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Determination of deep and shallow levels in conjugated polymers by electrical methods

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Abstract

Conjugated organic semiconductors have been submitted to various electrical measurement techniques in order to reveal information about shallow levels and deep traps in the forbidden gap. The materials consisted of poly[2-methoxy, 5 ethyl (2′ hexyloxy) paraphenylenevinylene] (MEH-PPV), poly(3-methylthiophene) (PMeT), and α-sexithienyl (αT6) and the employed techniques were IV, CV, admittance spectroscopy, TSC, capacitance and current transients. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Conjugated polymers have in common that you can locate a path with alternating single and double bonds somewhere in the molecule. The double bonds are made of overlapping p-orbitals which are relatively easily broken up. This makes the material (semi)conducting if it is possible to swap the position of the single and double bonds. The electrons are then delocalized along the backbone of the molecule. Furthermore, the π orbitals on neighboring molecules overlap with each other, especially when the molecular structures are flat, and therefore conduction can occur in three dimensions.

One of the most promising applications lies in the active element in displays and sensors. Because of the vast number of possible organic materials, they can be made to meet any requirements. For example, MEH-PPV has a band gap of approximately 2.5 eV and blue LEDS and detectors can be made from them. In fact, full-color displays, using three primary colors close to the CIE standards, and full-color scanners have already been made. They can also be used in for instance product tagging. In these low-end applications, silicon is overqualified for the job and their production cost prohibitively expensive. The great advantage that polymers offer is that they are easy to fabricate directly from solution and in contrast to inorganic semiconductors do not need surfaces with regularity at the atomic level; they do not have dangling bonds. Compare for instance the fabrication of our MEH-PPV devices, which were made by spin coating in ambient conditions (room temperature, room pressure and daylight) to the costly fabrication of GaN thin films or bulk crystals — a competitor for the blue LED. The thin GaN films require expensive MBE equipment running with ultra-high vacuum and well controlled environments, whereas the bulk materials require huge pressures. It is clear that the organic materials will be highly competitive in the consumer-electronics market of the future.

Semiconductor polymers still suffer from some problems. Most of these problems are caused by a lack of

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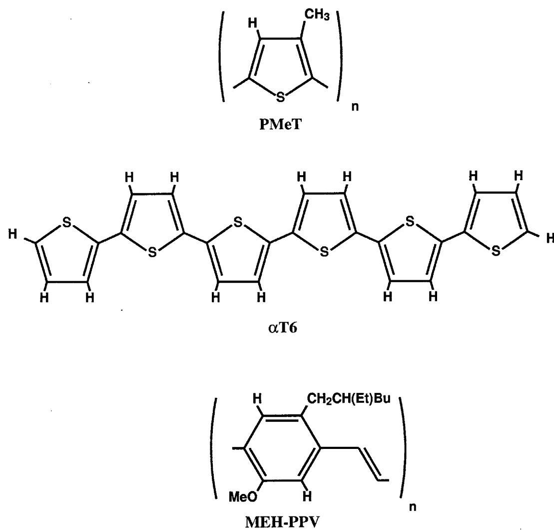

Fig. 1. The organic compounds studied in the current work. All contain a path along which the double and single bonds alternate. This causes delocalization of the charges and high conductivity.

understanding and control of the material properties. For instance, mid-gap states in wide-band-gap semiconductors have extremely long filling and emptying times. Hence, the understanding and possible elimination of these traps are mandatory for high-quality electronic devices. In the current work we review the possible experimental tools useful for the characterization of these novel semiconductors, especially applied to the deep and shallow levels. We will show how we can apply most of the standard techniques when we use them with care. Some critical remarks are placed where necessary.

The materials studied in the current work are PMeT (made by the Bangor group), MEH-PPV (made in Cambridge), and αT6 (made in Bologna). Fig. 1 summarizes these. Both PMeT and MEH-PPV are polymers with very long chains, while αT6 is an oligomer — a 'polymer' with constant, short chain length. These are just some examples of the vast number of possible structures.

2. Experimental details

The devices of the polymer PMeT were made by electro-polymerization, MEH-PPV by spin-coating the solution onto the substrates, and αT6 was deposited by vacuum sublimation. For the semiconductor/Al Schottky barriers the substrates were gold-coated glass plates where the gold-semiconductor interfaces produce good ohmic contacts. The aluminum electrodes where then vacuum sublimated on top of the polymers. For the hetero-junctions of silicon and the semiconductors, the substrates were heavily doped, n-type silicon single crystals. In that case, gold electrodes were made on top of the semiconductor. Circular electrodes with diameters of 1 and 2 mm were used.

After fabrication, the devices were exposed to air for long times before they were put in the measurement vacuum chamber. Gold wires were glued with silver paint to the substrate and the top electrode of a device. The chamber was then evacuated to 10^{-5} mbar so that it could be cooled or heated in the range 100–400 K. The temperature was measured with a thermocouple connected to a Keithley 2000 multimeter or a platinum, 100-Ω-standard resistor connected to an Oxford ITC 601 temperature controller. In either case, the sensor was placed close to the device to ensure accurate reading. The DC measurements were made with a Keithley 487 voltage source/picoammeter and the AC measurements (conductance G and capacitance C) were done on a Fluke PM6306 RCL bridge.

3. Results and discussion

3.1. Current–voltage measurements

The IV curves of all the three materials show good rectification ratios up to 10 000 at ± 1 V. In most cases the ambient conditions have a huge effect on this. For one device of Si/MEH-PPV, for instance, we found how prolonged vacuum conditions can increase the rectification ratio from 16 (see Fig. 2) to 2600 [1]. For the heavily-doped PMeT devices hysteresis effects can be observed which are attributed to the normal (depletion) capacitance discharge currents, $J_C = C\,dV/dt$ (with the term containing dC/dV ignored). This current is visible when it is large compared to the normal DC conductance.

The devices made from the hetero-junctions with silicon all show a plateau in the IV curves — a range of reduced voltage dependence of the current. This we ascribe to the presence of a substantial minority-carrier

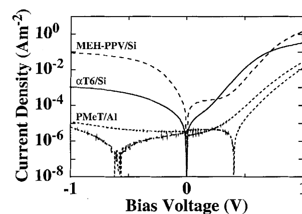

Fig. 2. Some IV curves of the studied materials. For the PMeT device a full-loop was made at a scanning speed of 1 mV/s and the observed hysteresis indicates a DC capacitance of 18 nF. The IV curves of the hetero-junctions both show a kink in the forward-bias range which we attribute to minority-carrier currents.

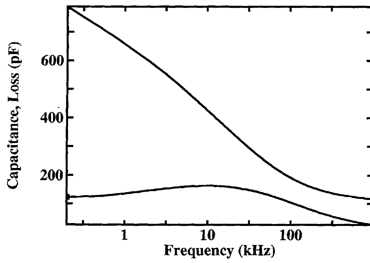

Fig. 3. Typical spectrum for a PMeT/Al Schottky barrier. The top trace shows the capacitance and the bottom trace shows the loss as a function of frequency. Up to the lowest frequencies the capacitance depends on the frequency indicating the presence of very deep level(s).

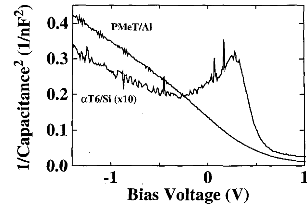

Fig. 4. Typical Mott–Schottky plots for a PMeT/Al Schottky barrier (at 200 Hz) and an αT6/Si hetero junction (at 60 Hz). The slope of the former indicates very high acceptor densities ($N_A = 10^{17}$ cm^{-3}). For reverse biases the slope changes slightly, indicating the presence of (a single) abundant deep level. For the hetero-junctions a peak is observed in forward bias, which can be assigned to minority-carrier currents.

(electron) current injected by the n-type silicon near zero bias [1]. Such currents are needed for good light-emitting devices where both types of carriers have to be brought together in the active region.

3.2. Admittance spectroscopy

Evidence for deep levels can be found in the measured capacitance (C) and loss (G/ω) as a function of the frequency. In the presence of only shallow levels, the measured capacitance should be flat up to a certain frequency, after which the measured capacitance switches to the much smaller value of the device-geometrical capacitance. In the presence of deep levels, the flat part of the C versus ω plot changes to a sloped part because the deep levels increasingly contribute to the capacitance when the frequency is lowered. Fig. 3 shows a typical plot of C and G/ω versus frequency for a PMeT/Al Schottky barrier. Up to the lowest frequencies the capacitance depends on the frequency, indicating deep levels present in the forbidden gap. For MEH-PPV and αT6 this effect is much smaller; the levels are more shallow here.

Note that at the frequency where the capacitance changes from the depletion value to the bulk value, the loss and the loss tangent $G/C\omega$ have a local maximum. The exact position of this peak depends reciprocally on the bulk resistance. Hence, from the temperature dependence of the value of this frequency we can determine the bulk activation energy [2]. For PMeT this energy was very high (0.47 eV) while for both MEH-PPV and αT6 this energy is 0.12 eV. The latter has to be placed in strong forward bias in order to be able to observe the peak.

3.3. Capacitance–voltage measurements

More evidence for deep levels can be found in the Mott–Schottky plots ($1/C^2$ versus V). The slope in a Mott–Schottky plot reveals the acceptor concentration, N_A. Note that in the presence of deep levels the slope can change with the bias, namely for voltages that put the Fermi level below the deep level somewhere in the depletion region. Fig. 4 shows such a plot with two different slopes for reverse and forward bias. This particular plot reveals a large acceptor concentration of $1–1.5 \times 10^{17}$ cm^{-3}. For both MEH-PPV and αT6 the plots are similar in shape, but the concentrations are typically an order of magnitude lower. For PMeT we also found that the apparent concentrations change when the device is placed under strong biases. After placing the device in strong forward bias for 20 min the slopes decrease and the apparent concentrations increase [2,3]. This is contradicting the common belief that the dopant ions in electro-deposited polymers can move under strong electrical fields. In that case the slopes would change in the other direction. What the cause is for the change in apparent acceptor concentration is not clear at this moment.

In the Mott–Schottky plots of the hetero-junctions (αT6/Si and MEH-PPV/Si) we observe on top of the linear behavior as described above some peaked structure in the small-bias range. This reduced capacitance is accompanied by an increased conductance and can be assigned to inductive effects of minority-carrier currents [4].

3.4. Transient spectroscopy

In the transients we also find evidence for deep levels. We recorded transients of the capacitance or DC current after switching the light or changing the voltage. By the illumination or bias the deep traps can be filled with holes which are, after switching off the light or switching the voltage back to its original value, re-emitted. The characteristic decay times of the transients are the trap-emptying times and these are exponentially depending on the trap depth divided by the temperature. For PMeT we recorded the slowest response times. Even at room temperature we recorded decay times in the order of 400 s in the optical-capacitance transients. See Fig. 5 for an example of such a transient.

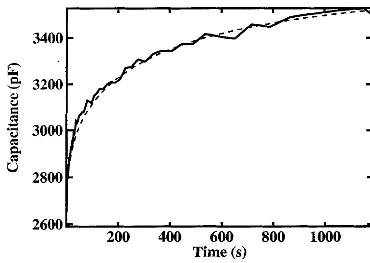

Fig. 5. Optical-capacitance transient for a PMeT/Al device. The extremely long decay time indicates a very large associated trap depth.

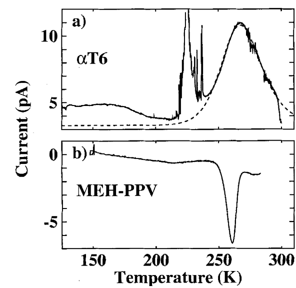

Fig. 6. TSC for αT6 (at 33 mK/s, cooled at +3 V bias) and MEH-PPV (at ca. 6 mK/s, cooled at +1 V). The peak in the former at 265 K can be related to a trap with depth 0.5 eV.

For MEH-PPV we made an extensive voltaic-transient-capacitance study and this revealed trap depths of 0.3, 0.45, 1.0 and 1.3 eV. Because here we used the n^+Si/MEH-PPV hetero junction we were able to observe both majority-carrier traps as well as minority-carrier traps [1,5]. By monitoring the transient amplitude as a function of the trap-filling time, we were able to determine that the trap that is visible at room temperature has point defect nature, rather than extended nature [1,5].

3.5. *Thermally stimulated current* (*TSC*)

For αT6 we did not find any transient response. This might be due to the fact that the cut-off frequency as described above for the loss tangents lies well below our measurement window (50 Hz–1 MHz) at 0 V and no response is expected from the interface. The best technique in such cases is to employ TSC, in which case the measurement is done at DC. The sample is cooled down at strong forward bias, thus filling all the traps. When it is warmed up without bias, the holes will be emitted when the emission time becomes appreciable. These holes drift towards the anode and a current is observed that mimics a reverse-bias current. When all the levels are emptied the current disappears again. For MEH-PPV we found a negative peak, in line with the above theory of a deep trap, see Fig. 6. The αT6 has a large positive peak at high temperatures and for this material we used the temperature controller to study it in more detail. The scanning rate dependence and overall fitting of the peak revealed that the associated trap is 0.5 eV deep.

In summary, the results presented here show that, in spite of the chemical differences between inorganic materials and conjugated polymers, the standard characterization techniques (CV, TSC and DLTS) can still be applied to these novel materials as long as care is taken. Polymers are low-mobility materials with large concentrations of deep impurities. Therefore one should use low-frequency-probing signals when doing AC measurements and long time scales when measuring transients.

Acknowledgements

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