-OMeTAD as HTL in the literature despite Cu₂O as HTL was use in this

research. This could be achieved by further improving the film morphology and crystalline quality of both the absorber and spiro-OMeTAD layer. Doping of spiro-OMeTAD by replacing it with other element might or can further modify the charge carrier concentration and mobility of HTL which was done using Cu_2O in this research work.

Table 7. Optimized parameters of the device.

Optimized parameters	ETL (ZnSe)	Absorber ($\text{CH}_3\text{NH}_3\text{SnI}_3$)	HTL (Cu_2O)
Thickness (μm)	0.0010	0.900	0.1800
Bandgap, E_g (eV)	3.60	1.4	---
mobility, μ_p ($\text{cm}^2\text{V}^{-1}\text{s}^{-1}$)	---	---	160

Table 8. Using SCAPS to report the photovoltaic parameters of cuprous oxide based perovskite solar cells, experimental work in the literature and simulated results.

Simulation	J_{sc} (mA/cm^2)	V_{oc} (V)	FF (%)	PCE (%)
Initial	32.44	0.89	67.77	19.65
Optimized μ_m of absorber	32.91	0.89	67.44	19.82
Optimized μ_m of ETL	33.51	0.92	68.33	21.11
Optimized μ_m of HTL	32.44	0.89	67.77	19.65
Optimized E_g of absorber	29.48	0.99	70.47	20.57
Optimized E_g of ETL	32.97	0.89	67.72	19.97
Optimized μ_p of HTL	32.44	0.89	67.99	19.72
Final optimization	31.01	1.01	70.94	22.28
Experimental parameters	18.67	0.68	47.43	6.09
Experimental parameters	31.59	0.92	79.99	23.36

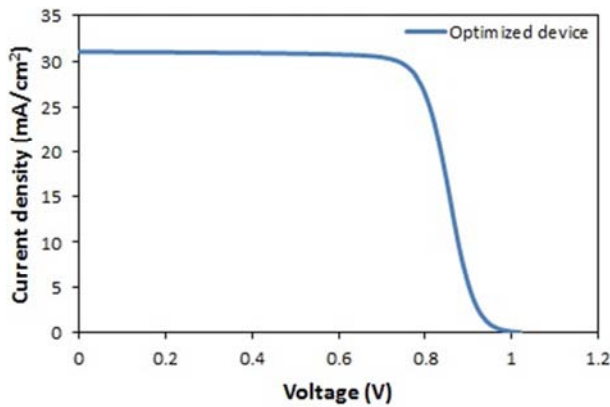


Figure 18. J-V curves of PSC with optimized parameters.

4. Conclusion

In conclusion, the objective of this research work was to use SCAPS-1D to study the integration of tin based ($\text{CH}_3\text{NH}_3\text{SnI}_3$) perovskite solar cell, cuprous oxide as HTL with ZnSe as ETL and its influence on the electrical performance while identifying some hindrances that limit this technology. In other to optimize the time and cost of tin based PSC. Numerical simulations have been done by adjusting parameters such as the thickness of absorber, ETL and HTL, bandgap of absorber and ETL and hole mobility for HTL using SCAPS-1D. The results show that Cu_2O as HTL has the potential to be used with perovskite absorber and can replace the Spiro-OMeTAD which is expensive and suffers from degradation. ZnSe as an ETL material can replace TiO_2 which is expensive. The highest PCE achieved is 22.28%, FF of 70.94%, J_{sc} of $31.01\text{mA}/\text{cm}^2$, V_{oc} of 1.01V which is the final optimized device. The thickness of the layers has a great influence on the performance parameters of the solar cells. After optimizing the thickness of all the layers,

PCE of 21.11% was obtained.

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