Charge conduction process and rectification effect in ITO/doped PPy/Ag device

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Received 25 February 2000; accepted 14 November 2000

Electrical, impedance and photovoltaic measurements with a thin film of PMB doped PPy and undoped PPy, using sandwich between Ag and ITO are explained in terms of p-type semiconducting behaviour of PMB doped-PPy (PMB:PPy) film and by the formation of Schottky barrier with Ag and ohmic contact with ITO. At low voltage region Ohm’s law is followed, while at high voltage region a space charge limited conduction is observed which is controlled by the exponential trap distribution.

The organic molecular and polymeric materials are emerging as a class of novel materials because of their potential applications in electronic and opto-electronic devices such as photovoltaic device, light emitting diodes and photorefractive devices, as these materials possess the special electrical and optical properties, low cost of processing and moreover their properties can modified by simple doping process\textsuperscript{12}. Photoinduced electron transfer process has been intensively studied in order to study the key steps in efficient conversion process. A great deal of theoretical and experimental work has shown that controlling the electron transfer rates requires control of both electronic and structural properties of the system\textsuperscript{3,4}.

In the present communication, a charge transfer complex is generated by employing the spatial arrangement of molecular donor and acceptor, which under illumination leads to the creation of photo carriers at the interface existing between molecular materials. The poly-pyrrole (PPy ), a well-known p-type organic semiconducting material, was doped with α α’ phenyl methyl substituted bipyridyl halide (PMB) which acts as an electron acceptor. The film of the material was developed by employing spin coating technique onto indium tin oxide (ITO) coated glass substrate. Silver (Ag) was used as a contact electrode, on the top of organic material. The active area of the device was about 1 cm\textsuperscript{2}. The J-V characteristics in dark as well as under illumination have been recorded. The J-V characteristics in dark shows the rectification effect, when the ITO electrode is made the positive with respect to Ag electrode. The rectification effect is due to the blocking contact which is formed between PMB doped PPy and Ag. The rectification effect improves on PMB doping. The position of Fermi level shift toward the valence band which results in the increase in the free carriers concentration, i.e., holes in the organic material, i.e., in PMB:PPy complex. The increase in dark conductivity on doping is due to the increase in the hole mobility. The various electrical parameters such as ideality factor, fill factor, barrier height, carrier mobility and conversion efficiency of the material have been evaluated and discussed.

Experimental Procedure

The thin films of PMB doped PPy having thickness of about 600 nm were made by spin coating technique using di-methyl formamide (DMF) as solvent on the indium tin oxide (ITO) coated glass substrate. The metallic Ag electrode was developed with silver paint on the top of the organic film for contact purpose. The J-V characteristics of the device were measured with a Keithley electrometer model 610C and a stabilised power supply. The ITO electrode was held at positive potential relative to Ag electrode. The impedance measurements were made with Keithley LCZ (Model 3330) impedance analyser. Temperature dependence of the current - voltage characteristics and impedance were measured in the range 300 - 370 K by controlling the temperature with the help of a digital temperature controller.

Results and Discussion

Current - Voltage characteristics

The current-voltage characteristics of ITO/ PMB:PPy/Ag device were recorded at room
temperature and shown in Fig. 1. The forward bias corresponds to the positive potential to the ITO electrode with respect to Ag. These characteristics shows the rectification effect. The forward bias corresponds to the positive potential to the ITO electrode with respect to Ag. These characteristics indicates the formation of the Schottky barrier at Ag-PMB:PPy interface in the device while the ITO forms the ohmic contact with PMB:PPy. This behaviour can be explained by the low work function of Ag and p-type semiconductivity of PMB:PPy layer. Above the voltage forward bias the current becomes almost linear which suggest that the current is limited by the series resistance of the bulk conductive region.

The data for forward bias are replotted at two temperatures in form of In (J) - voltage (V) and shown in Fig. 2 (J being the current density). It can be seen that the plot is non-linear. For low voltages the current is due to the shunt (leakage) resistance of the barrier and above it is limited by series resistance of organic layer. To describe such results the ideal Schottky diode equation

\[ J = J_o \left[ \exp \left( \frac{q(V - R_s)}{nKT} \right) - 1 \right] \]  

... (1)

where \( J_o \) is the saturation current density, \( V \) is voltage, \( K \) is Boltzmann constant and \( T \) is temperature in K. This equation must be modified to account (in the first approximation) for the resistivity of the bulk of PMB:PPy (\( R_s \)), for shunt resistance of the barrier (\( R_{sh} \)) and non-ideality of the barrier (ideality factor \( n \)).

The \( J-V \) characteristics then can be described as

\[ J = J_o \left[ \exp \left( \frac{q(V - R_s)}{nKT} \right) - 1 \right] + \frac{(V - R_s)J}{R_{sh}} \]  

... (2)

Here, Eq. (2) has been used to fit the experimental data using suitable computer program. The results are shown in Fig. 2 as solid lines. One can see that the agreement between experiment and theory is quite good. The junction parameters obtained from such fitting for the device at 300 K and 340 K are listed in Table 1. It is noted that diode ideality factor is greater than unity indicating the recombination of electrons and holes in the depletion region.

The saturation current density \( J_o \) imperfect junctions can be expressed as

\[ J = A^* T^2 \exp \left( - \frac{\phi_b}{KT} \right) + J_t \exp \left( - \frac{E_t}{KT} \right) \]  

... (3)

where \( A^* \) is the Richardson constant, \( \phi_b \) is the barrier height, \( J_t \) is the tunnelling saturation constant (proportional to the density of traps participating in the mechanism) and \( E_t \) is the depth of these traps. The first term accounts for thermionic emission over the barrier and second one is associated with indirect tunnelling (between traps) followed by a thermal jump over the barrier. It is assumed that the first term in Eq. (3) is dominant in our device and in such case, determination of saturation current density permits estimation of potential barrier height (\( \phi_b \)). The value of potential barrier height (\( \phi_b \)) at room temperature is listed in Table 1.

**Table 1—Electrical parameters of the Ag/PMB:PPy/ITO device at room temperature**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>( J_o )</td>
<td>( 1.2 \times 10^{-11} \text{ A/cm}^2 )</td>
</tr>
<tr>
<td>( \phi_b )</td>
<td>( 1.02 \text{ eV} )</td>
</tr>
<tr>
<td>( E_t )</td>
<td>( 0.34 \text{ eV} )</td>
</tr>
<tr>
<td>( n )</td>
<td>2.24</td>
</tr>
<tr>
<td>( \sigma_{sh} )</td>
<td>( 3.4 \times 10^{-8} \text{ S/m} )</td>
</tr>
<tr>
<td>( \mu )</td>
<td>( 5.475 \times 10^{-7} \text{ m}^2/\text{Vs} )</td>
</tr>
<tr>
<td>( p_s )</td>
<td>( 1.964 \times 10^{11} \text{ m}^{-3} )</td>
</tr>
</tbody>
</table>

![Fig. 1—\( J-V \) characteristics for Ag/PPy/ITO device in dark at room temperature](image1)

![Fig. 2—Semi-log plot of forward \( J-V \) response at different temperatures](image2)
The detailed information about the charge transport mechanism through PMB doped PPy have been obtained from the analysis of J-V characteristics at different temperatures as shown is Fig. 3. These curves show two distinct regions at each temperature: an ohmic region in low voltage region which extends up to a transition voltage ($V_x$) with slope about unity and space charge limited conduction (SCLC) controlled by exponential distribution of traps having slope between 7.3 at 300 K and 4.5 at 370 K.

Since the PMB:PPy behaves as a p-type organic semiconductor, the ohmic conduction is assumed entirely due to holes and described

$$J = q\mu N_v (Vd) \exp \left(-\frac{E_F}{KT}\right) \quad \ldots \quad (4)$$

where $N_v$ is the density of state in valence band which is taken as $10^{27} \text{ m}^{-3}$, $E_F$ is the position of Fermi level from the valence band, $\mu$ is the mobility of hole, $K$ is the Boltzmann constant and $T$ is the temperature.

By plotting the Log ($J$) against $1000/T$ in ohmic region i.e. at $V = 1$V (Fig. 4), the position of Fermi level $E_F$ and the product $\mu N_v$ can be determined from the slope and intercept in current axis of the straight line. The value of concentration of free holes in the organic layer can be determined from

$$\rho_o = N_v \exp \left(-\frac{-E_F}{KT}\right) \quad \ldots \quad (5)$$

where $\varepsilon$ is the permittivity taken as $3.0 \times 10^{-11} \text{ F/m}$ which is similar to other reported p-type organic semiconductors, $l$ is the ratio between the characteristics temperature ($T_c$) and ambient temperature ($T$). The exponential trap distribution may be described in terms of $T_c$ as

$$H(E) = \left( \frac{N_v}{KT_c} \right) \exp \left(-\frac{E}{KT_c}\right) \quad \ldots \quad (6)$$

where $H(E)$ is the trap density per unit energy range at an energy $E$ above the valence band edge and $N_v / KT_c$ is the value of $H(E)$ at valence band edge. It can be seen from the plots log ($J$) - log ($V$), in SCLC region for different temperatures are straight lines having slopes larger than 4.0 and decreases when the temperature increases. As a result of this behaviour it is clear that the straight lines intersect at a common point. The co - ordinates of this points are

![Fig. 3—Forward J-V characteristics for device Ag/PMB:PPy/ITO at different temperatures](image1)

![Fig. 4—Variation of log(J) with 1000/T in ohmic region](image2)
It is evident that the experimental curves \( \log(J) \) vs \( \log(V) \) is SCLC region, are straight lines with different slopes as predicted by the theory. When the temperature increases from 300 to 370 K the slopes decreases from 7.3 to 4.5 and then \( I \) decreases from 6.3 to 3.5. Using the values of \( I \), the characteristics temperatures is ranging from 1890 to 1260 K.

Furthermore, the co-ordinates of the intersection point of the lines are \( V_n = 10 \) V and \( J_m = 3.16 \times 10^{-3} \) A/cm\(^2\) as calculated from the square fit of experimental data. These co-ordinate values yield \( N_i = 2.6 \times 10^{23} \) m\(^{-3}\) and \( \mu = 3.0 \times 10^{-7} \) m\(^2\)/vs considering in Eq. (7), \( \varepsilon = 3.0 \times 10^{11} \) F/m and \( N_i = 10^{27} \) m\(^{-3}\).

Exponential trap distribution characteristics energy \( (E_i) \) by expression \( l = E_i / kT \) Fig. 5 shows the variation of \( E_i \) with temperature. The \( E_i \) varies from 0.16 to 0.11 eV as the temperature varies from 300 to 370 K. At the room temperature \( E_i \) has a value about 0.16 eV. As the temperature increases, \( E_i \) decreases to a value about 0.11 eV at temperature 370 K. The parameter is directly related to the steepness and depth of the exponential trap distribution, the smaller value indicating a much steeper distribution closer to the \( N_i \) level.

**Impedance measurements**

Fig. 6 display the plots of Re \((Z)\)-Im \((Z)\) at different biasing voltages. In this plot the frequency increases from right to left (40 Hz to 100 kHz). This figure shows the pronounced voltage dependence of the device impedance in the low voltage range. At high frequency the impedance in independent of bias voltage and show a small semi-circle close origin. The two semi-circles observed in the Cole-Cole plots also confirm the formation of junction at Ag-PPy interface in the ITO/PPy/Ag device. The device has high impedance at zero bias, no complete second circle is measurable even at frequency as low as 40 Hz. With increasing bias voltage, two distinct semi-circles are detectable. At higher voltage the right hand semi-circle disappears. The two semi-circles observed in the Re \((Z)\) and Im \((Z)\) plots which may be represented by a parallel combination of bulk resistance \( (R_b) \) and capacitance \( (C_b) \) in series with a parallel arrangement of the junction resistance \( (R_j) \) and capacitance \( (C_j) \). The low frequency semi-circle corresponds to junction region (right side) whereas the high frequency semi-circle corresponds to bulk region (left side).

From the diameter of the semi-circles observed in low frequency region, the junction resistance have been obtained. From junction resistance and the frequency \( (f_j) \) at which the maxima occurs, the junction capacitance have been calculated according to \( C_j = 1 / 2 \pi f_j R_j \). Similarly the bulk capacitance can also be estimated in same manner using the diameter of semi-circle observed in high frequency region. Thus the thickness of the bulk and the junction region can be calculated using \( C_j \delta_b = \varepsilon A / \delta_j b \). Using the value of \( \varepsilon = 3.0 \times 10^{11} \) F/m we obtained a thickness of bulk of \( \delta_b = 523 \) nm and a width of the depletion layer \( \delta_j = 45 \) nm. The sum of the \( \delta_j \) and \( \delta_b \) is almost equal to the thickness of the PMB:PPy layer, i.e., 600 nm.

It is observed that the curves in the impedance plane are not perfect semi-circles indicating the frequency dependence of conductivity and of
dielectric constant, as well as spatial in-homogeneities in the device thickness and dopant concentration.

References