Electrical characterization of ITO/PEDOT-PSS/MEH-PPV:PCBM organic diode

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The electrical characterization of organic diode with a configuration ITO/poly [2-methoxy-5-(2-ethyl)hexoxy-1,4-phenylenevinylene]:[6,6]-phenyl C_{61}-butyric acid methyl ester blend was analyzed by current-voltage and capacitance-voltage methods. The junction parameters of the diode were calculated from the current-voltage and capacitance-voltage data and are discussed. The ideality factor n and barrier height ϕ_b values of the diode were found to be 3.06 and 0.96 eV, respectively. The diode shows a non-ideal current-voltage behavior due to a high probability of electrons and holes recombining in the depletion region or series resistance and by the presence of an interfacial layer.

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1. Introduction

Organic semiconductors have been extensively investigated due to their electrical, optical and magnetic properties, in the recent years. These materials have wide applications in the electronic technology, such as Schottky diodes, solar cell, field effect transistor, light emitting diodes and etc [1-5]. Poly[2-methoxy-5-(2-ethyl)hexoxy-1,4-phenylenevinylene] (MEH-PPV) has been considered as one of the most potential conducting polymers for various optoelectronic applications [6]. The MEH-PPV acts as an electron donor (p-type semiconducting polymer) with a relatively low conductivity due to the low hole and electron mobilities, when compared to the inorganic semiconductor materials. Fullerene C_{60} is has special spherical π-electron carbon cluster and it is an organic semiconductor, because the band gap of solid C_{60} is in the range of 1.2–2 eV [7]. New organic semiconductors can be prepared using MEH-PPV and C_{60} organic compounds and so blend of these materials is likely to yield a new semiconductor material with improved electrical conductivities and optical properties. It has been observed in recent years that blends of organic semiconductors have been used in fabrication of electronic devices [8-9]. We have hoped that the knowledge of blend of organic semiconductors would provide future scope for electronic device applications.

In present study, the blend of MEH-PPV and C_{60} organic semiconductors was prepared as thin film on ITO to fabricate an organic diode. The electronic parameters such as barrier height, ideality factor, and series resistance of the organic diode were evaluated by current-voltage and capacitance-voltage measurements.

2. Experimental

Poly [2-methoxy-5-(2-ethyl)hexoxy-1,4-phenylenevinylene] (MEH-PPV) and [6,6]-phenyl C_{61}-butyric acid methyl ester (PCBM) and poly-(ethylene dioxythiophene) doped with poly-(styrene sulphonic acid) (PEDOT:PSS) organic materials were purchased from Sigma-Aldrich Co. In order to prepare organic device, firstly indium tin oxide (ITO) glass was washed successively by ethanol/acetone mixture deionized water in sequence, then dried in a clean chamber. PEDOT-PSS layer was deposited on ITO surface by spin coating (v=2000 rpm) and the PEDOT-PSS layer was annealed at 100 ^oC in a furnace. The blend of organic semiconductors was prepared as MEH-PPV and PCBM with the blending ratio of 1:4. The solution of the blend was homogenized for 10 min. and was mixed by an ultrasonic effect. Film of the MEH-PPV:PCBM blend was prepared by evaporating the solvent from a solution of the blend with subsequent drying of the film deposited on ITO [10-14]. The standard geometry of ITO/MEH-PPV:PCBM organic diode is the sandwich, as seen in Fig. 1. The diode contact area is 7.85×10^{-3} cm^2. The current–voltage (I-V) measurements were performed by a KEITHLEY 2400 sourcemeter and data of current-voltage measurements are recorded to a PC computer using a GPIB data transfer card. The capacitance–voltage (C-V) measurements were performed by a HIOKI 3532 LCR meter.

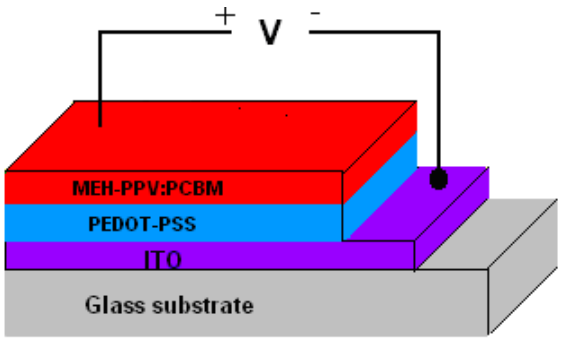


Fig. 1. Structure of the ITO/PEDOT-PSS/MEH-PPV:PCBM organic diode.

3. Results and discussion

3.1. I-V characteristics of the ITO/PEDOT-PSS/MEH-PPV:PCBM organic diode

The current-voltage (I-V) characteristics of the ITO/PEDOT-PSS/MEH-PPV:PCBM organic diodes are shown in Fig. 2. The I-V characteristics indicate a rectifying behavior and this confirms the formation of the ITO/PEDOT-PSS/MEH-PPV:PCBM interface. At lower voltages, the I-V characteristic of the diode shows the exponential rise.

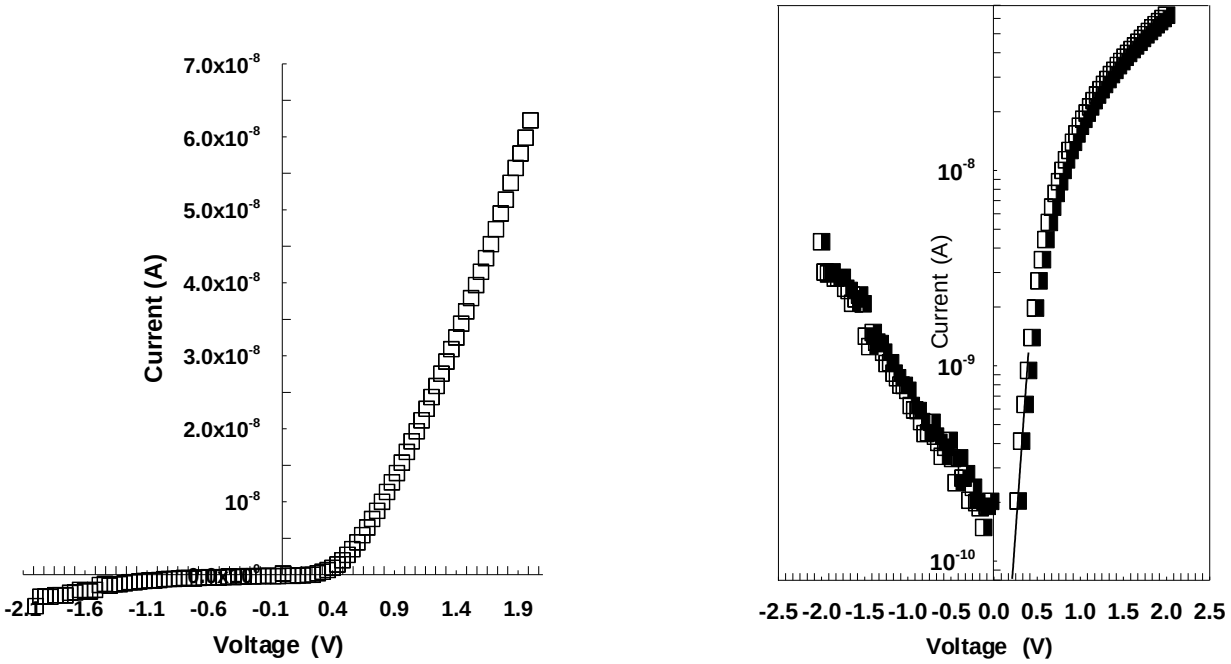


Fig. 2. I-V characteristics of the ITO/PEDOT- PSS/MEH-PPV:PCBM organic diode a) linear scale b) semilogarithmic scale.

The current-voltage characteristics of the diode are analyzed by the following relation [15]

$$I = I_o \exp\left(\frac{q(V - IR_s)}{nkT}\right)\left[1 - \exp\left(-\frac{q(V - IR_s)}{kT}\right)\right] \quad (1)$$

with

$$I_o = AA^*T^2 \exp\left(-\frac{q\phi_b}{kT}\right) \quad (2)$$

where n is the ideality factor, k is the Boltzmann constant, q is the electronic charge, A is the contact area, A^* is the Richardson constant, R_s is the series resistance, T is the temperature and ϕ_b is the barrier height. The saturation current was obtained from the linear portion intercept of logI at V=0. The barrier height was calculated using I_o (3.99×10^{-12} A) value and was found to be 0.96 eV. The ideality factor of the ITO/PEDOT-PSS/MEH-PPV:PCBM organic diode was calculated using the following equation,

$$n = \frac{q}{kT}\frac{dV}{d(\ln I)} \quad (3)$$

The n value was calculated from the linear portion of forward bias I-V curve in semi-logarithmic scale, as shown in Fig. 2 and was found to be 2.75. The ideality factor is an indicative of the interface uniformity. The obtained ideality factor suggests a non-ideal I-V behavior and this behavior of the diode may be due to high probability of electrons and holes recombining in the depletion region or presence of an interfacial layer [16]. The obtained n value is higher than 2, indicating that recombination current is dominant in this device. The I-V characteristics of the diode are affected by parasitic

resistances such series, R_s and shunt resistance, R_{sh}. These resistances are important factors in performance of the diode and the determination of these resistances is necessary to device performance. The R_{sh} value was determined from the lower current region of Fig. 2 and was found to be about 2.02×10^9 Ω. This resistance arises from the leakage of current through the ITO/PEDOT-PSS/MEH-PPV:PCBM device. At higher voltages, the current-voltage exhibits a non-linear behavior due to the changes in the depletion layer at the interface of the ITO/PEDOT-PSS/MEH-PPV:PCBM organic diode. This changes cause series resistance in the junction. The series resistance is significant in the non-linear of the I-V characteristics. The series resistance can be evaluated using a method developed by Cheung to determine the barrier height, ideality factor and series resistance. The Cheung's functions are expressed as follows [17],

$$\frac{dV}{d\ln(I)} = n\frac{kT}{q} + IR_S \tag{4}$$

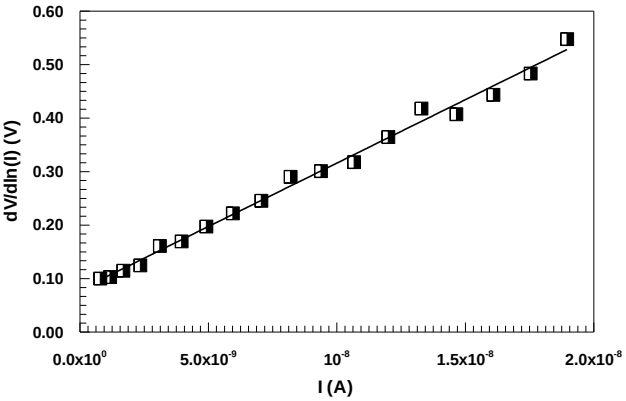
$$H(I) = V - n\frac{kT}{q}\ln\left(\frac{I_o}{AA^*T^2}\right) \tag{5}$$

and

$$H(I) = IR_S + n\phi_B \tag{6}$$

The plots of dV/dlnI-I and H(I)-I are shown in Fig. 3. The R_S and n values were determined from the slope and intercept of dV/dlnI-I plot and were found to be 2.37×10^7 Ω and 3.06, respectively. The ϕ_B and R_s values were calculated from the H(I)-I plot using obtained n value and were found to be 0.96 eV and 2.38×10^7 Ω. The average R_s value for the diode was found to be 2.37×10^7 Ω. The series resistance R_s is related to the interface of the diode and it is the sum total resistance value of the resistors in series and resistance in semiconductor device in the direction of current flow [18]. The MEH-PPV:PCBM organic semiconductor has low conductivity, therefore, the series resistance of the diode is very high. On the other hand, the bulk resistance, Poole-Frenkel and space charge limited current effects can cause higher values of ideality factor.

In order to analyze these effects, we plotted current-voltage characteristics in the form of logI-logV, as shown in Fig. 4. In a diode, when the higher carrier densities from one electrical contact are locally injected into material, the space charge limited currents may take place. If not so, the contact behaves as ohmic contact without carrier injection. The ohmic behavior in current-voltage characteristic breaks down at the space charge limit and the space charge limited current flows for higher voltages. The plot of logI-logV was analyzed using $I\propto V^m$ relation. The dominant charge transport mechanism for the diode was determined by obtaining m values from the slopes of linear regions in Fig. 4. The slope of first region is about 3.98, suggesting a SCLC with an exponential distribution of traps in the band gap of the organic semiconductor.



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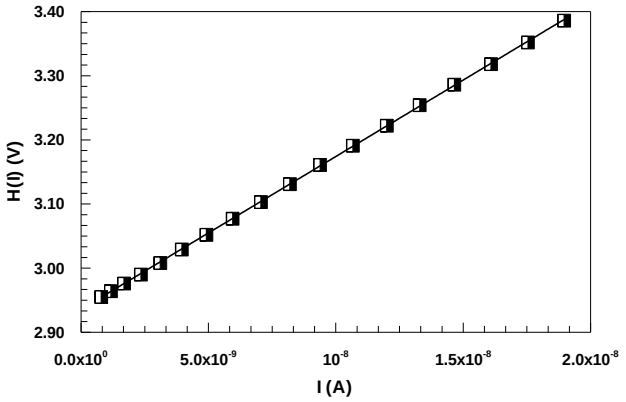

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Fig. 3. Plots of dV/dln(I)-I and H(I)-I of the ITO/PEDOT-PSS/MEH-PPV:PCBM organic diode.

This mechanism suggests that at higher voltages, the current is limited by space-charge accumulation. The space charge limited current mechanism by exponential distribution of traps is expressed by the following relation [19],

$$I = qA\mu N_v\left(\frac{\varepsilon_s}{qn_okT}\right)^l \frac{V^{l+1}}{d^{2l+1}} \tag{7}$$

where ε_s is the dielectric constant of organic semiconductor, l is a constant related to traps, n_o is the trap concentration per unit energy range at the conduction band edge, d is the thickness of the organic semiconductor, q is the electronic charge and A is the contact area. T_t value was determined from Eq. 7 and was found to be 1186 K. The characteristic energy of the exponential distribution of traps was calculated using T_t value and was obtained to be 0.101 eV. The equilibrium concentration of carrier charge in the conduction band is given by,

$$n_o = \frac{\varepsilon\varepsilon_o\theta}{qd^2}V_{tr} \tag{8}$$

where θ is described as follows,

$$\theta = \frac{n_o}{(n_o + n_t)} \tag{9}$$

where n_o and n_t are the free and trapped electrons densities respectively. The n_t and n_o values were obtained to be 4.68×10^{15} and 1.74×10^{14} cm^{-3} using θ value, respectively. The exponential trap distribution is expressed as,

$$n = n_o \, exp\left(-\frac{E}{kT_t}\right) \tag{10}$$

where n is the trap concentration per unit energy range at an energy E bottom conduction band edge. The total concentration of traps is defined as [19],

$$N_t = n_o k T_t \tag{11}$$

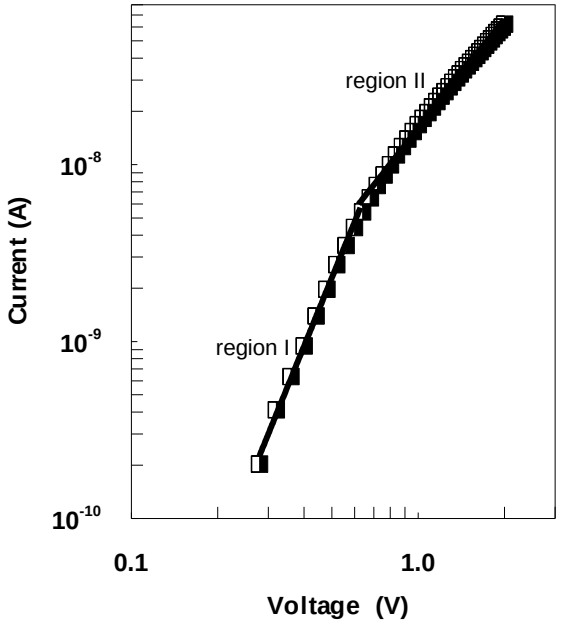

Fig. 4. Plot of I-V in logarithmic scale of the ITO/PEDOT-PSS/MEH-PPV:PCBM organic diode.

The N_t value for the organic diode was found to be 1.77×10^{13} $eV.cm^{-3}$. The slope of the second region shown in Fig. 4 was found to be 2, indicating the presence of space charge limited conduction. For an organic semiconductor with the localized traps, the space charge limited current is expressed by the well-known relation [20],

$$I = \frac{9}{8}\varepsilon_o \theta \varepsilon_s \mu \frac{A}{d^3} V^2 \tag{12}$$

where ε_o is the dielectric permittivity of vacuum, μ is the mobility of the charge carriers, θ is a trap-limiting parameter and d is the thickness of the film. The mobility μ for the device was determined using Eq. 12 and was found to be 1.65×10^{-7} $cm^2.V^{-1}.s^{-1}$. The obtained mobility value appears to be reasonable for organic semiconductors [21-22]

3.2. Capacitance-voltage characteristics of the ITO/PEDOT-PSS/MEH-PPV:PCBM organic diode

The capacitance-voltage (C-V) measurement of the device was performed at 100 Hz and plot of C^{-2}-V is shown in Fig. 5. This plot indicates a linear behavior, which confirms the formation of the junction between metal and organic semiconductor and thus, the plot of C^{-2} vs V can be analyzed by standard Mott-Schottky relation [15]

$$\frac{1}{C^2} = \frac{2(V_{bi} - V)}{qN_d \varepsilon_s A^2} \tag{13}$$

where V_{bi} is the built-in potential, N_d is donor concentration given by

$$N_d = \left(\frac{2}{q\varepsilon_s A^2}\right)\frac{dV}{dC^{-2}} \tag{14}$$

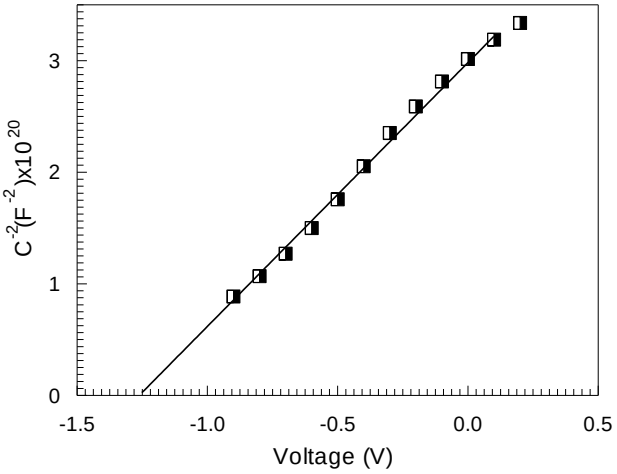

Fig. 5. Plot of C^{-2} vs V of the ITO/PEDOT-PSS/MEH-PPV:PCBM organic diode.

The values of V_{bi} and N_d can be obtained from the intercept and slope of C^{-2} vs. V plot by means of Eq. 13, respectively. The doping concentration N_d and the built-in potential V_{bi} were found to be 3.14×10^{15} cm^{-3} and 1.242 V, respectively. The barrier height can be obtained from C-V plot using the following relation,

$$\phi_b = C_2 V_{bi} + V_n \tag{15}$$

where V_n is the potential difference between the Fermi level and the bottom of the conduction band of semiconductor given by [15]

$$V_n = \frac{kT}{q} ln\left(\frac{N_c}{N_d}\right) \quad (16)$$

where N_c is the effective density of states in semiconductor conduction band. The ϕ_b value was determined using obtained V_p (0.32 V) value and was found to be 0.72 eV. The barrier height obtained from current-voltage measurements is higher than obtained from capacitance-voltage measurements. The obtained barrier height values from both the methods are not always the same, because the nature of the I-V and C-V measurements is different with each other.

4. Conclusions

The electrical charge transport properties of the ITO/PEDOT-PSS/MEH-PPV:PCBM organic diode have been investigated by current-voltage and capacitance-voltage characteristics. The diode indicates a non-ideal current-voltage behavior with ideality factor of 3.06. At higher voltages, the space limited current mechanism is dominant in the organic diode.

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