Effect of illumination intensity and temperature on open circuit voltage in organic solar cells

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The effect of illumination intensity and temperature on open circuit voltage (V_{oc}) in organic photovoltaic devices has been investigated. V_{oc} is observed to saturate at high illumination intensities. The illuminated *J-V* characteristics at different intensities intersect the dark characteristic at a single point. This intersection point is shown to be equal to the built-in voltage (V_{bi}) in the sample. A reduction in temperature shows increment in saturated V_{oc}. This increment in saturated V_{oc} is attributed to the variation of V_{bi} with temperature. A model has been presented that explains the observed behavior of V_{bi} at different temperatures. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3129194]

Organic photovoltaic (OPV) devices can play an important role in generating long-term clean and cheap energy.[1] Power conversion efficiencies and lifetime of these devices are not yet high enough for their commercial viability. Efforts are being made all over the world to understand the physics behind the operation and to improve the performance of these devices. The interpenetrating bulk-heterojunction tandem devices have shown a power conversion efficiency (η) of ~6.5%.[2] In order to optimize the power conversion efficiency and their reliability in various operating conditions, the complete understanding of device physics is of prime importance. There are various fundamental aspects regarding the physics of OPV devices that require attention. For example, contrary to the Si photovoltaic devices the forward bias current in OPV devices under illumination intersects the dark current and becomes more than the dark current. And another important issue is the origin of V_{oc}. For the design of future solar cells, it is important to understand whether the V_{oc} is a bulk property or an electrode property or a combination of both. It has been suggested that V_{oc} in OPV devices depends either on the difference of energies of highest occupied molecular orbital of the donor and lowest occupied molecular orbital of the acceptor[3,4] or on the difference of the work functions of anode and cathode (ΔW) used.[5] The variation of V_{oc} with temperature[6] and illumination intensity[7,8] cannot be explained by either of these models. Various models have been presented to explain the experimental observations in OPV devices[5,7] yet the physics behind the operation is not well understood and requires more work to be done. Schilinsky *et al.*[7] extended the standard Si one diode model and a good agreement with the experimental data at different illumination intensities was observed. By self-consistent calculations, Schilinsky *et al.*[7] showed the existence of a constant electric field in the OPV devices. This finding is an important contribution. The correction due to this electric field was applied to the observed short circuit current (J_{sc}). However, the effects of the electric field on the dark currents were not investigated. We have recently presented a model considering the effect of constant electric field on both the dark and photocurrent.[9] A model regarding temperature dependence of V_{oc} and V_{bi} in OPV devices is presented here. We investigate the effects of illumination intensities and temperature on V_{oc} in OPV devices and the observed results are interpreted theoretically.

The investigations have been carried out on an indium tin oxide (ITO)/copper phthalocyanine (CuPc) (20 nm)/C_{60} (40 nm)/bathophenanthroline (BPhen) (8 nm)/Al (150 nm) OPV device. The experimental details are given elsewhere.[10] The devices were illuminated with a white light halogen lamp at 200 mW/cm^2. Neutral density filters with different optical densities (ODs) were used to vary the incident illumination intensity. Figure 1 shows the *J-V* characteristics of CuPc/C_{60} cell at 300 K measured in dark and at different illumination intensities. Inset of Fig. 1 shows the variation of V_{oc} and J_{sc} with illumination intensity for the same sample. As expected both the J_{sc} and V_{oc} are observed to increase with the illumination intensity. J_{sc} is observed to increase linearly with the illumination intensity. On the other hand, V_{oc} increases with intensity of light, first rapidly and then slowly. V_{oc} is almost saturated at the high intensity of light used by us. The saturation of V_{oc} at high illumination intensities has also been suggested by Dhariwal *et al.*[11] for inorganic *p-n* junction solar cells and by Barker *et al.*[12] in OPV devices. The most interesting observation is that all the illuminated characteristics intersect the dark current at a single point (at $V=0.49$ V). Beyond this intersection point the illuminated currents become more than the dark current. This

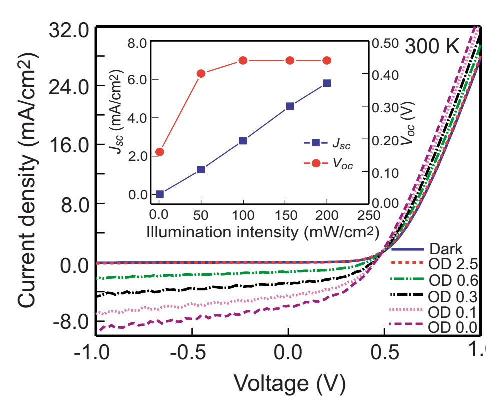

FIG. 1. (Color online) Dark and illuminated *J-V* characteristics of ITO/CuPc (20 nm)/C_{60} (40 nm)/BPhen (8 nm)/Al (150 nm) OPV device at 300 K. Inset shows the variation of J_{sc} and V_{oc} with the illumination intensities.

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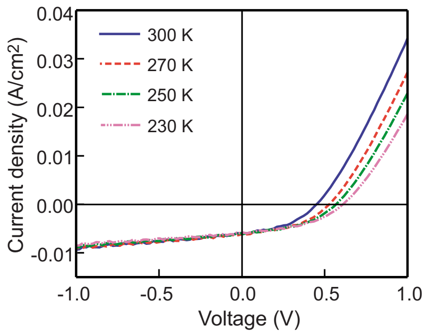

FIG. 2. (Color online) Illuminated *J-V* characteristics of the device under study, at different temperatures and 200 mW/cm^2.

behavior is quite contrary to that observed in case of inorganic photovoltaic devices, where the photocurrent always flows opposite to the junction the illuminated current is observed to be less than the dark current.[13] These interesting observation inferences that at this intersection point the photogenerated currents become zero. Numerical calculation shows that the photogenerated current is almost entirely due to drift caused by the internal electric field $(V_{bi}\text{-}V)/d$ and is given by[7,9,14]

$$J_L(V) = |J_{sc}| \quad \text{if} \quad \mu\tau \frac{(-V+V_{bi})}{d} > d,$$

$$J_L(V) = -|J_{sc}| \quad \text{if} \quad \mu\tau \frac{(V-V_{bi})}{d} > d,$$

$$J_L(V) = |J_{sc}|\mu\tau \frac{(-V+V_{bi})}{d^2} \quad \text{else}, \qquad (1)$$

where μ is charge carrier mobility, τ is charge carrier lifetime, V is the applied voltage, and d is the sample thickness. The zero photocurrent at the intersection point suggests that this intersection point would be the V_{bi}. This observation is quite important and a direct method for the determination of V_{bi} in an OPV device. It is quite clear from Eq. (1) that when the applied voltage increases beyond V_{bi} the direction of flow of photocurrent gets reversed and is now being added to the dark current. Therefore beyond V_{bi} the illuminated currents become more than the dark current. In this way the V_{bi} for this sample at room temperature is observed to be 0.49 V. The saturated V_{oc} at this temperature is observed to be 0.44 V, which is ~50 mV smaller than the V_{bi}. It is difficult to obtain a simple relation between V_{bi} and V_{oc} as the V_{oc} is affected by both the Dember potential and the internal resistance of the cell.[11,15] Therefore, we attribute the difference in saturated V_{oc} and the V_{bi} to the Dember potential and the internal resistance of the cell.

To investigate further the effect of temperature on V_{oc} and V_{bi} the illumination intensity of the sample was kept at its maximum 200 mW/cm^2 and the *J-V* characteristics were measured at different temperatures. The photocurrent under short circuit condition is observed to be weak dependent on temperature, which can either be attributed to temperature dependence of charge transport with shallow traps[16] or space charge effects.[17] Though V_{oc} is saturated at 100 mW/cm^2 at room temperature (see inset of Fig. 1), the reduction in temperature had still a quite significant effect on V_{oc}. The saturated V_{oc} increases monotonically as the temperature decreases. Figure 2 shows the illuminated *J-V* characteristics at different temperatures under the maximum illumination intensity of 200 mW/cm^2. The saturated V_{oc} is observed to increase further with reduction in temperature. At low temperatures, V_{oc} is observed to increase even beyond the V_{bi} (intersection point of dark and illuminated characteristics) at room temperature. Since V_{oc} is less than or equal to V_{bi} this observation is another important finding on the V_{oc} in OPV devices. To understand this behavior of saturated V_{oc}, the investigations were further carried out on the same sample for different illumination intensities at different temperatures. Figures 3(a) and 3(b) show the *J-V* characteristics of the same sample at 270 and 230 K under different illumination intensities. Interestingly even at 270, 250, and 230 K, all the illuminated currents intersect the dark current at the single points observed to be at 0.55, 0.63, and 0.71 V for 270, 250 (results not shown), and 230 K, respectively. These observations suggest the shifting of V_{bi} toward higher values at low temperatures.

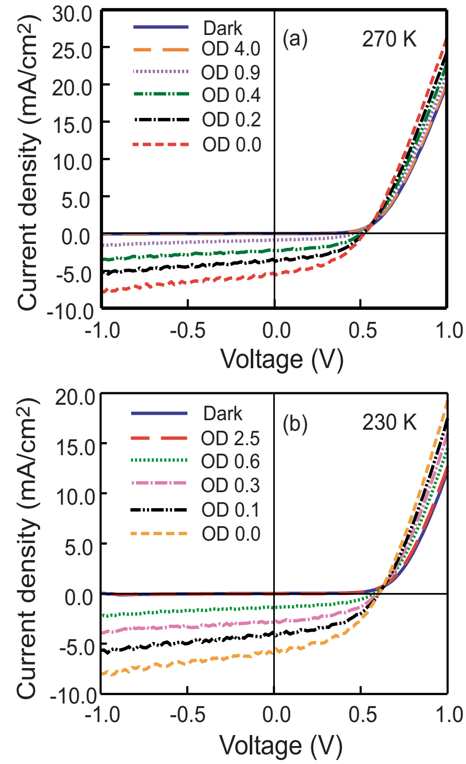

FIG. 3. (Color online) Dark and illuminated *J-V* characteristics of the sample under study, measured at (a) 270 K and (b) 230 K. Different curves show the characteristics at different illumination intensities. The initial illuminated intensity of the sample was maintained at 200 mW/cm^2.

We now present here the model on variation of V_{bi} with temperature. The Fermi level alignment results in the development of an electric field (built-in electric field) and the corresponding voltage developed in the device is known as V_{bi}. V_{bi} is actually the voltage which is required for flat band condition to occur.[5] It is demonstrated here that for large injection Schottky barriers and/or low temperatures V_{bi} is equal to ΔW. For very low Schottky barriers or an Ohmic contact V_{bi} is observed to be less than ΔW. It is well known that in the vicinity of Ohmic contacts an accumulation of charge carriers takes place, which results a significant band bending.[5,18] This band bending leads to a reduction in the voltage (δV) at which the flat band condition is reached in the bulk of the device.[18] We show that for a two Schottky junction diode, V_{bi} increases with reduction in temperature and tends to saturate at ΔW.

Let us consider the case for electrons with Schottky junctions, at anode and cathode. In thermal equilibrium the continuity and Poisson's equations will be written as

$$J = q\mu n(x)F(x) + qD_n \frac{\partial n(x)}{\partial x} = 0, \tag{2}$$

and

$$\frac{\partial F(x)}{\partial x} = -\frac{q}{\varepsilon\varepsilon_0} n(x), \tag{3}$$

where x is the distance from the anode ($x=0$ at the anode and $x=d$ at the cathode), ε and ε_0 are the dielectric constant of semiconductor and permittivity of free space, respectively, $n(x)$ is the electron density, $F(x)$ is electric field, and D_n is the diffusion coefficient for electrons. Using the Einstein relation $D_n = \mu kT/q$, Eqs. (2) and (3) give

$$\frac{\partial^2 F(x)}{\partial x^2} + \frac{q}{kT} F(x) \frac{\partial F(x)}{\partial x} = 0, \tag{4}$$

since $F(x) = -\partial V(x)/\partial x$, the integration of Eq. (4) gives

$$-V(x) = \frac{2kT}{q} \ln\left\{ \cosh\left[\sqrt{\frac{qC}{2kT}}(x - D) \right] \right\} + E, \tag{5}$$

where $V(x)$ is the potential distribution in the semiconductor, C, D, and E are the first, second and third constants of integration, respectively. The values of C, D, and E can now be obtained numerically from Eqs. (3) and (5) using the following boundary conditions:[13]

$$n(0) = N_c \exp\left(-\frac{\phi_1}{kT}\right), \tag{6}$$

$$n(d) = N_c \exp\left(-\frac{\phi_2}{kT}\right), \tag{7}$$

$$qV(0) = -\phi_1, \tag{8}$$

and

$$qV(d) = -\phi_2. \tag{9}$$

Here N_c is the effective density of states, ϕ_1 and ϕ_2 are the electron injection barriers at the anode and cathode, respectively. The charge density distribution can now be easily obtained from Eq. (3) as

$$n(x) = -\frac{\varepsilon\varepsilon_0 C}{q} \left\{ 1 - \tanh^2\left[\sqrt{\frac{qC}{2kT}}(x - D) \right] \right\}. \tag{10}$$

Equation (5) has been plotted along with Eq. (10) in Fig. 4 for different temperatures. Solid curves are for Eq. (5) whereas dashed curves represent Eq. (10). The values of the parameters used for these calculations are given in the caption of the figure. Reduction in temperature results into the reduction in diffusion coefficient (D_n), which leads to the reduction in band bending. The change in temperature would lead to change in diffusion current. As a result, the change in diffusion current would lead to change in drift current or in other terms to band bending. Therefore, the charge carrier density decreases with reduction in temperature. Assuming V_{bi} as the voltage required for the flat band condition to occur, it can be seen from Fig. 4 that V_{bi} increases as the temperature decreases. As V_{oc} has direct dependence on V_{bi},[11] the variation in saturated V_{oc} with temperature can be attributed to the variation of V_{bi} due to temperature variation. Also the incremental variation of V_{oc} beyond the V_{bi} value at room temperature can now be understood in terms of the increment in V_{bi} itself with reduction in temperature.

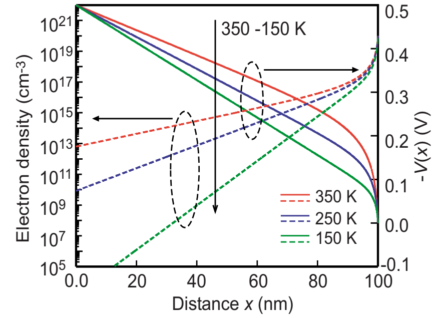

FIG. 4. (Color online) Distribution of potential $[-V(x)]$ and electron density at different temperatures in a semiconductor with ohmic contact at the cathode. The values of the parameters used in these calculations are $\phi_1 = 0.5$ eV, $\phi_2 = 0.0$ eV, $\varepsilon = 3$, $d = 100$ nm, and $N_c = 1 \times 10^{20}$ cm^{-3}.

In summary, we have investigated the effect of illumination intensity and temperature on V_{oc} in a CuPc/C_{60} OPV device. V_{oc} is observed to saturate at high illumination intensities. The illuminated J-V characteristics of device at different illumination intensities are observed to intersect the dark current at a common point. As photocurrent in OPV devices is completely field driven, the intersection point is the direct measure of V_{bi} in the sample. It is observed experimentally that V_{bi} shifts to higher values as the temperature is reduced. The theoretical interpretation has been presented to support the variation of V_{bi} with temperature. Electrode effects are observed to dominate the V_{oc} in the present device.

[1] S. C. Jain, M. Willander, and V. Kumar, *Conducting Organic Materials and Devices* (Academic, San Diego, 2007).
[2] J. Y. Kim, K. Lee, N. E. Coates, D. Moses, T. Q. Nguyen, M. Dante, and A. J. Heeger, Science **317**, 222 (2007).
[3] A. Gadisa, M. Svensson, M. R. Andersson, and O. Inganas, Appl. Phys. Lett. **84**, 1609 (2004).
[4] C. J. Brabec, A. Cravino, D. Meissner, N. S. Sariciftci, T. Fromhertz, M. T. Rispens, L. Sanchez, and J. C. Hummelen, Adv. Funct. Mater. **11**, 374 (2001).
[5] V. D. Mihailetchi, P. W. M. Blom, J. C. Hummelen, and M. T. Rispens, J. Appl. Phys. **94**, 6849 (2003).
[6] H. Kumar, P. Kumar, N. Chaudhary, R. Bhardwaj, S. Chand, S. C. Jain, and V. Kumar, J. Phys. D **42**, 015102 (2009).
[7] P. Schilinsky, C. Waldauf, J. Hauch, and C. J. Brabec, J. Appl. Phys. **95**, 2816 (2004).
[8] D. Chirvase, Z. Chiguvare, M. Knipper, J. Parisi, V. Dyakonov, and J. C. Hummelen, J. Appl. Phys. **93**, 3376 (2003).
[9] P. Kumar, S. C. Jain, V. Kumar, S. Chand, and R. P. Tandon, J. Phys. D **42**, 055102 (2009).
[10] H. Kumar, P. Kumar, R. Bhardwaj, G. D. Sharma, S. Chand, S. C. Jain, and V. Kumar, J. Phys. D **42**, 015103 (2009).
[11] S. R. Dhariwal, L. S. Kothari, and S. C. Jain, IEEE Trans. Electron Devices **23**, 504 (1976).
[12] J. A. Barker, C. M. Ramsdale, and N. C. Greenham, Phys. Rev. B **67**, 075205 (2003).
[13] S. M. Sze, *Physics of Semiconductor Devices* (Wiley, New York, 1981).
[14] C. Waldauf, P. Schilinsky, J. Hauch, and C. J. Brabec, Thin Solid Films **451–452**, 503 (2004).
[15] M. K. Han and W. A. Anderson, Tech. Dig. - Int. Electron Devices Meet. **1981**, 134.
[16] I. Riedel, J. Parisi, V. Dyakonov, L. Lutsen, D. Vanderzande, and J. C. Hummelen, Adv. Funct. Mater. **14**, 38 (2004).
[17] J. Nelson, Phys. Rev. B **67**, 155209 (2003).
[18] J. G. Simmons, J. Phys. Chem. Solids **32**, 1987 (1971).