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Analysis of deep levels in a phenylenevinylene polymer by transient capacitance methods

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Transient capacitance methods were applied to the depletion region of an abrupt asymmetric $n^+ - p$ junction of silicon and unintentionally doped poly[2-methoxy, 5 ethyl (2' hexyloxy) paraphenylenevinylene] (MEH-PPV). Studies in the temperature range 100–300 K show the presence of a majority-carrier trap at 1.0 eV and two minority traps at 0.7 and 1.3 eV, respectively. There is an indication for more levels for which the activation energy could not be determined. Furthermore, admittance data reveal a bulk activation energy for conduction of 0.12 eV, suggesting the presence of an additional shallow acceptor state. © 1999 American Institute of Physics. [S0003-6951(99)02308-6]

Poly[2-methoxy, 5 ethyl (2' hexyloxy) paraphenylenevinylene] (MEH-PPV) is an electroluminescent conjugated polymer now being developed as a material for use in display technology.^{1–5} It is well known that the luminescence is strongly affected by carrier traps which exist at energies within the band gap, and which may act as nonradiative carrier recombination centers, thus reducing the light emission efficiency. Time-of-flight measurements⁶ have shown that electrons, in contrast to holes, are strongly trapped in PPV. The resulting unbalanced electron and hole concentrations will have deleterious effects on luminescence efficiency. In addition, these deep levels may play an important role in the conduction mechanism.

Thermally stimulated currents in ITO/PPV/Al devices^{7,8} indicate the presence of several distinct gap states with energies in the range 0.05–0.2 and 0.6–1.0 eV. It was also reported⁹ that the current–voltage characteristics of ITO/PPV/Al devices can be fitted using an exponential distribution of traps with a characteristic energy of 0.15 eV. Deep traps have been assigned to the influence of the environment, while the shallow ones are assigned to doping by the ITO.⁸ However, it is clear that the microscopic nature of these trap states and their role in the charge transport need further investigation.

Although capacitance transient techniques, such as deep level transient spectroscopy (DLTS), have been acknowledged as one of the most powerful methods to detect and characterize electrically active defects in semiconductors, only a few studies¹⁰ have used these techniques to characterize semiconducting conjugated polymers. The work here represents the first use of capacitance transients to observe the thermal emission processes due to trapped carriers in MEH-PPV. In order to prime both minority and majority-carrier traps we used a p - n junction. Moreover, an abrupt asymmetric n^+ (silicon)– p (MEH-PPV) junction is preferred because the depletion layer is then mostly in the polymer side. Con-

sequently, the depletion capacitance will be more sensitive to traps in the lightly doped material, the MEH-PPV.

Thin films of MEH-PPV (0.1–0.2 μm thick) were deposited by spin coating onto n^+ -silicon substrates. Before deposition the silicon substrates were cleaned with diluted HF to remove any residual oxide layer and were rinsed several times in ultrapure water. After spin coating the films were immediately loaded into a turbopumped evaporator and gold was evaporated through a perforated mask to form an array of circular electrodes (2 mm in diameter). The devices were mounted in a temperature controlled sample holder located inside a steel chamber evacuated to less than 10^{-5} mbar. Small-signal admittance measurements over the range 50 Hz to 1 MHz were carried out with a Fluke PM 6306 RCL meter. The I – V curves were recorded with a Keithley 487 Picoammeter/voltage source. The sample temperature was varied in the range 100–300 K and measured with a chromel–alumel thermocouple placed on the substrate close to the devices. All the measurements were carried out in the dark. Despite all the precautions to minimize air exposure, it cannot be excluded that some residual oxygen was introduced during the spin coating deposition. This oxygen could have slowly diffused towards the silicon surface and created a very thin oxide layer. Such a layer offers little resistance to the passage of current, and the device may resemble a tunnel metal–insulator–semiconductor (MIS) diode.¹¹

The devices exhibit good diode behavior, with a typical current rectification ratio higher than 10^3 at a bias of $|0.5 \text{ V}|$ and an ideality factor of 1.6. Figure 1 shows the room-temperature current–voltage characteristics of a typical device. Figure 2 shows the loss (G/ω) and the capacitance (C) versus frequency at room temperature and at 116 K. The prominent loss peak and capacitance step—at 500 kHz at room temperature—is related with the RC time constant of the diode. This relaxation frequency decreases to below 1 kHz only when the device is cooled to the lowest tempera-

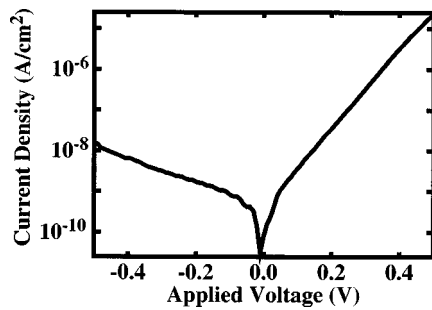


FIG. 1. I - V curve at room temperature showing the high rectification ratio (more than 1000) and ideality factor of 1.6.

tures. Therefore, using a low frequency ac voltage at 1 kHz, we can measure capacitance transients over a large temperature range, without limitations due to the diode time constant. The capacitance and conductance data plotted as a loss tangent ($\tan \delta = G/\omega C$) will show a peak at a particular frequency (ν_{\max}). It has been shown¹² that, assuming the depletion layer resistance is much higher than the bulk resistance, the temperature dependence of ν_{\max} should follow the same temperature dependence as the conductance of the bulk material. We can extract therefore the polymer bulk activation energy from the slope of a plot of $\ln(\nu_{\max})$ vs $1/T$. In our case E_a is 0.12 eV [Fig. 2(b)]. This may correspond to the shallowest ionized acceptor level responsible for conduction. From a plot of reciprocal square capacitance versus applied voltage, we estimated an ionized acceptor doping concentration of the order of 10^{16} cm^{-3} .

In obtaining trap levels from capacitance transients, it is important to pay attention to exponentiality since nonexponential decays can complicate the data analysis. The capacitance transients recorded usually show an immediate step-like response to the voltage change followed by a long-lived signal composed of, in our case, a small number of simple exponentials. The sign of the component depends on the character of the trap. For a majority trap, we expect a negative capacitance transient (upward trend), whereas the transient due to minority carrier trap is positive (downward trend).¹³

Figure 3 shows that, by an appropriate pulse scheme, it is possible to prime either the minority- or the majority-carrier trap levels. The majority carrier traps can be detected using a filling pulse of zero bias, and minority-carrier traps are revealed by injecting electrons into the polymer in a forward bias (1.0 V) pulse. A complication is that forward-

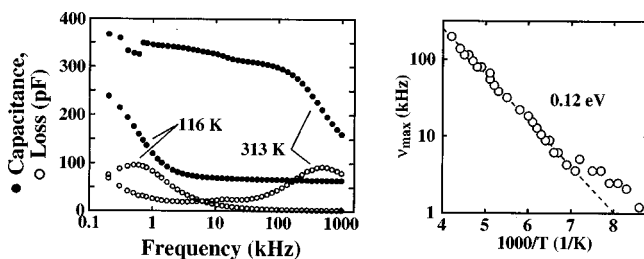


FIG. 2. (a) Capacitance (C ; solid circles) and loss ($1/\omega R$; open circles) for the two temperatures 313 and 116 K. The cut-off frequency of the diode moves from 500 to below 1 kHz. (b) Shows the position of the peak in the loss tangent ($\tan \delta = 1/\omega RC$) as a function of temperature. This reveals the bulk activation energy of 0.12 eV.

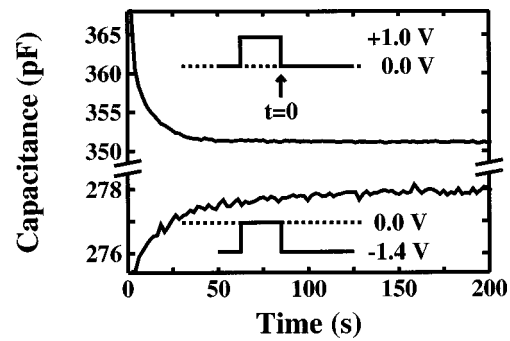


FIG. 3. By an appropriate bias pulse, the transient can be made to show a minority trap (top) recognizable by the downward trend, or majority trap (bottom) in an upward trend.

injecting bias pulses, because of the collapsing of the depletion range, can also significantly perturb the occupation of interface states (and give nonexponential contributions to the capacitance transients), which is not desirable because our interest is to prime only bulk traps. Therefore, during the experiments the sample was kept under zero bias and then subjected to a reverse step of -0.8 V . The corresponding transient capacitance under reverse bias was recorded at a series of stabilized temperatures to provide the time constants (τ).

Although we did not forward bias the p - n junction, we observe over certain temperature ranges a reversal in the sign of the capacitance change corresponding to a change from a majority-type behavior to a minority-type behavior. This reversal in the sign of capacitance change is illustrated in Fig. 4, where for a certain temperature both types of behavior are visible at the same time. The observation of minority-type transients suggests that electron diffusion from the n^+ silicon is enough to fill some minority traps in the polymer.

The activation energy of the trap is calculated by noting that the emission rate, $e_n = 1/\tau$, of the carriers from a trap of depth E_a at temperature T is given by Eq. (1) where k is the Boltzmann constant.¹³

$$e_n = 1/\tau \propto T^2 \exp(-E_a/kT). \quad (1)$$

The equation was applied to the data shown in Fig. 5. The solid and open circles represent majority and minority traps, respectively. There is a clear evidence for at least three trap levels, two minority ones (activation energies: 0.7 and 1.3 eV) and a majority one ($E_a = 1.0 \text{ eV}$). The data points related to these traps are so closely spaced, that the exact

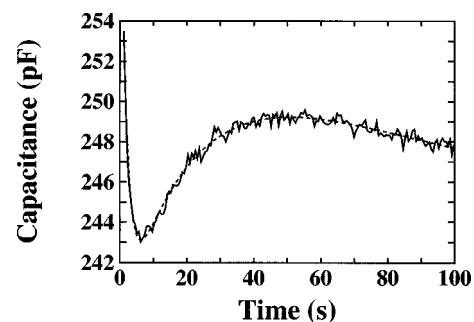


FIG. 4. When the emission rates of two traps are close enough together, transients can even have both types of behavior shown in Fig. 3 visible at the same time. The above picture reveals two minority traps and in between a majority trap.

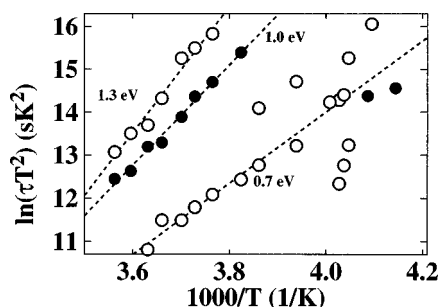


FIG. 5. Summary of the measurements. The corrected characteristic time of the transients τT^2 are plotted as a function of reciprocal temperature ($1/T$) to reveal the activation energies of the associated traps. Open circles represent minority traps while full circles correspond to majority traps.

determination of the time constants is cumbersome and depends for instance on the fitting procedure. Hence, the activation energy of the trap levels have a wide margin of error (about 0.2 eV). It has to be noted, however, that there is no doubt of the existence of the above mentioned levels.

In summary, transient capacitance spectroscopy techniques were applied to characterize carrier traps in unintentionally doped MEH-PPV. Our results show that, despite the chemical differences between inorganic semiconductors and conjugated polymers, the original junction DLTS technique proposed by Lang¹³ can be applied to these new materials. Furthermore, the use of a *p-n* junction enabled us to observe minority traps for the first time in MEH-PPV. Using this technique, a majority trap and two minority-carrier traps were found. The found activation energies agree with the values (0.6–1.0 eV) reported by others using thermally

stimulated currents in PPV prepared by the precursor route.^{7,8} The results provide evidence for more levels for which the activation energies could not be determined. Subsidiary experiments using admittance measurements gave a bulk activation energy for conduction of 0.12 eV, suggesting the presence of a shallow acceptor state.

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