Effect of electrical operation on the defect states in organic semiconductors

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Abstract We have investigated the role of the trapping process in degradation mechanisms of poly(9,9-dihexyl-fluorene-co-N,N-di(9,9-dihexyl-2-fluorenyl)-N-phenyla-mine) (PF) based diodes, after aging (at half lifetime) by electrical stress. By using the Charge based Deep Level Transient Spectroscopy, we have determined the trap parameters in PF light emitting devices. The mean activation energies of the traps are in the range 0.13–0.60 eV from the band edges with capture cross sections of the order of 10^{-18} to 10^{-20} cm^2. The trap densities are in the range of 10^{-16} to 10^{-17} cm^{-3}. Upon aging, no new trap levels have been found indicating that the electrical stress did not create additional defect level in the polymer in contrast to previous investigations on other organic materials, which reported that the degradation of devices in humid atmosphere lead to the onset of new traps acting as recombination centers. Furthermore, aging would not affect uniformly the defect levels in the polymer. Shallow trap states (below 0.3 eV) remain stable, whereas the enhancement in trap density of deeper trap levels (above 0.3 eV) have been observed, suggesting that degradation by electrical stress leads to an increase in density of deep levels.

1 Introduction

Since the launching of the first devices using organic semiconductors on the market [1], research on applications in this field have greatly progressed in the understanding of the physical processes as well as in improving the performance of commercial products. The potential applications comprise organic light emitting diodes (OLEDs), organic photovoltaic cells (OPCs), and organic field effect transistors (OFETs). The most promising products are OLEDs, and at present, small screens equipping cell phones, mp3 players using these devices are widely available. Compared to devices using conventional semiconductors, the organic diodes suffer from a lack of long-term stability. The lifetime of organic devices is an order or two less that that of equivalent inorganic ones and requirements for many applications are in the range of at least several tens thousands of hours [2]. In order to improve the lifetime, it is essential to control the degradation processes occurring in the organic semiconductors, but these processes have not fully understood so far. Several models have been proposed to explain the degradation behaviour [3]: diffusion of metal oxide atoms from the electrode, instability of the morphology, and ionic impurities. It is however obvious that degraded organic materials would contain an important amount of defects like conventional semiconductors [4] and degradation behaviour would accompany an important change in the defect states of the active materials. Recently, defect states in OLEDs have been investigated by several groups using electrical techniques such as Thermally Stimulated Currents (TSC) [5, 6] or Deep Level Transient Spectroscopy (DLTS) [7, 8]. These results gave interesting information on trap parameters in organic materials, which have been so far studied through models based on the transport in devices [9]. In particular, the relation between degradation and traps was examined in small molecule based devices [5, 10]. It has been demonstrated that aging of the organic

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materials exposed to specific atmospheres such as oxygen or humidity may favour the formation of new defects in the active layer [5]. However, degradation experiments have been carried out in artificial conditions, i.e., intentional exposure of the material to air or specific atmosphere, and it is not possible to relate these results to operational aging effects, which result from electrical stress during the operations. Kondakov et al. [10] performed capacitance–voltage measurements on diodes aged by electrical and temperature stresses and established that positive charge carriers that were trapped at the hole injection layer/electron transport layer interface are responsible for the exciton quenching upon aging. There is, however, no quantitative evaluation of the trap parameters in this work, and it was not possible to evaluate the importance of the defect formation in degraded devices. As for polymer-based devices, and to our knowledge, no direct measurements of defects have been carried out so far to correlate the defect formation and aging processes.

We report in this work the results obtained from measurements of electrical defects or traps in polyfluorene (PF) derivative based devices. The trap parameters in freshly prepared diodes were determined by using a variation of the conventional Deep Level Transient Spectroscopy (DLTS) then compared to those having been aged to half-life by electrical stress (the device lifetime being defined as the time for luminance to decay to 50% of its initial value). From the trap analysis, we discuss the role of defects in the aging process of the material and devices.

2 Experimental

Devices of structure Indium Tin Oxide (ITO)/polyethylene dioxythiophene: polystyrene sulfonate (PEDOT-PSS)/poly (9,9-dihexylfluorene-co-N,N-di(9,9-dihexyl-2-fluorenyl)-N-phenylamine) (PF-N-Ph)/Calcium (Ca)/Aluminium (Al) were fabricated using the following procedure. On cleaned ITO coated glass, a PEDOT-PSS layer of 80 nm thick was deposited by spin coating, and annealed under vacuum at 150 °C for 1 h. The active polymer thin film of thickness $\sim$100 nm was then deposited from a 10 mg/mL solution, followed by deposition of the cathode under vacuum with a base pressure of 10^{-7} mbar. The fabricated devices were encapsulated by a glass lit using an epoxy resin.

Current–voltage-luminance characteristics of devices were measured at room temperature using a Keithley 2400 coupled with a Photo Research Spectra Scan 650 radiance metre. Charge based DLTS (Q-DLTS) experiments were performed using an Iomtek Asmec set-up. All measurements were performed under vacuum and in the dark.
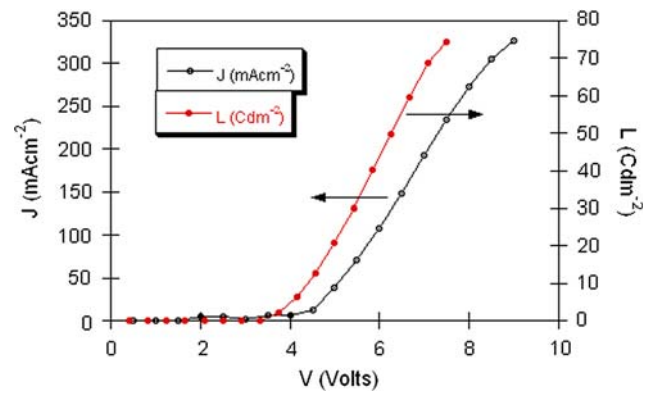

Fig 1 Current–voltage-luminance characteristics of a fresh ITO/PEDOT/PF/Ca/Al diode at T = 300 K

3 Results and discussion

Figure 1 shows the current–voltage-luminance of a freshly prepared diode at room temperature. The diode emits a blue light (λ = 444 nm) with a turn-on voltage $V_{to} \sim$ 4.5 V and a maximum luminance of L $\sim$75 cdm^{-2}. The lifetime of the diodes at this luminance was estimated to be $\sim$500 h.

In the conventional DLTS [11], traps in the semiconductor are filled by applying a voltage pulse of charging time t_c to the sample, which injects charge carriers into the sample, and changes the capacitance associated with a p–n junction or a Schottky barrier of the device. Next, the trapped charges are released in the external circuit and the variation of the sample capacitance ΔC is measured as a function of time. In the DLTS technique, detection of the capacitance change is performed by using a time window τ, which is related to the time interval between two measured times t_1 and t_2 by:

$$\tau = (t_1 - t_2)/[\ln(t_1/t_2)] \qquad (1)$$

For the Q-DLTS technique, the variation of the released charges ΔQ is measured instead of ΔC and the Q-DLTS spectrum is the plot of ΔQ as a function of τ. Whenever the rate emission $e_{n,p}$ of the trapped charges coincides with the window rate τ_m^{-1}, the charge variation ΔQ shows a maximum, provided that the ratio t_1/t_2 is constant. Trap parameters such as activation energy or trap level E_T, capture cross-section σ, and concentration N_T can be determined by measuring the Q-DLTS spectra as a function of the temperature [12].

Figure 2 shows the Q-DLTS spectrum obtained from a fresh device at T = 300 K, with an applied voltage of ΔV = +6 V, and different values of the charging time t_c. The spectra show five apparent peaks (denoted as A, B, C, D, and E) which are progressively saturated with increasing values of t_c. The relaxation time of each peak is then carefully determined from the spectra, and using these values, the decomposition of the Q-DLTS spectrum can be performed as shown in Fig. 2. The trap parameters such as activation
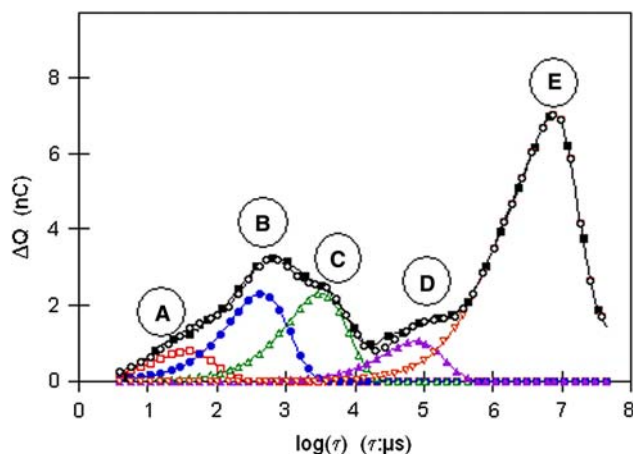
Fig. 2 Q-DLTS spectrum and resolved components of a fresh ITO/PEDOT/PF/Ca/Al diode at T = 300 K with the following experimental conditions: charging time t_c = 1 s, charging voltage ΔV = +6 V
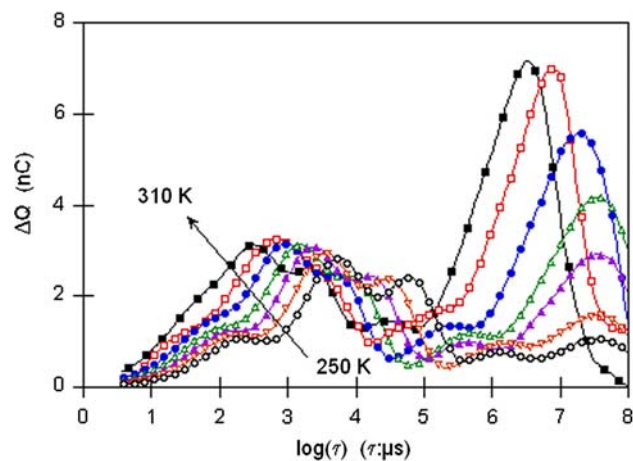

Fig. 3 Q-DLTS spectrum of a fresh ITO/PEDOT/PF/Ca/Al diode at different temperatures (250–310 K) with the following experimental conditions: charging time t_c = 1 s, charging voltage ΔV = +6 V

energy and capture cross-section can be determined by recording the spectra as a function of the temperature (Fig. 3), and by analysing the Arrhenius plot of the maximum of the spectra versus 1000/T [12] The results are given in Table 1. Previous investigations of carrier trapping in polyfluorene type polymers by using the TSC technique have shown that several trap types are present in the polymers [13]. One of these with a depth of 0.24 eV is assigned to hole traps and another with a depth of 0.6 eV is assigned to on chain keto defects, which are electron-like traps. These trap levels are comparable to those labeled B and E in our samples, although they were found distinctly in two different PF type polymers in the mentioned study. Furthermore, the concentration of different traps levels found in our devices are also in fair agreement with that estimated in recent studies on PF based diodes [14, 15].

Table 1 Trap parameters of a fresh ITO/PEDOT/PF/Ca/Al diode obtaine with a charging voltage of +6 V

Q-DLTS Peak	ΔV (V)	E_T (eV)	σ (cm^2)	N_T (cm^{-3})
A	+6	0.13	1.2×10^{-20}	1.5×10^{16}
B	+6	0.22	8.1×10^{-20}	4.4×10^{16}
C	+6	0.33	3.2×10^{-19}	4.4×10^{16}
D	+6	0.48	4.6×10^{-18}	2.0×10^{16}
E	+6	0.58	1.8×10^{-18}	1.4×10^{17}

The accuracies of parameter measurements are: $\Delta E_T = \pm 0.03$ eV; $\Delta\sigma/\sigma = \pm 0.5$; $\Delta N_T/N_T = \pm 0.3$

In order to determine the trap states in degraded devices, the fresh diode was electrically aged at half-life, and Q-DLTS measurements were performed under identical conditions as for the fresh device. Figure 4 shows the Q-DLTS spectra obtained in a device before and after aging at T = 300 K, with an applied voltage of +6 V, and a charging time of 1 s.

It can be seen that in the aged sample, the DLTS spectrum is similar in shape to that of the fresh one. Only some peaks has increased in intensity, but no new peaks are observed in the spectrum, indicating that the degradation of the sample is not accompanied by formation of new type of defects in the diodes. The trap parameters of the aged device were determined by using the same analysis as previously described and the results are shown in Table 2. It should be noted that in our experiments, the devices were aged during their normal operations and were not exposed to air. Therefore, it may be inferred that there is no direct relation between degradation processes in the studied devices and oxidation of the materials as suggested several previous investigations [16–18], and exposure of devices to air may artificially introduce defects to the material structure. We suggest that the aging increases the amount of
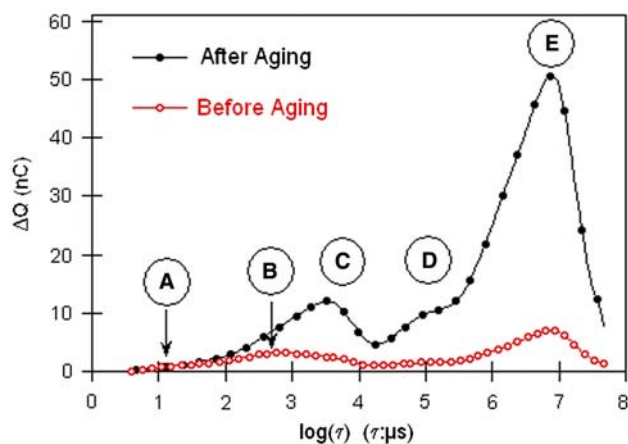

Fig. 4 Q-DLTS spectra of a fresh and an aged ITO/PEDOT/PF/Ca/Al diode at T = 300 K, with the following experimental conditions: charging time t_c = 1 s, charging voltage ΔV = +6 V

Table 2 Trap parameters of an aged ITO/PEDOT/PF/Ca/Al diode obtained with a charging voltage of +6 V

Q-DLTS Peak	ΔV (V)	E_T (eV)	σ (cm^2)	N_T (cm^{-3})	Ratio N_T aged/N_T fresh
A	+6	0.14	1.7×10^{-20}	1.5×10^{16}	~ 1
B	+6	0.25	1.0×10^{-19}	5.4×10^{16}	~ 1.2
C	+6	0.34	4.1×10^{-19}	2.1×10^{17}	~ 4.8
D	+6	0.49	5.5×10^{-18}	1.1×10^{17}	~ 5.5
E	+6	0.58	1.8×10^{-18}	9.6×10^{17}	~ 6.9

The accuracies of parameter measurements are: $\Delta E_T = \pm 0.03$ eV; $\Delta\sigma/\sigma = \pm 0.5$; $\Delta N_T/N_T = \pm 0.3$

existing defects (intrinsic defects) in material and/or devices without modifying their nature. In other words, the degradation results from a replication of structural defects under the working conditions of the device. In fact, trapping of carriers involves an amount of energy equal to the energy difference between two levels. When this energy is dissipated in the material, it causes structural damages to the region around the trap sites, and increases therefore their density. The available energy can also be transferred to a free charge carrier, making it more energetic and then can dissociate a molecule into radicals, which create then new traps. This explanation is consistent with the constancy of the different trap levels observed in fresh and aged devices. The nature of the defects in polyfluorene and its derivatives is not fully known. Previous studies have suggested that keto could be a source of defects in PF [19, 20], and the formation of fluorenone in devices were related to the decrease in performance. Furthermore, the degradation turns the blue emission color into a blue green one, which is not desirable. However, the devices in question were operating in air and were not protected, and oxidation and photo-oxidation of the material occurred. It is not excluded that such defects could exist in our samples and are introduced into the polymer during synthesis, but other defect formation possibilities, for instance interface instability [21], or structural disorder [22] have to be also considered, and further investigations are needed to clearly identify the nature of these defects.

4 Conclusion

The defects in PF based light emitting diodes have been examined by using the charge-based Deep Level Transient Spectroscopy technique. The Q-DLTS spectra of freshly fabricated ITO/PEDOT-PSS/PF/Ca/Al devices indicate five distinct levels with a density in the range of 10^{16} to 10^{18} cm^{-3}. After aging of the encapsulated devices by electrical stress, the decrease in performance of the diodes is accompanied by a noticeable increase in the density of several trap levels, but no new defect levels were observed. We suggest that the degradation of the copolymer is closely linked to the enhancement of the defects in these materials, and there is no evidence that these defects are directly introduced by oxygen with the formation of keto sites, as suggested previous studies.

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