

Defect states investigation in poly(2-methoxy,5-(2'-ethyl-hexyloxy)-1,4-phenylene vinylene) (MEH-PPV)

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Abstract

In this study, application of the charge based Deep Level Transient Spectroscopy (Q-DLTS) has been extended to poly(2-methoxy,5-(2'-ethyl-hexyloxy)-1,4-phenylene vinylene) (MEH-PPV) single layer diodes, whose cathode consisted of aluminium and anode of indium tin oxide (ITO). The results reveal a broad Q-DLTS spectrum, with at least two maxima, consistent with a complex distribution of trap states. Only the Q-DLTS maximum with the shortest relaxation time could be fully resolved over the temperature range used here (100–300 K), yielding activation energies and capture cross sections in the ranges 0.3–0.4 eV and 10^{-20} – 10^{-18} cm², respectively. It will be shown that this energy level is likely related to a majority-carrier (hole) trap, consistent with a Poole–Frenkel injection mechanism and p-type doping of the MEH-PPV film. The origin of the second (non-resolved) Q-DLTS peak will also be discussed.

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1. Introduction

For organic and polymer based devices, it is widely accepted that traps play a key role in the charge transport process, and hence influence the overall device operation [1]. Different techniques such as current–voltage characteristics [2], impedance spectroscopy [3], thermally stimulated currents [4], or deep level transient spectroscopy (DLTS) [5] have been used to determine the trap parameters in these materials. Two kinds of traps may exist within the bandgap of an organic semiconductor: shallow traps are those that can capture a carrier for a period much shorter than the transit time t_t while deep traps are those that can capture a carrier for a period much longer than t_t . Therefore, when a charge carrier is trapped in deep traps, it can no longer contribute to the transport. The importance of deep traps in organic materials has stimulated numerous experimental and theoretical studies in devices using these materials [6,7].

In this work, we have investigated the trap states of poly(2-methoxy,5-(2'-ethyl-hexyloxy)-1,4-phenylene vinylene) (MEH-

PPV), by using the charge based deep level transient spectroscopy or Q-DLTS [8]. This technique differs from the conventional DLTS by the measurements of the charge variation instead of the capacitance variation. The technique used here has been proved to be more precise in the determination of the trap parameters [7]. From the results, we shall discuss the influence of the present traps on the transport process using MEH-PPV as an active layer.

2. Experimental

MEH-PPV was purchased from Aldrich and used as such, without further treatment. Thin polymer films were spin-coated from polymer solution (11 mg/mL) on glass substrates, pre-coated with patterned indium tin oxide films (ITO) of sheet resistance 20 Ω/square. Prior to spin coating of the films, the ITO substrates were cleaned using trichloroethylene, followed by acetone and isopropanol. They were then rinsed in deionised water and blow dry in nitrogen. The thickness of the polymer film is ~400 nm. Aluminium was evaporated in high vacuum chamber ($\sim 10^{-6}$ mbar) to form single layer devices of active area of 7 mm². Q-DLTS experiments were carried out with a set-up already described in previous studies [7]. The spectra

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were recorded using a temperature range from 100 to 300 K in order to determine the trap energy level. All measurements were performed in vacuum, except a few current–voltage experiments, which were carried out in air as will be explained below.

3. Results and discussion

3.1. Current–voltage characteristics

Fig. 1 shows the current–voltage characteristics of an ITO-MEH-PPV-Al diode at a temperature of 300 K, both in air and under vacuum, plotted using a semi-logarithmic scale, with positive voltages applied to the ITO contact. Various models have been used to describe I – V characteristics of MEH-PPV devices. For instance, transport mechanisms have previously been discussed in term of an electrode-limited current due to a potential barrier to hole injection in the polymer layer [9]. In such a model, charge transport was thought to be controlled by field emission or Fowler–Nordheim tunnelling through the barrier. However, it has later been shown that bulk effects should also be taken into account owing to the low mobility of the charge carriers in polymer films [10,11]. Alternative approaches, describing conduction phenomena in polymer LEDs as being purely bulk-controlled mechanisms, have also proved to yield accurate account of transport phenomena [12].

In order to investigate the type of carrier transport that takes place in the devices studied here, the forward I – V characteristics shown in Fig. 1 have been plotted on a double logarithmic scale in Fig. 2. The I – V curve of the device in air can be divided into three regions, labelled A, B, and C. Regions A (below ~ 1 V) and C (above ~ 2 V) are well-described using a power law of the form: $I \propto V^\alpha$, with α taking the values 0.9 and 2.1, respectively in the case of regions A and C. The current flow can therefore be seen as nearly ohmic at low fields, and close to trap-free space-charge-limited (SCL) at higher fields, with region B being a transition region between the two regimes. The existence of region A suggests the presence of extrinsic carriers within the polymer film, which would indicate that gap states are likely present within the device. Indeed, it has

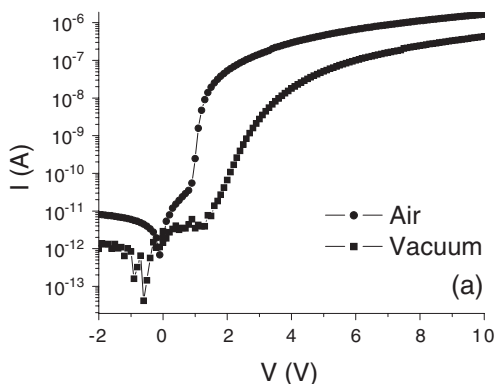


Fig. 1. I – V characteristics of an ITO/MEH-PPV/Al device measured at 300 K both in air and under vacuum using a semi-logarithmic scale.

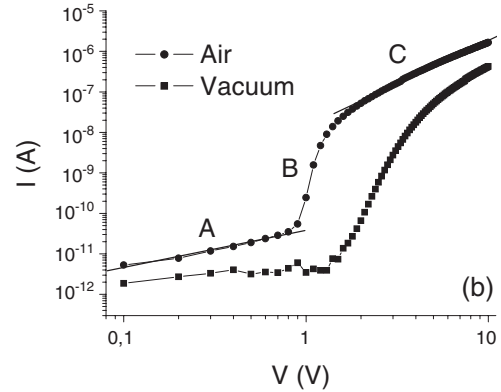


Fig. 2. I – V characteristics of an ITO/MEH-PPV/Al device measured at 300 K both in air and under vacuum using a double logarithmic scale.

been reported that exposure of polymer devices to air leads to a certain degree of p-type doping leading to a current flow at low fields, possibly controlled by the Poole–Frenkel mechanism as suggested by others [10]. Upon evacuation of the chamber, both the level of current and the shape of the I – V characteristic are significantly changed, the current intensity becoming lower when the device is placed under vacuum. The three regions described above can still be observed but the transition between regions B and C is not as sharp as when the device is in air. Instead, it is extended over a wider voltage range. Also, inspection of region A indicates that the density of extrinsic carriers has significantly decreased for the device in vacuum. Nevertheless, complete removal of traps upon evacuation is not likely, so that gap states are still expected to be present when the device is placed under vacuum.

3.2. Q-DLTS characteristics

In order to investigate the trap parameters in the devices, we performed Q-DLTS experiments on these structures. In this technique [8], a voltage pulse ΔV is applied for a short period of time t_C (charging time) to the sample, which is charged at a voltage V_0 (charging voltage) and kept at a constant temperature T . The time t_C was chosen here in order to allow complete filling of traps (see below). Next the applied voltage pulse was set to zero, so that the charges released from the traps could flow in the external circuit, resulting in a charge movement that could be measured in a time interval defined by two times t_1 and t_2 . As the variable, it is most convenient to use the time window τ defined by:

$$\tau = (t_2 - t_1) / \ln(t_2/t_1) \quad (1)$$

The Q-DLTS spectra were then obtained by plotting the charge transient $\Delta Q = Q(t_2) - Q(t_1)$ as a function of the time window. It can be demonstrated that the $\Delta Q(\tau)$ plot shows a maximum when the window rate τ^{-1} matches the emission one, assuming an exponential variation of the charge transient as a function of time. Under such an assumption, the trapped charges emission rate e is given by:

$$e = \sigma \Gamma T^2 \exp(-E_a/kT) \quad (2)$$

where E_a is the activation energy, σ is the capture cross section, and Γ is a constant. Both E_a and σ can then be determined respectively from the slope and intercept with the y -axis of an Arrhenius plot of the form $\ln(eT^{-2})$ versus $1/T$.

Fig. 3 shows the Q-DLTS spectra of an ITO/MEH-PPV/Al structure charged using a constant $V_0=0$ V and a pulse $\Delta V=10$ V, for different charging times t_C . It can be seen that the Q-DLTS spectra display two distinct peaks, denoted as peak I and II, and have an intensity which depends on t_C . Peak I becomes saturated when t_C reaches 500 ms whilst peak II is still growing for the maximum t_C of 1 s used here. This result suggests that the traps corresponding to the lower values of the time window τ (type I) can be entirely filled. However, traps of type II could not be filled even when using the maximum available $t_C=10$ s of the experimental set-up.

The parameters of the type I traps were then determined by recording the Q-DLTS spectra as a function of temperature. Fig. 4 shows the evolution of the spectra in the 250–310 K range for $V_0=0$ V and $\Delta V=10$ V. We note that at low temperatures, the relaxation time becomes longer. Furthermore, the Arrhenius curve derived from the data shown in Fig. 3 (see inset) yields a good straight line, indicating a thermally activated process with an activation energy $E_a=0.41$ eV and a capture cross section $\sigma=2 \times 10^{-18}$ cm². From the maximum amplitude of the Q-DLTS signal, the trap density N_t could also be evaluated [7,8] and was found to be approximately 1.5×10^{15} cm⁻³. By repeating the experiment at lower bias and using other samples, we obtained a distribution of the trap parameters in the ranges 0.3 to 0.4 eV and 10^{-20} to 10^{-18} cm² for the activation energy and capture cross sections, respectively.

It is interesting to discuss briefly the nature of the Q-DLTS peaks observed in these experiments. The barrier to electron injection at the cathode of ITO/MEH-PPV/Al devices has been reported to be 1.3 eV, whereas the one for hole injection at the anode is much lower, varying within the range 0.2–0.7 eV,

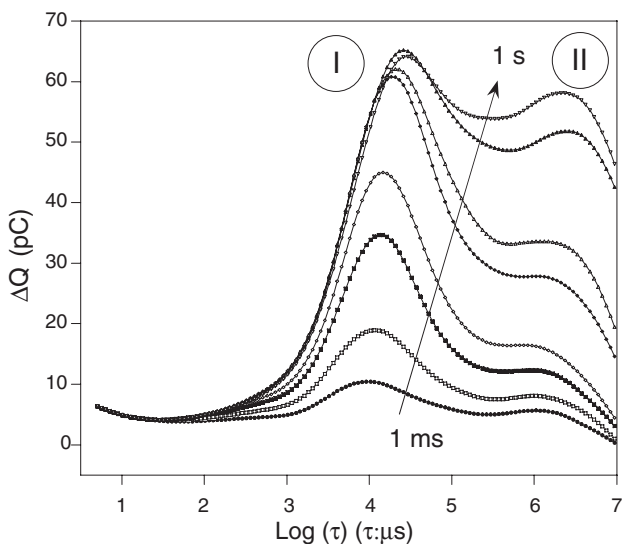


Fig. 3. Q-DLTS spectra obtained from an ITO/MEH-PPV/Al device at 300 K under vacuum using a charging voltage $V_0=0$ V, a voltage pulse $\Delta V=10$ V and different charging times t_C from 1 ms to 1 s.

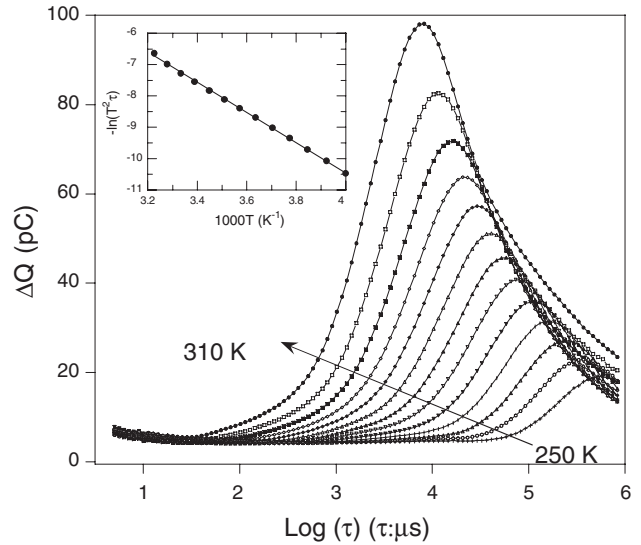


Fig. 4. Q-DLTS spectra obtained from an ITO/MEH-PPV/Al device under vacuum using a charging voltage $V_0=0$ V, a voltage pulse $\Delta V=10$ V, a charging from $t_C=1$ s for different temperatures within the range 250–310 K. Inset: Arrhenius plot derived from the data shown in Fig. 3.

depending on the preparation method of the ITO surface [11]. Besides, it is known that MEH-PPV is essentially a hole transporting material. Therefore, the current flow in the devices studied here is likely due essentially to holes, so that if traps are being filled upon carrier injection, they are more likely to be hole traps rather than electron traps. Thus, both Q-DLTS peaks of type I and II can preferentially be assigned to a flow of positive charge (i.e., holes) within the device. Note, however, that polymers are known to have low carrier mobility values, resulting in relatively long dielectric relaxation times, so that a contribution of the free charge to the Q-DLTS signal is not ruled out, as has recently been observed in the case of capacitance–voltage measurements [13]. Nevertheless, a contribution of extrinsic carriers to the current flow, as inferred from the above I – V characteristics, is consistent with a hole, acceptor-like trap. The activation energies of 0.3–0.4 eV found here for the type I peak compare favourably with the one of 0.3 eV reported for MEH-PPV devices on the basis of capacitance transient measurements, and also assigned to a majority carrier trap [14]. In contrast, assignment of peak II is made more difficult since it could not be completely resolved from the measurements made here. However, we note that this peak has a long relaxation time and could therefore be related to deeper traps. In addition, because of the hole-only character of the devices used, they would also be hole traps. In fact, deep hole traps have also been proposed as a feature of the band scheme of MEH-PPV [14].

4. Conclusion

The parameters of a trap distribution that exists in the active layer of MEH-PPV hole-only devices have been determined by using the Q-DLTS technique. It was shown that hole traps with a density of 10^{15} cm⁻³ and an activation energy of about 0.4 eV are likely present in the polymer film. Such defects

may be responsible for the presence of extrinsic carriers within MEH-PPV films, as observed from inspection of the I – V characteristics at low fields. They could then contribute to the conduction mechanisms by adding a Poole–Frenkel component, at least in the case of devices prepared in ambient atmosphere [10]. Deeper hole traps are also thought to be present in the polymer layer, but their parameters could not be determined in the present study.

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