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To cite this version:
Yong Huang, S. Aharon, Alain Rolland, Laurent Pedesseau, Olivier Durand, et al.. Influence of Schottky contact on the C-V and J-V characteristics of HTM-free perovskite solar cells. EPJ Photovoltaics, EDP sciences, 2017, 8, pp.85501. <10.1051/epjpv/2017001>. <hal-01495026>

HAL Id: hal-01495026
https://hal.archives-ouvertes.fr/hal-01495026
Submitted on 24 Mar 2017

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Influence of Schottky contact on the C-V and J-V characteristics of HTM-free perovskite solar cells

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Received: 30 September 2016 / Received in final form: 14 December 2016 / Accepted: 3 January 2017 © Y. Huang et al., published by EDP Sciences, 2017

Abstract The influence of the Schottky contact is studied for hole transport material (HTM) free CH3NH3PbI3 perovskite solar cells (PSCs), by using drift-diffusion and small signal models. The basic current-voltage and capacitance-voltage characteristics are simulated in reasonable agreement with experimental data. The build in potential of the finite CH3NH3PbI3 layer is extracted from a Mott-Schottky capacitance analysis. Furthermore, hole collector conductors with work-functions of more than 5.5 eV are proposed as solutions for high efficiency HTM-free CH3NH3PbI3 PSCs.

1 Introduction

Due to their potential for photo-induced carrier separation [1], various Hetero-Junction Solar Cells (HJSCs) have been experimentally [2,3] and theoretically [4,5] investigated. Selected doped functional materials are added on each side of the Light Harvesting Material (LHM) to select photo-induced carriers. The electron transport material (ETM) is used to extract photo-induced electrons and block holes, while the hole transport material (HTM) has a complementary function. HJSCs based on low-cost, easy processed [6–8] and highly absorbing [9, 10] semiconductor [11] halide perovskites have indeed led to high Photon-to-electron Conversion Efficiency (PCE) rising from 3.8% (2009) up to 22.1% (2016). Nowadays, these values are very close to the record value of silicon based solar cells (25.6%) [12].

As predicted from the detailed balance principle [13], if no defect-assisted recombination occurs in LHM and if the cell open circuit voltage (VOC) equals to LHM’s energy band gap (Eg) divided by elemental electron charge (q) the silicon based and the Perovskite based Solar Cells (PSC) should achieve maximum PCE of 44% and 37%, respectively. However, due to limited Internal PL quantum yield (iQY) and non-zero entropy, the maximum VOC [14] is smaller than Eg:

\[ q\text{VOC} = E_g - T \Delta S - k_B T \ln \text{iQY} \] (1)

where T is the absolute temperature and k_B is the Boltzmann constant. If optical losses are weak and the contacts are almost ideal, an open circuit voltage (VOC) of about 1.2 V is expected for CH3NH3PbI3 [15]. In pace with the enhancement of stability [16,17], the influence of defects was weakened down to an acceptable level [18, 19], while the band offsets between the LHM and ETM or HTM remain major factors impeding PCE [15, 20–23].

ZnO nanorods [24] or PCBM [25], ETM [26] are able to minimize the band offset at the conduction band minimum (CBM) and allow building almost ideal contact at ETM/LHM interface. However HTM very often present large band offsets at valence band maximum (VBM) and low carrier mobility [23,27–29]. Alternatively, PSC without HTM layer was proposed as a solution towards high efficiency. After Etgar and coworkers early directly deposited gold on CH3NH3PbI3 and demonstrated that the CH3NH3PbI3 material can be simultaneously considered as a light harvester and a hole conductor, leading to PCE of 8% [30]. Then porous carbon film was used as contact for fully printable HTM-free PSCs with efficiency of 12.8% [17]. And PSCs with single-walled carbon nanotubes as hole collector achieved efficiency of 15% [31,32]. In such case, solar cells benefit from fewer interfaces, and the optical and electrical losses in the HTM layer are eliminated as well. In Figure 1, the architecture of the HTM-free CH3NH3PbI3 PSC is schematic represented by comparison to that of classical PSC. Gold for example, is directly connected with CH3NH3PbI3 as the hole collection electrode and a Schottky contact is formed [33].

To get an insight into the HTM-free PSC operation, di-rect current and small signal simulation analyses [5,34–37]
were performed including basic semiconductor models: the Poisson equation, the current continuity equation and a drift-diffusion model. The critical transport and recombination processes in solar cells can thus be quantitatively analyzed. Nevertheless, few numerical analyses were dedicated up to now to HTM-free PSCs. In our work, the basic current-voltage (J-V) and capacitance-voltage (C-V) characteristics of HTM-free CH$_3$NH$_3$PbI$_3$ based PSCs are studied with drift-diffusion and small signal models [38], which are integrated in Silvaco Atlas simulator [39].

2 Numerical modeling

The physical model is numerically simulated in Atlas by solving a set of coupled equations including Poisson’s equation (2), continuity (3a) and (3b) and transport equations (4a) and (4b) for electrons and holes densities. These equations link together the electrostatic potential profile and the charge distributions, and describe the evolution of electron and hole densities under external bias and light illumination, including carrier transport, generation, and recombination processes. The bimolecular recombination model corresponds to the formula (5). The trap-assisted recombination model is described in formula (6), (7a) and (7b), while the photo-induced carrier generation processes are introduced through complex refractive index of materials. Simulations were carried out under equilibrium and small AC conditions, with and without ΔE1.5 sun illumination, in order to obtain J-V and C-V characteristics of HTM-free CH$_3$NH$_3$PbI$_3$ PSCs

\[ \Delta \psi = -\frac{\rho}{\varepsilon} \]  

where \( \psi \) is the potential, \( \rho \) is the charge density and \( \varepsilon \) is the dielectric constant.

\[ \frac{\partial n}{\partial t} = \frac{1}{q} \text{div} J_n + G_n - R_n \]  

(3a)

\[ \frac{\partial p}{\partial t} = \frac{1}{q} \text{div} J_p + G_p - R_p \]  

(3b)

where \( n(p) \) is the electron (hole) density, \( t \) is the time, \( J_n (J_p) \) is the electron (hole) current density, \( G \) and \( R \) are the generation and recombination rates respectively. The footnotes \( n(p) \) is related to electron (hole).

\[ \vec{J}_n = -q\mu_n n \nabla \phi_n \]  

(4a)

\[ \vec{J}_p = -q\mu_p p \nabla \phi_p \]  

(4b)

where \( \mu \) is mobility and \( \phi \) is the quasi-Fermi level

\[ R_{\text{SRH}} = \frac{pm - n_t^2}{\tau_n \left[ p + n_i \cdot \exp \left( \frac{-\Delta E}{k_B T} \right) \right] + \tau_p \left[ n + n_i \cdot \exp \left( \frac{\Delta E}{k_B T} \right) \right]} \]  

(6)

\[ \tau_n = \frac{1}{S I G n \cdot v_n \cdot N_t} \]  

(7a)

\[ \tau_p = \frac{1}{S I G p \cdot v_p \cdot N_t} \]  

(7b)

The Shockley-Read-Hall (SRH) recombination mechanism is described by equation (6) \( \tau \) is the charge carrier lifetime for trap-assisted process. The relationship between \( \tau \) and trap density \( N_t \) (Eq. (7)) depends on the traps capture cross section (SIG) and the thermal velocity \( (v) \). \( \Delta E \) is the absolute energy difference between the trap level and the intrinsic Fermi level \( (E_i) \) in the bulk. \( E_i \) is approximately located in the middle of energy band gap. If \( \Delta E = 0 \), the maximum of SRH recombination rate is obtained. In other words, the deep trap centers lead to the highest recombination rates and are harmful for photo-induced carrier extraction. We set \( \tau_n = \tau_p \) and \( \mu_n = \mu_p \) to reduce the number of parameters in the present work.

3 Basic properties of HTM-free PSC

A basic modeling of HTM-free Perovskite Solar Cells (PSCs) studied experimentally by Etgar’s group [40], relies on TiO$_2$/CH$_3$NH$_3$PbI$_3$/Au architecture with a computed static band alignment shown in Figure 2. Heavily n-type doped ETM anatase (TiO$_2$) [41–43] and hole collector gold are added on each sides of lightly n or p-doped CH$_3$NH$_3$PbI$_3$ [1,44,45]. Under thermal equilibrium and short circuit condition, the Fermi-level \( (E_f) \) remains constant as reference through the device, and the band offsets at each interface yield two potential barriers. It is clear that the major potential drop \( \Delta \psi \) is located in the CH$_3$NH$_3$PbI$_3$ layer. Therefore, the major part of the electrical current originates from carrier drifting rather than carrier diffusion. The main properties of the materials used for the simulation are summarized in Table 1, including \( \chi \), \( E_g \), the doping level \( (N) \), the effective masses of electron and hole \( (m_e^* \& m_h^*) \) and the relative dielectric constant \( (\epsilon_r) \). The thickness of TiO$_2$ and CH$_3$NH$_3$PbI$_3$ layers are both equal to 300 nm. The work function (WF) of gold is 5.1 eV [33,46]. An Ohmic contact is considered...
Table 1. Main properties of the materials.

|       | $X$ (eV) | $E_g$ (eV) | $N$ (cm$^{-3}$) | $m_e^*$ & $m_h^*$ ($m_0$) | $\varepsilon_r$ ($\varepsilon_0$) |
|-------|----------|-----------|----------------|--------------------------|----------------------------------|
| HOIP  | 3.9      | 1.6       | $n = 4 \times 10^6$ or $p = 8 \times 10^6$ | $0.23 \& 0.29$           | 70                               |
| TiO$_2$ | 4.1      | 3.3       | 1e19           | 5.6 & 5.6                | 31                               |

Notes: HOIP means CH$_3$NH$_3$PbI$_3$; * indicates fitting parameter.

3.1 Capacitance characteristics

In order to obtain efficient energy conversion in solar cells with low mobility LHM, a high built-in potential ($V_{bi}$) is necessary to prevent significant losses due to carrier recombination processes competing with charge extraction processes [52]. In our case, a Schottky contact [53] is formed at interface CH$_3$NH$_3$PbI$_3$/Au. Therefore, $V_{bi}$ can be extracted from a Mott-Schottky capacitance analysis. The device architecture in our work is shown together with the circuit in Figure 3. The capacitance expression is given by:

$$
\frac{1}{C^2} = \frac{2}{qA\varepsilon_0} \left( \frac{1}{N\varepsilon_r} \right) \left( V_{bi} - V_{bias} + \frac{k_BT}{q} \right)
$$

where $C$ is the junction capacitance, $A$ is the junction area, $\varepsilon$ is the vacuum permittivity, $N$ is the activated dopant density in semiconductor and $\varepsilon_r$ is the relative permittivity. In our work, a small signal analysis [38] is used to simulate $C$-$V$ characteristics of HTM-free CH$_3$NH$_3$PbI$_3$ PSC. The signal frequency is set at 1 kHz for simulation, as in practical measurement. The theoretical characteristics is presented in Figure 4 and compared to available experimental data [40]. In order to fit the experimental data, an effective interfacial layer (IF) was introduced into the architecture for each type of CH$_3$NH$_3$PbI$_3$. For n-doped CH$_3$NH$_3$PbI$_3$, the IF of 8.5 nm is heavily n-doped and located between Au and CH$_3$NH$_3$PbI$_3$. For p-doped CH$_3$NH$_3$PbI$_3$, the IF of 3.4 nm is heavily p-doped and located between TiO$_2$ and CH$_3$NH$_3$PbI$_3$. The doping level of each IF is equal to 2e19 cm$^{-3}$. The influence of IF is further discussed at the end of the section.

As the bias reversely increases, the extension of the depletion region starts at the CH$_3$NH$_3$PbI$_3$/Au interface, then goes through the CH$_3$NH$_3$PbI$_3$ and finally into the TiO$_2$. Because of the different $N$ and $\varepsilon_r$ values in both CH$_3$NH$_3$PbI$_3$ and TiO$_2$, $C$-$V$ curves under reverse bias are bent into two stages. Similar phenomena were observed.
for III-V semiconductors [54, 55]. The roughly constant capacitance at stage II is due to the heavy doping level in TiO$_2$, in comparison with the smaller slope related to the small doping level in CH$_3$NH$_3$PbI$_3$. The point A in Figure 4 corresponds to the transition point of the depletion region from stage I to stage II. According to expression (8), the $V_{bi}$ of a finite CH$_3$NH$_3$PbI$_3$ layer is extracted from the intersection (IS) as pointed out in Figure 4. The fluctuations of experimental data at stage II can be explained by non-uniform doping in the TiO$_2$ layer. Because of the huge effective surface area of nano-porous TiO$_2$ [56–58] and the rough surface of CH$_3$NH$_3$PbI$_3$ layer [58], it is risky to extract $N$, $\varepsilon_r$ or thickness ($d$) of CH$_3$NH$_3$PbI$_3$ from the expression (8) and classic parallel plate capacitance expression (9), directly. In the model the effective area of capacitance interface ($A_{eff}$) is around two times as large as the active area of practical gold electrode

$$C = \frac{\varepsilon_r\varepsilon_0 A_{eff}}{d}. \quad (9)$$

If more uniform growth of material layers for HTM-free PSCs is achieved in the future, it will be possible to extract more quantitative information from C-V measurements, related to $N$, $\varepsilon_r$, and the thickness of the CH$_3$NH$_3$PbI$_3$ layer.

### 3.2 Photovoltaic characteristics

Due probably to the different growth procedures employed by the experimental groups, some deviations are found for the absorption coefficients values of CH$_3$NH$_3$PbI$_3$ in reference [59]. For that reason, the absorption coefficient curve used in our simulation was rather obtained by fitting the experimental IPCE spectrum data. In Figure 5, the simulated J-V characteristics under 1 sun illumination are presented along with experimental data. A good matching to the experimental J-V curve is achieved based on n-type CH$_3$NH$_3$PbI$_3$ when its $\tau = 80$ ns and $\mu = 0.2$ cm$^2$/Vs. These empirical values are consistent with commonly measured values for the CH$_3$NH$_3$PbI$_3$ material. The paper will only discuss n-doped CH$_3$NH$_3$PbI$_3$ based PSCs in the following sections, because a better agreement with experimental C-V and J-V characteristics is obtained in this case.

From the comparison of the experimental and computed C-V characteristics (Fig. 4), it is necessary to assume that a heavily n-doped IF exists at the CH$_3$NH$_3$PbI$_3$/Au contact. Alternative hypotheses with layers containing acceptors or surface states, were explored but without success. Indirect evidences of the existence of such an IF can be found in the report of Liu’s group [33]. Using ultraviolet photoemission spectroscopy (UPS), these authors indeed showed that during the deposition of the gold contact, the Fermi level undergoes a progressive shift. Noteworthy, the presence of metal nano particles [60] or charged ions [61–63] at the interface was discussed by other groups. This Fermi level shift is simulated in the present work by introducing an effective and highly n-doped CH$_3$NH$_3$PbI$_3$ IF. The high density of positive ionized charges in the IF leads to a reduction of the $V_{bi}$ from 0.9 to 0.6 V, in good agreement with the experimental value (Fig. 4).

The static band alignment and potential profile with and without IF are represented in Figures 6a and 6b, to have an insight into the device operation. Even though
the band offset at the CH$_3$NH$_3$PbI$_3$ surface is pinned by the gold contact, the effective potential drop across the CH$_3$NH$_3$PbI$_3$ layer is lowered by the presence of the IF. As a consequence, the losses due to carrier recombination processes increase and the efficiency of PSC decreases from 11% to 8%, as shown in Figure 5. A thick IF has clearly a detrimental effect on the photovoltaic efficiency. It is indeed possible to enhance the efficiency by increasing the WF of the metal used for the Schottky contact. In Figure 7a, $V_{OC}$, fill factor and efficiency are presented as a function of WF. These parameters are improved until saturation is reached for a WF value of 5.6 eV, while the short circuit current ($J_{SC}$) is almost constant and equal to 19 mA/cm$^2$. The efficiency of HTM-free PSC can be enhanced up to 17% (Fig. 7a) by this way, and as stated before further enhancements could also be expected by improving the intrinsic properties of the perovskite.

Furthermore, as shown in Figure 7b, the efficiency of HTM-free CH$_3$NH$_3$PbI$_3$/Au interface, as the WF of the metal increases up to 5.6 eV, larger than the VBM of CH$_3$NH$_3$PbI$_3$ (5.5 eV). As a result, the overall $V_{bi}$ in CH$_3$NH$_3$PbI$_3$ becomes almost saturated. When the carrier recombination rate is small enough, the $J_{SC}$ mainly depends on absorption properties and is almost independent of $V_{bi}$.

Palladium [46, 64] or Selenium [65] are examples of hole collector conductors with WF larger than 5.5 eV.

5 Conclusion

In summary, a detailed investigation of C-V and J-V characteristics of HTM-free CH$_3$NH$_3$PbI$_3$ PSC has been proposed, based on the drift-diffusion model and small signal analysis. The simulation results are in good agreement with experimental data. An effective heavily doped interfacial layer was introduced at the interface to fit the C-V characteristics. It is also shown in this work that, an increase of WF of the hole collector conductor, is expected to enhance the PSC efficiency.

The work at FOTON was supported by French ANR Super-sansPlomb project.

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Cite this article as: Y. Huang, S. Aharon, A. Rolland, L. Pedesseau, O. Durand, L. Etgar, J. Even, Influence of Schottky contact on the C-V and J-V characteristics of HTM-free perovskite solar cells, EPJ Photovoltaics 8, 85501 (2017).