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Electrical study of impurity states in conjugated polymers

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Abstract

Schottky diodes resulting from an intimate contact of aluminum on electro-deposited poly(3-methylthiopene), PMeT, have been studied by admittance spectroscopy, capacitance-voltage and current-voltage measurements, and optically-induced current transients. The loss-tangents show the existence of interface states that can be removed by vacuum annealing, also visible in the transients. Furthermore, the CV curves don't substantiate the idea of movement of the dopant ions.

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A common approach to studying impurity states in semiconductors is to measure the small transients (of current or capacitance) related to carrier capture and emission processes at the impurity states. The various DLTS techniques are good examples. Alternatively, the impurity states can be studied in the frequency domain by measuring the AC conductance of a barrier depletion-region as a function of frequency (admittance spectroscopy). In this contribution we show that the AC impedance of a Al-PMeT Schottky diode is very sensitive to the presence of surface states introduced by ambient air. The presence of these surface states also strongly affects the shape of the optically-induced current-transients. Furthermore, C-V plots are strongly influenced by placing the device in strong bias fields.

The PMeT used in this study was made by electrodeposition on a gold substrate from an electrolytic medium, as described previously[1]. On top of the 0.3 μm thick polymer, electrodes of aluminium (2 mm diameter) were deposited by evaporation to form Schottky barriers with rectification ratios up to 1000 at ±1 V. These samples were exposed to air for long periods of time prior to the electrical measurements.

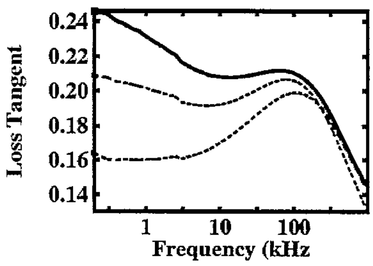

Figure 1. *Loss tangent $1/\omega RC$ as grown (top, solid) and after heat treatment at 38 °C (bottom, dashed) and airing for two hours (middle, dashed)*

The AC measurements were done on a Fluke PM6306 RCL bridge and the DC scans on a Keithley 487 Picoammeter. During all measurements, the samples were mounted in a cryostat at high vacuum (10^{-5} mbar).

Figure 1 shows tanδ (($1/\omega RC$) as a function of frequency. The as-grown device shows a significant low frequency dispersion, which can be removed by heating the device to 38°C in vacuum. After airing for two hours the low frequency dispersion partially recovers. If the device is modeled by a circuit of two RC loops in series, one representing the bulk and one representing the depletion layer[2, 3], the observed change in loss tangent after annealing is due to an increase in the depletion layer resistance R_d. The fact that this process is so fast even at low temperatures and is related to the ambient circumstances indicates that it is taking place at the surface of the device. It is likely that surface states are generated, probably owing to the presence of absorbed atmospheric oxygen.

At the same time, the optical induced current transients show a similar behavior: The as-grown sample has a complicated transient (recording I(t) after switching

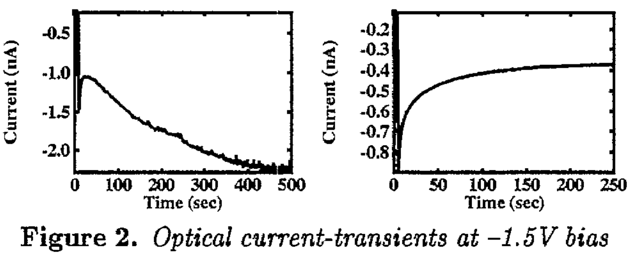

Figure 2. *Optical current-transients at −1.5V bias for the as-grown sample (left) and the annealed sample (right).*

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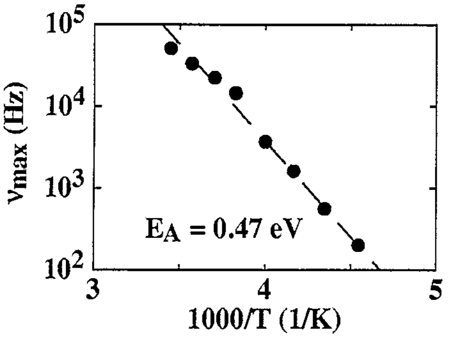

Figure 3. *Arrhenius plot of the position of the maximum of the loss tangent of Figure 1.*

the illumination) at strong reverse bias, while for the annealed device the transient becomes simple. One thing to note is that the transients have a remarkable 'square-root-exponential' behavior $I(t)=A\exp(-\sqrt{t/\tau})$, indicating extended defects with multi-charge capture; each charge feels the Coulombic field of the other captured charges and is trapped more slowly (see Figure 2).

The bulk activation energy can be evaluated from the temperature dependence of the position of the maximum of peak in the loss tangent, since it should be linearly dependent on the bulk conductance ($1/R_b = R_0^{-1}\exp(-E_A/kT)$) [1, 2]. Figure 3 shows the result: $E_A = 0.47$ eV.

One of the main criticisms about devices made from electropolymerized polymers is that the dopants can move under the influence of the strong electric fields present at the interface. We have tested this assumption by placing the device in strong reverse and forward biases and looking at the change in the acceptor concentrations. For forward biases, the aluminum electrode is placed on a negative voltage, and hence, the mostly negatively charged acceptor atoms are expected to move away from the interface, resulting in a reduction of the acceptor concentration, N_A. This concentration can immediately be seen in a Mott-Schottky plot: Since the capacitance of the depletion layer is proportional to $\sqrt{N_A/(V_{bi}-V)}$, with V the bias and V_{bi} the built-in voltage, the slope in a plot of $1/C^2$ vs. V is proportional to $1/N_A$, the acceptor concentration [4]. Figure 4 (top) gives a typical Mott-Schottky plot after placing, 'resetting', the device in strong reverse bias for 1 hour. The two slopes indicate two impurity levels ($N_A=2\cdot10^{16}$ cm^{-3}, $N_B=8\cdot10^{16}$ cm^{-3}) [1]. For different resetting voltages, the slopes are different. Figure 4b (bottom) gives a summary of this effect. For forward biases, the slopes decrease, indicating an *increase* of the acceptor concentration. This is directly opposite to what we expected on the assumption of mobility of ions. On the other hand, it seems more likely that the change in slope is due to charges trapped at the interface with extremely long detrapping times (longer than the time it takes to complete a CV measurement (1 min)).

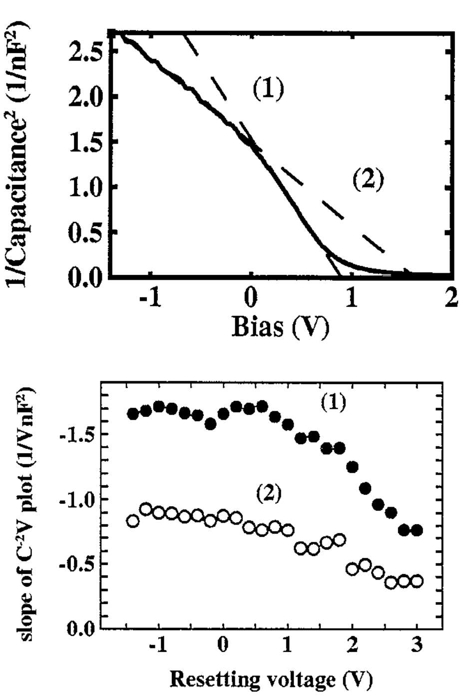

Figure 4. *Top: Typical Mott-Schottky plot after 'resetting' the device in strong reverse bias (-1.4 V). The slopes 1 and 2 are proportional to the acceptor concentrations ($1/N_A$ and $1/[N_A+N_B]$ respectively, with A and B being different acceptor(level)s [1]). Bottom: The slopes of the top plot as a function of the resetting voltage.*

In conclusion, surface states, probably due to absorbed oxygen, create a large dispersion in tanδ and have a marked effect on the shape of the optically-induced current transients. The slopes of Mott-Schokkty plots are affected by the driving field on the sample just before the C-V plot is recorded. The effect is opposite to the one expected due to movement of doping ions (PF_6^-), however. This suggests that at these doping levels the ions do not move. We argue that the changes in slopes are due to changes in occupation of surface states induced by the field.

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