

Correspondence

Influence of metal cathode for organic photovoltaic device performance

ARTICLE INFO

Keywords:

Organic photovoltaic
Metal electrode
Charge extraction
Series resistance
Open circuit voltage

ABSTRACT

Influences of metal electrode on the performance of organic photovoltaic device were studied. An appropriate energy level was set between HOMO of donor material and LUMO of acceptor material used to fabricate device and metals with workfunction above, below and within this appropriate range were selectively chosen to form electron collecting electrode. Metals which can form an Ohmic contact showed enhanced power conversion efficiency, while metals forming a Schottky type contact showed poor power conversion efficiency. Series resistances showed characteristic values for each range. Open circuit voltages were in the same order with power conversion efficiency, showing a dependence on injection barrier at negative electrode contact. The power conversion efficiency of low workfunction metal electrode (i.e. calcium electrode device) was higher than that of gold electrode where the electron extraction is spontaneous process.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

Polymer photovoltaic devices can be fabricated by a spin casting of the solution. Since the spin coating is quite simple preparation method, a polymer-based organic photovoltaic (OPV) device becomes a cost-effective one, providing a way to obtain the cheapest renewable energy which is comparable to the cost of fossil energy sources. Recent rapid improvements in the power conversion efficiency elicit anticipation for commercial OPV devices in the near future. However, the conversion efficiency is still far from a commercially viable value, which is estimated as about 10% [1], and still not close to the approximate maximum value of 11% [2]. Therefore, further improvements in the efficiency of polymeric solar cell are strongly required. The primary reason of low efficiency in OPV might be low quantum yield due to their intrinsic photoconduction process such as exciton generation, diffusion and ionization. The typical structure of OPV is transparent electrode/hole transporting layer/photoactive layer/metal electrode. Indium tin oxide (ITO) is usually used as a transparent, positive electrode with high workfunction and the low workfunction metals such as aluminum or calcium are used as negative electrode contact.

For an achievement of power conversion efficiency close to the theoretically expected value, it is quite important to perform a basic study on the device structure and performance relationship. Required condition for high conversion efficiency of OPV is higher carrier extraction, which can be obtained by optimizing device structure. Engineering of interfaces at transparent hole extraction electrode, hole transporting layer, active layer formed by polymer blend, and electron extraction metal electrode are significantly important in order to extract maximum charge output. Open circuit voltage (V_{oc}) is another factor to be considered to increase power conversion efficiency. Open circuit voltage which represents the built-in potential in fabricated device is mainly determined by the energy difference between the HOMO of donor material and the LUMO of acceptor material which are contacting to form the

hetero-junctions, while the influence of injection barrier should be also considered since the accumulation of charge carriers at interface give rise to a diffusion current that must be compensated with drift current at open circuit [3].

In this study, for a photo-active polymer material blends composed of poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl-C₆₀-butyric acid methyl ester (PCBM), most widely used materials for OPV, effects of metal electrode on the power conversion efficiency were studied. Since HOMO of donor material (i.e. P3HT) is 5.1 eV and LUMO of acceptor material (i.e. PCBM) is 4.3 eV, an appropriate workfunction level of metal seems to lie between 4.3 and 5.1 eV as shown in Fig. 1. We assume the efficient extraction of electron when workfunction of metal as the anode (electron extraction) is in this range. We have analyzed the effect of metal electrode on the open circuit voltage, current density, series resistance, and the power conversion efficiency.

2. Experiments

Our photovoltaic cell consists of four conventional cell size of 0.04 cm² active area which formed by a resin cured insulator layer on top of 1 in. by 1 in. ITO coated glass. ITO glass was cleaned by boiling in chloroform, isopropyl alcohol and acetone for 30 min in each solvent, sonification for 15 min in 50:50 isopropyl alcohol and acetone solution, and finally rinsed with de-ionized water. PEDOT:PSS (poly(3,4-ethylene dioxythiophene):poly(styrene sulfonate) aqueous dispersion [Baytron® P] stock solution was spin coated at 2000 rpm for 40 s to form about 35 nm thick film, working as a hole extraction layer, then was baked at 200 °C for 10 min in a nitrogen environment glove box. A typical example of sample preparation is as follows: 2.4 wt% of P3HT and PCBM blend with 1:0.6 ratio by weight was dissolved in anhydrous chlorobenzene and was spin coated on prepared PEDOT:PSS coated ITO glass at 2500 rpm for 40 s. The thickness of resulting active layer was 220 nm and pre-annealed at 150 °C for 10 min. A chosen metal was

deposited on top of the active layer by a thermal evaporation at 10^{-6} to 10^{-7} Torr (150 nm in thickness), and prepared device was post-annealed at 120°C for 10 min. In the case of LiF/Al electrode, 0.8 nm thick LiF buffer was inserted and 150-nm thick aluminum was thermally deposited. Low workfunction metals employed in this study (calcium and magnesium) were deposited on top of active layer with thickness of 30 nm as an electron extraction electrode and 100-nm thick aluminum layer was evaporated for protection of reactive electrode. All of the processing was performed in the glove box with high purity nitrogen environment.

Thickness of coated film was measured with surface profiler (TENCOR®, P-10 α -step). Oriel class A type solar simulator (IEC 904) with Oriel reference cell (calibrated data taken by NREL) was used as a light source and all measurement was performed under 1 sun condition ($100\text{ mW}/\text{cm}^2$). The measurements were not corrected for reflection losses and light absorption in the ITO electrode. Current–voltage characteristics were determined with Keithley 2400 source-measure unit.

3. Results and discussions

Even though several reports [3–9] point out the change of open circuit voltage (V_{oc}) with various metal electrode, it is generally expressed that V_{oc} is only determined by the energy level difference between HOMO of donor material and LUMO of acceptor material. Since power conversion efficiency is directly related with V_{oc} , it is very important to know how to control V_{oc} . It is also important to investigate the combined effects of metals electrode on series resistant, open circuit voltage and current density in order to control power conversion efficiency as one expect.

Aluminum was known as an optimum electrode for P3HT:PCBM blend system since its workfunction (4.20 eV) is approximately aligned with LUMO of PCBM and it forms a stable electrode. It is well known that aluminum forms an Ohmic contact with P3HT:PCBM active layer [5,7]. Current extraction is quite prompt and conversion efficiency is high. Typical current density–voltage curve (J – V curve) is given in Fig. 2. In order to eliminate edge effect [10,11], all measurements were performed with masked device, where only active area was exposed to incident light. Open circuit voltage was 0.52 V, short circuit current was $9.27\text{ mA}/\text{cm}^2$, fill factor was 0.53 and power conversion efficiency was 2.54%.

It is well known that LiF used in organic light emitting diodes (OLED) acts as a buffer layer and causes a band bending and tunneling [12,13]. Since operating mechanisms of OPV and OLED are exactly reverse, the role of LiF buffer layer at the interface between active layer and metal electrode in OPV device is interesting subject [14,15]. Mihailitchi et al. [16] reported that there was no barrier energy for electron extraction between LiF/Al electrode with PCBM as an acceptor material. LiF/Al electrode showed best performance among several high workfunction metal electrodes (i.e. Ag, Au, Pd).

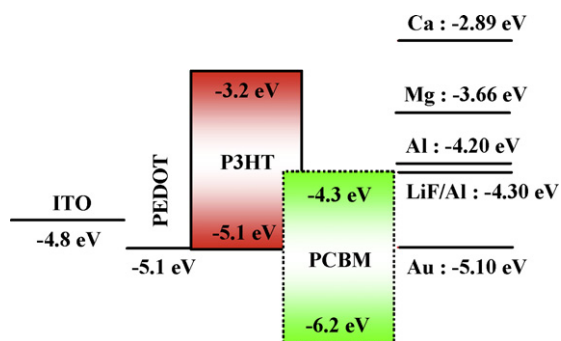


Fig. 1. Energy band diagram of OPV device.

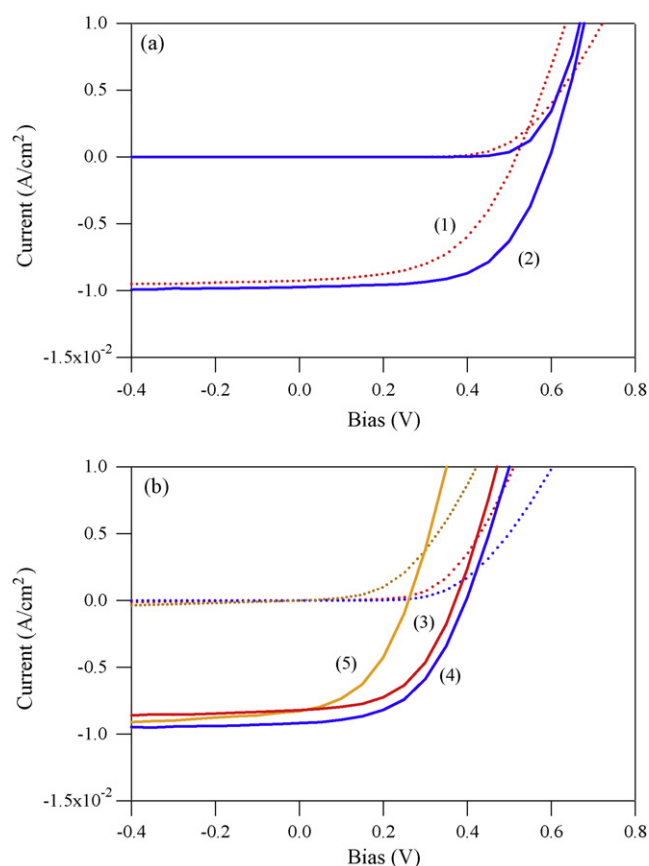


Fig. 2. J – V curve of chosen metal electrode: (a) Al electrode (1) and LiF/Al electrode (2); (b) Ca electrode (3), Mg electrode (4) and Au electrode (5).

Our experimental data showed same tendency and charge extraction was enhanced and conversion efficiency was increased about 40% (from 2.54 to 3.54) compared to that of aluminum electrode. The increase of V_{oc} is not significant, but shows a value of 0.60 V, which is 0.08 V higher than that of device with aluminum electrode.

Calcium was chosen as a negative electrode with low workfunction (2.89 eV) which is below appropriate range. Aluminum was over coated for protection of calcium electrode. Calcium has been used quite open recently, since the long term stability of OPV with calcium/silver or calcium/aluminum contact is much better than that of Al or LiF/Al [17]. Due to the workfunction of calcium (2.89 eV), which is significantly lower than LUMO of PCBM (4.3 eV), it forms a Schottky type contact [3,18] as well as a non-spontaneous electron extraction process. Because of the formation of space charge limited condition, power conversion efficiency should be decreased and the experimental data showed decrease in power conversion efficiency to 1.58 which is about 40% reduction in efficiency compared to the condition of PCBM–Al contact (efficiency is 2.54 using aluminum electrode). As an electrode with intermediate low-work function (3.66 eV), magnesium was also employed for the device fabrication. Due to the reactive property of magnesium, aluminum was also over coated for protection. As expected, all characteristic values of the device properties were in between values of calcium and aluminum. It still forms a Schottky type contact so that large energy is required for efficient carrier conduction (electron extraction) into metal electrode. Therefore, magnesium electrode behaves close to calcium electrode. The power conversion efficiency decreases to 1.85 which is about 30% reduction in efficiency compare to a device with the aluminum electrode. Another possible explanation for low V_{oc} and conversion efficiency at Ca and Mg elec-

Table 1
Characteristics of different metal electrode devices.

Sample	Metal electrode	Work function (eV)	V_{oc} (V)	J_{sc} (mA/cm ²)	FF	Efficiency	R_s (Ω cm ²)
1	Ca/Al	2.89	0.37	−8.21	0.52	1.59	8.28
2	Mg/Al	3.66	0.40	−9.17	0.51	1.85	8.96
3	Al	4.20	0.52	−9.27	0.53	2.54	3.24
4	LiF/Al	4.30	0.60	−9.74	0.61	3.54	2.87
5	Au/Al	5.10	0.26	−8.28	0.44	0.94	7.06

trodes, although minor effects at high-vacuum evaporation process, is the reaction of calcium or magnesium at the interface of the active layer, which might prevents the efficiency charge collection, hereby causing decrease in charge extraction [19,20].

Gold was chosen as a negative electrode with high-work-function material (5.10 eV), which is clearly above the appropriate range. Even though workfunction of gold is higher than HOMO of donor material so that it forms a Schottky type contact [3,18], charge extraction should be prompt since the potential energy flow is spontaneous reaction. However, the energy difference between the active layer and gold electrode is so high that it cannot form an Ohmic contact [5,7], which reduces charge extraction. Since work-function of gold is higher than HOMO of donor molecule (i.e. P3HT), hole can be injected from metal electrode back to the active layer, which causes recombination with electron to form an exciton. As a result of this recombination, all factors such as open circuit voltage, current density and fill factor are lower than that of other metal electrode so that the conversion efficiency is the lowest of all tested metal electrode. Conversion efficiency drop to 0.94 which is reduction of 60% compare to that of aluminum.

The bulk resistance of OPV can be divided into series resistance and shunt resistance. Shunt resistance is a parallel resistance in circuit of OPV and represents resistance against leak current so that conversion efficiency is high when shunt resistance is high. While series resistance represents resistance against current flow so that it should be minimized in order to obtain high conversion efficiency. This series resistance can be obtained from the slope of current density-voltage (J-V) characteristics curve (the inverse of slope in the J-V curve represents the bulk series resistance). As summarized in Table 1, devices prepared with metal electrode possessing workfunction close to the appropriate range (Al and LiF/Al) showed significantly low series resistance compared to the case of other electrodes. The trend shown in Table 1 is quite reasonable since series resistance represents resistance to current flow. Energy level difference from LiF/Al electrode (workfunction is 4.30 eV which is known to be a zero potential barrier) to gold electrode is about 0.8 eV while that for calcium electrode is 1.41 eV so that the series resistance for calcium electrode should be higher than that of gold electrode. Because of the possible recombination caused by an injection (overflow) of hole from negative electrode, open circuit voltage of gold electrode is lower than that of calcium electrode while series resistance of device prepared with gold electrode is less than that of calcium electrode. From these results it can be concluded that series resistance is not scaled with the extent of current flow; it rather depends on the main difference of energy levels.

Magnesium and gold are the metals with workfunction which is just outside of appropriate range; however, the short circuit current and open circuit voltage using these metals showed huge differences as shown in Fig. 3. Magnesium electrode caused less decrease in factors, while gold electrode caused more pronounced decrease in all factors (I_{sc} , V_{oc} , and efficiency). Power conversion efficiency of low workfunction metal electrode (i.e. magnesium) was twice of that of high workfunction metal electrode (i.e. gold). Also open circuit voltage was changed (from 0.40 V to 0.26 V) when metal electrode was changed from magnesium to gold. Unlike the Ohmic contact (Al or LiF/Al), the negative electrodes of Ca, Mg, and Au are forming a non-Ohmic contact. Therefore, the experimen-

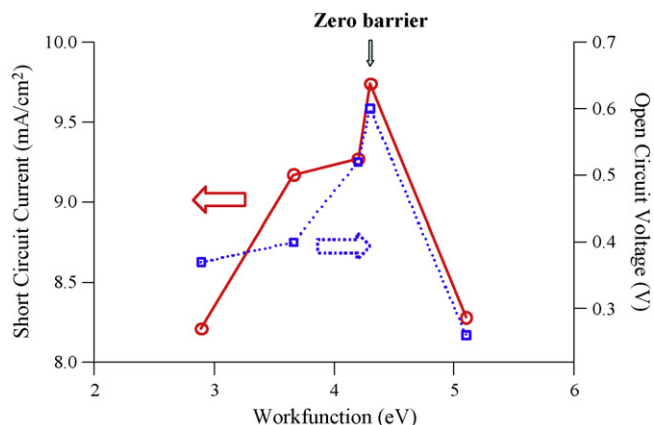


Fig. 3. Change of short circuit current and open circuit voltage as a function of metal workfunction.

tal open circuit voltage is dramatically influenced by the change of work function, as seen in the linear relationship with V_{oc} and LUMO + Fermi level of electrodes [16]. The more concrete explanation of these phenomena (relationship between open circuit voltage and conversion efficiency decrease) is that recombination of hole-electron at Au-PCBM contact is more pronounced when the work function of metal electrode is higher than the HOMO of donor material.

4. Conclusion

The role of metal electrode on the performance of polymer/fullerene solar cells has been studied. The power conversion efficiency of low workfunction metal electrode (i.e. calcium electrode device), which electron extraction is not a spontaneous (i.e. in the direction of low Gibbs free energy direction) process, was higher than that of gold electrode which electron extraction is spontaneous process. Because of the built-in potential within the device, electron extraction from active layer to metal electrode was possible by overcoming high energy barrier. The device prepared with metal electrode which workfunction is in the appropriate range showed superior performance than that of outside of the appropriate range. The upper limit of the V_{oc} can be set to the difference of the acceptor LUMO and the donor HOMO levels. The contact materials are one of the key parameters to alter the performance of the OPV. Series resistance solely depends on the energy level differences between LUMO of acceptor material and metal electrode workfunction. The general trend was that the higher open circuit voltage, the higher the power conversion efficiency.

Acknowledgments

This work was supported by the Korea Science and Engineering Foundation (KOSEF) grant funded by the Korea government (MOST) (No. R01-2006-000-10087-0). This work was also partially supported by GRR program of Gyeonggi province (66944, Development of high efficiency solar cells).

References

- [1] C.J. Brabec, J.A. Hauch, P. Schilinsky, C. Waldauf, *MRS Bull.* 30 (2005) 50.
- [2] L.J.A. Koster, V.D. Mihailetchi, P.W. Blom, *Appl. Phys. Lett.* 88 (2006) 093511.
- [3] C.J. Brabec, A. Cravino, D. Meissner, N.S. Sariciftci, T. Fromherz, M.T. Rispens, L. Sanchez, J.C. Hummelen, *Adv. Funct. Mater.* 11 (2001) 374.
- [4] C.M. Ramsdale, J.A. Barker, A.C. Arias, J.D. MacKenzie, R.H. Friend, N.C. Greenham, *J. Appl. Phys.* 92 (2002) 4266.
- [5] V.D. Mihailetchi, L.J.A. Koster, P.W.M. Blom, *Appl. Phys. Lett.* 85 (2004) 970.
- [6] C.J. Brabec, A. Cravino, D. Meissner, N.S. Sariciftci, M.T. Rispens, L. Sanchez, J.C. Hummelen, T. Fromherz, *Thin Solid Films* 403 (2002) 368.
- [7] H. Frohne, S.E. Shaheen, C.J. Brabec, D. Müller, N.S. Sariciftci, K. Meerholz, *Chemphyschem* 9 (2002) 795.
- [8] E. Kymakis, I. Alexandrou, G.A.J. Amaratunga, *J. Appl. Phys.* 93 (2003) 1764.
- [9] L.J.A. Koster, V.D. Mihailetchi, R. Ramaker, P.W.M. Blom, *Appl. Phys. Lett.* 86 (2005) 123509.
- [10] A. Cravino, P. Schilinsky, C.J. Brabec, *Adv. Func. Mater.* 17 (2007) 3906.
- [11] M.-S. Kim, M.-G. Kang, L.J. Guo, J. Kim, *Appl. Phys. Lett.* 92 (2008) 133301.
- [12] S.T. Zhang, X.M. Ding, J.M. Zhao, H.Z. Shi, J. He, Z.H. Xiong, H.J. Ding, E.G. Obbard, Y.Q. Zhan, W. Huang, X.Y. Hou, *Appl. Phys. Lett.* 84 (2004) 425.
- [13] S.E. Shaheen, G.E. Jabbour, M.M. Morrell, Y. Kawabe, B. Kippelen, M.-F. Nabor, R. Schlaf, E.A. Mash, N.R. Armstrong, *J. Appl. Phys.* 84 (1998) 2324.
- [14] W.J.H. van Gennip, J.K.J. van Duren, P.C. Thüne, R.A.J. Janssen, J.W. Niemantsverdriet, *J. Chem. Phys.* 117 (2002) 5031.
- [15] C.J. Brabec, S.E. Shaheen, C. Winder, N.S. Sariciftci, P. Denk, *Appl. Phys. Lett.* 80 (2002) 1288.
- [16] V.D. Mihailetchi, P.W.M. Blom, J.C. Hummelen, M.T. Rispens, *J. Appl. Phys.* 94 (2003) 6849.
- [17] R. De Bettignies, J. Leroy, M. Firon, C. Sentein, *Synth. Met.* 156 (2006) 510.
- [18] S. Karg, W. Riess, V. Dyakonov, M. Schwoerer, *Synth. Met.* 54 (1993) 427.
- [19] P. He, F.C.K. Au, Y.M. Wang, L.F. Cheng, C.S. Lee, S.T. Lee, *Appl. Phys. Lett.* 76 (2000) 1422.
- [20] M. Kiy, I. Biaggio, M. Koehler, P. Günter, *Appl. Phys. Lett.* 80 (2002) 4366.

Yong Seok Eo^{a,b}, Hee Woo Rhee^b,
Byung Doo Chin^c, Jae-Woong Yu^{a,*}

^a Center for Energy Materials Research, Korea
Institute of Science and Technology, P.O. Box 131,
Cheongryang, Seoul 130-650, Republic of Korea

^b Department of Chemical Engineering, Sogang
University, Seoul 121-742, Republic of Korea

^c Department of Polymer Science and Engineering,
Dankook University, Jukjeon-dong, Suji-gu, Yongin,
Kyeonggi 448-701, Republic of Korea

* Corresponding author. Tel.: +82 2 958 5325;
fax: +82 2 958 5309.
E-mail address: jwyu@kist.re.kr (J.-W. Yu)

14 April 2009

Available online 1 July 2009