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Impact of work function of back contact of perovskite solar cells without hole transport material analyzed by device simulation

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ABSTRACT

The impact of the work function of a metal back contact on lead methylammonium tri-iodide based perovskite solar cells without hole transport material (HTM) was analyzed using device simulation. The elimination of the HTM is attractive in terms of the simplification of device structure and fabrication process. In the solar cell, a back junction is formed by the perovskite absorber and metal back contact. The device simulation revealed that the elimination of the HTM did not change the built-in voltage (V_{bi}) of the device when the work function of the metal back contact (ϕ_M) was similar to the valence band maximum of the absorber ($E_{v\_absorber}$). In the HTM-free structure, V_{bi} showed a high value if ϕ_M was equal to or deeper than $E_{v\_absorber}$. In contrast, when ϕ_M was shallower than $E_{v\_absorber}$, V_{bi} monotonically decreased, resulting in the decrease in open-circuit voltage of the device. The results showed the importance of the ϕ_M matching to maintain V_{bi}, which is useful guideline for the design of the HTM-free perovskite solar cells.

1. Introduction

The first application of organometal halide perovskite, i.e., $CH_3NH_3PbI_3$ and $CH_3NH_3PbBr_3$, to photo sensitizer was reported in 2009 [1]. The perovskite absorber was in the form of nanocrystalline particles in dye-sensitized solar cell configuration. After the first report of all-solid state thin film mesoscopic solar cells based on $CH_3NH_3PbI_3$ in 2012 [2], the perovskite absorbers, such as $CH_3NH_3PbI_3$ and $CH_3NH_3PbI_{3-x}Cl_x$, gathers much attention as excellent novel absorber materials for high efficiency and cost-effective solar cells [3–11]. Initially, the perovskite solar cells employed mesoporous structure [2–7] using scaffold layers such as porous TiO_2. However, the elimination of the mesoporous layers, i.e. planar junction architecture, also enables to achieve high efficiency [8–11]. The flexibility of the structures was realized by high absorption coefficient and excellent carrier transport property of the absorbers [4,12]. Interestingly, one more elimination, i.e. the elimination of a hole transport material (HTM), also worked well [13–18]. The HTM-free perovskite solar cells employed back contacts with deep work function such as Au (−5.1 eV) [13–16] and carbon (−5.0 eV) [17,18]. The highest efficiency reported so far is 12.8% [18] using carbon as a back contact. These eliminations are attractive from the view points of structure and process simplifications, which should be useful for cost reduction. Also, the elimination of the HTM may lead to improve the stability of the devices because the HTM can be one of the origins of degradation. Nevertheless, the reason why the HTM can be eliminated is not understood completely. The understanding of device operation mechanism is essential for the optimization of the device structure, which leads to the efficiency improvement. From the analogy of the early date of developments in crystalline silicon and thin-film compound solar cells using Schottky junction [19–21], the work function of a metal back contact should be an important parameter to obtain a reasonable built-in voltage (V_{bi}) of the devices. For the understanding of the device operation, device simulation is a powerful tool, which was widely applied to inorganic semiconductor solar cells [22–28]. In contrast, device simulation studies on the perovskite solar cells are not enough. The exciton type of the perovskite materials is Wannier type [29], and the device structure of the perovskite and inorganic semiconductor solar cells, such as $Cu(In,Ga)Se_2$ (CIGS), are similar. Therefore, device simulators used in CIGS solar cells can be applied to the perovskite solar cells. In this study, the impact of the elimination of the HTM was analyzed using the Solar Cell Capacitance Simulator (SCAPS) developed by University of Gent [30] together with the optimum design of the work function of the back contact.

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2. Device simulation parameters

The device simulator SCAPS ver. 3.2.01 was used as simulation platform. In the simulation, the perovskite solar cells employed planar junction architecture with layer configuration of transparent conductive oxide (TCO)/blocking layer (BL)/absorber/HTM/metal back contact. In the case of the HTM-free structure, the HTM was simply removed from the above structure. Table 1 summarizes the base parameter set of each layer in the simulation. Here, N_A and N_D denote acceptor and donor densities, ε_r is relative permittivity, χ is electron affinity, E_g is band gap energy, μ_n and μ_p are mobility of electron and hole, and N_t is defect density. The physics parameters of TCO, BL, absorber and HTM are based on those of SnO_2:F, TiO_2, and $CH_3NH_3PbI_{3-x}Cl_x$, 2,2′,7,7′-tetrakis(*N*,*N*-*p*-dimethoxy-phenylamino)-9,9′-spirobifluorene (Spiro-OMeTAD), respectively. The thicknesses of each layer were taken from an experimental report on high efficiency perovskite solar cells with planar junction architecture [9]. The interface defect layers of IDL1 and IDL 2 were inserted between BL/absorber and absorber/HTM (or absorber/metal) interfaces to consider interface recombination. The parameters of IDL1 and IDL2 were set to be identical to those of the absorber except high defect density. One of the most important parameters to determine the absolute value of the efficiency (Eff) is N_t of the absorber. In this study, N_t of the absorber was set to be 2.5×10^{13} cm^{-3} to adjust electron and hole diffusion length (L_n and L_p) to be 1 μm, which is an experimentally reported value for high quality perovskite material [4]. The other parameters not included in Table 1 were set to be identical in each layer; effective density of states of conduction band (N_C) and valence band (N_V) were set to be 2.2×10^{18} and 1.8×10^{19} cm^{-3}, respectively. Thermal velocity of electron and hole was 10^7 cm/s. Defect energy level was located at the center of E_g and defect type was neutral. Energetic distribution was Gaussian with characteristic energy of 0.1 eV. Capture cross section of electron and hole was 2×10^{-14} cm^2. Pre-factor A_α was 10^5 to obtain absorption coefficient (α) calculated by $\alpha = A_\alpha(h\nu - E_g)^{1/2}$. In this study, the conduction band offset of BL/absorber and the valence band offset of absorber/HTM, which are important parameters to determine interface recombination, were set to be zero because the consideration of the band offsets makes this analysis too complicated and we should focus on the effect of the elimination of HTM in this study. The effect of the band offsets will be reported elsewhere.

The band diagram of the perovskite solar cell calculated with the parameter set showed that the absorber was fully depleted and the solar cell had an *n*-*i*-*p* structure. An experimental report using electron beam induced current measurement also pointed out the *n*-*i*-*p* structure of the perovskite solar cells [33]. The current density–voltage (*J*–*V*) characteristics calculated with above assumption gave the solar cell parameters of short-circuit current density (J_{sc}) of 22.2 mA/cm^2, open-circuit voltage (V_{oc}) of 1.03 V, fill factor (FF) of 80.0% and efficiency of 17.9%. FF was higher than experimental values [9,10] because no additional series resistances such as sheet resistance of the TCO and contact resistances were considered in the simulation. Beside this, reasonable J_{sc} and V_{oc} consistent with experimental reports [9,10] were obtained, demonstrating that this simulation can be used and the parameter set is not far from that in the real devices. In this calculation, the work function of the metal back contact (ϕ_M) was set to be identical to the Fermi level of the HTM of −5.39 eV (relative to vacuum level), which is almost similar to the valence band maximum of the absorber ($E_{v\_absorber}$) of −5.45 eV, to adjust a majority carrier barrier height at the HTM/metal interface to be zero, which is an ideal case. In the HTM-free structure, a back junction is formed by the absorber and the metal back contact. Thus, the energy difference between $E_{v\_absorber}$ and ϕ_M should affect the solar cell performance. In the next section, the effects of the elimination of the HTM and the variation of ϕ_M are discussed by simply removing the HTM from the structure and varying ϕ_M.

3. Results and discussion

Fig. 1 exhibits the band diagrams of the perovskite solar cells (a) with HTM and (b) without HTM with different $E_{v\_absorber} - \phi_M$. Here, $E_{v\_absorber}$ and ϕ_M indicate energy position relative to vacuum level and $E_{v\_absorber}$ is −5.45 eV from Table 1. Thus, positive and negative values of $E_{v\_absorber} - \phi_M$ indicate that the work function of the metal back contact is deeper and shallower (relative to vacuum level) than the valence band maximum of the absorber, respectively. As clearly shown in the figures, the absorbers are completely depleted, which is consistent with the experimental report [33]. In the HTM-free structure, when ϕ_M is equal to and deeper than $E_{v\_absorber}$, i.e. $E_{v\_absorber} - \phi_M = 0.0$ and 0.3 eV in Fig. 1(b), a high V_{bi} identical to the case with the HTM can be obtained. Here in Fig. 1(b), the two band diagrams are overlapped. However, if the ϕ_M is shallower than $E_{v\_absorber}$, i.e. $E_{v\_absorber} - \phi_M = -0.3$ and −0.6 eV in the figure, V_{bi} monotonically decreases, which leads to the reduction in the electric field across the absorber.

Fig. 2 shows the *J*–*V* curves of the HTM-free perovskite solar cells with different $E_{v\_absorber} - \phi_M$. A *J*–*V* curve for the perovskite solar cell with the HTM and with the identical ϕ_M to the Fermi level of the HTM is also shown by a dashed line in the figure. When ϕ_M is in the adequate range to maintain high V_{bi}, the similar *J*–*V* curves are obtained regardless of the presence of the HTM, which is well understood from the band diagrams shown in Fig. 1. Here, we should note that the direct deposition of the metal on the perovskite absorber in the real devices may lead to an increase in the defect density at the interface. However, the excess carrier densities by light irradiation at the back junction (absorber/metal) are significantly smaller than that at the front junction (BL/absorber), and thus the effect of the defect density at the back junction should be limited.

In Fig. 2, the *J*–*V* curves for $E_{v\_absorber} - \phi_M = 0.0$, 0.2 and 0.4 eV are overlapped, which is consistent with the band diagrams of Fig. 1. On the other hand, the *J*–*V* curves for $E_{v\_absorber} - \phi_M < 0.0$ eV, i.e. shallower ϕ_M than $E_{v\_absorber}$, monotonically shift to lower voltage with moving ϕ_M upward to vacuum level. The shift resulted

Table 1
Base parameter set in simulation. For HTM-free structure, HTM was simply removed from the structure.

Parameter	TCO (SnO_2:F)	BL (TiO_2)	IDL1 (defect layer)	Absorber ($CH_3NH_3PbI_{3-x}Cl_x$)	IDL2 (defect layer)	HTM (Spiro-OMeTAD)
Thickness (nm)	500	50	10	330	10	350
N_A (cm^{-3})	–	–	–	–	–	2×10^{18} [4]
N_D (cm^{-3})	2×10^{19}	10^{16}	10^{13}	10^{13}	10^{13}	–
ε_r	9.0	9.0	6.5	6.5 [9]	6.5	3.0 [31]
χ (eV)	4.00	3.90	3.90	3.90 [29]	3.90	2.45 [32]
E_g (eV)	3.50	3.20	1.55	1.55 [5]	1.55	3.00 [32]
μ_n/μ_p (cm^2/V s)	20/10	20/10	2.0/2.0	2.0/2.0 [3]	2.0/2.0	$2 \times 10^{-4}/2 \times 10^{-4}$ [32]
N_t (cm^{-3})	10^{15}	10^{15}	10^{17}	2.5×10^{13}	10^{17}	10^{15}