Model of mixing ratio dependence of built-in voltages in organic bulk heterojunction solar cells

Y. WANG[a], C. MA[a], R. WANG[a], R. LI[a], Y. PENG[a,b*]
[a]School of Physical Science and Technology, Lanzhou University, Lanzhou 730000, China
[b]The Key Laboratory for Magnetism and Magnetic Materials of the Ministry of Education, Lanzhou University, Lanzhou 730000, China

Bulk heterojunction has emerged over the past years as a promising structure for organic solar cells. Different materials for electron and hole contact are usually used for most optimized devices, which results in a built-in voltage. Based on the double Gaussian distribution of density of states of bulk junction materials, a numerical model for the built-in voltage of bulk heterojunction solar cells is developed. The result show that the built-in voltage of a bulk heterojunction solar cells is strongly dependent on the mixing ratio. Compared with the built-in voltage of the pure devices (with pure donor material or pure acceptor material), the built-in voltage of bulk heterojunction solar cell is larger than the smaller but smaller than the larger of the built-in voltages of the two pure devices. The result also show that the built-in voltage increases with the increase of the cathode Fermi level, which is characterized by two plateaus related to the filling of the LUMOs of the acceptor and that of the donor, respectively.

1. Introduction

Compared with the inorganic solar cells, such as the silicon solar cells, the organic solar cells (OSCs) can be cheaper fabricated, and can be made on large size flexible substrate. Usually the organic solar cells can be made in planar heterojunction structure and bulk heterojunction structure. Due to the higher dissociation efficiency of the photogenerated excitons, the conversion efficiency of bulk heterojunction solar cells is higher than that of planar heterojunction solar cells,   and becoming the competitive structure of OSCs. Usually different electrode materials for electron and hole contact are used in OSCs, which results in a built-in voltage, , because U_{bi} sets the upper limit of the open-circuit voltage [1], and hence directly related to the conversion efficiency. The energy conversion efficiency (η_p) of a solar cell can be described as :

$$\eta_p = \frac{U_{oc}J_{sc}FF}{P_{in}}$$

where U_{oc}, J_{sc} ,FF and P_{in} are the open-circuit voltage , short-circuit current density, fill factor (*FF*) and the intensity of input light , respectively , the volue of *FF* is between 0 and 1. Obviously , under the condition of given J_{sc}, *FF* and $P_{in,}$ the energy conversion efficiency of OSC increases with the open –circuit voltage . The relevant experimental results show that the open-circuit voltage increases with the input light . As U_{bi} *sets the upper limit of $U_{oc.}$ The further research on the built –in voltage*

of OSC is very important.
When neglecting band bending due to charges near the electrodes, U_{bi} for MOSM structures can be described as [2]:

$$U_{bi} = \text{Min}(W_a, E_H) - \text{Max}(W_c, E_L), \quad (1)$$

Where W_a and W_c are the anode and cathode Fermi level, E_H and E_L are the mean values of HOMO and LUMO levels of the organic in respective to vacuum. For bulk heterojunction solar cells, the built-in voltage under MIM approximation can be formulated as

$$U_{bi} = \text{Min}(W_a, E_{HA}, E_{HD}) - \text{Max}(W_c, E_{LA}, E_{LD}) \quad (2)$$

Where E_{HA} and E_{LA} are the mean values of HOMO and LUMO levels of the acceptor, and E_{HD} and E_{LD} are that of the donor in respective to vacuum. Under the condition of single carrier transport approximation, M. Kemerink et.al. derived a analytical expression for the built-in voltage. Unfortunely, the mixing ratio (ζ)is not included in that formal ,it is only applicable for the planar heterojunction solar cells and can not use in the bulk-heterojunction solar cells. By using the Guassian distribution of energy states in organic semiconductor density, we proposed a numerical model for the calculation of the analysed the mixing ratio dependence of the built-in voltage .The rusult show that compared with the built-in voltage of the pure devices, the built-in voltage of bulk heterojunction solar cells is larger than the smaller but smaller than the larger of the built-in voltages of the two pure devices. The result

also show that the built-in voltage creases with the increase of the cathode Fermi level, which is characterized with two plateaus. This conclution is an indispensable guider for making the BHJ SOCS.

2. Model

Organic semiconductor thin films are either amorphous, or polycrystalline in structure, which is disordered in comparison with regular inorganic crystals. The essential effect of disorder is to split the electronic transport orbital bands of the corresponding regular crystal lattice into a series of localized states. To a good approximation the density of states of LUMOs $g_L(E)$, and HOMOs $g_H(E)$ display a Gaussian profile[3-4]. The energy distribution of DOS in a bulk heterojunction structure is [5-6]

$$g_H(E) = \frac{(1-\zeta)N_{HA}}{\sqrt{2\pi}\sigma_{HA}}\exp\left(-\frac{\left(E-E_{HA}\right)^2}{2\sigma_{HA}^2}\right) + \frac{\zeta N_{HD}}{\sqrt{2\pi}\sigma_{HD}}\exp\left(-\frac{\left(E-E_{HD}\right)^2}{2\sigma_{HD}^2}\right) \tag{3}$$

$$g_L(E) = \frac{(1-\zeta)N_{LA}}{\sqrt{2\pi}\sigma_{LA}}\exp\left(-\frac{\left(E-E_{LA}\right)^2}{2\sigma_{LA}^2}\right) + \frac{\zeta N_{LD}}{\sqrt{2\pi}\sigma_{LD}}\exp\left(-\frac{\left(E-E_{LD}\right)^2}{2\sigma_{LD}^2}\right) \tag{4}$$

Here ζ is the mixing ratio, which is defined as the quotient of molar density of the donor to the total. N_{HA}, N_{LA}, E_H and E_L are the total density of HOMO, the total density of LUMO, the mean energy of HOMOs and the mean energy LUMOs of the acceptor, respectively. σ_{HA} and σ_{LA} are the variance of HOMO levels and the variance of LUMO levels. N_{HD}, N_{LD}, E_H, E_L, σ_{HD} and σ_{LD} are the corresponding parameters of the donor.

Generally the occupation of HOMO and LUMO energy states obey Fermi-Dirac statistics. In inorganic semiconductor devices, interface states at metal-semiconductor interfaces play an important role due to dangling bonds. But in the case of organic semiconductor devices, the density of interface states is generally negligible lower because of molecular bonding of organic solids. Neglecting the contribution of interface states, the hole and electron concentration at anode-organic interface (x=0), p_0 and n_d, are described by Equation (5) and (8), respectively.

$$p_0 = \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty}\frac{\frac{(1-\zeta)N_{HA}}{\sigma_{HA}}\exp\left(-\frac{\left(E-E_{HA}-\Delta\phi_a\right)^2}{2\sigma_{HA}^2}\right) + \frac{\zeta N_{HD}}{\sigma_{HD}}\exp\left(-\frac{\left(E-E_{HD}-\Delta\phi_a\right)^2}{2\sigma_{HD}^2}\right)}{1+\exp\left(\frac{W_a-E}{k_\mathrm{B}T}\right)}dE \tag{5}$$

Here k_B and T are Boltzmann constant and device temperature, respectively. $\Delta\varphi_a$ is the image-force lowering of the energy barrier at the anode-organic interface, which depends on the electric field at x=0, F_0. By single carrier transport approximation near the contacts, that is, hole transport dominates in the area near the anode, while electron transport dominates in the area near cathode, F_0 and $\Delta\varphi_a$ can be expressed as [7-8]

$$F_0 = -\sqrt{\frac{2k_BTp_0}{\varepsilon_\mathrm{r}\varepsilon_0}} \tag{6}$$

$$\Delta\phi_\mathrm{a} = q\sqrt{\frac{q|F_0|}{4\pi\varepsilon_0\varepsilon_\mathrm{r}}} \tag{7}$$

Analogously, the electron density near the cathode can be expressed as

$$n_d = \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty}\frac{\frac{(1-\zeta)N_{LA}}{\sigma_{LA}}\exp\left(-\frac{\left(E-E_{LA}+\Delta\phi_c\right)^2}{2\sigma_{LA}^2}\right) + \frac{\zeta N_{LD}}{\sigma_{LD}}\exp\left(-\frac{\left(E-E_{LD}+\Delta\phi_c\right)^2}{2\sigma_{LD}^2}\right)}{1+\exp\left(\frac{E-W_c}{k_\mathrm{B}T}\right)}dE \tag{8}$$

where $\Delta\varphi_c$ is the image-force lowering of the energy barrier at the cathode-organic interface (Figure 1). p_0 and n_d are calculated iteratively by setting a staring value of zero for both $\Delta\varphi_a$ and $\Delta\varphi_c$.
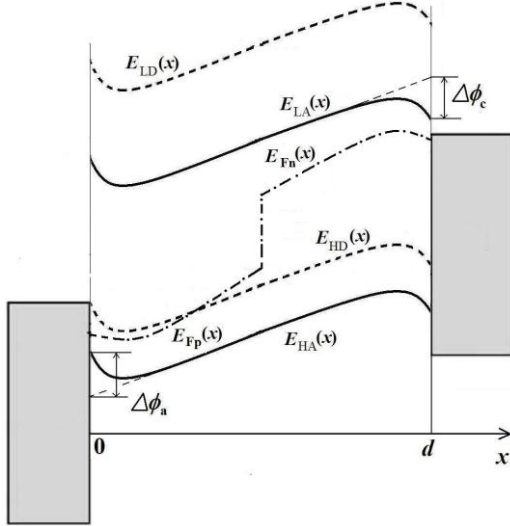

Fig. 1. Schematic energy level diagram in a bulk heterojunction solar cells.

Let the electric potential at $x=d$ be the quasi Fermi level at $x=0$, $E_{Fp}(0)$, and the quasi Fermi level at $x=d$, $E_{Fn}(d)$, are calculated from following equations:

$$\int_{-\infty}^{\infty} g_H \left[E, E_{HA}(0), E_{HD}(0) \right] f_h (E, E_{Fnd}) dE = p_0 , \quad (9)$$

$$\int_{-\infty}^{\infty} g_L \left[E, E_{LA}(d), E_{LD}(d) \right] f_e (E, E_{Fnd}) dE = n_d \quad (10)$$

Where $E_{HA}(0)=E_{HA}+\Delta\varphi_a$, $E_{HD}(0)=E_{HD}+\Delta\varphi_a$, $E_{LA}(d)=E_{LA}-\Delta\varphi_c$, and $E_{LD}(d)=E_{LD}-\Delta\varphi_c$. The built-in voltage U_{bi} is the difference of the quasi Fermi levels at the two contacts:

$$U_{bi} = E_{Fn}(d) - E_{Fp}(0). \quad (11)$$

3. Results and discussion

Fig. 2 shows the calculated dependence of built-in voltage on the mixing ratio for P3HT:PCBM bulk heterojunction solar cells with a given cathode workfunction for different anode work functions. The parameters used are listed in Table 1. It is seen that the built-in voltage of the bulk heterojunction solar cells is larger than the pure PCBM device, but smaller than that of the pure P3HT devices, and decreases with the increase of the mixing ratio. This is because the built-in voltage in the device anode/P3HT/Al is larger than that of the device anode/PCBM/Al, and this can be elucidated with help of Equation (1). First of all, the built-in voltage from Equation (1) in the two devices are nearly equal, about 0.5eV. In addition, in device anode/PCBM/Al, the anode and cathode Fermi level located fully in the energy gap of PCBM, which results in a limited charge accumulation near the two contacts. While in the case of device anode/P3HT/Al, the HOMO level of P3HT is just near the anode workfunction, and thus there is a high accumulation of holes near the anode, which results in a larger built-in voltage than the device anode/PCBM/Al.

Table 1. The HOMO and LUMO levels of donor and acceptor materials.

Material	HOMO	LUMO	Reference
OC1C10-PPV	5.20	3.4	[9]
P3HT	4.90	2.9	[10]
Si-PCPDTBT	5.30	3.6	[11]
C60	6.20	4.5	[12]
PCBM	6.41	4.0	[13]

Table 2. Comparison of calculated U_{bi} with measured open-circuit voltages.

Device structure	Weight mixture ratio	Mole mixure ratio ζ	U_{OC} (V)	U_{bi} (V)
ITO/PEDOT/ OC1C10-PPV:PCBM/LiF/Al	1:4	0.484	0.90 [14]	1.410
ITO/PEDOT/ OC1C10-PPV:PCBM /Ag	1:4	0.484	0.70 [14]	0.9115
ITO/PEDOT:PSS/ P3HT:C60/Al	3:2	0.867	0.37 [15]	0.6204
ITO/PEDOT/ Si-PCPDTBT: C$_{70}$-PCBM /LiF/Al	1:2	0.483	0.57 [11]	1.436
ITO/PEDOT/ P3HT:PCBM /Al	1:1.08	0.835	0.59 [16]	0.6892

The calculated dependence of the built-in voltage on the cathode workfunction is shown in Figure 3. As the Fermi level of the cathode increase form -4.3eV, the built-in voltage increases and reaches a plateau of -1.12V at a cathode Fermi level of -4.0eV. The built-in voltage increases again at a cathode Fermi level of -3.6eV, and reaches the second plateau with a buil-in voltage of 1.37V. The origin of the two plateaus is the double Gaussian distribution of the density of states of the bulk heterojunction. The beginning of first plateau means the full occupation of the LUMOs of the acceptor, and the beginning of the second plateau indicates a full occupation of the LUMOs of the donor material.

value of Ubi, if the light intensity illuminating the OSC is sufficiently large. As experimental data of Ubi for bulk heterojunction solar cells are scars, we made a comparison between calculated Ubi and UOC from experiments. The calculated Ubi for several bulk heterojunction solar cells are listed in Table 2, together with the values of open-circuit voltage from experiment. By the calculation, workfunctions of ITO/PEDOT:PSS, LiF/Al, Al and Ag electrode are taken to be 5.2eV, 3.68eV, 4.28eV and 4.35eV, respectively. It is seen that all the calculated Ubi values are above the corresponding values of open-circuit voltages as expected.

4. Conclusions

A numerical model for the built-in voltage of bulk heterojunction solar cells is developed. The result show that the built-in voltage of a bulk heterojunction solar cells is dependent on the mixing ratio. Compared with the built-in voltage of the pure devices, the built-in voltage of bulk heterojunction solar cells is larger than the smaller but smaller than the larger of the built-in voltages of the two pure devices. The result also show that the built-in voltage increases with the increase of the cathode Fermi level, which is characterized with two plateaus.
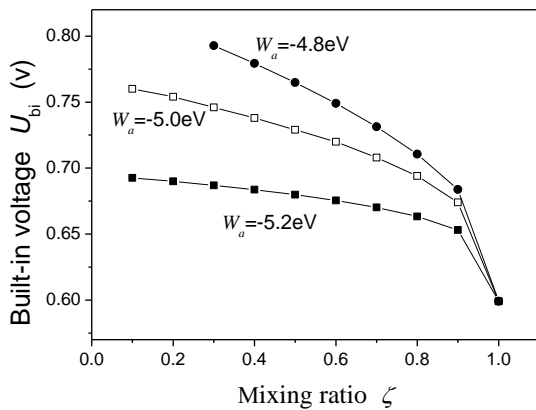
Acknowledgements

Fig. 2 The calculated dependence of the built-in voltage in P3HT:PCBM bulk heterojunction solar cells for different anode workfunctions. The parameters used are Wc=-4.3eV, T=300K, d=100nm.

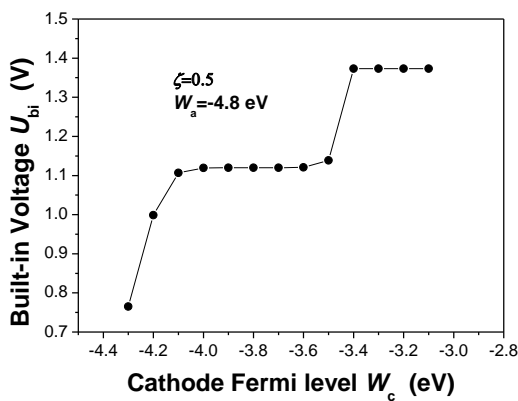*Fig. 3 Calculated dependence of the built-in voltage on the cathode workfunction. The parameters used are ζ=0.5, W_a=-4.8eV and T=300K.*

The built-in voltage of an OSC sets the upper limit of its open-circuit voltage, that is, the Uoc tends to reach the

References

[1] L. J. A.Koster, V. D. Mihailetchi, R. Ramaker, P. W. M. Blom, Appl. Phys. Lett. **86**, 123509 (2005)
[2] Y. Q. Peng W. M. Meng R. S. Wang, C. Z Ma, X. S. Li, H. W. Xie, R. H. Li, M. Zhao, J. T. Yuan, Y. Wang, Appl. Surf. Sci. **255**, 8010 (2009)
[3] H. Baessler, Phys. Stat. Sol. (b), **107**, 9 (1981)
[4] Y. Q. Peng, S. Sun, C. A. Song, Material Science in semiconductor Processing, **8**(4), 525 (2005)
[5] Y. Q. Peng, J. H. Yang, C. A. Song, Applied Physics A **83**(2), 305 (2006)
[6] Y. Q. Peng, J. H. Yang, F. P. Lu, Q. S. Yang, H. W. Xin, X. S. Li, C. A. Song, Appl. Phys. A, **86**, 225 (2007)
[7] M. Kemerink, J. M. Kramer, H. H. P. Gommans, R. A. J. Janssen, Appl. Phys. Lett. **88**, 192108 (2006)
[8] S. M. Sze, Physics of Semiconductor Devices, Wiley-Interscience, p148 (2007)
[9] I. Riedel, V. Dyakonov, phys. stat. sol. (a) **201**(6), 1332 (2004)

[10] A. D. Pasquier, H. E. Unalan, A. Kanwal, S. Miller, M. Chhowalla, Appl. Phys. Lett. **87**, 203511 (2005)

[11] M. C. Scharber, M. Koppe, J. Gao, F. Cordella, M. A. Loi, P. Denk, M. Morana, H.-J. Egelhaaf, K. Forberich, G. Dennler, R. Gaudiana, D. Waller, Z. G Zhu, X. B. Shi, and C. J. Brabec, Adv. Mater. **22**, 367 (2010)

[12] B. P. Rand, J. Li, J. G. Xue, R. J. Holmes, M. E. Thompson, S. R. Forrest, Adv. Mater. **17**, 2714 (2005)

[13] R. Valaski, L. M. Moreira, L. Micaronind, I. A. Huemmelgen, J. Appl. Phys. **92**(4), 2035 (2002)

[14] V. D. Mihailetchi, L. J. A. Koster, P. W. M. Blom, Appl. Phys. Lett. **85**(6), 970 (2004)

[15] Cheng Li, Y. H. Chen, S. A. Ntim, and S. Mitra, Appl. Phys. Lett. **96**, 143303 (2010)

[16] V. Chellappan, G. M. Ng, M. J. Tan, W.-P. Goh, F. R. Zhu, Appl. Phys. Lett. **95**, 263305 (2009)

_____

*Corresponding author: yqpeng@lzu.edu.cn