Transient capacitance measurements of the transport and trap states distributions in a conjugated polymer

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Abstract

We have performed transient capacitance measurements on indium tin oxide/poly(*p*-phenylenevinylene)/Al diodes which have a depletion region type Schottky barrier at the polymer/Al interface. We show that both the transport and trap state distributions within the polymer can be determined from the results and present a fully consistent model that describes the observed behaviour in terms of a de-trapping of carriers from a discrete trap level to a Gaussian distribution of transport states. © 2000 Elsevier Science B.V. All rights reserved.

Conjugated polymers, exemplified by the archetypal poly(*p*-phenylenevinylene) (PPV), have attracted widespread interest due to their potential for use as the emissive material in commercial electroluminescent displays [1]. There is, however, relatively little direct experimental information concerning the nature of charge transport in these materials. One major issue is how the transport states are distributed in energy. This has important implications for transport theories based on band-like motion, polaronic relaxation or hopping. Indirect evidence comes from optical absorption spectroscopy and site selective fluorescence measurements, which show that the *neutral* singlet exciton excited states in PPV are inhomogeneously distributed in energy [2,3]. It is then often assumed that the *charged* transport states will reflect the same level of energetic disorder [4]. Such transport state disorder has been directly studied for xerographic material systems by detailed analysis of the field and temperature dependence of the charge carrier mobilities [4]. Results for three conjugated polymers have recently been analysed in a similar manner [5,6], but the analysis is more ambiguous due to the limited measurement range, scatter in the results and deviations from expected behaviour [5]. No direct measurements have been reported for PPV. In addition, no further techniques have been used to directly measure the distribution of transport states in conjugated polymers.

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Another important issue that affects conduction in these materials is the presence of charge traps. Despite their clear effects on device performance, relatively few studies have been carried out to measure the energies of traps in electroluminescent polymer devices [7,8]. A technique traditionally used to study traps in inorganic semiconductor devices is deep level transient spectroscopy (DLTS) [9,10]. Here we show that this transient capacitance technique can also be applied to study traps in electroluminescent polymers and other organic semiconductors. We show further that it can be used to determine the material's transport states distribution. A fully consistent model is presented in which the approximations normally used for DLTS analysis are avoided. The observed capacitance transients for PPV can then be successfully modelled in terms of the de-trapping of carriers from a discrete trap level to a Gaussian distribution of transport states.

In standard DLTS, a small AC test signal is used to measure the depletion width capacitance. This width depends upon the total amount of charge stored within the depletion region. By applying a voltage pulse, it is possible to fill any bulk traps or interface states within the depletion region by momentarily pulling them below the Fermi level. The emptying of charge from these traps can then be measured using the variation of the depletion width capacitance with time. However, nearly all polymer LEDs are fully depleted. The level of accidental extrinsic impurity dopants is too low to form a depletion region type Schottky barrier smaller than the width of the device (<200 nm) [11]. A notable exception arises for the ITO/(PPV)/Al structures fabricated at the University of Bayreuth, Germany. In these devices, the level of p-type doping is large enough (10^{16}–10^{17} cm^{-3} In-Cl$_3$ dopants) that a depletion region can form at the PPV/Al interface that has a much narrower width between 50 and 150 nm [12]. Here we report measurements of these ITO/PPV/Al devices. Note, that spectroscopically the Bayreuth material is the same as other samples of PPV, an indication that the differences are restricted to doping levels and not other chemical effects.

To prepare devices the Bayreuth PPV precursor polymer (tetrahydrothiophenium leaving group) was spread with a Doctor blade onto ITO coated glass substrates (Balzers, 60 Ω/□) and then converted under vacuum at 160°C for 2 h. The top Al electrode was thermally deposited through a shadow mask. Two different polymer film thicknesses, 200 and 600 nm, were used. The average device area was 0.045 cm^2. Measurements were made using a Solartron Schlumberger SI 1260 impedance/gain-phase analyser. Temperature measurements (accuracy: ± 0.1 K) were conducted using an Oxford Instrument CCC 1204 closed cycle, Helium exchange gas cryostat. Some 20 devices were measured in total, and the results presented here are representative of typical devices.

Fig. 1 shows the capacitance–voltage (C–V) characteristics of a typical 200 nm thickness device in the form of a $1/C^2$ versus V plot recorded at a measurement frequency ω_{rf} of 117 Hz. The device was tested at 295 K in He after being stored under vacuum (rotary pump) and then exposed to ambient atmospheric conditions for two days. Three different curves were recorded with a 24 h interval between subsequent measurements. Each of the curves shows two distinct slopes as a function of bias. This behaviour is the classic characteristic for a Schottky diode that has majority carrier traps
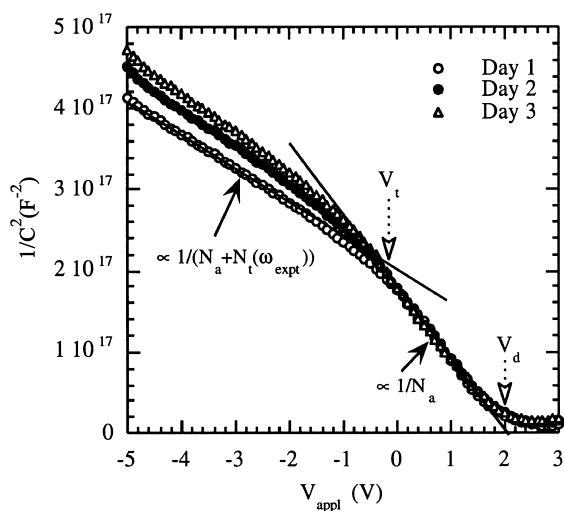

Fig. 1. Inverse capacitance squared, $1/C^2$, against applied bias, V_{appl}, of a 200 nm thick ITO/PPV/Al device. Recorded at 1 day intervals in He atmosphere after exposure to air.

whose charged state, when empty, is of the same sign as the ionised dopant centres [10, Fig. 6.17]. The larger gradient at positive bias arises from the InCl$_3$ acceptor dopants, density N_a, and is proportional to $1/N_a$, with an intercept that gives the diffusion potential V_d. The smaller gradient at negative bias arises from the combination of acceptor dopants, N_a, and those traps that can empty on the time scale of the experiment, $N_t(\omega_{expt})$. This gradient is proportional to $1/(N_a + N_t(\omega_{expt}))$, where ω_{expt} is determined by the sweep rate of the measurement (2 s per data point, 160 s for the whole scan) and is of order of the fastest trap emptying rates found in the measured capacitance transients (see below) [10]. $N_t(\omega_{expt})$ therefore gives a lower limit to the true trap density. As expected, $N_t(\omega_{expt})$ decreases with increasing measurement frequencies and increasing experimental sweep rates. The bias at which the slope changes (V_t) is that where, with increasing positive bias, the traps are pulled below the Fermi level at the interface and become effectively permanently filled. They can then no longer respond in the experiment.

The measured values of the acceptor density N_a, zero bias depletion width x_d ($V = 0$) and diffusion potential V_d for the devices in this work are very similar to those reported in the literature [12]. The values of $N_t(\omega_{expt})$ lie between 0.9×10^{17} and 3.6×10^{17} cm^{-3}. Devices with large N_a also have large $N_t(\omega_{expt})$, so that some of this scatter is almost certainly due to variations in active device area A (the calculated densities are proportional to $1/A^2$). If the trap states were to lie at the interface, the values of V_t should give the trap depth from $E_t = q(V_d - V_t) + E_F$. However, the calculated values are much too large ($E_t \gg E_g/2$), suggesting that the trap density varies with depth, N_t increasing with distance from the Al/PPV interface. Fig. 1 also shows that under He atmosphere, V_t shifts to more negative bias and N_t decreases with time. This decrease of trap density with time under a dry inert gas atmosphere is consistent with the DLTS results below, which identify this trap state as being due to exposure to air.

Fig. 2 shows the change of the capacitance with time for a typical 200 nm thick device on a log-linear plot. The data were recorded at 295 K for an applied quiescent bias of -1 V after being stored
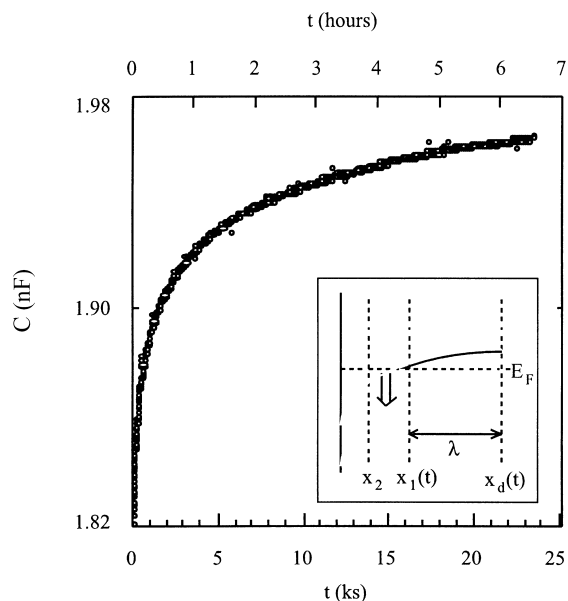

Fig. 2. Log-lin plot of transient capacitance, C, against time, t, of a 200 nm thick ITO/PPV/Al device. Insert shows model of depletion region assumed in analysis.

overnight (15 h) at 0 V. This transient is very typical of all those observed, although for most experiments, the capacitance was not recorded for such a long time. The sign of the transients shows that the amount of positive charge in the depletion region decreases. This, combined with the C–V measurements, indicates that we are probing majority p-type carrier traps of the acceptor type that are neutral when filled and negatively charged when empty. The length of the transient (the traps are still emptying after 7 h) suggests that the traps are very deep within the energy gap. The change in capacitance over the duration of the transient is about 50% of the change in the capacitance between -1 V and 0 V applied bias in the C–V measurement. This indicates that $N_t > N_a$, consistent with the C–V results.

If $N_t > N_a$, then one might expect all the free extrinsic p-type carriers to be trapped so that the devices would be permanently fully depleted. However, the results in Figs. 1–4 show that a depletion region must be present. The traps themselves being of the acceptor type (neutral when full, negatively charged when empty) may donate p-type carriers when they form. Also, it has been

shown that ITO forms an ohmic contact with PPV for positive carriers [13]. Such a contact will offer no barrier to carrier injection and will supply all the carriers needed by the bulk material. It will effectively act as an infinite reservoir of free carriers. Hence, the ITO contact will always allow detailed carrier balance to be maintained across the ITO/PPV interface and within the PPV, supplying or removing any excess p-type carriers captured or emptied from the traps.

All of the observed transients are non-exponential, which is not unexpected for a disordered organic solid in which the transport states, the traps, or both, are believed to be distributed in energy. Optical absorption spectroscopy and spectral dispersion measurements (via site-selective fluorescence) of PPV show that the neutral exciton excited states have a Gaussian energy distribution and it has therefore been suggested that the transport states might also have a similar distribution [2,3]. The transient capacitance decay rate does not vary with the applied quiescent bias level V_{appl}, so the transients cannot be due to the decay of a distribution of interface states. In addition, the transients cannot then be due to the decay of a distribution of bulk traps. Detailed modelling indicates further that N_t would need to be three to four orders of magnitude smaller than observed in the C–V experiments [14]. The transient results have therefore been modelled by considering the de-trapping of carriers from a discrete trap level to a Gaussian distribution of positive carrier transport states. This is shown schematically in the inset to Fig. 3.

As $N_t > N_a$, the small trap density approximation cannot be used. The change of the depletion width $x_d(t)$ with time is calculated from

$$\frac{2\varepsilon_r\varepsilon_0}{q}(V_d - V_{appl} + V^*)$$
$$= N_a x_d(t)^2 + N_t x_1(t)^2 - N_t f(t)\{x_1(t)^2 - x_2^2\}, \quad (1)$$

where V_{appl} is the applied quiescent bias and V^* is a fitting parameter that allows for charge stored in fast interface states or fast bulk traps or spatial variations in N_t. $x_1(t)$ is the distance from the cathode to the point at which the trap level intersects the quasi Fermi level when the device is held
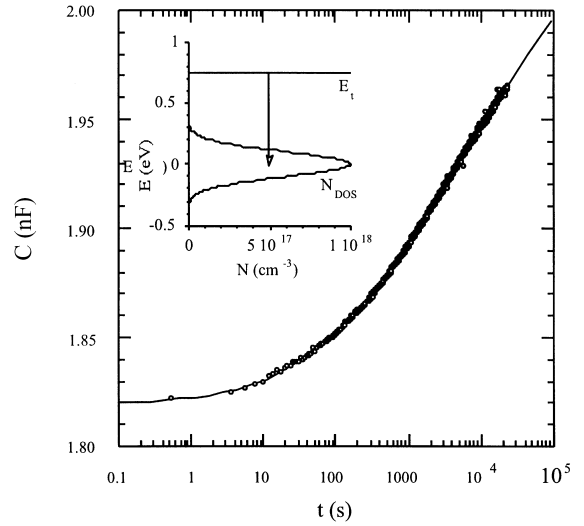

Fig. 3. Fit of model to results in Fig. 2 on a lin-log plot. Parameters used in fit are $\sigma = 0.10$ eV, $E_t = 0.75$ eV, $v = 10^8$ s^{-1} and $N_t = 5.1 \times 10^{17}$ cm^{-3}. Insert shows physical picture of decay model.

at quiescent bias (see inset in Fig. 2). x_2 is the same distance during the filling voltage pulse. $f(t)$ is the variation with time of the trapped charge between $x_1(t)$ and x_2 [10]. $x_1(t)$ and x_2 are calculated from the depletion width by subtracting the parameter λ where $\lambda^2 = 2\varepsilon_r\varepsilon_0(E_t - E_F)/qN_a$. This model assumes the depletion region approximation. It also assumes that N_a does not vary with distance from the cathode as shown by the very linear $1/C^2$ versus V plots of similar devices [12]. At the average field in the depletion region, V_d/x_d, the p-type carrier mobility in the Bayreuth PPV has been determined by time-of-flight (TOF) measurements to be of order 10^{-5} cm^2 V^{-1} s^{-1} at room temperature [15]. The average transit time of a carrier across the depletion region should then be of order 10 μs. It is therefore assumed for simplicity that re-trapping is negligible on the time scales of the experiment. The decay function $f(t)$ is calculated by integrating at different times t over a normalised Gaussian distribution $N_{Gauss}(g_t)$ of trap depths $g_t + E_t$,

$$f(t) = \int N_{Gauss}(g_t)$$
$$\times \exp\left\{-v\exp\left(\frac{-(g_t + E_t)}{kT}\right)t\right\}dg_t. \quad (2)$$

This corresponds to the physical picture in the inset to Fig. 3, with v the attempt-to-escape frequency. Given that this is an energetically disordered polymer in which the trap capture cross-section is defined by the physical size of the trapping site, the density of states N_{DOS} is the molecular density and conduction is by hopping transport, it is assumed that v has a temperature dependence of the form $\exp(-E_a/kT)$, where E_a is an activation energy associated with the zero-field carrier thermal velocity. E_a is expected to be about an order of magnitude less than E_t and should be contained within the estimated error in the latter of ± 0.05 eV. $f(t)$ was calculated for a range of different E_t, v and Gaussian widths σ. Eq. (1) can be reduced to a quadratic form to find $x_d(t)$ and hence calculate the variation of C with t. A fit to the results is then obtained by varying V^* and N_t. The relative permittivity was taken to be $\varepsilon_r = 3.8$, as previously measured [12]. N_{DOS} was taken as 8×10^{20} cm^{-3} as previously calculated [11].

Fig. 3 shows the fit of our model to the transient shown in Fig. 2. An excellent match is obtained for this data as, indeed, was also the case for all of the other measured transients. We find that the model constrains the Gaussian width σ to be 0.10 ± 0.02 eV. Theoretical modelling suggests that for the charge transport states, σ should be 1.5 times greater than that for the neutral exciton excited states [4]. Spectral dispersion measurements of PPV give a Gaussian distribution of neutral exciton excited states with a width of 0.08 eV [3]. This implies a charge transport state σ of 0.12 eV, in excellent agreement with the results in this work.

Transients were recorded at a range of temperatures between 240 and 320 K. The lower limit was defined by the freezing out of the acceptor dopants and the upper limit by the temperature range of the cryostat. However, due to spatial variations in N_t, it was also important to avoid large changes in temperature since this would change the depth probed within the depletion region. In traditional DLTS experiments on inorganic semiconductors using a fixed rate window, the peak widths are of the order of about 40 K, so this temperature range is typical. Fig. 4 shows capacitance transients at 300, 280 and 260 K fitted to the model with a constant N_t. The value of N_a
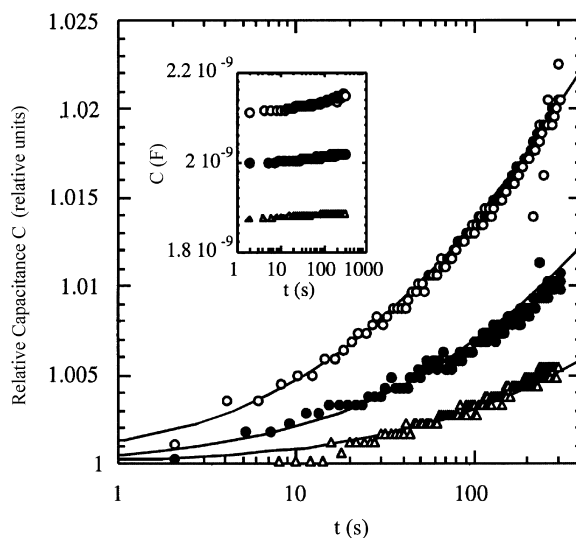

Fig. 4. Variation of relative capacitance, C_{rel}, against time, t, at 300 K (open circles), 280 K (filled circles) and 260 K (open triangles). Solid lines are fits to model at these temperatures for $\sigma = 0.10$ eV, $E_t = 0.75$ eV, $v = 10^8$ s^{-1} and $N_t = 6.0 \times 10^{17}$ cm^{-3}. Data and fits have been normalised to C of fits at $t = 10^{-5}$ s for illustration purposes. Insert shows unnormalised original data.

used at each temperature was measured directly from the corresponding C–V plots. All of the results gave a trap depth $E_t = 0.75 \pm 0.05$ eV and an attempt-to-escape frequency $v = 10^8$ s^{-1}. The value of v is large, but is in good agreement with previous estimates and values in the literature [7,11]. The trap depth deduced is in very good agreement with the energies of 0.75 and 0.8 eV found respectively from p-type carrier TOF activation and thermally stimulated current (TSC) measurements on the same Bayreuth PPV [8,15]. The TSC measurements show that the traps are due to exposure to air, in good agreement with the results shown in Fig. 1. However, oxygen is generally considered to be an n-type carrier trap in molecular materials, and given that the ionisation potential of PPV is 5.2 eV suggests that water or water combined with oxygen is the most likely culprit. We note in this context that a combined spectroscopic and theoretical examination of the influence of air on the electronic structure of PPV (prepared from a specific type of precursor polymer) identified the dominant role of water

molecules that form complexes with the polymer backbone through hydrogen bond like interactions [16].

At a distance between 30 and 50 nm from the cathode (modelled for $E_t = 0.75$ eV) N_t is found to be of order 4–7×10^{17} cm^{-3}. Capacitance transients were recorded for different quiescent bias levels at constant pulse height to determine whether there is any spatial variation in N_t. The results showed a constant increase in N_t with distance from the cathode, approximately doubling in magnitude between 40 and 56 nm.

In summary, our transient capacitance measurements show that DLTS provides a suitable means to directly probe the shape of the transport DOS in doped organic semiconductors. We have been able to very successfully model the results for PPV on the decay of a discrete bulk trap state to a Gaussian distribution of transport states. The results give the first *direct* evidence that the transport states in PPV are indeed energetically disordered and that their Gaussian width is, as expected, 1.5 times greater than that of the neutral excited states [4]. The measured Gaussian width of 0.10 ± 0.02 eV and trap depth of 0.75 ± 0.05 eV are in very good agreement with results in the literature for PPV, derived from other indirect and unrelated measurements. The positive majority carrier traps are of the acceptor type (neutral when full, negatively charged when empty) and are associated with exposure of the device to air.

Finally, we note that doped organic semiconductors with the carrier densities needed to form suitable Schottky barriers are not limited to the PPV samples reported here. Such materials are important for use in organic field effect transistors (FETs) and the information on bulk traps and interface states extracted from DLTS can be helpful in understanding their operation. The DLTS technique could be even more widely applied to organic semiconductors if dopants such as FeCl$_3$ can be used to increase carrier densities to the point that a depletion region can form at one of the interfaces.

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