PULSE TRANSIENT METHOD USED FOR ANALYSIS OF TEMPERATURE MODULATED SPACE CHARGE LIMITED CURRENTS

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INTRODUCTION

Space charge limited currents (SCLC) plays a key role in studies of the localised energy states distribution into a forbidden energy band gap of inorganic and/or organic semiconductors. The shape (slope) of the current-voltage characteristics reflect the amount of trapped electrons (holes) injected into the semiconductor on the change of the Fermi energy level [1[1], 1[2]]. Utilising the temperature modulated space charge limited current (TM SCLC) characteristics it began to be possible to determine the energetic position of the states responsible for the electron (hole) trapping [1[3], 1[4], 1[5]]. The method was used as a semistationary: the measurement was performed as a slow temperature wobbling near the room temperature. However, the method fails when the activation energies are low ($\sim kT$) because the experimental error of the steepness determination from the Arrhenius dependence of electric current ($\ln I = \mathrm{f}(1/T)$) significantly increases in this region. In this contribution, we present a modification of the method that does not suffer such drawback. It is based on pulse transient method conventionally used to determine heat properties (diffusivity, thermal conductivity, specific heat) [1[5], 1[7]]. From the time-dependence of the electric current it is possible to both, find a window with current modulated by temperature change, but in particular, to determine the activation energy of the current, even thus is the current change very low (so-called Child's law). If higher activation energies are present, it is possible to determine the behaviour of the measured semiconductors for several temperatures.

EXPERIMENTAL

The experimental set-up is similar to the apparatus designed at the Institute of Physics, Slovak Academy of Science (Thermophysical Transient Tester 1.02). A Peltier heater with one side kept on a constant temperature is on the other side heated by square current pulse (see Figure 1). The heat is then transferred to a glass substrate with a thin film of the measured semiconducting material. The temperature of the equilibrated side of the Peltier heater is measured by platinum resistance thermometer (PRT). The differential temperature between the constant side and the temperature of the glass substrate is measured by comparatively connected thermocouples.

The impression of voltage on the semiconducting sample contacts causes the electric current flow. The time of equilibrating of the amount of the current flowing depends on the SCLC regime and on the voltage applied. At the time of partial stabilising of the electric current, the sample is heated enough to create an extra current caused by a redistribution of the electric charge inside the semiconductor. The time behaviour of the current change is proportional to the change of the sample temperature monitored by the electrometer. The measured data are automatically collected via HPIB and RS232 data bus lines during the experiment. The measurement can be performed both under vacuum and protective atmosphere of inert gas (e.g. Argon).
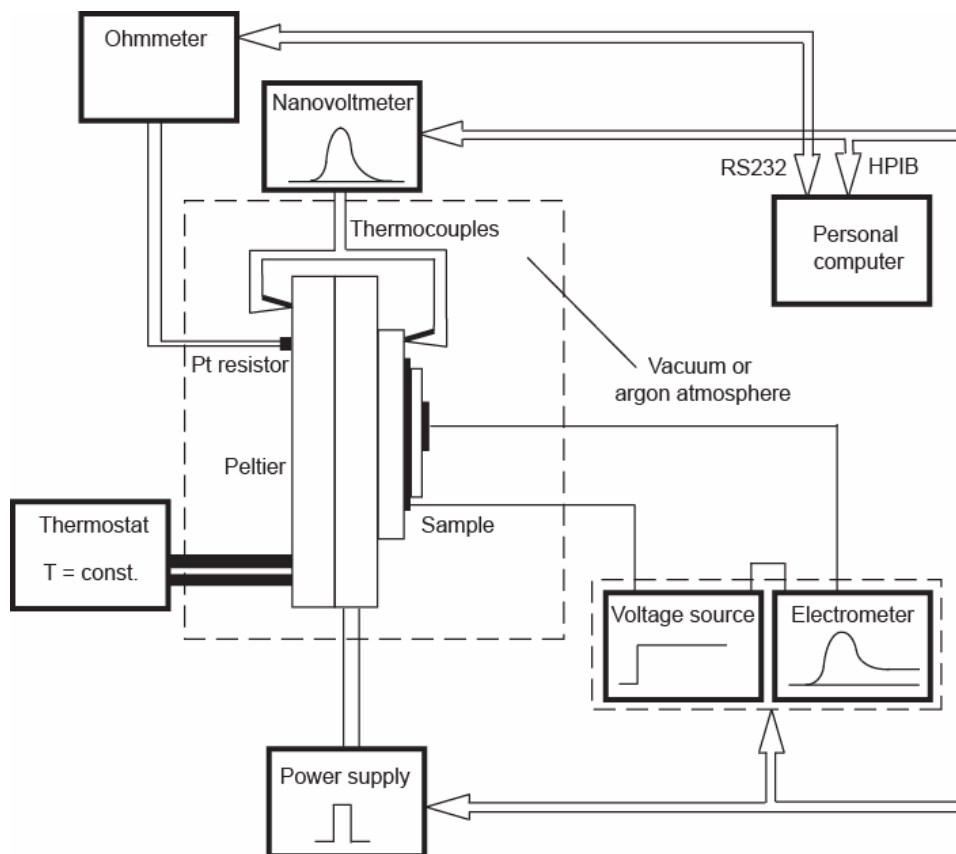
Figure 1 The apparatus for the pulse transient TM SCLC measurement. See text for further details.

RESULTS AND DISCUSSION

The organic semiconductor (derivative of *1,4*-diketo-*3,6*-difenyl-pyrrolo-[3,4-c]-pyrrol (DPP), see Figure 2 on the left) was dissolved in the mixture of toluene and chloroform (2:3). To dissolve them completely an ultrasonic bath was used. Using the spin–coating method, a thin layer of the material was prepared on a glass substrate with ITO electrode. The glass substrate was previously coated with PEDOT (Aldrich) layer to accomplish better injection of positively charged carriers (holes) into the analysed material. The sandwich structure of the sample was completed with vacuum evaporated Alq3 (to reduce the injection barrier for electrons) and aluminium top electrode (see Figure 2 in the middle. The microphotograph of the prepared DPP layer is shown in the Figure 2 on the right (20× magnified). The layer was clearly microcrystalline because of the low molecular weight of the DPP.
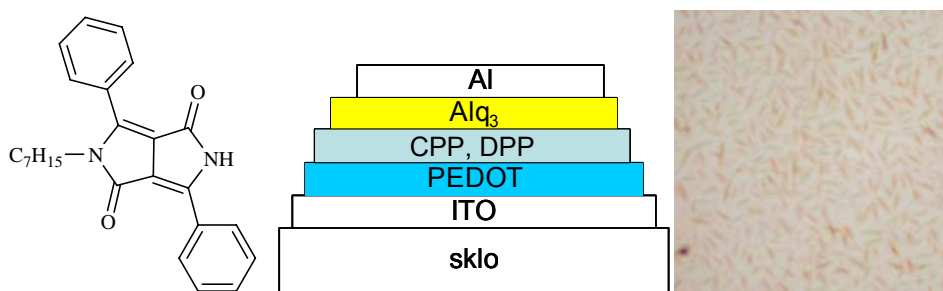

Figure 2 Left: the chemical structure of the analysed DPP, in the middle: schematic representation of the measured structure and right: microphotograph (20× magnified) of the spin-coated layer.

The measurement was performed as follows: Voltage was applied to the sample at the time $t = 0$ s. After equilibrating of the current flowing ($t = 120$ s), the sample was heated by a heat pulse from the Peltier heater. The power was typically $P = 40$ W (i.e. with energy Q = 735 J, and time $\Delta t = 18$ s). This caused a reorganisation of the electric charge between the delocalised energy states of the semiconductor (valence and conduction band), and the localised energy states (forbidden band gap). This led to a further change of the electric current I caused by the temperature change of the sample (see Figure 3). It is obvious that this change depends on the activation energy of the electric current (the energy needed to overcame the barrier between the available energy states). When the activation energy is low (~ kT) the change of the temperature has to be much larger than for samples with high activation energy (> 3kT).

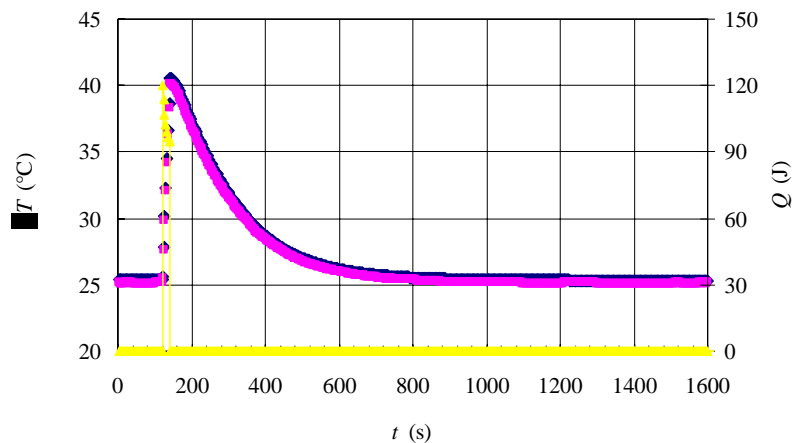*Figure 3 The time dependences of the sample temperature on the heat pulse (Q = 735 J, Δt = 18 s) for two different measurements (0.1 V and 4.64 V).*

As can be seen from the Figure 4 it is obvious that in our case the change is nearly not observable. This implies that the activation energy is very small. The change is however observable from the Arhenius law dependence of the electric current (Figure 4) on the temperature (Figure 3), i.e. the dependence of log (I) = f(1/T), see Figure 5.
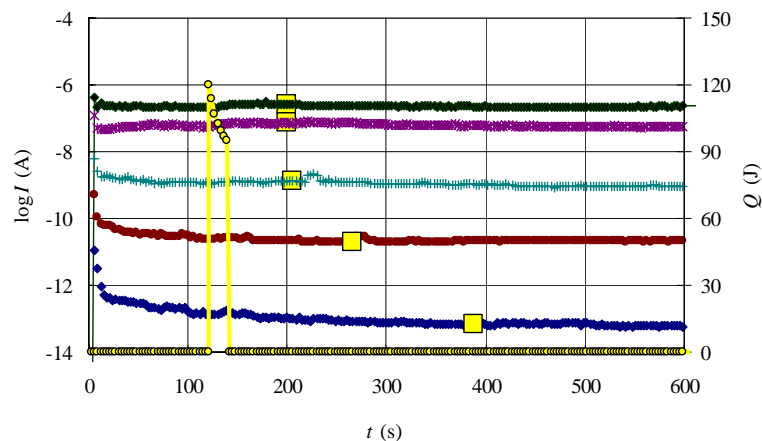

Figure 4 The time dependences of the current after the impression of stepwise voltage (t = 0 s) *and pulse heat power (*t = 120 s, Q = 735 J, Δt = 18 s). The marked areas were used to determine the activation energy of the current-voltage characteristics.*

When small voltage is applied (so-called ohmic current), the electric current behaviour of the Arhenius dependence during the heating and cooling of the sample ($U \sim 0.1$ V) is apparently

different than for higher voltages (so-called SCLC regime $U > 0.5$ V). The difference between the heating and cooling parts is not observable for high voltages.
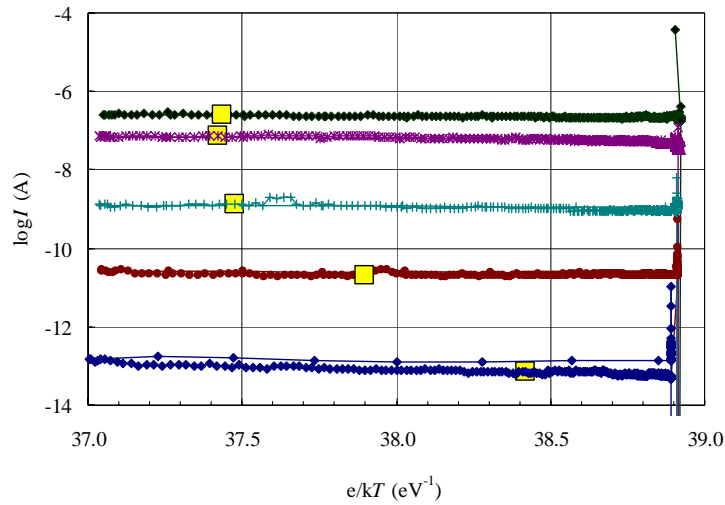

Figure 5 The Arhenius dependence of the electric current on the temperature for different biases (from the bottom 0.1 V, 1.0 V, 1.78 V, 3.73 V and 4.64 V). The marked areas were used to determine the activation energy of the current-voltage characteristics.

The activation energies of the current-voltage characteristics (see Figure 6) E_a and the pre-exponential factor of the electric current I_0 were determined from the parts where the change of the current is not influenced by the voltage applied (marked by the squares). These values were used to determine the electric current for selected temperature ($T = 300$ K)
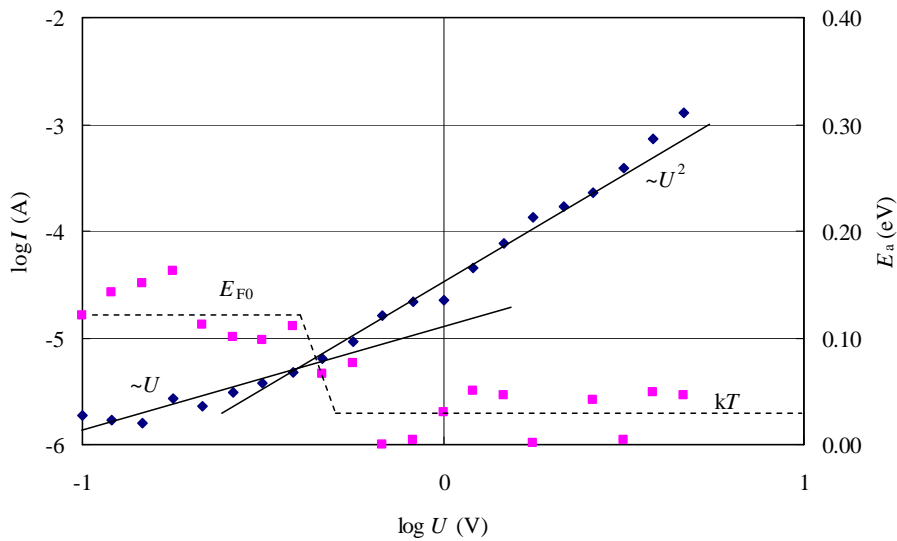
$$I = I_0 \exp\left(-\frac{E_a}{kT}\right). \tag{1}$$

Figure 6 Current-voltage characteristic and activation energies determined by the pulse transient TMSCLC for temperature T *= 300 K*

From the analysis of the ohmic region (voltages $U < 0.5$ V) one can see that the position of the Fermi energy level is $E_{F0} \sim 0.12$ eV and thus, the current can be expressed as

$$I = e\,\mu\,N_c \exp\left(-\frac{E_{F0} - E_c}{kT}\right) \frac{S\,U}{L}, \qquad (2)$$

where e is the elementary charge, μ is the mobility of the charge carriers, N_c is the concentration of states in the conduction band, E_c is the location of the edge of the conduction band, L is the thickness of the sample and S is the area of the measuring contacts. In the case of intrinsic semiconductor where the Fermi energy level lies in the middle of the forbidden band gap, the width of the gap is $\Delta E_g \sim 0.24$ eV. However, this doesn't have to be this case. Since the optical gap of the analysed material is ~ 2.5 eV and of the PEDOT is ~ 1.4 eV the actual position of the Fermi level have to be different.

The behaviour in the SCLC region implies that the activation energy $E_a < kT \sim$ const., the slope of the current-voltage dependence is $m \sim 2$ and the current will be determined by the Childs law

$$I = \frac{9}{8}\varepsilon\varepsilon_0\mu\frac{U^2}{L^3}, \qquad (3)$$

where $\varepsilon\varepsilon_0$ is the permitivity of the measured material.

CONCLUSION

The contribution discusses utilization of pulse transient method for heat dependent electric current characteristics of semiconducting material measurement and analysis. From the preliminary analysed data it is apparent that the method originally developed to measure the heat parameters can be successfully used also in this area. The first results obtained from the analysis also suggest the validity of the pulse transient temperature modulated space charge limited currents (pulse transient TM SCLC).

ACKNOWLEDGMENTS

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