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Electronic levels in MEH-PPV

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Abstract

pn-Junctions of MEH-PPV on top of heavily doped n-type silicon were used in electrical measurements. Through deep-level transient-spectroscopy (DLTS)-like measurements, four traps (two majority and two minority traps) could be identified on top of the shallow acceptor level responsible for conduction. Furthermore, evidence is found for interface states. © 2000 Published by Elsevier Science S.A. All rights reserved.

Keywords: Polymers; Traps; DLTS; MEH-PPV

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1. Introduction

One application of conjugated polymers is the active material in LEDs and — ultimately — in electronic displays. To control the efficiency of such devices, it is important to have a knowledge of all the impurities, which can act as non-radiating recombination centers, thus, killing the electro-luminescence. While deep-level transient-spectroscopy (DLTS) is the most common technique for the characterization of electronic levels in semiconductors, it is actually of limited use for polymers because they suffer from low-carrier mobility, series-resistance effects, and non-exponential decays. For materials impaired by these drawbacks, it is preferred to use a precursor method of DLTS based on analyzing the complete decay curve of the capacitance, instead of using a windowing technique, which uses only a fraction of the data [1]. Furthermore, low-frequency AC-probing of the capacitance is needed and the transients should be recorded in the order of minutes, rather than milliseconds. For these reasons, commercial DLTS equipments, normally operating at 1 MHz, cannot be employed. In this work, we demonstrate the usefulness of low-frequency capacitance-transient techniques in determining trap levels in poly[2-methoxy, 5-ethyl-(2′-hexyloxy)-*para*-phenylenevinylene], MEH-PPV.

On the other hand, even if we have full control over the recombination paths, the performance of the LED is still limited by the balance of carriers of both types injected into the active region. In the current work, we show how we find evidence for the injection of minority carriers from the n-type silicon into the polymer.

The MEH-PPV used in this study was deposited by spin-coating onto heavily doped n^+-silicon substrates. The films were roughly 1-μm thick. Although just before deposition, the silicon was etched in diluted HF, a thin oxide layer (≤ 30 Å) cannot be excluded, creating effectively an MIS tunneling structure. On top of the polymer, circular electrodes of gold were evaporated (2-mm diameter). The capacitance transients were recorded on a Fluke PM 6306 RCL meter, while the *I–V* curves were acquired with a Keithley 487 voltage source/picoammeter. The temperature was varied in the range of 100–300 K.

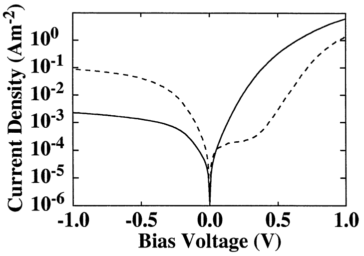

Fig. 1. *I–V* curves of a device (Si/MEH-PPV/Au) before (dashed) and after (solid) placing in vacuum for several weeks.

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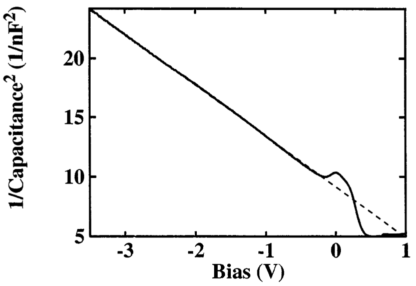

Fig. 2. Mott–Schottky plots, $1/C^2$ vs. V, of the device after 2 weeks in vacuum, recorded at an AC frequency of 1 kHz. From the reverse bias data, an ionized acceptor concentration of 6.6×10^{15} cm^{-3} can be derived (assuming $\varepsilon_r = 5$), see the dashed line.

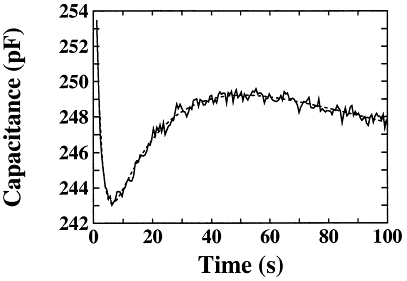

Fig. 3. An example of a complex capacitance transient that reveals three trap levels: a fast and a slow minority-carrier trap and, in between, a majority carrier trap. The transient was recorded at -5°C after switching the voltage from 0 to -1.4 V.

Fig. 1 shows the I–V curves of a device before and after placing it for several weeks in vacuum. The original scan shows a plateau and rectification inversion over a small voltage range, which are normally associated with a minority-carrier behavior in MIS tunnel diodes. Minority-carrier injection occurs when the Fermi level at the interface is closer to the minority-carrier band than to the majority-carrier band [2]. This is likely caused by the pinning of the Fermi level at interface states. The solid curve in the same figure shows that the effects are removed by the persistent vacuum conditions showing that they are related with species present in the air. Our forthcoming publication will give more details on this minority-carrier effects. Capacitance–voltage measurements indicated a free carrier density of 7×10^{15} cm^{-3} at room temperature (see Fig. 2).

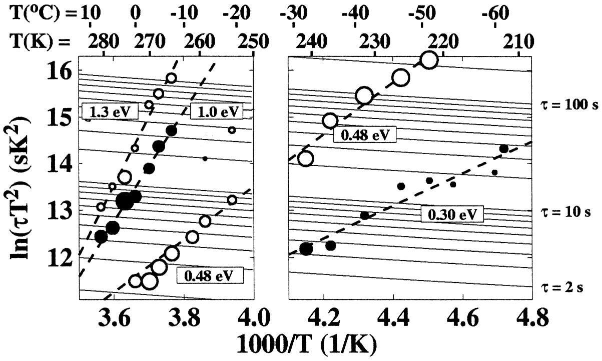

Fig. 4. Decay times, τ, as a function of temperature for two runs. Solid circles denote majority-type transients, while open circles indicate minority-type trap levels. The area of each point is proportional to the transient amplitude ($\times5$ in right plot). From this plot, the trap level depths E_a can be determined according to Eq. (1).

Table 1
Level depth data

Label	Type	Energy (eV)
AF0	acceptor	0.12
AF1	majority	1.0
DF1	minority	1.3
AF2	majority	0.30
DF2	minority	0.48

Two of the devices have been subjected to a voltaic capacitance-transient study. In this, the bias voltage of the device is suddenly changed and the capacitance is monitored over time. The capacitance depends on the amount of charge stored in the interface region on the levels. Charges can rapidly be emitted from shallow levels and the corresponding capacitance changes fast upon the bias switch, whereas deep levels can be recognized by a slow capacitance transient. The emission rate e_n, the reciprocal of the transient time τ, depends on the level depth E_a and the temperature T [3]:

$$\epsilon_n = 1/\tau \propto T^2 \exp(-E_a/kT), \tag{1}$$

Furthermore, majority trap levels show themselves as a ''restoring'' transient; the initial fast change of the capacitance due to the dopant (acceptor) level is partly undone when the charges are emitted from the deep levels. This is in contrast to the transients from minority traps, which have a transient that has the same sign as the initial fast response.

In this work, a series of transients was recorded at different temperatures, ranging from 100 to 300 K. To each transient, a curve was fitted that consisted of a limited number of exponential decays (up to three). Fig. 3 shows

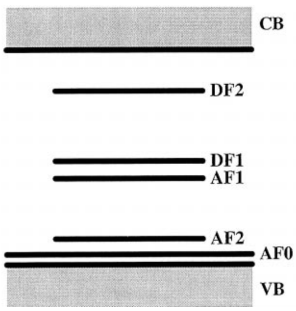

Fig. 5. Summary of the levels found in the capacitance-transient study. See also Table 1.

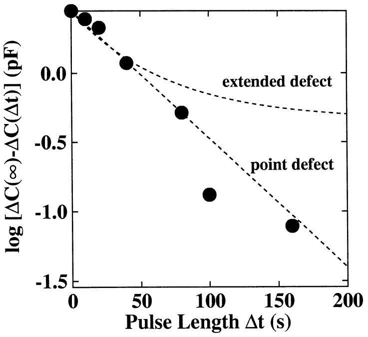

Fig. 6. Pulse-length dependence of the transient amplitude revealing that the corresponding level AF1 originates from a point-like defect rather than an extended defect.

an example of a complex transient with a triple-exponential behavior. In the few cases where the number of exponentials was not clear or when the quality of the fit was bad, the data were rejected. The trap level depths were then determined by fitting Eq. (1) to the series of decay times (τ) found (see Fig. 4). Table 1 summarizes the levels found in this capacitance-transient study, and Fig. 5 shows the relative energetic position in the band gap of MEH-PPV. It also shows the shallow acceptor level depth held responsible for the conduction, which was found in the temperature dependence of the lost tangent.

At room temperature, the temperature is stable enough to determine the nature of the defect responsible for the transient. For single-charge point-defects, the amplitude of the transient $\Delta C(\Delta t)$ depends exponentially on the filling pulse width Δt (the time spent at 0 V before switching back to -1.4 V), while for multi-charge (extended) defects, every charge trapped makes the transient slower [4,5]. A plot of log[$\Delta C(\infty)$-$\Delta C(0)$] vs. Δt will be a straight line in the former case, while it will bend upwards for the latter. The data in Fig. 6 show that the trap level AF1 originates from a point-like defect.

In summary, it has been shown that a successful DLTS-like experiment can be performed on MEH-PPV. Apparently, the measurement technique designed for the classic semiconductors (Si, GaAs, etc.) also works very well for conjugated organic materials, although the transients are in a different time regime (minutes, rather than milliseconds) and a lower AC-probing frequencies has to be employed. Four new trap levels have been found. At the moment, their microscopic identification and their role in the reduction of luminescence are not yet clear. Future studies will try to resolve that.

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