VIBRONIC STATES AND ELECTRONIC PROPERTIES OF ALUMINIUM JUNCTIONS WITH MELT-PROCESSED POLY[3-(2,5-DIOCTYLPHENYL)THIOPHENE] (PDOPT)

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ABSTRACT: Poly[3-(2,5-dioctylphenyl)thiophene] (PDOPT) becomes a semiconducting film when spin coated or caste from a chloroform solution. The optical absorption spectrum of spin coated thin films was measured using UV/Vis/NIR spectrophotometer which showed a forbidden energy gap of about 2.02 eV. In addition, two shoulders were observed on each side of the absorption peak. These kinks are the vibrational modes of double and single bonds in PDOPT that resonate at shorter and longer wavelengths, respectively. The electronic properties of melt-processed PDOPT in the form of Al/PDOPT/ITO sandwich structure were analyzed using current-voltage characteristics and complex impedance spectroscopy. The I-V curves were found to be symmetrical and non-linear, where the current across the junction was limited by the series resistance due to the oxide of aluminium at the Al/PDOPT interface governed by space charge limited current (SCLC). The impedance spectra (IS) showed part of a single semicircle on Cole-Cole co-ordinates manifesting one geometric capacitance. This is modelled by one parallel RC electrical circuit, usually obtained from metal-semiconductor (MS) devices.

Key words/phrases: Absorption spectrum, impedance spectroscopy, PDOPT, thermionic emission, vibronic state

INTRODUCTION

In spite of their interesting structural, physical, chemical and electrical characteristics, the use of conducting polymers in electronic applications requires the solution of several problems (Bredas and Chance, 1990; Salaneck *et al.*, 1991). Synthesis of conjugated polymers continues to be of interest to both the

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fundamental and applied research communities (Menon *et al.*, 1996). Recently, a number of new highly conducting thiophene based polymers have been synthesized (Pei *et al.*, 1994) among which PDOPT is one of these. More recently, many other derivatives of thiophene were synthesized by the Organic Chemistry group at Chalmers University in Sweden, and are being tested for their semiconducting properties in different devices such as polymeric light-emitting diodes (PLEDs).

The electrical properties of conducting polymers are mainly determined by their core structure, as morphology, average chain length, doping level; however, the knowledge of other parameters such as oxygen and water contents which can strongly influence the features of devices based on these polymers is of utmost importance. For instance, it was reported that oxygen present in polypyrrole, PPy, doped with BF_3^- (Inganas and Lundstrom, 1984/85), or polystyrene-sulphonate, PSS, (Bantikassegn Workalemahu *et al.*, 1993) which cannot be eliminated by de-aeration, gives rise to an insulating thin film of oxides of aluminium and/or the dangling polystyrene-sulphonate at the interface between aluminium and the PPy polymer.

The quantum efficiency of polymer-based devices such as PLEDs is highly influenced by the injection of electrons and holes at the respective electrodes that sandwich the semiconducting polymer (Parker, 1994). Although there has been a breakthrough in the area of PLEDs that perform continuously for thousands of hours (Burroughes *et al.*, 1990; Gustafsson *et al.*, 1992; Berggren *et al.*, 1994; Chen *et al.*, 1996), the mechanism of charge transport has not yet been fully understood. In view of the current arguments, both electron-phonon coupling and electron-electron interaction should be considered in the analysis of the conduction mechanism in conjugated polymers. There are numerous reports on polymeric diodes made from, for example, thiophene oligomers (de Leeuw and Lous, 1994; Lous *et al.*, 1995), poly(3-alkylthiophene) (Gustafsson *et al.*, 1991; Gomes *et al.*, 1993) and poly[3-(4-octylphenyl)-2,2'-bithiophene], PTOPT, (Bantikassegn Workalemahu and Inganas, 1997a), Schottky barrier characteristics were observed, where the current at a forward bias were limited by the bulk resistance.

One of the major conditions for using semiconducting polymers as active materials in devices is the ease and simplicity of processing steps to construct the device. It was reported that melt-processed poly(3-octylthiophene), P3OT, in the

form of Al/P3OT/Au sandwich structure, showed a rectifying Schottky barrier characteristics (Sundberg *et al.*, 1990).

In this work a melt-processed PDOPT has been used as an active semiconducting material. The chemical structure of PDOPT (see Fig. 1) is such that two octyl chains are attached at the 2- and 5- sites of the phenyl ring, which in turn, is bonded to the 3- position of the thiophene monomer. In addition to increasing the solubility of the polymer, the side chains are supposed to keep the planar geometric conformation when thin solid films of the polymer are prepared either by spinning or casting from a chloroform solution. The planar conformation of solid thin films of polymers is believed to increase their conductivity. We have measured the optical absorption of spin coated PDOPT films to deduce its forbidden energy gap. Two vibronic states in the absorption spectrum were also identified. Moreover, the electrical properties of melt-processed Al/PDOPT/ITO sandwich structures, see Fig. 2, were characterized with the help of current-voltage measurements as well as complex impedance spectroscopy techniques.
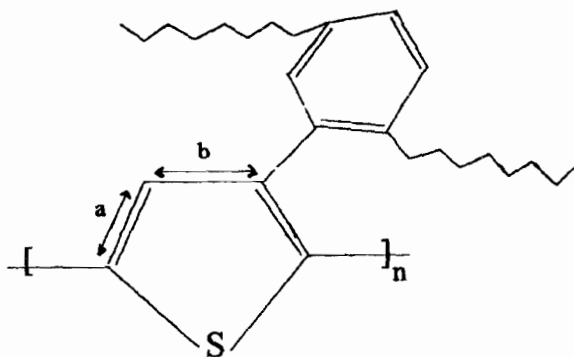

Fig. 1. The chemical structure of PDOPT and optical absorption-induced vibration modes of the double bond (arrow a) and single bond (arrow b).
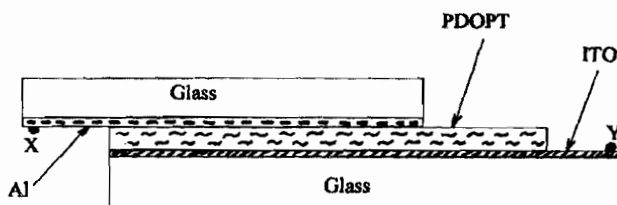

Fig. 2. The Al/PDOPT/ITO device of melt-processed sandwich structure. Points X and Y indicate positions for electrical contacts.

EXPERIMENTAL

A chloroform solution of PDOPT was prepared with a concentration of 5mg/ml for both absorption spectra and I-V and IS measurements. For optical characterization, thin films of PDOPT were spin coated on glass substrates at a rate of 600 rpm yielding a uniform, high quality reddish solid films of about 200 - 300 nm thickness. The PDOPT-on-glass was then placed in the sample compartment of Perkin Elmer λ19 UV/Vis/NIR spectrophotometer. With the help of the ultraviolet computerized spectroscopy software, UVCSS, and the interfaced PC, the optical absorption of PDOPT was recorded (Fig. 3) and analyzed.
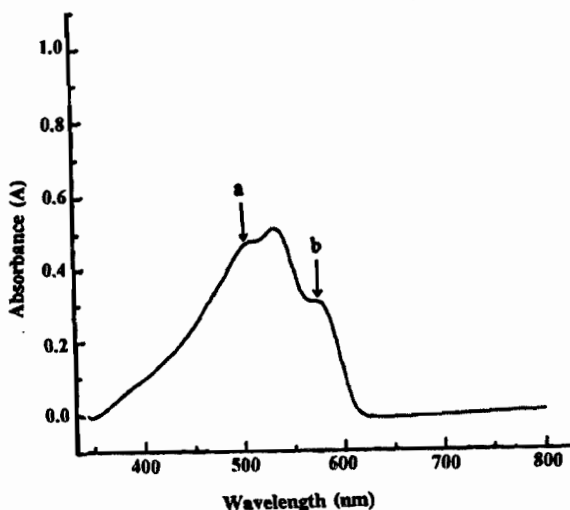
Fig. 3. Optical absorption spectroscopy of PDOPT thin films. Points a and b depict the vibronic states of the double and single bonds, corresponding to arrows a and b of Fig. 1, respectively.

For electrical characterization, two electrodes were prepared separately. A transparent conducting indium-doped tin oxide, ITO, on glass was cut to a size convenient for the experiment, washed with distilled water and rinsed with ethanol. The second electrode was aluminium evaporated on glass under a low pressure of about 10^{-5} Torr and had about the same size as the ITO/glass. Solid films of PDOPT having a thickness of 10 – 15 μm were prepared by dropping the chloroform solution onto the ITO/glass and waiting until the volatile chloroform solvent had evaporated. Then PDOPT/ITO-glass was heated on a hot plate to the melting point of PDOPT (about 160° C). The second electrode, Al/glass, was pressed to the polymer until intimate-contact adhesion was

achieved. The device was cooled down to room temperature before starting the electrical measurements. The Al/PDOPT/ITO structure, Fig. 2, provided a means of current-voltage and complex impedance measurements. The active area of the device was about 0.4 cm^2. The samples were kept in the dark, at room temperature in dry air during all measurements. Current-voltage characteristics were measured with an HP 4140B pico-ampere meter (pA) together with an HP 16058A test fixture, Fig. 4. The applied voltage was scanned between -4V and +4V. The complex impedance was measured using an HP 4192A LF Impedance Analyzer. The bias voltage applied to the diode ranged between -3V and +3V, in steps of 1V. For every bias voltage used, a sinusoidal oscillating voltage of $V_{rms} = 10$ mV was applied. The frequency was automatically scanned between 500 Hz and 10^6 Hz for each bias. The complex impedance spectra, known as Cole-Cole plot, (Cole and Cole, 1941), as a function of frequency and bias voltage were generated, Fig. 5, and analyzed.
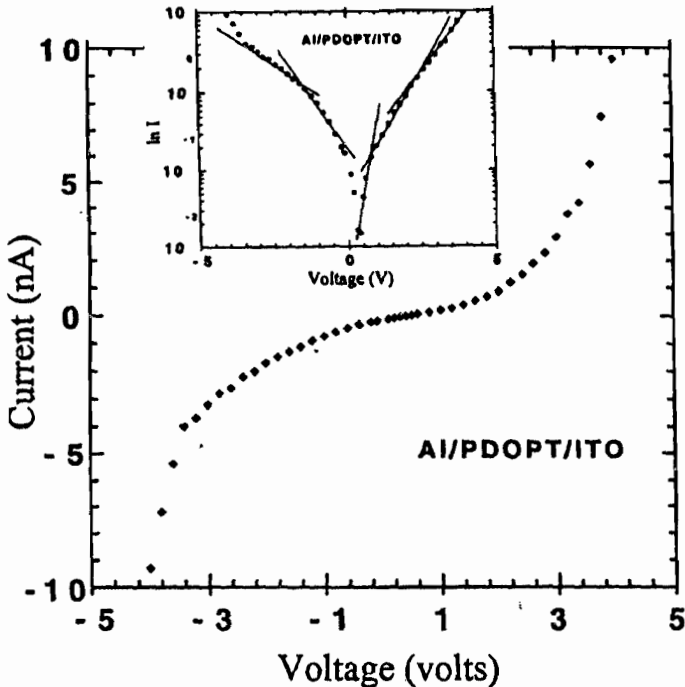

Fig. 4. The current-voltage characteristics of A*l*/PDOPT/ITO diode. The inset shows a semi-log plot of the I-V curve, where there are many possible ways of charge transport mechanisms (Pope and Swenberg, 1982).
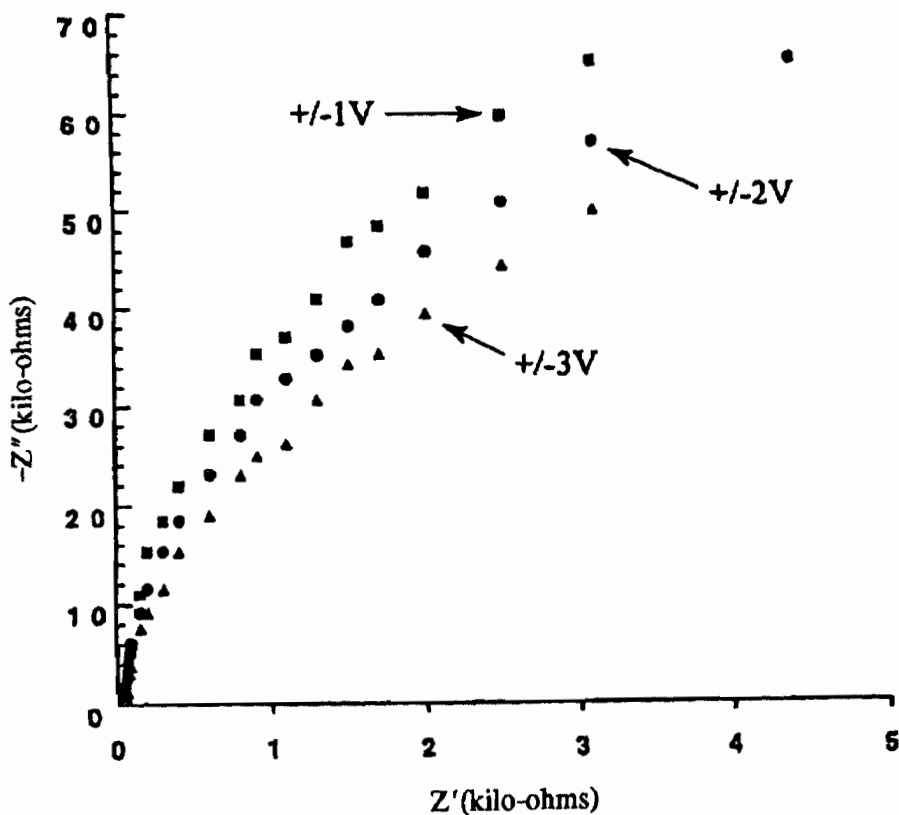
Fig. 5.   The complex impedance spectroscopy of the device shown in Fig. 2, where
         Z' and Z" are the real and imaginary axes of the Cole-Cole plot,
         respectively.

RESULTS AND DISCUSSION

Conjugated polymers and (in most cases) their derivatives fall in the category
of semiconductors, in terms of their conductivity scale, with forbidden gap
energies ranging between 1.5 eV (Pei *et al.*, 1994; Bantikassegn Workalemahu
and Inganas, 1997b) and 3 eV. As a newly synthesized thiophene derivative,

thin films of PDOPT were used in optical absorption measurements. Moreover, melt-processed Al/PDOPT/ITO sandwich structures were prepared for current-voltage and complex impedance analyses.

Optical absorption

A computer interfaced PE spectrophotometer driven by UVCSS software was used to measure the absorption spectra in the wavelength range between 350 nm and 800 nm. The absorption spectrum is shown in Fig. 3. From the figure it can be seen that the interband optical transition for PDOPT, as determined by the onset of the π-π^* transition, is at a wavelength of about 610 nm. Using quantum theory of light, the corresponding energy is calculated from the relation: $E = hc/\lambda$, where h is Planck's constant, c is speed of light in vacuum, and $\lambda = 610$ nm $= 6.1 \times 10^{-7}$ m is the wavelength of the absorbed light at a position of the onset. The energy thus calculated is $E = 3.232 \times 10^{-19}$ J $= 2.02$ eV. This energy corresponds to the difference in energy scale between the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO), or the conduction and valence bands, respectively. In the language of semiconductor physics, it is the forbidden gap energy, $E_g = 2.02$ eV, which asserts that thin films of solid PDOPT are semiconductors. Unlike the optical absorption spectra of neutral and doped PTOPT (Bantikassegn Workalemahu and Inganas, 1997a), the absorption spectrum of neutral PDOPT shows two additional shoulders within the absorption width, as indicated by points a and b in Fig. 3. These are signatures of vibronic states associated with the higher resonance frequency at about 500 nm (peak value corresponding to point a) for the vibration of the double bonds of the polymer. The second shoulder (point b) corresponds to a lower resonance frequency at about 575 nm, which accounts for the vibration of the single bonds. The double bonds, having greater force constant than the single bonds, have higher resonance frequency, and therefore, absorb light of higher energy (smaller wavelength) than the single bonds.

Current-voltage characteristics

Figure 4 shows the current-voltage (I-V) characteristics at room temperature in the dark of Al/PDOPT/ITO device where the polymer was made to adhere on both electrodes by heating it to its melting point and pressing the electrodes together. The I-V characteristics are symmetrical and non-linear. At lower values of bias voltage, the junction becomes highly resistive.

The interpretation of the I-V curve lies in the heart of the general relation known as thermionic emission/diffusion equation, which has two extreme limiting cases. Case 1: If the device forms a depletion region at the metal/semiconductor interface such that it yields a rectifying current-voltage characteristics, then the current density and the voltage have an exponential relation (Sze, 1981) given by:

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

where J is current per unit area, J_0 the reverse saturation current density, q the electronic charge, V the applied forward voltage, T the absolute temperature, k the Boltzmann constant, and n the ideality factor of the diode. The important point of case 1 is that, for equation (1) to hold at a forward bias voltage where the current turns on exponentially, the current density J must be much greater than the reverse saturation current density J_0, i.e., $J >> J_0$. Case 2: On the other extreme, if it turns out to be that $J << J_0$, then equation (1) can be expanded and approximated to give

$$V \approx (nkT/qJ_0)J \tag{2}$$

which is Ohm's Law. In such a case the I-V curve becomes symmetric and linear (ohmic).

However, if the current-voltage characteristics is such that it is neither $J >> J_0$, nor $J << J_0$, i.e., intermediate between the two limits, then the I-V curve becomes non-ohmic and non-rectifying. It is symmetrical and non-linear. This is exactly the case with our melt-processed diode, where there is a thin insulating layer at the Al/PDOPT interface because the aluminium was exposed to air before the formation of the junction.

All measurements of current-voltage characteristics may involve more than one type of charge transport mechanisms such as tunnelling, generation-recombination, and leakage currents (Barus and Donoval, 1993). There is a strong evidence for this argument because the semi-log plot of the I-V curve, see the inset of Fig. 4, has several slopes each linear region corresponding to one type of charge transfer mechanism. Probably the strongest influence on

current limitation arises from the series resistance which indicates the electrical transport that is dominated by space charge limited current (SCLC) (Pope and Swenberg, 1982; Gomes *et al.*, 1993; Lous *et al.*, 1995). In such a case, similar to the interface properties of Al/polymers doped with large polymeric anion junctions (Bantikassegn Workalemahu *et al.*, 1993), no Schottky barrier is formed. The I-V curves become non-linear and symmetrical.

Complex impedance spectroscopy

Impedance spectroscopy (IS) is a powerful method of characterizing the electrical properties of materials and their interfaces with conducting electrodes (Macdonald, 1987). It may be used to investigate the dynamics of bounded or mobile charges in the bulk or interfacial regions of any kind of solid or liquid material that conducts electronically (electrons and/or holes), ionically or mixed electronic-ionic conductors, and even insulators (dielectric). We focus only on one technique which enables us to measure the complex impedance directly (separate real and imaginary components) as a function of frequency and applied bias voltage.

Figure 5 shows the IS results of the interface between melt-processed PDOPT and aluminium. For each curve, the frequency increases in traversing from right to left. For each of the -3V, -2V, and -1V reverse bias, and 1V, 2V, and 3V forward bias voltages, onto which a sinusoidally oscillating voltage of $V_{rms} =$ 10 mV is added, the frequencies range between 500 Hz and 10^6 Hz. The filled points are the measured co-ordinates of the real and imaginary parts of the complex impedance. Theoretically a Cole-Cole plot is a semicircle with its centre, the "zero-frequency" and the "infinite-frequency" intercepts iie on the Z_{real} axis (Cole and Cole, 1941). In most actual measurements, however, the "zero-frequency" intercept is obtained by extrapolation. The Cole-Cole plot thus generated is part of a depressed semicircle, each measured point being characteristic of the corresponding frequency value.

In IS measurements, diodes are commonly analyzed using electrical equivalent circuit shown in Fig. 6. The complex impedance spectra of Al/Polymer/ITO sandwich structures, where the conjugated polymers were doped with macromolecules of polymeric anions such as PSS⁻, showed two slightly overlapping semicircles (Bantikassegn Workalemahu and Inganas, 1996, 1997b).

These can be modelled by an equivalent circuit consisting of two parallel RC circuits in series. However, devices made of neutral polymers as active semiconducting materials (Bantikassegn Workalemahu, 1998) and those doped with small anions such as ClO_4^- or PF_6^- (Bantikassegn Workalemahu and Inganas, 1997a) manifest a single semicircle that can be represented by one parallel RC circuit.

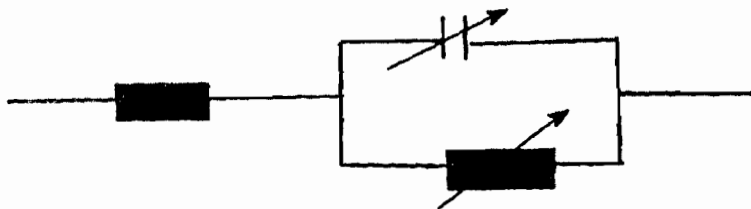**Fig. 6. An equivalent circuit for Aℓ/PDOPT/ITO sandwich structure as modelled from the Cole-Cole plot of Fig. 5.**

A depressed single semicircle observed in the IS measurements of a melt-pro-cessed PDOPT/Al interface suggests that there exists one time constant (Plocharski *et al.*, 1997), and therefore, one transport process (electronic). Moreover, it confirms the formation of a single barrier at the Al/PDOPT junction that limits charge transport through the diode. There is no evidence for an overlapping second semicircle due to a barrier at the interface with the ITO electrode. The parameters obtained from the Cole-Cole plots are listed in Table 1, where R is the resistance (real part of the impedance) related to the electronic conductivity of PDOPT. The capacitance C is calculated from the relation of constant phase element (CPE) whose impedance depends on frequency according to the expression

$$-Z'' = (\omega C)^{-1} \tag{3}$$

where $\omega = 2\pi f$ is the angular frequency. Thus knowing the value of -Z'' and the frequency f at which this impedance yields the time constant $\tau = 1$, *i.e.*, where the phase angle $\theta = 45°$ and -Z'' has a maximum value, the geometric capacitance C is obtained. R_C is a contact resistance in series with the single parallel RC, which remains constant at all bias voltages.

Table 1. **Parameters extracted from the Impedance Spectroscopy plot of Fig. 5. V_b is the applied bias voltage [(-) for reverse and (+) for forward], and the rest are values of electrical parameters indicated in Fig. 6.**

V_b(volts)	R(KΩ)	C(pF/cm²)	R_c(Ω)
±3	7	0.44	50
±2	9	0.44	50
±1	10	0.45	50

The resistance R decreases with increasing bias voltage, almost identically for both reverse and forward. For instance, the plot at +2V nearly coincides with that at -2V. This is consistent with the symmetric nature of the I-V curve depicted in Fig. 4. However, the capacitance remains fairly constant for all applied bias voltages indicating that there is no significant variation of the depletion width with the polarity and magnitude of the applied voltage. Hence, the diode is non-rectifying, once again indicating the consistency with the current-voltage curve.

The formation of an interfacial insulating thin layer between aluminium and the polymer bulk has several possible routes. One of the factors is formation of oxides of aluminium even if the metal is vacuum deposited (Inganas and Lundstrom, 1984/85). The melt-processed diode would have thicker oxide layer due to the exposure of Al/glass to air prior to junction formation. In our earlier studies of Al/polymer junctions (Bantikassegn Workalemahu and Inganas, 1996, 1997a,b; Bantikassegn Workalemahu, 1998), it was reported that neutral polymers as well as those doped with small anions resulted in a metal-semiconductor (MS) type diodes where the IS is a single depressed semicircle. The results of this investigation (where PDOPT is neutral) are also the same, re-enforcing the fact that neutral conjugated polymer/metal junctions form only one barrier at the interface.

The fact that the geometric capacitance, formed by the oxide layer sandwiched between the aluminium and the conducting bulk of PDOPT, remains constant at

different bias voltages indicates that there is no significant variation in the thickness of the depletion layer which might change the dielectric constant. In addition to low mobility of charge carriers in conjugated polymers (less than 0.1 $cm^2/V.s$), the oxide of aluminium at the Al/PDOPT interface adds up to the series resistance. Hence the I-V curve shows a space charge limited current (SCLC). Further investigations on spin-coated thin film of PDOPT with vacuum deposited Al contact might be necessary to compare the charge transport mechanism.

CONCLUSION

We have identified the possible vibronic states of a neutral conjugated polymer PDOPT from an optical absorption spectra. The double bonds vibrate at a resonant frequency of about 500 nm, while the single bonds vibrate at about 575 nm. A melt-processed Al/PDOPT/ITO diode was constructed, whose current-voltage characteristics is symmetrical and non-linear. The charge carrier transport mechanism is dominated by the space charge limited current. The complex impedance spectra show a single geometric capacitor connected in parallel with a resistor (one parallel RC circuit). The capacitance is bias voltage independent, while the resistance decreases with increasing bias (reverse or forward) voltage.

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REFERENCES

1. Bantikassegn Workalemahu (1998). Complex impedance spectroscopy of the interface between aluminium and emeraldine base polyaniline. *SINET: Ethiop. J. Sci.* **21**(1):51–66.

2. Bantikassegn Workalemahu, Dannetun, P., Inganas, O. and Salaneck, W.R. (1993). Absence of Schottky Barrier formation in junctions of Al and polypyrrole polyelectrolyte polymer complexes. *Thin Solid Films* **224**:232–236.

3. Bantikassegn Workalemahu and Inganas, O. (1996). The electrical properties of junctions between aluminium and doped polypyrrole. *J. Phys. D: Appl. Phys.* **29**:2971–2975.

4. Bantikassegn Workalemahu and Inganas, O. (1997a). Electronic properties of junctions between aluminium and neutral or doped poly[3-(4-octylphenyl)-2,2'-bothiophene]. *Synth. Met.* **87**:5–10.

5. Bantikassegn Workalemahu and Inganas, O. (1997b). Electronic properties of junctions between aluminium and doped poly(3,4-ethylenedioxythiophene). *Thin Solid Films* **293**:138–143.

6. Barus, M. and Donoval, D. (1993). Analysis of I-V measurements on CrSi2-Si Schottky barrier structures in a wide temperature range. *Solid State Electronics* **36**:969–675.

7. Berggren, M., Inganas, O., Gustafsson, G., Rasmusson, J., Andersson, M.R., Hjertberg, T. and Wennerstrom, O. (1994). Light-emitting diodes with variable colours from polymer blends. *Nature* **372**:444–445.

8. Bredas, J.L. and Chance, R.R. (eds) (1990). *Conjugated Polymeric Materials: Opportunities in Electronics, Optoelectronics and Molecular Electronics*. Kluwer, Dordrecht.

9. Burroughes, J.H., Friend, R.H., Burn, P.L. and Holmes, A.B. (1990). Light-emitting diodes based on conjugated polymers. *Nature* **347**:539–541.

10. Chen, S.-A., Chuang, K.-R., Chao, C.-I. and Lee, H.-T. (1996). White light emission from electroluminescence diode with polyaniline as the emitting layer. *Synth. Met.* **82**:207–213.

11. Cole, K.S. and Cole, R.H. (1941). Dispersion and absorption in dielectrics: I. Alternating Current characteristics. *J. Chem. Phys.* **9**:341–351.

12. de Leeuw, D.M. and Lous, E.J. (1994). Metal-Insulator-Semiconductor Schottky-type diodes of doped thiophene oligomers. *Synth. Met.* **65**:45–53.

13. Gomes, H.L., Taylor, D.M. and Underhill, E.U. (1993). Charge transport in poly(3-methylthiophene) Schottky barrier diodes. *Synth. Met.* **55-57**:4076–4078.

14. Gustafsson, G., Inganas, O., Sundberg, M. and Svensson C. (1991). Rectifying metal/poly(3-hexylthiophene) contacts. *Synth. Met.* **41-43**:499–504.

15. Gustafsson, G., Cao, Y., Treasy, G.M., Klavetter, F., Calaneri, N. and Heeger, A.J. (1992). Flexible light-emitting diodes made from soluble conducting polymers. *Nature* **357**:477–479.

16. Inganas, O. and Lundstrom, I. (1984/85). Electronic properties of metal/poly-pyrrole junctions. *Synth. Met.* **10**:5–12.

17. Lous, E.J., Blom, P.W.M., Molenkamp, L.W. and de Leeuw, D. M. (1995). Schottky contacts on a highly doped organic semiconductors. *Phys. Rev.* **B 51**:17251–17258.

18. Macdonald, J.R. (ed.) (1987). *Impedance spectroscopy, emphasizing solid materials and systems.* John Wiley & Sons, New York.

19. Menon, R., Yoon, C.O., Moses, D. and Heeger, A.J. (1996), in Skotheim, T.A., Elsenbaumer, R.L. and Reynolds, J.R. (eds.). *Handbook of conducting polymers*, 2nd ed. Mercel Dekker, New York.

20. Parker, I.D. (1994). Carrier tunnelling and device characteristics in polymer light-emitting diodes. *J. Appl. Phys.* **75**:1656–1666.

21. Pei, Q, Zuccarello, G., Ahlskog, M. and Inganas, O. (1994). Electrochromic and highly stable poly(3,4-ethylenedioxythiophene)switches between opaque blue-black and transparent sky blue. *Polymer* **35**:1347–1356.

22. Plokarski, J., Drabik, H. and Ciach, T. (1997). Electrorheological properties of polyphenylene suspensions. *Synth. Met.* **88**:139–145.

23. Pope, M. and Swenberg, C.E. (1982). *Electronic Processes in Organic Crystals.* Oxford University Press, New York.

24. Salaneck, W.R., Clark, D.T. and Samuelsen, G. (eds.) (1991). *Science and applications of conjugated polymers.* Adam Hilger, Bristol.

25. Sundberg, M., Gustafsson, G. and Inganas, O. (1990). Rectifying metal-polymer contacts formed by melt processing. *Appl. Phys. Lett.* **57**(7):733–737.

26. Sze, S.M. (1981). *Physics of semiconductor devices.* Wiley, New York.