

## Utilization of low cost metals as back contact with Perovskite Solar Cell

Najmin Ara Sultana<sup>1</sup>, Md Obidul Islam<sup>2</sup> and Zahid Hasan Mahmood<sup>3</sup>

<sup>1</sup>Department of EEE, Rajshahi University of Engineering & Technology, Rajshahi, Bangladesh

<sup>2,3</sup>Department of EEE, University of Dhaka, Dhaka, Bangladesh

E-mail: najminee@gmail.com, obidulapece@gmail.com, zahid@du.ac.bd

Received on 14.02.2017, Accepted for publication on 18.06.2017

### ABSTRACT

Organic halide perovskite-based solar cells have high photovoltaic conversion efficiency, because the materials show superior optoelectronic behavior, lower defect density and broader absorption spectra. A better understanding of the relationships between material parameters, device architectures and performances is still required for the continued development of the solar cell. This paper represents how the work function of metals can affect their photovoltaic characteristics. Comparatively cheap metals such as Al, Ag and C have been studied as the back contact electrodes for perovskite solar cell. The general trend observed is that the shunt resistance and open-circuit voltage of the devices decrease with the decreasing work function of the contact metal. Spiro-OMeTAD and TiO<sub>2</sub> have been used as hole transporting material and electron transporting material respectively in this solar cell. The results have showed that the materials of high work function can produce good ohmic contact with HTM. Maximum efficiency of 27.67% have been found for C-based perovskite solar cell.

**Keywords:** Perovskite solar cell; back contact; simulation; wx-AMPS.

### 1. Introduction

The perovskite solar cell is a new category of solar cell using organic-metal halide perovskite materials as the light absorber. Owing to its excellent optoelectronic behaviour, good stability, easy fabrication process and high photoconversion efficiency (PCE) organometal halide based hybrid perovskite has been attracting the great attention to the recent solar cell researchers. Perovskite, a crystal structure, is usually represented as ABX<sub>3</sub> where A is an organic/inorganic cation, B is divalent small metallic cation (Pb/Sn) and X is halide ion (I/Cl/Br) that binds to both cations [1]. In 1979, Salau recognized that the perovskite is a good absorber for solar cells[2] due to its extremely good electron and hole diffusion ability, very wide absorption wavelength range[3]. In 2009, Miyasaka remigrated perovskite in photovoltaics and obtained efficiency 3.81% and 3.13% for MAPbI<sub>3</sub> and MAPbBr<sub>3</sub> based solar cells, respectively [4]. It has been upgraded to 22.1% at KRICT/UNIST recently [5].

One vital issue in the build-out of perovskite solar cells was moving from the liquid-electrolyte-based dye sensitized solar cell (DSSC) towards a solid state device to overcome the drawbacks of using liquid electrolyte and dye[6]. Unlike DSSC, in perovskite solar cell, the liquid electrolyte is replaced by a solid state hole transporting material alternative and the absorber material perovskite is used instead of dye to create a fully solid state electronic dye sensitized solar cell. The absorber material is used in centre of the solar cell to harvest the solar energy[7]. Immense knowledge and optimal use of all layers of solar cells are the very important matter in the fabrication of solar cells. Dopant concentration, mobility of charge carrier, surface properties of the electron transporting material (ETM) and hole transporting material (HTM) and energy band

alignment with absorber are vital factors to conduct the charge carriers to the front and back contacts.[8] Efficient collection of the charge carriers would be obtained only when work function of the front contact material is almost equal to or somewhat greater than conduction band minimum of ETM and at the mean time there would be barrier for holes. Likewise, high work function material as back contact can produce an ohmic contact for holes and electrostatic barrier for electrons in HTM [7].

The structure of the employed device is p-i-n type with low p-type doped CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> sandwiched between a n-type material (TiO<sub>2</sub>) and p-type 2, 20, 7, 70-tet-rakis (N, N0-dimethoxyphenylamine)-9, 90-spirobifluorene (spiro-OMeTAD) layer. TiO<sub>2</sub> is a semiconducting material as well to harvest a portion of the solar spectrum and spiro-OMeTAD is an organic hole transporting material. In perovskite solar cells, Au and Ag are usually used as back contact metal. Ag is used in the form of thin film layer [9], embedded mesh in the PET substrate covered by a conductive polymer [10] and in an alloy form as a substrate for HTM or ETM. In 2013, efficiency of 15.4% have been reported for PSC with Ag-contact by vapour deposition [11]. But until now Au/spiro-OMeTAD structure contributes higher efficiency. Recently Krishna et al investigated that efficiency of 22.35% can be achieved for similar structure of PSC with Au-contact [12]. However high price of Au is a drawback to commercialization of PSCs. Aim of this study is optimizing a comparatively low cost metal contact for PSC with high efficiency. On the other hand, chemical and photochemical stability is also an important factor in selection of a metal. Relatively low cost materials Al, Ag and C, normally used in optoelectronic devices have been investigated to analysis the performances of the PSC here. This study helps to optimize and improve the modules as well as to realize the role of work function of back contact.

## 2. Model and Simulation

The structure of a perovskite solar cell is shown in Fig. 1. It consists of about 90 nm( $\text{TiO}_2$ ) ETM layer over an FTO film, followed by a 400 nm perovskite over-layer, 400 nm spiro-OMeTAD (HTM) and a metal contact. To study the role of different metal contacts, performances of the PSC have been simulated.



**Fig. 1:** Model of Perovskite Solar Cell. ( $\text{TiO}_2$  as ETM, Perovskite ( $\text{MAPbI}_3$ ) as absorber and spiro-OMeTAD as HTM).

**Table 1:** Work Function of metals used in simulation

Metal	Work Function (eV)
Al	4.06
Ag	4.26
C	5

**Table 2:** Material parameters used in simulation

Electrical properties	$\text{TiO}_2$	$\text{MAPbI}_3$	spiro-MeOTAD
$\epsilon_r$	100	30	3
$\mu_n$ ( $\text{cm}^2/\text{v-s}$ )	0.006	50.0	0.0002
$\mu_p$ ( $\text{cm}^2/\text{v-s}$ )	0.006	50.0	0.0002
$N_A, N_D$ ( $\text{cm}^{-3}$ )	$5.0 \times 10^9$	$2.1 \times 10^{17}$	$3.0 \times 10^{18}$
Eg (eV)	3.2	1.5	2.91
$N_C$ ( $\text{cm}^{-3}$ )	$1.0 \times 10^2$	$2.5 \times 10^{20}$	$2.5 \times 10^{20}$
$N_V$ ( $\text{cm}^{-3}$ )	$2.0 \times 10^0$	$2.5 \times 10^{20}$	$2.5 \times 10^{20}$
Affinity(eV)	4.0	3.93	2.2

In this study one-dimensional numerical analysis tool, wx-AMPS, has been used to modeling perovskite solar cell and obtained the results. Table 1 shows the work functions of different low cost metals which can be utilized as back contact with HTM in the PSC.[13,14] Table 2 shows the simulation parameters of different materials used in PSC layers.[12,15,16] The work function of 4.4 eV has been used for front contact (FTO).[12] For simulation, temperature has been used 300K as default and to get all the results, AM1.5 illuminations have been used.

## 3. wx-AMPS

The wx-AMPS program is an update of the very well-known solar cell simulation tool AMPS-1D (Analysis of microelectronic and photonic structures-1D) [18]. This program is designed based on three basic semiconductor equations and it is well adapted to modeling various hetero- and homo-junctions, multi-junction, and Schottky barrier devices. It is a computer aided numerical analysis of solar cells by solving Poisson's equation and the hole and electron continuity equations.[17] Generally the Poisson's equation is:

$$\frac{d\psi}{dx} \left( -\epsilon(x) \frac{d\psi}{dx} \right) = q [p(x) - n(x) + N_D^+(x) - N_A^-(x) + p_t(x) - n_t(x)] \quad (1)$$

where,  $N_D^+, N_A^-$  are the concentrations of ionized donors and acceptors,  $n, p$  are the concentrations of free electrons and holes,  $n_t, p_t$  are the concentrations of trapped electrons and holes,  $\epsilon$  is the dielectric permittivity of semiconductor,  $\psi$  is the electrostatic potential, and  $q$  is the electron charge.

The transport characteristics of an electronic device can be derived by the continuity equation for the holes and electrons. The continuity equations in steady state conditions are:

$$\frac{1}{q} \frac{dJ_n}{dx} = R_n(x) - G(x) \quad (2)$$

$$\frac{1}{q} \frac{dJ_p}{dx} = G(x) - R_p(x) \quad (3)$$

where,  $R_n, R_p$  are electrons and holes recombination velocities for direct band-to-band and indirect transitions,  $J_n, J_p$  are electron and hole current density, and  $G$  is the optical generation rate which is expressed as a function of  $x$  is,

$$G(x) = -\frac{d}{dx} \sum_i \Phi_i^{FOR}(\lambda_i) + \frac{d}{dx} \sum_i \Phi_i^{REV}(\lambda_i) \quad (4)$$

where,  $\Phi_i^{FOR}$  and  $\Phi_i^{REV}$  are, respectively, the photon flux of the incident light and the light reflected from the back surface at a wavelength,  $\lambda$  of  $i$  at some point  $x$ , depending on the light absorption coefficient, and the light reflectance in the forward and reverse direction. The governing equations (1), (2), and (3) must hold at every position in a device, and the solution to these equations involves determining the state variables  $\psi(x)$ , the  $n$ -type quasi-Fermi level  $E_{Fn}$ , and the  $p$ -type quasi-Fermi level  $E_{Fp}$  or, equivalently,  $\psi(x)$ ,  $n(x)$ , and  $p(x)$ , which completely defines the system at every point  $x$ . Because the governing equations for  $\psi(x)$ ,  $E_{Fn}$ , and  $E_{Fp}$  are non-linear and coupled. They cannot be analytically solved. There must be boundary conditions imposed on the set of equations. The Newton-Raphson technique is used in AMPS. To be specific, the solutions to equations (1), (2), and (3) must satisfy the following boundary conditions:

$$\begin{aligned}\psi(0) &= \psi_0 - V \\ \psi(L) &= 0\end{aligned}\quad (5)$$

$$J_p(0) = -qS_{p0}[p_o(0) - p(0)]$$

$$J_p(L) = qS_{pL}[p(L) - p_o(L)]$$

$$J_n(0) = qS_{n0}[n(0) - n_o(0)]$$

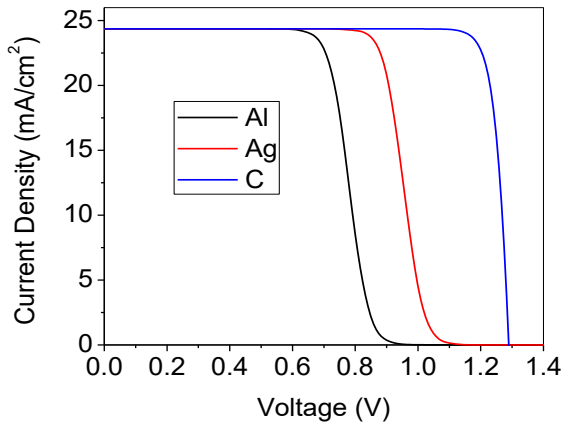
$$J_n(L) = -qS_{nL}[n_o(L) - n(L)]$$

$S_{p0}$ ,  $S_{pL}$ ,  $S_{n0}$ , and  $S_{nL}$  appearing in those conditions are effective interface recombination speeds for holes and electrons at  $x = 0$ , and  $x = L$ .

wx-AMPS solves three coupled differential equations each subject to boundary conditions (equ. 5) and then calculates the electrostatic potential and the quasi-Fermi level for holes and electrons at all point in the solar cell. Once these values are known as a function of depth, it is straight forward to calculate the carrier concentrations, electric fields and currents, and device parameters like the open-circuit voltage ( $V_{oc}$ ), short circuit current density ( $J_{sc}$ ), fill-factor (FF), and the efficiency ( $\eta$ ). The performance of a solar cell is defined by these parameters.

#### 4. Result and Discussion

Figure 2 exhibits the Current density versus voltage curve of perovskite cell with Al, Ag and C metal contacts. A considerable effect of using different metal is found here. The carbon contact performs better as compared to aluminium and silver contacts, due to its larger open circuit voltage and stiffer J-V curve. Table III presents the photovoltaic performances of PSC with Al, Ag and C metal contacts.

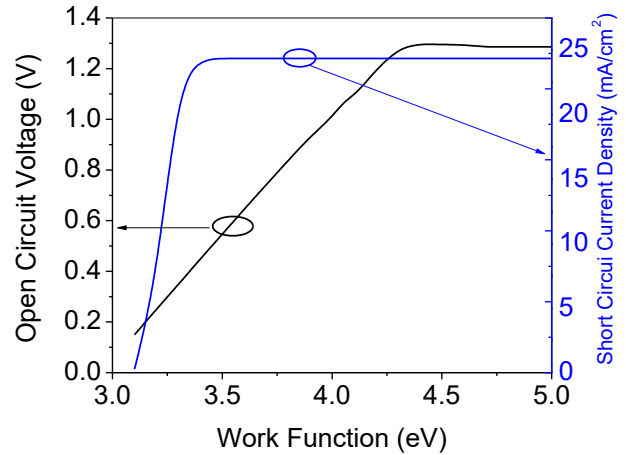


**Fig. 2:** Current density versus Voltage curves for  $\text{TiO}_2/\text{CH}_3\text{NH}_3\text{PbI}_3/\text{spiro-OMeTAD}$  cell using different metal contacts.

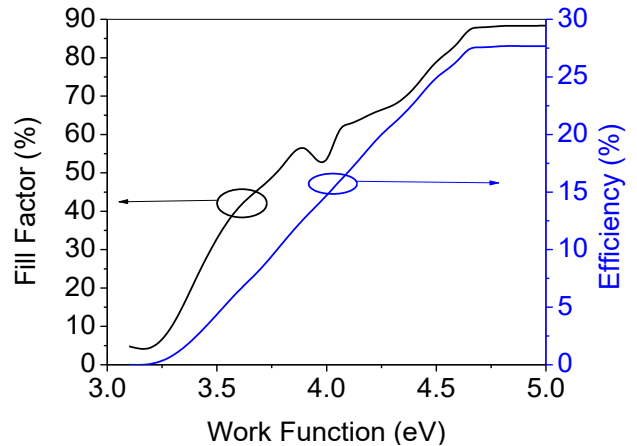
**Table 3:** Photovoltaic characteristics of  $\text{TiO}_2/\text{MAPbI}_3/\text{spiro-OMeTAD}$  cel

Work Function (eV)	$V_{oc}$ (V)	$J_{sc}$ ( $\text{mA}/\text{cm}^2$ )	Fill Factor (%)	PCE (%)
4.06	1.0698	24.3681	61.2389	15.964
4.26	1.2416	24.3682	66.6389	20.1625
5.00	1.2859	24.3685	88.33	27.6782

Figure 3 depicts the variation of open circuit voltage and Short circuit current density with work function of metal contacts. For work functions greater than  $3.5\text{eV}$ , there is almost no change of short circuit current density and for work functions greater than  $4.4\text{eV}$ , slight variation of open circuit voltage is observed. It is seen that both  $V_{oc}$  and  $J_{sc}$  are maximum at the larger range of work function. Carbon contact leads to larger value of open-circuit voltage ( $V_{oc}$ ) and short-circuit current density ( $J_{sc}$ ) for its larger work function than aluminum and silver contacts.



**Fig. 3:** Variation of Open Circuit Voltage & Short Circuit Current Density with Work Function.



**Fig. 4:** Photovoltaic performances of PSC with the variation of work function.

Fill factor and Photovoltaic conversion efficiency versus work function of metal contacts are displayed in Figure 4. Both fill factor and efficiency are increased with increasing work function. But as we observed this is not true always. From the figure it is seen that at some particular range of work function, fill factor slightly decreases with increase of efficiency. This is because performance of a solar cell also depends on  $V_{oc}$  and  $J_{sc}$ . Photovoltaic conversion efficiency of PSC increases almost linearly with work function up to 4.6eV. But work functions larger than 4.6 eV causes small changes of efficiency.

## 5. Conclusion

The role of different metals as a back contact electrode on the performance of PSCs has been studied. Results show that C is the optimum metal for use with spiro-OMeTAD as the back contact. This is due to the high stability and high work function of C (about 5.00 eV). It is very low cost material as compare to other metals used in PSCs. At the same time Ag provides the better performance compared to Al electrode. High work function led to suitable band bending at the HTM-metal interface. For solid state perovskite solar cells, carbon forms low interfacial resistance with the HTM. Although Ag is the second-most used metal contact, it has a stability problem [20]. On the other hand, C has a very good performance with spiro-OMeTAD. Efficiencies of 15.96%, 20.16% and 27.67% have been obtained for Al, Ag and C-based ( $TiO_2$ /MAPbI<sub>3</sub>/spiro-OMeTAD) cells. In future, perovskite cell with carbon contact can be fabricated in laboratory for commercialization instead of gold or silver.

## Acknowledgements

The authors thank Bernabé Marí Soucase for a critical reading of the manuscript. Also thank Prof. Rockett, Dr. Yiming Liu of UIUC and Prof. Fonash of PSU for wx-AMPS simulator.

## References

1. S. Luo and W.A. Daoud. *J. Mater. Chem. A*, 3, 8992-9010.
2. A.M. Salau, *Sol. Eergy Mater.* 2(3), 327-332, 1980.
3. Yecheng Zhou and Angus Gray-Weale, "A numerical model for charge transport and energy conversion of perovskite solar cell", *Phys. Chem. Chem. Phys.*, 2016, 18, 4476.
4. T. Miasaka, A. Kojima, K. Teshima and Y. Shirai, *J. Amer. Chem Soc.* 131(17), 6050-6051, 2009.  
NREL: [https://en.wikipedia.org/wiki/Perovskite\\_solar\\_cell](https://en.wikipedia.org/wiki/Perovskite_solar_cell).
6. W. Tress, N. Marinova, T. Moehl, S. M. Zakeeruddin, Mohammad Khaja Nazeeruddin and M. Grätzel, "Understanding the rate-dependent J-V hysteresis, slow time component, and aging in CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> perovskite solar cells: the role of a compensated electric field," *Energy Environ. Sci.*, 2015, 8, 995
7. S. Fonash, *Solar Cell Device Physics*, 2<sup>nd</sup> ed. (Elsevier, 2012).
8. W. J. Yin, J. H. Yang, J. Kang, Y. Yan and S. H. Wei, *J. Mater. Chem A* 3, 8926-8942, 2015.
9. K. Hwang, Y.S.Jung, Y.J.Heo, F.H.Scholes, S.E.Watkins, J. Subbiah, D.J.Jones, D.Y.Kim and D. Vak, *Adv. Mater.*, 2015, 27, 1241-1247.
10. Y. Li, L. Meng, Y.M. Yang, G. Xu, Z. Hong, Q. Chen, J. You, G. Li, Y. Yang and Y. Li, *Nat. Commun.*, 2016, 7, 10214.
11. Mingzhen Liu, Michael B. Johnston & Henry J. Snaith "Efficient planar heterojunction perovskite solar cells by vapour deposition", 9 September 2013/vol501/nature/395
12. Krishna R. Adhikari, Shekhar Gurung, Binod K. Bhattarai and Bernabe Mari Soucase, "Comparative study on MAPbI<sub>3</sub> based solar cells using different electron transporting materials," *Phys. Status Solidi C* 13, No. 1, 13– 17 (2016).
13. Herbert B. Michaelson, "The work function of the elements and its periodicity," *J. Appl. Phys.* 48, 4729-4733 (1977).
14. The 84th Edition of the CRC Handbook of Chemistry and Physics. 12-124.  
<https://wiki.illinois.edu/wiki/display/solarcellsim/Simulation+Software>
15. Md. Sharafat Hossain, Nowshad Amin and Takhir Razykov, "Prospects of back contacts with back surface fields in high efficiency Zn<sub>x</sub>Cd<sub>1-x</sub>S/CdTe solar cells from numerical modeling," Vol. 8, No. 3, March 2011, p. 187 – 198
16. "A Manual for AMPS-1D", The center for Nanotechnology Education and Utilization, The Pennsylvania State University, PA 16802
17. Yiming Liu, Yun Sun and Angus Rockett, "A new simulation software of solar cells—wxAMPS," *Solar Energy Materials & Solar Cells* 98 (2012) 124–128.  
[refractiveindex.info/?shelf=main&book=C&page=Peter](http://refractiveindex.info/?shelf=main&book=C&page=Peter)
18. F. Behrouznejad, S. Shahbazi, N. Taghavinia, Hui-Ping Wud and Eric Wei-Guang Diao, *J. Mater. Chem. A*, 2016, 4, 13488