Vol. 94 (1998) *ACTA PHYSICA POLONICA A* No. 3

Proc. of the XXVII Intern. School on Physics of Semiconducting Compounds, Jaszowiec 1998

ELECTRICAL CHARACTERIZATION OF SEMICONDUCTING POLYMERS

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Schottky diodes resulting from an intimate contact of aluminum on electrodeposited poly(3-methylthiopene) were studied by admittance spectroscopy, capacitance–voltage measurements and voltaic and optically-induced current and capacitance transients. The loss tangents show the existence of interface states that can be removed by vacuum annealing. Furthermore, the $C-V$ curves contradict the idea of movement of the dopant ions.

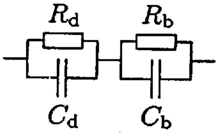
PACS numbers: 73.61.Ph, 73.40.-c

Polymers have a promising future, because they are easy to produce and their properties can be engineered to fit many requirements, for instance in lightweight large-area displays. The number of possible polymers is vast. One of the most promising ones is poly(3-methylthiopene) (PMeT). In the current study we try to shed some light on the question of the electronic properties of this material when used in a Schottky barrier.

The PMeT used in this study was made by electrodeposition on a gold substrate. On top of the 1 μm thick polymer, electrodes of aluminum (2 mm diameter) were deposited by evaporation to form in 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.

For the DC measurements ($I-V$) we made use of a Keithley 487 PicoAmmeter and the AC measurements (capacitance and AC resistance) were performed on a Fluke PM6306 RCL bridge. During all measurements, the samples were mounted in a cryostat at high vacuum (10^{-5} mbar) at room temperature.

To model the admittance spectroscopy data, we made use of a circuit consisting of two RC loops, see the scheme:



where "d" denotes the depletion layer and "b" — the bulk [1]. If $R_b \ll R_d$ and $\omega^2 R_b R_d C_d^2 \gg 1$, the loss tangent ($\tan\delta = 1/\omega RC$) of this circuit is equal to

$$\tan\delta = \frac{\omega C_d R_b}{1 + (\omega R_b)^2 (C_d + C_b) C_b}, \tag{1}$$

which has a maximum at a frequency

$$\omega_{\max} = \frac{1}{R_b}\sqrt{\frac{1}{C_b (C_b + C_d)}}. \tag{2}$$

Figure 1a shows the loss tangent spectrum of the as-grown device. The values that best fit this spectrum are presented in Table. After annealing at relatively low temperatures in vacuum, the low-frequency loss tangent is reduced, see Fig. 1b. In the fit parameters of Table it can be seen that it is mainly due to an increase in the depletion layer resistance, R_d.

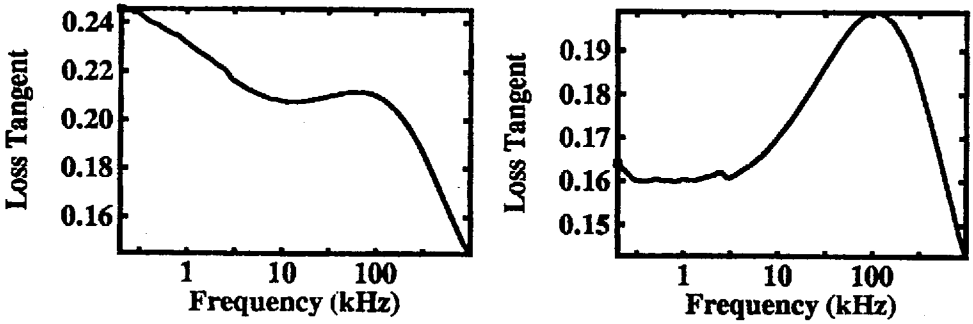


Fig. 1. Loss tangent 1/ωRC (a) as grown, (b) after heat treatment at 38°C.

TABLE

Device parameters obtained from the spectra.

	Before anneal	After anneal
R_d	1 MΩ	7 MΩ
C_d	1.5 nF	1.3 nF
R_b	2 kΩ	2 kΩ
C_b	500 pF	500 pF

This process is reversible; after airing the sample for some time (say 2 hours), the spectra change back to their original shape. The fact that this process is so fast and is related to the ambient circumstances indicates that it is taking place at the surface of the device. It is likely that interface states are generated, enabling tunneling through the Schottky barrier.

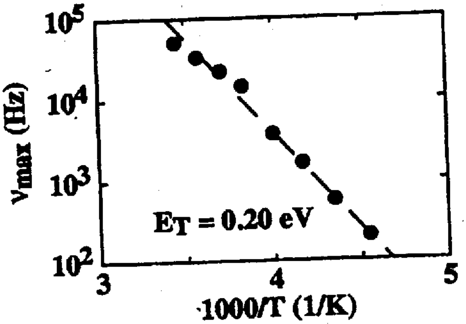


Fig. 2. Arrhenius plot of the position of the maximum of the loss tangent of Fig. 1, revealing an activation energy $E_A = 0.2$ eV.

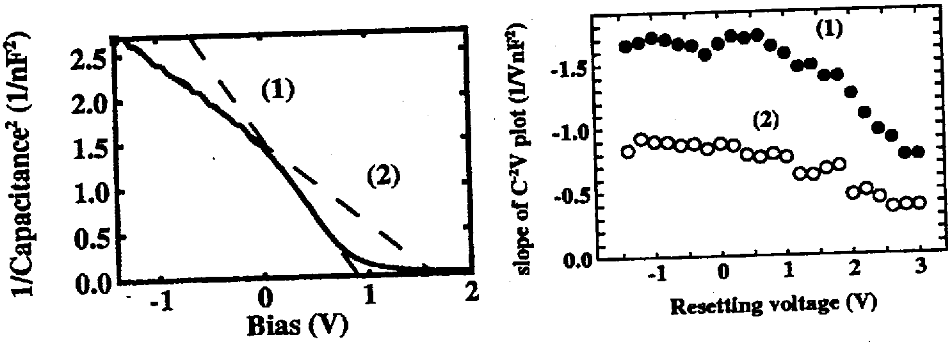


Fig. 3. Left: typical Mott-Schottky plot after "resetting" the device in strong reverse bias (-1.4 V). The slopes 1 and 2 are proportional to the acceptor concentrations ($1/N_A$ and $1/(N_A + N_B)$ respectively, with A and B being different acceptor(level)s [3]). Right: the slopes of the plot on the left as a function of the resetting voltage.

The position of the peak in the loss tangent can give valuable information about the acceptor level. If we assume that the number of free carriers in the bulk, and hence the resistance, R_b, has an exponential behavior over temperature, $R_b = R_0 \exp(E_A/kT)$, the position of the maximum of the loss tangent, according to Eq. (2), should follow the same dependence. Therefore, an Arrhenius plot of the position of $\omega_{\max}$ can reveal the acceptor level depth E_A. Figure 2 shows the result: $E_A = 0.2$ eV.

In conclusion, admittance spectroscopy, in the form of the loss tangent, can give a good identification of the quality of the interface and give an estimation of the activation energy of the acceptor responsible for the charge transport in bulk material.

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 [2]. Figure 3a 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. For different resetting voltages, the slopes are different. Figure 3b gives a summary of this effect. For forward biases, the slopes decrease, indicating an *increase* in the acceptor concentration. This is directly opposite to what we expected on the assumption of mobility of ions.

Acknowledgment

This work was supported by a European TMR grant, contract number FMRX-CT96-0083 (DG 12 – BIUO).

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