Effect of Absorber Layer Thickness on the Performance of Bismuth-Based Perovskite Solar Cells

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Abstract—Theoretical study of methyl-ammonium bismuth halide perovskite solar cells, (CH\textsubscript{3}NH\textsubscript{3})\textsubscript{3}Bi\textsubscript{2}I\textsubscript{9}, was carried out using a one-dimensional Solar Cell Capacitance Simulator (SCAPS-1D) software. The performance of the tested device architectures largely depends on the thickness of the absorbing layer, with the combination of electron transport, and hole transport layers. Thus, the bismuth perovskite absorber layer was optimized by varying the thickness and also, the thicknesses of the different charge-transport materials such as Spiro-OmeTAD, copper(I) oxide (Cu\textsubscript{2}O), and copper(I) iodide (CuI) as hole transport layer (HTL), and phenyl-C\textsubscript{61}-butyric acid methyl ester (PCBM), poly(3-hexylthiophene-2,5-diyl) (P3HT), zinc oxide, and titanium dioxide as electron transport layer (ETL). The best performance in terms of the power conversion efficiency (PCE) was recorded for the device with Cu\textsubscript{2}O as the HTL and ZnO as the ETL with the absorber layer thickness of 200 nm. The working temperature of the device was varied from 295 to 320 K and the effects of temperature on various device architectures were investigated. Results obtained indication that the efficiency of the bismuth perovskite solar cells can be improved by optimizing the thickness of the absorber layer and utilizing an appropriate combination of HTLs and ETLs.

Keywords: methyl-ammonium bismuth perovskite, SCAPS, HTL, ETL, PCE
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1. INTRODUCTION

Organic-inorganic hybrid lead halide perovskite solar cells have attracted tremendous attention due to a combination of its low cost, as a result of low-temperature processing [1] and its increasing efficiency [2, 3]. The commercialization of this technology has been impeded by the toxicity of lead (Pb) [4] and the instability of the device at relatively high humidity [5, 6]. Methyl-ammonium tin halide perovskite has been investigated [7] and reported to exhibit a power conversion efficiency (PCE) of 6% [7]. Nonetheless, it is highly unstable [8] due to oxidations from Sn\textsuperscript{2+} to the stable form Sn\textsuperscript{4+} in ambient conditions [7]. Germanium (Ge) has also been used to replace Pb and was reported to exhibit a high degree of stability [9], but very low PCE [10]. The use of an all-inorganic Pb-free cesium tin-germanium tri-iodide (CsSn\textsubscript{0.5}Ge\textsubscript{0.5}I\textsubscript{3}) was investigated, and a PCE of 7.11% was reported [11]. Bismuth (Bi) has been reported to be a promising material for a Pb-free hybrid organic-inorganic perovskite solar cells because of it is friendliness to the environment [12] and boasts of good stability under humid conditions [13]. An energy storage device fabricated with bismuth material was reported to maintain almost 84.8% of its initial maximum capacitance after a charge-discharge over 1000 cycles [12]. Bi-based solar cell device achieved an increase in PCE from 0.04 to 0.17% when processed by a modified spin-coating process. The increase in PCE was due to the size of the perovskite crystals, which was affected by the concentration of the solution, coupled with the speed of the rotation for effective layer coverage [14]. Bismuth perovskites prepared by two-step solution deposition realized a PCE of 0.21%, which was attributed to an improvement in the morphology of the film and improved absorption [15]. Several techniques have been investigated to improve the PCE of perovskite solar cells by employing novel materials and novel device architectures. Improvement in PCE can also be achieved by altering the electron transport layer (ETL) and hole transport layer (HTL) of the devices, because these materials and their interfaces with the perovskite are of prime significance in con-
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The Poisson equation is

$$\frac{d^2 \varphi(x)}{dx^2} = -\frac{e}{\varepsilon_0 \varepsilon_r} \left( p(x) - n(x) + N_D - N_A + \rho_p - \rho_n \right).$$

(3)

The drift–diffusion equations are

$$J_n = D_n \frac{dn}{dx} + \mu_n n \frac{d\varphi}{dx},$$

(4)

$$J_p = D_p \frac{dp}{dx} + \mu_p p \frac{d\varphi}{dx},$$

(5)

where \( J_n \) and \( J_p \) are electron and hole current density, \( R \) is the recombination rate, \( G \) is the generation rate, \( \varphi \) is the electrostatic potential, \( e \) is the electron charge, \( \varepsilon_0 \) is the vacuum permittivity, \( \varepsilon_r \) is the relative permittivity, \( p \) and \( n \) are hole and electron concentration, \( N_D \) is charged impurities of the donor, \( N_A \) is charged impurities of the acceptor, \( \rho_p \) and \( \rho_n \) are holes and electron distribution.

The proposed architecture of the solar cell device is presented in Fig. 1, where FTO stands for fluorine-doped tin oxide.

The device comprises three main layers: ETL, HTL, and the perovskite layer, which is the absorber layer sandwiched between the ETL and HTL [19]. Two other important layers that make up the cell are the top and bottom contact layers with the arrows indicating the direction of illumination of light. These contacts are responsible for collecting the separated electron-hole pairs, where the top contact collects the electrons and the bottom contact collects the holes when light of 1000 W/m² at 300 K with air mass of 1.5 global spectrum is illuminated on the device. The thickness of the Bi-based perovskite (the absorbing layer) was varied from 100 to 500 nm to ascertain the optimum thickness for a different combination of transport materials; CuI|(CH₃NH₃)₃Bi₂I₉|ZnO, Cu₂O|(CH₃NH₃)₃Bi₂I₉|ZnO, Cu₂O|(CH₃NH₃)₃Bi₂I₉|TiO₂, and CuI|(CH₃NH₃)₃Bi₂I₉|TiO₂. With this optimized thickness, the effect of the working temperature of the illuminated light was observed by varying temperature from 295 to 320 K for the different device architectures. The thickness of other layers of the device was maintained throughout the simulation. Various parameters for this study were obtained from different literature and experimental works [5, 17, 22–27] and are summarized in Table 1.

Table 2 presents the list of parameters used for the simulation of the organic transport layer or the electron transport material (ETM) namely the PCBM, P3HT and the SPIRO-OMETAD.

These parameters were obtained from various theoretical and experimental data available in [5, 17, 22–27].
3. RESULTS AND DISCUSSION

3.1. Absorber Layer Thickness Optimization

The thickness of the absorber layer is important in determining the PCE of a solar cell device. A very small thickness will result in a lower absorption rate that leads to a decrease in PCE. Similarly, a very thick absorber layer will mean difficulty of the charge carriers to travel to the charge collectors, ultimately leading to recombination that will decrease the PCE of the device [28]. Therefore, an optimum layer thickness is necessary for the effective absorption of photons for the generation of electron-hole pairs and successful migration to the charge collectors. The result obtained indicates changes in the PCE of the device as the thickness of the absorbing layer changes. For all the cell structures having inorganic transport materials, the efficiency of the device increases as the absorber thickness increases, up to a maximum point (optimum thickness), where the best efficiency of the device is obtained as shown in Fig. 2a.

The increase in efficiency is due to the increase in solar cell characteristics because a thick absorbing layer will absorb more photons, leading to the genera-
tion of more electron and hole pairs. The efficiency starts to decrease beyond the optimum thickness due to the recombination of the generated electrons and holes as a result of the longer distance the charges have to travel for diffusion, as shown in the figure. This optimum thickness observed for all four-cell structures corresponds to 200 nm, and a maximum PCE of 6.1% has been obtained from the device with Cu2O/ZnO as the hole/electron transport material and corresponds to the established optimum thickness of the Bi-based perovskite solar cell.

For the devices with organic transport materials, the PCE of the cell structures is presented in Fig. 2b. The PCE increases as the thickness increases due to amplified charge carriers at 300 nm and decreases afterward due to the recombination of current beyond this maximum point. The optimized thickness obtained from the different cell structures having organic transport materials is 300 nm, and the cell structure with PCBM, a PCE of 5.81% was obtained for the optimum thickness.

### 3.2. Effect of Temperature

The working temperature was varied from 295 to 320 K to study the effects on the solar cell parameters. The energy of electrons increased as the temperature increases, leading to a decrease in the band gap of the material [21]. Figure 3a presents the different cell structures showing similar PCE as the temperature increases with exception of the device with CuI/TiO2 as the hole/electron transport material.

The CuI/TiO2 hole/electron material showed the least PCE of 2.3% as the temperature increased. It can, therefore, be explained that this material experiences more recombination [13], and the interface of the transport material layers and the absorber layer are not compatible, which could be due to poor adhesion between the layers. The cell device with Cu2O/ZnO as
the hole/electron transport materials displayed a maximum of PCE of 6.05% at a temperature of 295 K. Beyond this temperature, the PCE slightly decreases and could probably be due to temperature-activated charge transport in the charge transport layers that affects the series resistance and the fill factor.

For the devices fabricated with organic transport materials, as shown in Fig. 3b, the PCE of the cell structure with PCBM decreased with increasing temperature from 5.68 to 5.62%, whilst that of the cell having P3HT increased with increasing temperature from 5.4 to 5.50%. This decrease in PCE as the temperature increases can be attributed to an increase in series resistance due to a decrease in carrier diffusion length [19]. The best efficiency was obtained by the cell structure with PCBM and corresponds to 5.68% at 295 K.

CONCLUSIONS

In this work, four different cell structures with different combinations of inorganic electron and hole transport materials (ZnO and TiO₂; CuI, Cu₂O) and two cell structures using two electrons and a single hole transport material (PCBM, P3HT and Spiro-OmeTAD) was simulated with SCAPS-1D software. For each device structure, the thickness of the bismuth-based absorbing layer was varied between 100 to 500 nm. The optimum performance was obtained from the device with inorganic electron and hole transport materials, Cu₂O/(CH₃NH₃)₃Bi₂I₉/ZnO, with an efficiency of 6.1%, at a thickness of 200 nm. The best performing device with organic transport materials, Spiro-Omedad/(CH₃NH₃)₃Bi₂I₉/PCBM, had an efficiency of 5.8%, at a thickness of 300 nm. The working temperature was also varied from 295 to 320 K and it was observed that the performance of the different cell structures had no significant change with temperature variation. It can also be deduced from the plots that the choice of electron and hole transport materials to be employed in any given device is of paramount importance.

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CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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