THE OPTIMUM PERFORMANCE OF POLYMER SOLAR CELLS

By

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ABSTRACT

A model for an ideal bulk heterojunction solar cell has been developed . The model is compared with measurements from MDMO : PPV / PCBM solar cells . The performance of the cell is found to be governed by the offset of the highest occupied molecular orbital of the electron donor and the lowest unoccupied molecular orbital of the electron acceptor . It is also governed by the offset of the lowest unoccupied molecular orbital of the acceptor and the lowest unoccupied molecular orbital of the donor . The results also show that the performance depends strongly on the work function of the anode and the thickness of the solar cell . Material development is required for development of low – band gap cells to optimize the utilization of solar radiation . The optimum band gap is about 1.5 e V .

الملخص :

تم تطوير أنموذج لخلية شمسية غير متجانسة. ثم تمت مقارنة ذلك الأنموذج بقياسات من خلية شمسية من نوع MDMO:PPV/PCBM ولقد وجد أن أداء الخلية يتحكم فيه الفرق في الطاقة بين أعلى مدار ممتلئ في العنصر المانح للإلكترون وأدنى مدار فارغ في العنصر المستقبل للإلكترون. وكذلك فإنه يخضع لفرق الطاقة بين أدنى مدار فارغ في العنصر المستقبل وأدنى مدار فارغ في العنصر المانح. كذلك فقد أظهرت النتائج أن أداء الخلية يعتمد بشكل كبير على دالة الشغل في المهبط وسمك الخلية. كذلك فقد وجد أنه هنالك حوجة لتطوير المواد بحيث تكون ثغرة الطاقة حوالى 1.5 eV.

INTRODUCTION

Photovoltaic devices prepared from blends of conjugated polymers and fullerene derivatives are promising candidates for solar energy conversion , due to their mechanical flexibility, lightweight, and potential low cost of fabrication .The efficient photo- response of these devices originates from the ultra fast electron transfer from the conjugated polymer (donor) to the fullerene (acceptor) [1]. Over the last few years, a sustained effort has been made to improve the performance of these solar cells.

In the ongoing attempt to maximize the efficiency of polymer-based photovoltaic devices, many research effort have been done. That included improvement of the device structure, as well as the proper choice of electrode materials [2,3] , and blend layers [4] .

The ongoing research include also development of new polymers. Low-band gap polymers are especially attractive as they promise to increase the absorption of solar photons , especially near the peak of solar emission .

The first organic solar cells were based on single thermally evaporated molecular organic layers , sandwiched between two metal electrodes of different work functions. The behavior of these devices can be explained by the metal-insulator-metal (MIM) model[5]. The photoactive region is often very thin (less than the diffusion length of the exciton) . Since both positive and negative photo-excited charges travel through the same material, recombination losses are generally high. Results from single layer organic solar cell show that the typical conversion efficiency is below 0.14% [6].

Double layer devices ,were introduced in many combinations ,to replace the single layer cells[7].In such devices only excitons created within the distance of 10-20 nm(diffusion length of the exciton)from the donor-acceptor interface,can reach the interface,where the excitons are dissociated into free charge carriers. This leads to the loss of absorbed photons further away from the interface, and leads to low quantum efficiencies [8].

Recently,most of the work has been on the blend organic solar cell.It consists of a blend of an electron donor and an electron acceptor.It exhibits a donor-acceptor phase separation ,that each donor –acceptor interface is within a distance less than the exciton diffusion length of each absorbing site. The bulk

heterojunction (BHJ) concept provides a large interfacial area between the donor and acceptor phases, where charge separation occurs [9] .

Optimization of bulk heterojunction solar cells

Photo-excitations in organic materials do not lead directly to free charge carriers,as in inorganic materials,but to bound electron-hole pairz (excitons). The excitons can be dissociated at interfaces of materials with different electron affinities.Usually the polymer ,electron donor, is blended with the electron acceptor, [6,6]-phenyl-C16–butyric acid methyl ester (PCBM) ,due to its high electron affinity.After dissociation ,a pair of a hole in the donor and an electron in the acceptor is formed across the interface .The internal electric field separates the pair into free charge carriers .The free hole and the free electron are then transported through the donor and acceptor to the electrodes.The lifetime of the separated charges in such blend has to be sufficiently long in order to be transported to the electrodes .This limits the thickness of the blend to about 100 nm [10] .

The power efficiency , η , is given by

$$\eta = (FF)\, I_{sc}\, V_{oc}\, P^{-1} \qquad (1)$$

where FF is the fill factor ,I_{sc} is the short circuit current ,V_{oc} is the open circuit voltage , and P is the solar power incident on the cell .

The short circuit current is determined by the photon absorption and the internalconversionefficiency.Theamountofabsorbedphotonscanbe increased by increasing the thickness. As the thickness increases the possibility of recombination losses increases, due to the low charges mobility . The electron mobility in poly(3-hexylthiophene) (P3HT):PCBM at 300 ^{0}K is about $10^{-8}\, m^2 V^{-1} s^{-1}$, and that of the hole is even lower , by a factor of about 5000 [11] . The recombination losses decrease the fill factor .

When the cell is illuminated, the open-circuit voltage (V_{OC}) is given by

$$q\, V_{OC} = F_n - F_p \qquad (2)$$

where F_n and F_p are the electron and hole quasi-Fermi levels, and q is the elementary charge. The upper limit for the V_{OC} is given by the potential offset of the highest occupied molecular orbital of the donor $(HOMO)_D$ and the lowest unoccupied molecular orbital of the acceptor $(LUMO)_A$ [9] .This indicates that F_n aligns with the $(LUMO)_A$ and F_p aligns with the $(HOMO)_D$.

$$q\,V_{OC} = (HOMO)_D - (LUMO)_A \qquad (3)$$

Effect of the positive electrode

The cell was prepared at the Polymer Laboratory of the University of Addis Ababa. Indium tin oxide (ITO) was used as a transparent anode. A solution of (3, 4,-ethylenedioxy thiophene/poly (styrene sulafonate) PEDOT :PSS, with concentration of 5 mg/ml, was spin coated on top of the ITO. The blend consists of poly[2-methoxy-5-(3′,7′- dimethyloctyloxy)-p-phenyleneviylene] (MDMO : PPV) as electron donor and PCBM as electron acceptor, in a 1:4 weight ratio. The blend was spin coated on top of the PEDOT: PSS. The aluminum electrode was evaporated over the blend at a pressure of about $6\times10^{-6}\,mb$. The cell was illuminated with a $0.3\,W\,m^{-2}$ lamp . The measurements were taken at $300\,^{o}K$. The area of each solar cell was $1.5\,mm^{2}$.

Measurements for the current and voltage were taken for two identical cells , except for the anodes . In one of them the anode was ITO and in the other it was PEDOT: PSS (coated on ITO) . The work function of the PEDOT: PSS (5.2 eV) matches the HOMO level of the MDMO : PPV (5.2 eV) [12,13], which results in ohmic contact for holes . The work function of the ITO is (4.3 eV) [13] . Fig.1 shows the (HOMO) and the (LUMO) of the donor and acceptor , and the work functions of the electrodes .

The results of the measurements are shown in Fig.2 . The PEDOT:PSS makes an ohmic contact with $(HOMO)_D$. It is seen that the PEDOT:PSS layer has increased the current significantly. The short circuit current has increased by more than four times, Table.1. The open circuit voltage has decreased from 1.0 V to about 0.7 V . It seems that the ohmic contact resulted in a voltage drop of 0.3 V.

Similar results has been obtained by Scharber et al [12]. The voltage drop could be due to band bending [14].
For ohmic contact , Eq.3 can be written as

$$q\,V_{OC} = (HOMO)_D - (LUMO)_A - 0.3 \qquad (4)$$

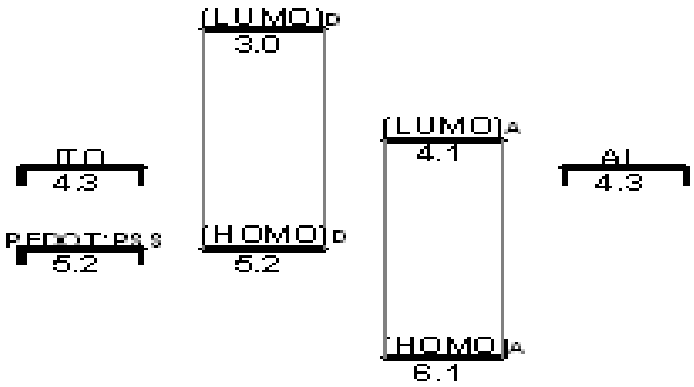

Fig.1 Energy –band diagram of the BHJ solar cell .

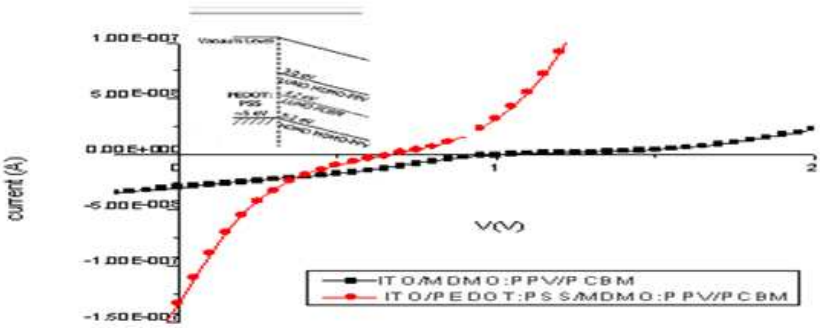

Fig. 2 Effect of the work function of the anode on the current-voltage characteristics .

Table .1 The work function (Φ_m) of the anode , open circuit voltage (V_{oc}), and short - circuit current (I_{sc}) .

anode	Φ_m (eV)	V_{oc} (V)	I_{sc} (A)
PEDOT:PSS	5.3	0.7	1.34×10^{-7}
ITO	4.3	1.0	2.95×10^{-8}

Open circuit voltage

The absorbed photons generate excitons which dissociate at the heterojunction interface.

The exciton binding energy is about 0.5 eV [15] .This requires that the offset between the $(LUMO)_A$ and the $(LUMO)_D$ to be about 0.5 eV. Then we can write

$$(LUMO)_A - (LUMO)_D = (HOMO)_A - (HOMO)_D = 0.5 \text{ eV} \quad (5)$$

The band-gap of the donor is given by

$$(HOMO)_D - (LUMO)_D = E_g \quad (6)$$

Subtracting Eq . (6) from Eq . (4)

$$(LUMO)_A - (LUMO)_D = E_g - q\,V_{OC} - 0.3 \text{ eV} \quad (7)$$

When substituting the value of the $(LUMO)_A$ - $(LUMO)_D$ offset in Eq .(7) ,

$$0.5 = E_g - q\,V_{OC} - 0.3$$

$$q\,V_{OC} = E_g - 0.8 \text{ eV} \quad (8)$$

Eq. (8) gives the V_{OC} of an ideal BHJ solar cell in which :

a- The electrodes make ohmic contact with the blend.

b- The difference between the electron affinity of the acceptor and that of the donor is 0.5 eV.

It has to be noted that the HOMO of the MDMO: PPV is 5.2 eV, and the LUMO of the PCBM is 4.1 eV [16]. Eq.3 gives an open circuit voltage of 1.1 V for these values. This is approximately similar to the measured value of the V_{oc} when the ITO was used as an anode.

The measurements gave open–circuit voltage of about 0.7 V and an efficiency of 2.8 % , when the PEDOT : PSS was used as an anode . From the UV-VIS absorption spectrum the band-gap of the blend was found to be about 2.1 eV.

By substituting the value of the band-gap in Eq .(8), we obtain a value of 1.3 V for V_{OC} .This is 0.6 V higher than the measured value of V_{OC} . Eq.(8) is based on the assumption that the $(LUMO)_A$ - $(LUMO)_D$ offset is 0.5 eV . The LUMO level of MDMO : PPV is 3.0 eV [16] , while that of the PCBM is 4.1 eV. The $(LUMO)_A$ - $(LUMO)_D$ offset is 1.1 eV. This energy is more than the energy (0.5 eV) needed for the exciton dissociation and the electron transfer from the donor to the acceptor. About 0.6 eV would be dissipated as heat.

If the LUMO level of the PCBM could be raised to the 3.5 eV level, the V_{OC} would increase by 0.6 eV , Eq.(4). The possibility of variation of the LUMO of the PCBM has been proven experimentally , [17] . A change of the $(LUMO)_A$ by 0.6 eV would increase the efficiency to a value of 5.2 % .

Fill factor

The effect of thickness on fill factor was studied by taking measurements from three solar cells with thicknesses: 25 nm ,40 nm and 60 nm. Fig.3 shows the variation of the fill factor with thickness . The fill factor decreases as the thickness increases. Charge recombination seems to increase as the thickness increases, while photons absorption increases as the thickness increases. The thickness needs to be optimized for maximum efficiency .

Fig.4 shows the short–circuit current and the open circuit voltage for blend thicknesses of 25 nm , 40 nm and 60 nm. The V_{OC} seems to be approximately independent of the blend thickness. The short –circuit current is maximum at 40 nm thickness.

Band gap

In order to generate an electron-hole pair , the photon energy has to be greater than the band-gap . If the band-gap is decreased , photons of lower energy (from the visible and I.R.) can be utilized, and hence the current will be increased . Since the open circuit voltage is proportional to the band-gap , Eq. (7) , the voltage decreases when the band-gap is decreased . The band-gap has to be optimized according to the spectral distribution of solar radiation .

It has been shown that, at air mass one and 300 ^{o}K temperature, the optimum band-gap is about 1.5 eV [18] . The efficiency of a BHJ solar cell with 1.5 eV

band-gap is about 1.5 times that with band-gap of 2.1 eV. Material development is required to produce a BHJ solar cell with 1.5 eV band-gap

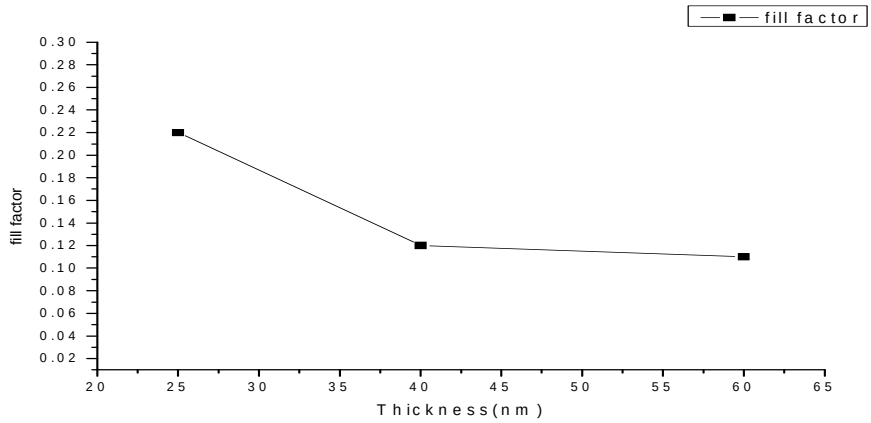

Fig.3 Variation of fill factor with thickness .

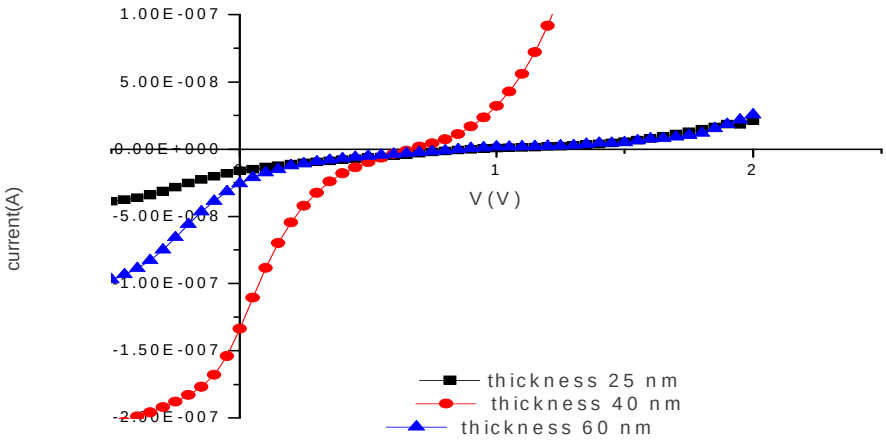

Fig.4 Current-voltage characteristics for three cells with thicknesses : 25 nm , 40 nm and 60 nm .

CONCLUSION

A model for an ideal BHJ solar cell has been proposed . The model has been compared with measurements from MDMO : PPV /PCBM solar cells .

The maximum limit for Voc is given by the offset of $(HOMO)_D$ - $(LUMO)_A$. It is noticed that small voltage drop (about 0.3 V) has to be sacrificed when the anode makes an ohmic contact with $(HOMO)_D$ .The ohmic contact is a necessity . It has increased the I_{sc} by about four times (when a layer of PEDOT:PSS was coated on the ITO) .

The electron acceptor is preferably to have a lowest unoccupied orbital which makes $(LUMO)_A$-$(LUMO)_D$ offset of about 0.5 e V . Higher values of the offset results on the reduction of the V_{oc} . Lower values of the offset may not be sufficient to break the excitons into free charge carriers .

The thickness of the cell has to be optimized for maximum efficiency . As the thickness increases , the photons absorption increases , but the fill factor decreases .

Material development is required to produce low band gap BHJ solar cells . The optimum band gap is about 1.5 e V .

REFERENCES

1. **Sariciftci, N. S. Smilowitz, L. Heeger, A. J. and Wudl ,F. (1992).** Science 258, 1474
2. **Alem,S. de Bettignies,R.. Nunzi,J.M. Cariou,M. (2004).** Appl. Phys. Lett.84
3. **C.J. Brabec,C.J. Cravino,A.Meissner,D. Sariciftci,N.S. Fromherz,T. Rispens,M.T. Sanchez,L. Hummelen,J.C. (2001).** Adv. Funct. Mater. 11,374
4. **Zhang, F.L. Gadisa,A. Inganas,O. Svensson,M. Andersson,M.R. (2004).** Appl. Phys. Lett. 84,3906
5. **Hoppe, H. Sariciftci, N. S. (2004).** J. Mat. Chem., Vol. **19**, 1924
6. **Godisa,A. Kassegn ,B. (2002).** Synthetic Metal 129,179-185
7. **Tang, C.W. (1986).** Appl. Phys. Lett., Vol. **48**, 183
8. **Winder, C. Sariciftci, N.S. (2004).** J. Mat. Chem., Vol. **14**, 1077
9. **Lungenschmied, C.Dennier, Neugebauer G.H.Sariciftci, N.S.and.Echernfreund, E. (2006).** Appl.Phys. Lett.89,223519
10. **Lenes, M. Koster, L.J.A. Mihailetchi, V.D.and Blom, P.W.M. (2006).**Thickness dependence of the efficiency of polymer:fullerene bulk heterojunction solar cells , Appl. Phys. Lett. 88, 243502-1-243502-3

11. **Mihailetchi, V.D. Xie, H. de Boer, B.. Koster, L .J.A and Blom , P. W.M. (2006).** Charge transport and photocurrent in Poly (3-hexylthiophene): Methanolfullerene bulk-heterojunction solar cells , Adv.Funct Mater. 16, 699-708
12. **Schaber, M.C. Muhlebacher, D. Koppe, M. Denk, P. Walldouf, C. Heeger, A.J. and Brabec, C.J. (2006).** Design rules for donors in bulk-heterojunction solar cells – towards 10% energy-conversion efficiency, Adv.Mater. 0000,1-6
13. **Muhlbacher,D.Neugebauer,H.Cravino,A.Sariciftci,N.S. van Duren, J.K.J. Dhanabalan,A. van Hal,P.A and Janssen, R.A.J. (2002).** Comparison of electrochemical and spectroscopic data of the low-band polymer PTPTB , Mol. Cryst. Liq.Cryst.385, 205-212
14. **Mihailetehi, V.D. Blom, P.W.M. Hummelen,J.C. and Rispens, M.T. (2003).** Cathode dependence of the open-circuit voltage of polymer:fullerene bulk heterojunction solar cells , J.Appl. Phys. 94,10,6849-6854
15. **Bassler, H. Arkhipov, V.I. Emelianova, E.V. Gerhard, A.Hayer,A. Im,C. and Rissler, J. (2003).** Exciton in π-conjugated polymer, Synth. Met.135-136, 377-382
16. **Muhlbacher,D.Neugebauer,H.Cravino,A. Sariciftci, N.S. van Duren, J.K.J. Dhanabalan,A. van Hal, P.A. and Janssen, R.A.J. (2002).** Mol .Cryst. Liq.Cryst. 385
17. **Kooistra, F.B. Knol,J. Kastenberg,F. Popescu, L.M. Verhees, W.J. H. Kroon, J.M.and Hummelen, J.C. (2007).** Increasing the open circuit voltage of bulk-heterojunction solar cells by raising the LUMO level of the acceptor ,Org. Lett. 9,4
18. **Sze, S.M.. (1985).** Semiconductor devices, physics and technology. John Wiley and sons . New York.