ELECTRONIC PROPERTIES OF POLY[3-(2″,5″-DIHEPTYLOXYPHENYL)-2,2′-BITHIOPHENE]/AL JUNCTIONS

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ABSTRACT: Junctions between a single layer of Poly[3-(2″,5″-diheptyloxyphenyl)-2,2′-bithiophene] and aluminium are studied by means of current–voltage and capacitance-voltage characteristics, and complex impedance spectroscopy. The results indicate the formation of a Schottky barrier type at Poly[3-(2″,5″-diheptyloxyphenyl)-2,2′-bithiophene]/Al interface. Parameters such as the reverse saturation current, the barrier height and the ideality factor are extracted from the I-V curves. The Cole–Cole plots of complex impedance spectroscopy reveal part of a single semicircle, which can be modeled as a single parallel RC circuit. This suggests that the device is a metal-semiconductor (M-S) type. Capacitance per unit area as well as the width of the depletion layer are obtained from the complex impedance analysis. The built-in potential and the charge carrier concentration are also calculated from C-V curves.

Key words/phrases: Electronic properties, built-in potential, depletion width, impedance spectroscopy, schottky barrier

INTRODUCTION

Electrical contacts to semiconductors are critical elements in a number of important technologies. Metal/semiconductor interfaces form the basis of many rectifiers, metal-semiconductor field-effect transistors, sensors and other surface junction devices.

Conjugated polymers exhibit a range of interesting properties as organic semiconductors. The semiconducting property of a conjugated polymer is derived from delocalised π - bonds formed by the overlap of P_z orbitals at each site along the polymer chain. Attempts to use conjugated polymers in devices have been hindered to some extent by their poor processability. However, many research works have been directed towards synthesizing processable conducting polymers (Fang, et al., 1992). It was found that when side chains are attached to the polymers, their processability and solubility are greatly enhanced (Bantikassegn Workalemahu and Inganas, 1997).

With improvements in the polymer processing, it has become possible to fabricate a range of thin films which are active in semiconductor devices that include field effect-transistors (Horowitz et al., 1993), light-emitting diodes (Bruan and Heeger, 1991), Schottky barrier devices (Gardner and Tan, 1989; Bantikassegn Workalemahu and Inganas,

1997; Granstrom et al., 1998), organic solar cells (Abay Gadisa and Bantikassegn Workalemahu, 2002). Poly[3-(2″,5″-diheptyloxyphenyl)-2,2′-bithiophene], a polythiophene derivative whose structure is depicted in Fig. 1(a), is soluble in organic solvents such as chloroform.

There are many methods of determining the Schottky barrier heights such as photo-electric, C – V and I – V measurements (Sze, 1981). The I – V measurement approach is the most popular and commonly used method mainly because of its simplicity. In this regard, we have used the I – V characterization, augmented with the complex impedance and C – V analysis, and report the electronic properties of junctions between poly[3-(2″,5″-diheptyloxyphenyl)-2,2′-bithiophene] and Al shown schematically in Fig. 1(b). Current-voltage characteristic in the dark is measured to obtain the device parameters from the plot of log (current density) versus applied voltage. Thermo ionic emission theory is applied to extract the parameters. Capacitance-voltage measurement is used to investigate the formation of the depletion region and evaluate the built-in potential and the charge carrier concentration. Complex impedance spectroscopy is measured for further investigation of the existence of a depletion region and to obtain the capacitance per unit area of the cell as well as the depletion region widths.

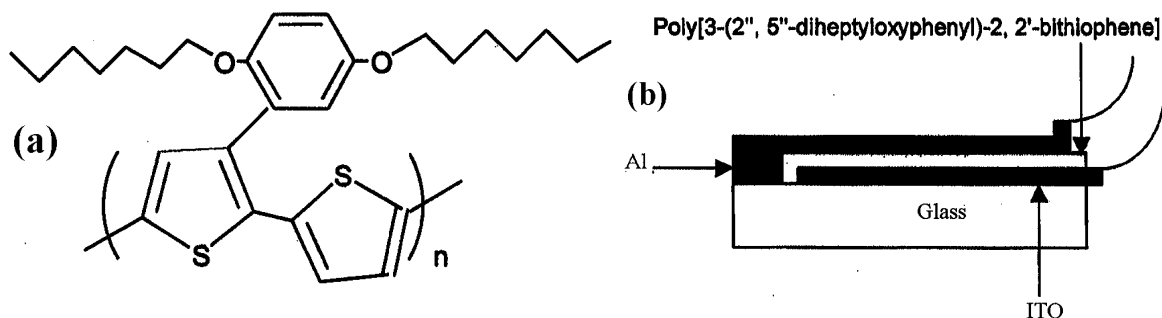* Author to whom all correspondence should be addressed.

Fig. 1. Structure of poly[3-(2",5"-diheptyloyphenyl)-2,2'-bithiophene] (a) and the schematic of the device (b).

EXPERIMENTAL DETAILS

Indium tin oxide (ITO) coated glass was cleaned with distilled water, methanol, and rinsed with acetone. About two-third of the 3cm x 3cm ITO/glass substrate is covered by photo resist and then exposed to a mixture of concentrated HCl, HNO₃ and water, 48:4:48 by volume, so as to etch out the ITO part that was not covered by the photo resist. The etched portion of the ITO/glass provides a region convenient for electrical contacts to the aluminium deposited later. The photo resist is removed using acetone, and the surface was again washed with distilled water and methanol, and rinsed with acetone and dried in air. Poly[3-(2",5"-diheptyloxyphenyl)-2,2'-bithiophene] is dissolved in chloroform to give a concentration of 5mg/ml, which is spin coated on the ITO/glass substrate at about 6000 rpm that yielded a thin uniform film of thickness about 100 nm. Strips of the polymer are removed from the etched part as well as from ITO/glass to allow electrical contact without damaging the device. Finally, aluminium strips are evaporated on top of the polymer at a pressure of 5.5×10^{-6} mBar, as a required metal contact to the polymer, using Eward 306 vacuum evaporator. Part of Al is over the polymer/ITO while the remaining portion is over the glass from which the ITO is etched out. The effective area of the device is about 0.2 cm².

Current-voltage characteristics in the dark are measured with HP 4140B Pico- Ammeter together with HP 16055A Test fixture. The applied voltage is scanned between +2V and –2V. The complex impedance analysis is measured with LF HP 4192A Impedance Analyser. The bias applied to the diode is between +2V and –2V in steps of 1V, and the frequency is scanned between 500 Hz and 500 kHz. For every applied d.c. bias voltage, a sinusoidal oscillating voltage of V_{rms} = 10 mV is applied. Cole-Cole plots are then generated and analysed. Capacitance-voltage measurements are obtained under bias voltage scanned between –2V and 0V using LF HP 4192A Impedance Analyser for a frequency fixed at 5 kHz.

CURRENT-VOLTAGE MEASUREMENTS

Figure 2(a) is a plot of current density, J, versus V for ITO/poly[3-(2",5"-diheptyloxyphenyl)-2,2'-bithiophene]/Al structure, which shows a rectification behaviour of the device. A semilog plot of the current density versus applied voltage, depicted in Figure 2(b) shows an exponential increase in the forward bias voltage between 0.4 and 0.9 V due to the formation of a depletion layer between a low work function metal (Al) and poly[3-(2",5"-diheptyloxyphenyl)-2,2'-bithiophene]. The exponential behaviour is observed to disappear above 1.5 volts as a result of space charge limited bulk resistance. According to the Schottky barrier theory, p-type semiconductors form a rectifying junction at the interfaces with low work function metals (Sze, 1981).

The exponential dependence of current on forward bias can be analysed using thermoionic emission theory given by (Sze, 1981).

$$J = J_0[\exp(\frac{qV}{nkT}) - 1] \qquad (1)$$

where J_0 is the reverse saturation current density given by:

$$J_0 = A^* T^2 \exp(\frac{-q\phi_b}{kT}) \qquad (2)$$

where A* is the effective Richarson constant, taken to be 120 A/cm²K² at room temperature for free electron (Bantikassegn Workalemahu, 1998), ϕ_b is the barrier height, n the ideality factor of the diode, k the Boltzmann constant and, T the absolute temperature.
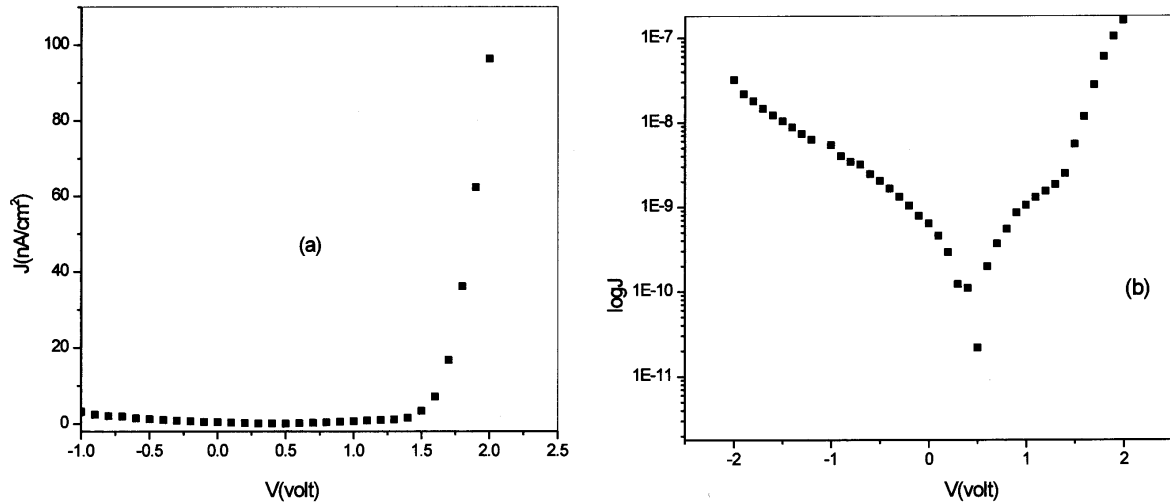
Fig. 2. (a) Current density versus voltage curve and (b) logJ-V characteristics. All parameters are extracted from curve (b).

The ideality factor of the diode can be derived from the inverse of slope lnJ versus V as:

$$n = \frac{q\Delta V}{kT\Delta \ln J} \qquad (3)$$

By applying equation (2) to the linear part of Fig 2(b), the reverse saturation current density, J_0, is obtained as an intercept of the linear part with the V = 0 axis. Thus the ideality factor n, and the barrier height, ϕ_b, are calculated and listed in Table 1 together with the rectification ratio, γ.

Table 1. Parameters obtained from the I – V curve.

Parameter	J_0	ϕ_b	n	γ
Value	$3 \times 10^{-11} A/cm^2$	1.02 eV	1.8	5

The value of J_0 obtained is small compared to the experimentally measured current density, which implies that current flow is blocked for the reverse bias voltage (Sze, 1981). Moreover, the barrier height for small J_0 is high. This suggests the formation of a depletion layer when a low work function metal and a p-type semiconductor (Al/polymer in our case) are in contact (Chung *et al.*, 1994). The ideality factor for an ideal Schottky barrier diode is one. The ideality factor being more than one in this case indicates the presence of recombination effects at the depletion layer (Seanor, 1992). The rectification ratio of the device is small compared to devices made of other polythiophene derivatives such as PTOPT (Bantikassegn Workalkemahu and Inganas, 1997).

We have noticed in Fig. 2 the existence of several linear regions in the forward bias that could be attributed to the existence of more than one charge transport mechanisms such as Ohmic tunneling, Schottky emission and Poole-Frankel, as well as the effects of series and shunt resistances. These effects collectively cause low charge mobility in the device (Girma Goro and Bantikassegn Work-alemahu, 1999).

C-V MEASUREMENTS

The capacitance per unit area of the depletion layer at the interface is given by (Sze, 1981):

$$C = \frac{\varepsilon \varepsilon_0}{W} \qquad (4)$$

where W is the depletion width, ε_0 is the permittivity of free space, and ε is the dielectric constant of the polymer taken to have a value of 3. Considering the abrupt approximation, the density of charges at space charge region is $\rho = qN_a$, where N_a is the dopant concentration per unit volume. The relationship between C and the applied voltage is given by (Tomozawa *et al.*, 1987).

$$\frac{1}{C^2} = \frac{2(V_{bi} - V)}{q \varepsilon \varepsilon_0 N_a} \qquad (5)$$

where V_{bi} is the built-in potential and q is the electronic charge.

A plot of C^{-2} versus applied voltage generally gives a straight line if the abrupt approximation is valid. The intercept of the straight line with the abscissa of the plot gives the built-in potential.

Figure 3 is a plot of C^{-2} versus V at 5 kHz fixed frequency. The plot does not yield a single straight line, except for the values between –1.5 and - 0.1 volts. This may be due to inhomogeny of the impurity charge carrier concentration in the sample, *i.e.*, dopant concentration is not constant throughout the polymer (Bantikassegn Workalemahu and Inganas, 1997). The linear portion of the plot of C^{-2} versus V indicates the existence of the depletion region in the sample. The slope of the linear part is found to be negative, which implies the contact is made between Al and a p-type polymer. From the slope of this line, the dopant concentration can be calculated as (Rideout, 1975).

$$N_a = \frac{-2}{q \varepsilon \varepsilon_0} \frac{dV}{dC^{-2}} \tag{6}$$

The built-in voltage, V_{bi}, and the carrier concentration, N_a, were calculated from the plot to give 0.4 V and 2×10^{17} cm^{-3}, respectively.
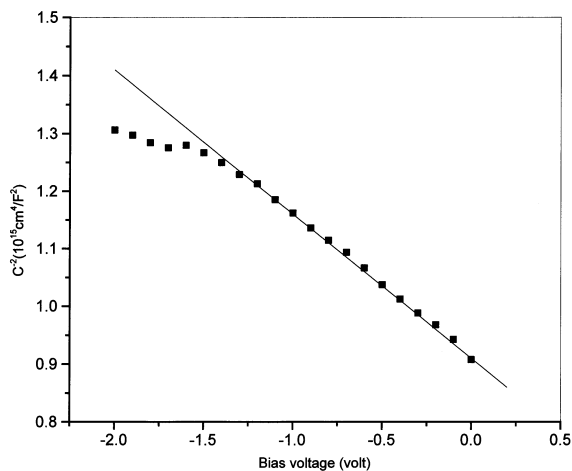
Fig. 3. Inverse square capacitance versus voltages characteristics.

COMPLEX IMPEDANCE SPECTROSCOPY

Information about the resistance of the bulk and Schottky junction can be obtained from complex impedance measurements as well (Gustafsson *et al.*, 1990). Figure 4 show the complex impedance as a function of frequency at particular bias voltages at room temperature. The frequency range is between 0.5 kHz and 500 kHz, and the bias volt-

age used are –2V, -1V, 1V and 2V. The filled points are the measured co-ordinates representing the real and imaginary parts of the complex impedance, which are characteristic of a given frequency.
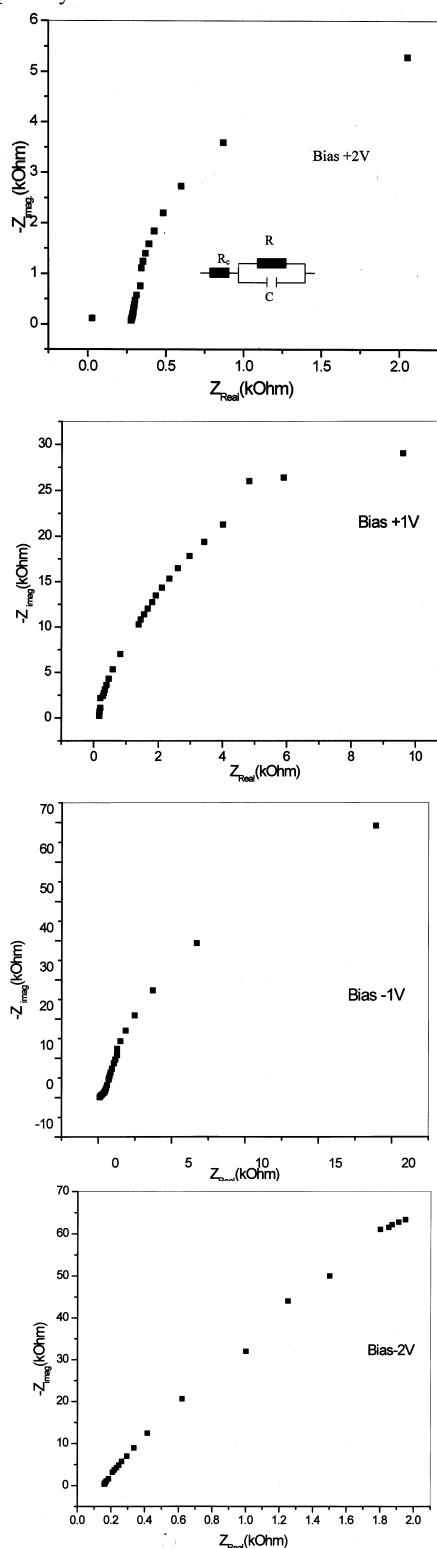
Fig. 4. Cole-Cole plots of ITO/ poly[3-(2″,5″-diheptyloy-phenyl)-2,2′- bithiophene]/ Al diode. The equivalent circuit model is shown in the in set of Fig. 4a.

An ideal Cole-Cole plot of a complex impedance spectroscopy gives a semicircle with its center, the zero-frequency, and the infinite-frequency intercepts on the Z_{real} axis (Bantikassegn Workalemahu, 1999). The zero-frequency limit is usually obtained by extrapolation. The highest frequency intersection of the semicircle with the real axis of the impedance plot is assumed to be the contact resistance, R_c. The value of R_c is usually small and is estimated to be about 100 Ω. The Cole-Cole plots depicted in Fig. 4 are part of a single semicircle. The diameters of the semicircles are big for the reverse bias voltages, while the diameters decrease with increasing (positive) bias voltages being the smallest at the highest forward voltage. In other words, the resistance is larger for a reverse bias than for the forward bias. It indicates an increase in the depletion width and the barrier height at the reverse bias voltages, which is consistent with the rectification behavior of the I-V curve shown in Fig. 2. The complex impedance of the diode can be modeled by an equivalent one parallel RC circuit in series with the contact resistance, as shown in the inset of Fig. 4. The values of the capacitance per unit area, C, and the depletion widths, W, are calculated from the plots and shown in Table 2.

Table 2. Parameters obtained from the Cole-Cole plots of Fig. 4.

V (volt)	2	1	-1	-2
C (F/cm²)	14x10⁻⁸	4x10⁻⁸	2.3x10⁻⁸	2x10⁻⁸
W (nm)	5	66	115	133
R (kΩ)	5	30.4	69.7	73

The results show that capacitance of the device increases with increasing bias voltage while the depletion width decreases with increasing bias voltage. This is because at forward bias voltages the width of the depletion layer, that acts as the dielectric separation, decreases.

CONCLUSION

Electronic properties of a single layer poly[3–(2″,5″-diheptyloxyphenyl)-2,2′-bithiophene]/Al junction have been studied. Thermoionic emission theory has been applied to explain current-voltage characteristics of the diode. All the measurements of current – voltage and capacitance-voltage characteristics on this sandwich structure confirm the existence of a Schottky barrier type between Al and a p-type polymer. The C–V characteristics have been also understood by the Schottky barrier model, but with inhomogeneous charge carrier concentration. The inhomogeneous nature of the carrier concentration may arise due to migration of the carriers under the applied voltage. Together with the I-V curve, the complex impedance analysis has shown the existence of a depletion region, which is a typical characteristic of a metal/semiconductor junction. The single semicircle of the Cole-Cole plot, modeled by a parallel RC circuit, is sufficient to account for a single element equivalent circuit where there are no extra layers at the interface. Various device parameters have been calculated from the J-V and C-V measurements and complex impedance analysis.

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