A Memory Effect in the Current-Voltage Characteristic of a Low-Bandgap Conjugated Polymer

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Summary

Diodes formed by electrodeposition of the low-bandgap polymer poly(4-dicyano methylene-4H-cyclopenta[2,1-b:3,4-b']dithiophene), PCDM, onto glass slides coated with indium tin oxide (ITO) and furnished with evaporated aluminium counterelectrodes exhibit a reversible bistability in their current-voltage characteristics. Applying +5 V to the ITO electrode induces a 'high' conductance state while applying -5 V induces a 'low' conductance state. The effect is identical in most respects to recent observations in diodes formed from thin films of chromium-doped SrZrO_3 sandwiched between SrRuO_3 and gold electrodes. A number of mechanisms are discussed but the evidence points to the controlling influence of an interfacial depletion layer at the ITO-polymer interface. It is also shown that the high capacitances associated with such layers can lead to higher than expected displacement currents being generated during the automated collection of I-V data. The presence of such currents distort the I-V characteristics in the low-bias, low-current regime.

I. INTRODUCTION

There is now considerable interest in fabricating polymer integrated circuits, see for example the recent reports of logic circuits based on thin film MISFET devices¹⁻³ and driver circuits for optical displays⁴. The development of a non-volatile, polymeric memory element would increase both the versatility and range of applications of such circuits. In an on-going study⁵ of the low bandgap polymer poly(4-dicyanomethylene-4H-cyclopenta[2,1-b:3,4-b']dithiophene), PCDM, formed by electrodeposition of the corresponding carbon-bridged dithienyl monomer (see inset figure 1) we have identified a reproducible, reversible, voltage-induced switching phenomenon. The effect appears to be similar in most respects to that observed recently by Beck et al⁶ in a potential memory element formed from a thin film (~300 nm) of chromium-doped SrZrO₃ sandwiched between a SrRuO₃ bottom electrode and a gold top electrode. Evidence obtained from the present study highlights the role of interfacial depletion regions in controlling diode currents.

II. EXPERIMENTAL

Films of PCDM ~200 nm thick were grown on indium tin oxide (ITO) coated glass substrates following our previously reported procedures⁵. This involved electrochemical deposition from a solution of the monomer in nitrobenzene to which tetrabutylammonium tetrafluoroborate (TBATFB) was added as a supporting salt. Preparation of the monomer followed a well-established synthetic route^{7,8}. After deposition, the polymer was dedoped to extract the tetrafluoroborate, BF₄⁻, anions, washed in acetone and dried under a stream of dry nitrogen. Diodes were formed by evaporating circular aluminium contacts, 2.5 mm² in area and 300 nm thick, onto the free surface of the polymer films in a turbo-pumped vacuum system (Balzers TSH170) at 10⁻⁵ torr. DC characteristics were obtained at pressures <10⁻⁵ torr using an I-V plotter (HP model 4140B) incrementing in steps of 0.1 V and allowing 60 s between readings for currents to stabilise. Voltage sweeps normally commenced after

allowing currents to stabilise for 80 s with either -5V or + 5 V applied to the lower ITO electrode.

Film thickness and morphology were determined using a Digital Instruments, Nanoscope IIIA AFM. The optical absorption spectrum of the polymer was obtained in transmission using a UV-visible spectrometer (Hitachi model U2000).

III. RESULTS AND DISCUSSION

AFM micrographs of the electrodeposited film showed it to be densely packed and relatively uniform (RMS roughness 8.3 nm over a $2 \times 2 \mu\text{m}^2$ area). UV-visible spectroscopy confirmed the formation of a polymer with the π - π^* transition centred at ~ 900 nm as reported by Ferraris and Lambert⁸ and corresponding to an energy gap < 1.4 eV.

The current-voltage (I-V) characteristics of the diodes investigated here were superlinear, with currents rising through some 5 orders of magnitude between 0.1 V and 5 V. At the lower end of the range, the characteristics displayed two features, both of which were sensitive to the sweep direction of the applied voltage. These features are seen in figure 1 in which only the section of the I-V characteristic between ± 0.5 V is plotted. (The full sweep covers the range ± 5 V). Firstly, we note that the device current changes polarity at a non-zero voltage which is dependent on sweep direction. Such an effect was reported by Riel et al⁹ for multilayer organic light emitting diodes (OLEDs) and ascribed loosely to interfacial space-charges in their diodes. Secondly, we note that the device displays two conductance states: 'high' when sweeping from +5 to -5 V and a 'low' when sweeping in the opposite sense. Such an effect was reported by Beck et al⁶ in diodes formed from thin films of chromium-doped SrZrO₃ sandwiched between SrRuO₃ and gold electrodes.

AC admittance measurements carried out on our diodes (not reported here) show a marked dispersion at low frequency arising from the presence of a depletion region at one of

the electrodes similar to that reported for poly(3-methylthiophene) Schottky diodes¹⁰. The capacitance of this layer, which dominates device behaviour at low frequencies, typically ranged from 10 - 30 nF. (This contrasts with a capacitance of ~ 0.5 nF calculated from the device geometry assuming a relative permittivity of ~ 7). The stepwise application of voltage in the present work, which approximates to a voltage ramp of ~ 1.7 mV/s, therefore, is expected to generate a displacement current (CdV/dt) in the range 17 to 50 pA rather than the 0.8 pA or so based on the geometrical capacitance of the diode. In figure 1, it is seen that for a voltage sweep starting at +5 V the displacement current (device current when $V = 0$) is equal to - 44 pA and for the reverse sweep is equal to +14 pA, in good agreement with estimates based on the depletion layer capacitance. That the magnitudes differ for the two sweep directions reflects changes in the capacitance of the depletion layer, a point to which we will return later. A consideration of the displacement currents in the I-V characteristics of their OLEDs would explain all the dynamic effects reported by Riel et al⁹. Nevertheless, their approach is useful in identifying the presence of interfacial, space-charge layers (including depletion layers) in diodes without resorting to ac admittance measurements. However, careful interpretation is required for multilayer structures where Maxwell-Wagner-type dispersions can occur.

Figure 2 is a double-log plot of the full I-V characteristics after correcting for the relevant displacement current in order to reveal the true low-voltage behaviour. As can be seen, when sweeping from + to - the device remains in the high state. When sweeping from - to + the device switches reproducibly between its two conductance states at $|V| \sim 1$ V. In the 'high' state a V^3 dependence is observed over most of the voltage range. In the 'low' state, an ohmic regime at low voltages undergoes a rapid transition ($I \propto V^5$) to the 'high' state. (This reproducible switching is not caused by sample breakdown). Over the range ± 1 V, the

conductances of the two states differ by an order of magnitude. Apart from an even sharper transition occurring at ~ 0.5 V in their case, the behaviour here is almost identical to that observed by Beck et al⁶ in their oxide diodes.

As reported 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' state. After applying +3 V to the diode to induce the 'high' state and decrementing to +0.5V or -0.5V, it is seen (figure 3) that the device currents decay exponentially with time constants of 2600s and 1500s respectively. Thus the application of negative voltages, encourages the relaxation of the 'high' conductance state, which begins even at low positive voltages. Clearly by -5 V this process is complete.

The reversible transition between 'low' and high' states in chromium-doped SrZrO₃ was tentatively ascribed to charge transfer processes via donor and acceptor levels (Cr³⁺ and Cr⁴⁺) although the exact mechanism for producing the two distinct conductance states was not explained. In the present work, it is unlikely that all the BF₄⁻ dopant was removed from the polymer during dedoping. Hence electron transfer to and from acceptor molecules could occur here also.

The transition from the 'low' to the 'high' conductance states near ± 1 V is reminiscent of the transition from a trap-controlled space-charge-limited current (SCLC) to a trap-free SCLC when the trap-filled-limit voltage is exceeded. In the present devices, though, this latter regime is characterised by a V^3 dependence rather than the square law relation predicted by Lampert¹¹, i.e.

$$J = \frac{9}{8} \epsilon \epsilon_0 \mu \frac{V^2}{d^3} \quad (1)$$

where $\epsilon \epsilon_0$ is the absolute permittivity of the semiconductor, d its thickness and μ the carrier mobility. Two possible explanations suggest themselves for this discrepancy.

(i) A V^3 dependence is predicted¹² when traps are distributed in energy. The rapid change in conductance near ± 1 V would then arise from the filling of a set of deeper traps located below a manifold of shallower distributed states.

(ii) In a number of conjugated polymers the carrier mobility is a function of applied field, E , the mobility generally increasing with field following a Poole-Frenkel-type dependence (mobility $\propto \exp(E/E_0)^{1/2}$).¹³ It is conceivable that such an effect could lead to a V^3 dependence over a limited range of applied voltages.

A trap-controlled SCLC does not, however, explain the persistence of the ‘trap-free’ SCLC over the whole range when sweeping the applied voltage from + 5 V to - 5 V. This would require that traps filled under a high positive electric field should remain filled for long periods of time or until a negative field of similar magnitude is applied. On the otherhand, when the extreme of the positive voltage ramp is restricted to +2 V, trap-filling is immediately reversed when the voltage is reduced.

Arguments can be constructed which involve configurational changes in the polymer in the environment of the filled trap such that the release of carriers now requires a change in the entropy term in the Gibbs energy function. Under such conditions the escape frequency, ν , given by¹⁴

$$\nu = \nu_0 \exp \frac{\Delta S}{k} \exp - \frac{E_t}{kT} \quad (2)$$

where ν_0 is the attempt-to-escape frequency and ΔS the change in entropy required to effect an escape from a trap of depth E_t . Thus, negative values of ΔS increase the residence time of carriers in the traps. Detailed spectroscopic analysis of electrically stressed films would be required to confirm the presence of such configurational changes.

The results presented in figure 1 may suggest a simpler explanation though. It is known that, at electrode polymer interfaces Schottky barriers are readily formed in which

the depletion region is composed of a layer of unscreened dopant ions.¹⁰ Since the dopants are not chemically bound to the polymer they may undergo a slow drift under the action of an applied electric field hence changing the capacitance of the depletion layer. Such a change will manifest itself as a change in the displacement current measured during a voltage sweep. Capacitance-voltage measurements (not reported here) provide some evidence that a depletion region exists at the polymer/ITO interface. The different displacement currents seen for positive and negative voltage sweeps in figure 1 can then be explained in terms of an increase in the depletion capacitance caused by a drift of negatively charged BF_4^- ions to this interface when +5 V is applied to the diode and a reversal of this process under negative bias. Indeed, as already noted, the reversal occurs, albeit more slowly, even under reduced positive bias as evidenced by the data in figure 3.

The 'low' conductance state is then seen to be associated with current limitation through the depletion layer which is overcome when $|V| > 1$ V. Following the application of a +5 V bias, the accumulation of dopant ions at the ITO interface leads to a reduction in the width of the depletion layer and hence an increase in its transparency to charge flow until such time as the excess ions are dispersed under high negative bias. The 'high' state probably reflects the true I-V characteristic of the polymer which is likely to be space-charge-limited with a field dependent mobility.

These results confirm the findings of Riel et al⁹ that the control of interfacial space-charge layers, particularly depletion regions, is important for maximising current flow through organic diodes. As shown here, these layers can also give rise to a reversible switching phenomenon which may find application in memories. Such a possibility has been suggested for a similar effect reported by Beck et al⁶ in their oxide diodes in which interfacial space-charge layers are also likely to play a role.

IV. CONCLUSIONS

It has been shown that Al/PCDM/ITO diodes display a reversible switching effect which is similar in all respects to that reported for diodes formed from thin films of chromium-doped SrZrO₃ sandwiched between SrRuO₃ and gold electrodes. In the polymer diodes investigated here a number of possible mechanisms have been discussed but the most plausible explanation is that the effect is likely to arise from the presence of an interfacial depletion layer at the ITO electrode. Normally, at low bias voltages the depletion layer controls charge flow through the device. However, either a high field, achieved when $|V|$ exceeds ~ 1 V, or an increase in dopant density in the layer, achieved rapidly when V exceeds about +3 V, can render the layer transparent to charge flow.

It has also been shown that in the low-bias, low-current regime, I-V characteristics of organic diodes are influenced by the presence of displacement currents which may be greater than expected where high-capacitance space-charge layers are present.

When corrected for the displacement current, the I-V characteristic of our diodes in the 'high' state probably reflects the true behaviour of the polymer which is seen to undergo a transition from an ohmic to a V^3 dependence as the bias increases.

ACKNOWLEDGEMENTS

The authors are grateful to the Engineering and Physical Sciences Research Council (UK) and BNFL for supporting this work through the award of a CASE studentship to one of us (CAM).

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Figure Captions

Figure 1 The low-bias section of the I-V characteristics of an Al/PCDM/ITO diode showing the presence of displacement currents (curves do not pass through the origin) and two conductance states. The 'high' conductance was obtained by sweeping the voltage from +5 V to -5 V. The 'low' conductance state was achieved when sweeping in the opposite sense.

Figure 2 Double-log I-V plots showing the symmetrical nature (with respect to polarity) of the two conductance states of an Al/PCDM/ITO diode. The 'high' state was obtained by sweeping the voltage from + 5 V while the 'low' state was induced by starting the sweep at - 5 V.

Figure 3 Temporal relaxation of the 'high' conductance state at + 0.5 V (●) and - 0.5 V (○). The high state was induced by applying + 3 V to the ITO electrode.