Effects of space-charge at the conjugated polymer/electrode interface

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Abstract

Films of the polymer poly(4-dicyanomethylene-4H-cyclopenta[2,1-b:3,4-b']dithiophene (PCDM) were electro-deposited onto indium tin oxide (ITO) coated glass substrates. The formation of a polymer was confirmed by the presence of an absorption band at ~900 nm (~1.4 eV) previously attributed to a π - π^* transition. Diodes formed by evaporating aluminium counterelectrodes onto the films displayed non-linear current-voltage characteristics that were independent of voltage polarity. Interestingly, at low applied voltages, the diodes exhibited two, stable, reversible conductance states differing by about an order of magnitude. The effect is similar to that reported recently in diodes formed from chromium-doped SrZrO₃. Ac admittance measurements carried out over a range of frequency coupled with the voltage dependence of the device capacitance at low frequency, suggests that the two states arise from the presence of a field-dependent space-charge at the ITO/PCDM interface.

1. Introduction

Electronic devices formed from conjugated polymers have received considerable attention in recent years with much research effort focused on the fabrication of efficient light emitting diodes¹⁻⁶. Significant progress has been achieved also in developing active polymer devices and even integrated circuits⁷⁻¹¹ in which the carrier mobility is comparable with that in amorphous silicon¹². The polymers utilised to date have relatively high bandgap, *ca.* 2 eV or greater, i.e. double that of silicon. Therefore, synthesising and characterising low bandgap polymers for electronic applications is of interest.

It is known that, the bandgap of a polymer may be reduced by increasing the quinoid character of the π -conjugated system at the expense of its aromaticity. A successful design strategy for achieving this is to introduce an electron withdrawing group at the sp^2 carbon bridging the 4,4-positions of a bithienyl precursor.^{13,14} We have adopted this approach previously to synthesise the electroactive polymer poly(4-dicyanomethylene-4H-cyclopenta[2,1-b:3,4-b'] dithiophene (PCDM)^{14,15} the bandgap (E_G) of which is reported to be below 1 eV.¹³ Here, we present the results of a much more extensive investigation into films of this polymer electrodeposited onto an indium tin oxide (ITO) substrate

Electrical measurements on diodes formed from these films reveal the presence of a space-charge layer at the electrode-polymer interface. The space-charge influences the low-field conductance of the devices as suggested by Riel et al¹⁶, although their interpretation of their data is questionable. In view of its importance to device operation, such an effect needs to be correctly understood. In the present case, a sufficiently high applied field changes the space-charge density, giving rise also to an interesting memory effect in the low-field conductance which is identical in most respects to that reported in inorganic oxides by Beck et al¹⁷.

2. Experimental

Synthesis of the target monomer 4-dicyanomethylene-4H-cyclopenta[2,1-b:3,4-b'] dithiophene (CDM), see inset figure 1(a) has been described fully elsewhere.¹⁸ Briefly, the method described by Jordans and co-workers¹⁹ was used to synthesise 4H-cyclopenta[1,2-b;3,4-b']dithiophene-4-one (CDT). This material was then used to synthesise CDM via a piperidine-catalysed Knoevenagel condensation reaction using malonitrile. Finally, CDM was polymerised by electrochemical deposition onto ITO-coated glass substrates, 5 cm x 1 cm in area, in a class II semiconductor clean room.

Prior to film deposition, the substrates were rinsed initially in cold and then hot ultra-pure water (Millipore SuperQ system with an activated carbon, nuclear grade deioniser and a 0.2 μm point-of-exit filter). This was followed by a thorough wash in concentrated Decon 90 (Scientific Services Ltd., UK) and final rinses in cold and then hot ultra-pure water. Potentiostatic polymerisation was performed in a standard three-electrode cell controlled using an EG+G potentiostat/galvanostat (Model 273, Princeton Applied Research) connected to a differential electrometer cell. Electrodeposition of PCDM was achieved from a solution of CDM monomer (0.01 mol dm^{-3}) in nitrobenzene (99% Aldrich chemicals, UK) using tetrabutylammonium tetrafluoroborate (TBATFB, 0.1 mol dm^{-3} , 99% Aldrich chemicals, UK) as the supporting salt. After preparation, the solution was stored in a sealed container in the dark at 277 K and degassed for 20 minutes immediately prior to use by purging the solution with dry nitrogen.

The polymerisation cell consisted of a 50 ml glass beaker, washed in ultra-pure water and acetone and dried in an oven prior to use, into which 40 mL of the monomer solution was introduced. Electrodes were suspended in the solution by copper connecting wires held in the PTFE cap to the cell. The ITO-coated glass slide formed the working electrode, platinum foil 7 mm x 6 mm in area formed the secondary electrode while a clean

silver wire acted as a quasi-reference electrode.

Following our previously reported procedures^{8,20,21} deposition of the polymer was carried out in two stages; a short nucleation step, in which 2.0 V (vs. Ag) was applied to the working electrode for 10 s, followed by the main growth step when the potential was reduced to 1.6 V (vs Ag) and applied for the time necessary to grow a film of predetermined thickness. Subsequently, the film was dedoped, i.e. the TBATFB dopant required for polymer growth was removed, by reducing the applied potential to 0.0 V (vs. Ag). When the recorded current had fallen below 20 μ A the potential was maintained for a further 300 s to remove as much of the dopant as possible. The coated substrate was then recovered from the solution, thoroughly rinsed in acetone to remove residual monomer prior to drying under a stream of dry nitrogen and storage under vacuum. Since some variability was detected in the surface resistance of different ITO substrates (nominally 20 Ω /square), for one experiment, films of different thickness were grown on the same substrate by raising the substrate in stages out of the monomer solution during film growth.

Circular aluminium contacts, 2.5 mm² in area and 300 nm thick, were evaporated onto the free surface of the polymer films to form sandwich structures for electrical characterisation. The evaporation was carried out in a turbo-pumped vacuum system (Balzers TSH170) at a pressure of 10⁻⁵ torr.

For electrical characterisation, the completed devices were placed in a specially designed sample holder located in a chamber evacuated to a pressure of < 10⁻⁵ torr. The DC characteristics were obtained over the range $\pm$ 5 V using an I-V plotter (HP model 4140B) normally incrementing in steps of 0.05 V or 0.1 V and allowing 60 s between readings. Scans normally commenced after allowing the currents to stabilise for 80 s with -5V applied to the lower ITO electrode, although some test scans began at +5V.

Small-signal AC admittance measurements over the range 20 Hz – 1 MHz were made using a precision LCR meter (HP model 4284) with a test signal of 50 mV. Sample temperature was controlled using a Eurotherm (model 19e) temperature controller connected to a small resistance heater attached to the sample holder. The sample temperature was measured using a chromel/alumel thermocouple linked to the temperature controller.

Film morphology was investigated using a DI Nanoscope IIIA Atomic Force Microscope (AFM) operating in tapping mode. Film thickness was also determined using the AFM by scoring the polymer using a sharp blade and peeling a section away from the substrate to create a step. The optical absorption spectrum of the deposited polymer was obtained in transmission using a UV-visible spectrometer (Hitachi model U2000).

3. Results

A number of polymer films were prepared for this study with several working devices formed in each. All devices showed the same general pattern of behaviour but differed in detail, depending on exact fabrication conditions. Except, where otherwise indicated, the results presented are representative of those grown under the conditions described in section 2.

3.1 Film morphology

The deposited films were relatively uniform in thickness over the central area of the substrate where the devices were formed. They were, however, more nodular in appearance than those grown on gold-coated microscope slides²¹. The RMS roughness over an area 2 μm x 2 μm was typically 8.3 nm. Increasing the scanned area to 5 μm x 5 μm , thereby including the largest nodules, increased the RMS roughness to 13.3 nm (maximum height = 165 nm) for a nominally 100 nm thick film.

3.2 Optical properties

Figure 1 shows the UV-visible spectrum for (a) CDM monomer in solution, (b) a

film of CDM monomer deposited onto ITO using the Langmuir-Blodgett technique and (c) an electro-deposited film of PCDM. The sharp cut-off for wavelengths below ~300 nm in (b) and (c) is due to absorption in the ITO substrate. The monomer spectrum displays a broad band below ~400 nm arising from the overlap of π - π^* transitions. These are present also in the LB film and in the polymer. The monomer solution displays a charge transfer band at ~ 600 nm related to the CN..S dipole of the monomer.²² In the LB film, where molecules adopt a highly ordered parallel configuration, the strong interaction of adjacent dipoles significantly attenuates this band. Some reports^{13,18} attribute the weak feature centred at approximately 900 nm (~1.4 eV) in the polymer to π - π^* transitions in the polymer i.e. excitation of electrons from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) and corresponding, therefore, to the polymer bandgap. The low intensity of this band, however, may cast some doubt on this interpretation. A dependence on dopant concentration seen in the present work suggests that this feature may arise from sub-bandgap transitions possibly involving (bi)polaron states. If so, then the strong band at ~ 500 nm (~2.5 eV) may represent the intrinsic bandgap.

3.3 DC characteristics

The raw data obtained from the I-V plotter displayed the same low-voltage hysteresis and voltage offsets reported by Riel et al¹⁶. Such effects arise from the presence of a significant displacement current as explained in the following. The stepwise application of 0.05 V per 60 s to obtain the data in figure 2 approximates to a voltage ramp, dV/dt , of ~ 0.83 mV/s. Therefore, superimposed on the conduction current will be a displacement current $I_d = C dV/dt$. Here, C corresponds to the effective, low frequency capacitance of the device. Since, the geometrical capacitance of the devices is < 1 nF (see later), the displacement current was expected to be < 1 pA. However, for voltage sweeps in the range ± 2 V and ± 5 V the measured displacement currents (device current flowing

when $V = 0$ V) were 8.3 pA and 14.4 pA respectively when sweeping from - to +, and -10.4 pA and -44.4 pA when scanning from + to -. (Doubling the sweep speed doubled the currents flowing at 0 V, confirming that they were indeed displacement currents). The inference is that, the capacitance dominating device behaviour at low frequencies is typically in the range 10 - 50 nF and much greater than the geometric capacitance of the device. It also appears that when the device is taken to high positive voltages the effective capacitance increases. We will return to this point later.

Aluminium makes a rectifying contact to many conjugated polymers including thiophene-based polymers.⁸ The current-voltage (I-V) characteristics of the present diodes were expected, therefore, to show strong rectification. After correcting for the relevant displacement currents, however, the I-V characteristics (figure 2) are almost identical for both polarities and virtually independent of the direction of the voltage sweep when this is restricted to the range ± 2 V. When the range is extended to ± 5 V the I-V plots, while remaining insensitive to voltage polarity, now become sensitive to the direction of the voltage sweep. The device now switches reproducibly between two conductance states. Starting the voltage sweep at +5 V induces a 'high' conductance while starting at - 5 V induces a 'low' conductance state at the lower voltages. In the 'high' state a V^n dependence ($n \sim 3$) is observed over most of the voltage range. In the 'low' state, an ohmic regime at low voltages undergoes a rapid transition to the 'high' state when $|V|$ exceeds ~ 1 V. Consequently, in the range ± 1 V, the conductances of the two states differ by an order of magnitude. Apart from an even sharper transition which occurs at ~ 0.5 V in their case, the behaviour here is almost identical to that observed by Beck et al¹⁷ in diodes formed from chromium-doped SrZrO₃ sandwiched between a SrRuO₃ bottom electrode and a gold top electrode. This same general pattern of behaviour was found in all the devices tested here. For the reduced sweep range, ± 2 V, the I-V plot is always in the 'low' state at the lowest

voltages but undergoes a transition to the 'high' state when $|V|$ is greater than ~ 1 V.

The occurrence of the persistent 'high' state when sweeping the voltage from +5 V correlates with the observation of a larger displacement current and thus higher capacitance. The geometry of the device is unlikely to change significantly during a voltage sweep. The effective device capacitance is likely, therefore, to be associated with an interfacial space-charge in the device, for example a depletion region at one or other of the electrodes²⁰. Accordingly, we undertook a detailed investigation of the device admittance to confirm this point.

3.4 Admittance measurements

Capacitance (C) and loss (conductance/angular frequency, G/ω) curves (figure 3(a) and (b)) were obtained in 5°C steps from room temperature to 80°C allowing 30 mins between sets of measurements for the sample temperature to stabilise. (For clarity we only include data obtained every 20°C in figure 3). Cooling the device in 5°C steps to room temperature resulted in identical curves. AC admittance plots show a strong dispersion, with a relaxation frequency lying in the range 20 - 600 Hz depending on sample temperature. Our earlier studies²⁰ showed that such a dispersion was related to the formation of a rectifying contact at the junction between the aluminium contact and the electrodeposited film of poly(3-methylthiophene). Although the I-V plots (figure 2) for the Al/PCDM/ITO diodes show little or no rectification, nevertheless, it is likely that a Schottky barrier has been created. The present data provides evidence also for a second, much smaller, temperature-independent dispersion at approximately 1 MHz (see inset diagram in figure 3(a) and (b)).

In a further series of experiments, a number of subtle changes were observed in the admittance plots upon *increasing* the thickness of the polymer film from 60 to 120 nm (achieved by increasing the growth time from 60 to 600s):

- (i) a shift of the low-frequency dispersion to lower frequencies,
- (ii) a reduction in the frequency-independent capacitance in the mid-frequency range
- (iii) a shift of the high frequency dispersion to higher frequencies.

The dependence of device capacitance on applied voltage may be used to confirm the presence of a depletion region at one of the contacts. Figure 4 shows that the low-frequency capacitance, measured at 20 Hz, is certainly dependent on voltage. However, when the data is displayed in the form of a Mott-Schottky plot (open circles) it does not follow the simple linear relationship expected²³ viz.

$$C_d^{-2} = \frac{2}{q\epsilon\epsilon_0 N_A} (V_B + V) \quad (1)$$

where C_d is the depletion capacitance per unit area, q the electronic charge, $\epsilon\epsilon_0$ the absolute permittivity of the polymer, N_A the doping density and V_B the height of the Schottky barrier.

4 Discussion

4.1 AC Admittance

Following our previous work on polymeric Schottky diodes²⁰, the low-frequency admittance data is modelled by a series-parallel combination of capacitances and resistances representing the depletion and bulk regions of the diode (figure 5(a)). A resistance R_S is included in figure 5(b) to represent the series resistance associated with one of the electrodes²⁴. This is probably the ITO substrate since the high frequency dispersion is absent when diodes are formed on gold.

The equivalent circuit in figure 5(a) may be represented by a capacitance C_P in parallel with a conductance G_P so that the admittance Y_P can be written as

$$Y_P = G_P + j\omega C_P \quad (2)$$

where ω is the angular frequency, and

$$C_P = C_g + \frac{C_{LF} - C_g}{1 + (\omega\tau_{LF})^2} \quad (3)$$

$$G_P = G_{LF} + \frac{G_a}{1 + (\omega\tau_{LF})^2}. \quad (4)$$

Here $C_g (= C_d C_b / (C_d + C_b))$ is the series sum of the barrier and bulk capacitances, C_{LF} the effective low-frequency capacitance of the structure given by

$$C_{LF} = \frac{C_d R_d^2 + C_b R_b^2}{(R_d + R_b)^2} \quad (5)$$

and G_{LF} the low frequency or DC conductance $(R_d + R_b)^{-1}$. The AC conductance, G_a is given by

$$G_a = \omega^2 \frac{R_d R_b (R_d C_d - R_b C_b)^2}{(R_d + R_b)^3} \quad (6)$$

and τ_{LF} the circuit relaxation time by

$$\tau_{LF} = \frac{R_d R_b}{R_d + R_b} (C_d + C_b). \quad (7)$$

Therefore, the circuit displays a Debye-like dispersion²⁵ and at low frequency, it is readily seen that so long as $R_d \gg R_b$, then $C_P \sim C_d$ and $G_P \sim R_d^{-1}$. At high frequency $C_P = C_b C_d / (C_d + C_b)$ which reduces to $C_P \sim C_b$ if $C_d \gg C_b$. In the presence of a series resistance, R_S , as in figure 5(b) then equations (3) - (4) may be re-derived yielding a total admittance Y_T given by

$$Y_T = G_T + j\omega C_T \quad (8)$$

where

$$\tau_{LF} = \frac{R_d R_b}{R_d + R_b} (C_d + C_b), \quad (9)$$

$$G_T = \frac{(R_P + R_S) + \omega^2 C_P^2 R_P^2 R_S}{(R_P + R_S)^2 + \omega^2 C_P^2 R_P^2 R_S^2} \quad (10)$$

and $R_p = G_p^{-1}$. Again, a Debye-like dispersion is expected though now modified by the frequency dependence of C_p and G_p . For two, well-separated processes and so long as $R_s \ll R_p$ then the relaxation time, τ_{HF} , of this second, higher frequency dispersion is $C_p R_s$. As ω tends to infinity, then G_T and C_T asymptote to R_s^{-1} and 0 respectively.

The Cole-Cole plot²⁶ in figure 3(c) allowed the components of the equivalent circuit in figure 5(b) to be evaluated. The main dispersion follows a semicircle whose centre lies slightly below the horizontal axis. It is, therefore, slightly broader than predicted by a single relaxation time. This is not unexpected because the local variations in film thickness will lead to local variations in R_b the bulk resistance of the film.

The inset diagram in figure 3(c) shows that, by following the main dispersion anticlockwise, a curve through the data points can be extrapolated to the horizontal axis yielding a capacitance of $\sim 7 \times 10^{-10}$ F. At even higher frequencies, the data points rise again as the second dispersion becomes dominant. The extrapolated capacitance represents the high frequency limit of equation (2) and corresponds to the bulk capacitance, C_b , of the diode. Thus, with $C_b = 7 \times 10^{-10}$ F, a film thickness of 220 nm and a sample area of 2.5 mm², we estimate the relative permittivity, ϵ , of the polymer to be ~ 7 , a value typical of conjugated polymers e.g. for PMeT $\epsilon \sim 5$.²⁰

The depletion region capacitance was deduced from figure 3(c) by extrapolating the low frequency data to the horizontal axis. Thus, C_d is estimated to be $\sim 3.2 \times 10^{-8}$ F and independent of temperature between 23°C and 80°C. In this temperature range, therefore, all dopant species in the depletion region are ionised. Significantly, the value estimated for C_d is consistent with the range of values predicted from the displacement currents. Furthermore, if we assume that the relative permittivity of the polymer is ~ 7 , then the width of the depletion layer is calculated to be ~ 5 nm.

To obtain values for the resistive elements of the equivalent circuit it is necessary

to recast equations (2) - (4) and (8) - (10) into the corresponding impedances i.e.

$$Z_p = \frac{1}{Y_p} = \frac{1}{G_p + j\omega C_p} \quad (11)$$

and

$$Z_T = \frac{1}{Y_T} = \frac{1}{G_T + j\omega C_T} \quad (12)$$

and to replot the data in the complex impedance plane. Thus, the series resistance was found to be $\sim 400 \Omega$ and independent of temperature. On the other hand, between room temperature and 80°C , the bulk resistance decreased by about an order of magnitude from $\sim 45 \text{ K}\Omega$ to $\sim 4 \text{ K}\Omega$, corresponding to an activation energy of $\sim 0.36 \text{ eV}$ for the AC conductivity of the bulk polymer.

From equation (7) it is readily deduced that when $R_d \gg R_b$ and $C_d \gg C_b$, then $\tau_{LF} \sim R_b C_d$. Since C_d was temperature independent (figure 3) then any temperature variation of τ_{LF} must arise from R_b . Figure 6 is an Arrhenius plot of the frequency $\nu_m (= 1/2\pi\tau_{LF})$ at which the loss reaches a maximum. The linear slope yields an activation energy of 0.45 eV in reasonable agreement with the initial estimate from the complex impedance plots (see above) but significantly greater than the value of 0.25 eV observed in poly(3-methylthiophene).²⁰

From the UV-visible absorption spectrum in figure 1, the bandgap of the undoped PCDM polymer investigated here is believed to be $\sim 1.4 \text{ eV}$ but possibly could be as high as 2.5 eV . Therefore, the activation energy for AC transport in the bulk polymer is likely to be associated with a hopping mobility.

The model presented above readily explains also the effect of increasing the film thickness on the admittance plots. Firstly, the bulk capacitance, C_b , is expected to decrease, thus reducing the time constant, $\tau_{HF} \sim C_b R_s$, of the high frequency dispersion. Secondly, the bulk resistance, R_b , will increase, thus increasing the time constant, $\tau_{LF} \sim$

$C_d R_b$, of the low frequency dispersion. All these predictions are consistent with observations.

4.2 Capacitance-Voltage Characteristics

If the films are p-type, as is the case for other thiophene-based polymers, the dependence of the low-frequency capacitance on applied voltage in the range ± 1 V (figure 4), provides some evidence for the presence of a depletion region at the polymer-ITO junction rather than at the polymer-Al junction. However, applying equation (4) even over this limited voltage range leads to unrealistically large values of the barrier potential at the ITO electrode (> 3 eV) and doping densities $> 10^{25} \text{ m}^{-3}$ in the polymer.

A reduction in the depletion resistance, R_d , as the applied voltage increases would explain the rapid increases in the Mott-Schottky plots above ± 2 V. With forward (negative) voltage across the junction, R_d is expected to decrease owing to a reduction in the depletion region width. For reverse (positive) voltages, the electric field at the ITO-polymer interface increases as the depletion region expands. This will reduce R_d either through a field-enhanced carrier generation rate in the depletion region or through increased field-assisted thermal emission over the potential barrier at the junction. Equation (5) shows that, when R_d becomes small, the capacitance measured at low frequency is reduced. For sufficiently small values of R_d ($\ll 1/\omega C_d$), it will tend towards C_b the bulk capacitance of the diode. A reduction in R_d is likely also to manifest itself at the lower applied voltages. This is confirmed in figure 7 where Cole-Cole plots are presented for a range of applied voltages both positive and negative. Above about 60°C the low frequency dispersion shifts to sufficiently high frequencies to enable C_d to be measured unambiguously (figure 3). Nevertheless, when applied voltages exceed about ± 1 V, the Debye-like behaviour is completely swamped making it impossible to obtain accurate estimates of C_d . The change in slope of the C-V plot around 0 V probably reflects the different mechanisms controlling R_d in forward and reverse bias.

4.3 DC characteristics

ITO/PCDM/Al devices display two stable conductance states whose behaviour, in most respects, is identical to that observed in chromium-doped SrZrO₃ diodes. As for the oxides, the 'low' conductance state of the polymer diodes is stable for many months. We have, additionally, investigated the stability of the high conductance state²⁷ and shown that it relaxes with a time constant ranging from ~45 mins at +0.5V down to ~25 mins at -0.5 V.

Beck et al¹⁷ tentatively ascribed the transition between 'low' and high' states to charge transfer processes via donor and acceptor levels (Cr³⁺ and Cr⁴⁺). In the present work, it is unlikely that the dedoping step removed all the TBATBF dopant from the film. Hence, an electron transfer involving the BF₄⁻ anion could occur here also. However, since the mechanism proposed by Beck et al¹⁷ lacks detail we cannot proceed further down their line of reasoning.

Furthermore, the evidence presented here points clearly to the important role of interfacial space-charges. Differences in work function lead to the formation of a Schottky barrier at the polymer/ITO interface in which the space-charge is defined by a thin layer (5 nm) of ionised acceptors (BF₄⁻). Under positive bias, additional acceptors drift to the polymer/ITO interface, reducing further the width of the depletion region. The consequent increase in the depletion region capacitance results in an increase in the measured low-frequency capacitance of the device and thus an increase in the magnitude of the displacement current when sweeping the applied voltage from + to -. The reduction in depletion region width is sufficient also to allow tunnelling to occur through the Schottky barrier over the whole voltage range so that currents become bulk limited. After sweeping the voltage to -5 V, the acceptor density at the ITO interface relaxes to its equilibrium value resulting in a wider, more resistive depletion region. When reversing the sweep, a

transition from bulk-limited conduction to barrier-limited conduction at the lower applied voltages explains the rapid changes in current seen at about ± 2 V.

In the present devices, the bulk currents, although likely to be space-charge limited, are characterised by an approximate V^3 dependence rather than the square law relation predicted by Lampert²⁸, i.e.

$$J = \frac{9}{8} \epsilon \epsilon_0 \mu \frac{V^2}{d^3} \quad (13)$$

where $\epsilon \epsilon_0$ is the absolute permittivity of the semiconductor, d its thickness and μ the carrier mobility. This discrepancy may be explained by the presence of an exponential trap distribution²⁹ or a field-dependent mobility³⁰.

5. Conclusions

We have shown that, films of the polymer poly(4-dicyanomethylene-4H-cyclopenta[2,1-b:3,4-b'] dithiophene (PCDM) electrodeposited onto ITO substrates are dense and relatively uniform in thickness. Typically, the RMS roughness was 13.3 nm over a $5 \mu\text{m} \times 5 \mu\text{m}$ area. When compared with an LB film of the monomer, the UV-visible spectrum of the polymer displayed a new albeit weak absorption band centred ~ 900 nm (1.4 eV) which has been attributed to the π - π^* transition of the polymer. However, this feature may arise from sub-bandgap transitions in which case the intrinsic gap is ~ 2.5 eV. Further work is necessary to confirm this point.

The I-V characteristics of the devices displayed no rectification. On the contrary, I-V plots were essentially independent of voltage polarity. Surprisingly, they did display two, stable, voltage-controlled conductance states, almost identical in behaviour to that reported for chromium-doped SrZrO_3 diodes. In the present case, the effect is related to a thin depletion region formed at the polymer/ITO interface. It is postulated that the field-induced changes in space-charge density in the depletion layer cause a change from

electrode to bulk limited transport in the devices. These findings may be significant for the operation of conjugated polymer devices at low-voltages. They also suggest a possible strategy for fabricating polymer memory elements through control of interfacial space-charge.

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FIGURE CAPTIONS

- Figure 1** UV-visible spectra of (a) CDM monomer (inset) in a 1:1 solution of CH_2Cl_2 and CH_3CN , (b) a film of CDM monomer LB-deposited onto ITO and (c) an electrodeposited film of PCDM.
- Figure 2** Current-voltage (I-V) characteristics of an ITO/PCDM/Al diode. The characteristics were obtained by sweeping the voltage through the ranges ± 2 V and ± 5 V at a rate of 0.1 V per minute. The data has been corrected for displacement currents to reveal the true dependence at low voltages. Four voltage regimes are identified, -V to 0 ($\circ$), 0 to +V ($\bullet$), +V to 0 (∇) and 0 to -V ($\blacktriangledown$).
- Figure 3** Effect of temperature on (a) the capacitance, C, and (b) the loss, G/ω , of an ITO/PCDM/Al diode. (Measurements were made every 5°C but for the sake of clarity only the curves corresponding to 23°C ($\circ$), 40°C (∇), 60°C ($\square$) and 80°C ($\diamond$) are presented). (c) capacitance and loss data plotted in the complex plane (Cole-Cole plot).
- Figure 4** The voltage dependence of the low-frequency capacitance ($\bullet$) and the same data replotted as a Mott-Schottky plot ($\circ$) to test the relationship in equation (4). The results were obtained at 20°C and represent the 20 Hz data extracted from successive frequency sweeps with the applied dc voltage incremented from +5 V to -5 V.
- Figure 5** (a) Equivalent circuit of a device in which the bulk material, represented by C_b and R_b , is in series with an interfacial (depletion) layer represented by C_d and R_d . In (b) the series resistance R_s of the electrode is included.
- Figure 6** Arrhenius plot of the frequency, ν_m , at which the loss reaches a maximum for increasing ($\bullet$) and decreasing ($\circ$) temperatures.

Figure 7 Cole-Cole plots showing the effect of applying both positive and negative bias to the ITO electrode. ($T = 60^{\circ}\text{C}$).