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TRANSPORT IN POLYMERS

Electron Transport in Polyethyleneterephthalate

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Abstract—The electron transport is studied experimentally by measuring pulsed radiation-induced conductivity in polyetheleneterephthalate under bulk irradiation of polymer films by fast electron pulses in a small-signal regime. Numerical simulation is performed using a multiple trapping model with an exponential energy trap distribution. It is shown that, contrary to the reported interpretation of this phenomenon, there is no electron extraction to electrodes under these experimental conditions. In reality, the electron dispersive transport in PET occurs in the presence of the monomolecular capture of electrons by deep traps of biographic origin.

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Up to now, polyethyleneterephthalate has been widely used as a material for screen-vacuum thermal blankets of low-orbit spacecraft. Such materials should have a reduced ability to accumulate space charges, which create strong electric fields. This leads to the appearance of electrostatic discharges and ultimately, to the failure of the onboard electronics of spacecraft.

The main parameter that controls the magnitude of the electric field in the polymer bulk when it is irradiated with electrons is the electrical conductivity of this polymer. In this case, electrical conductivity is the sum of two terms: dark electrical conductivity and radiation-induced electrical conductivity. Since PET is a good dielectric, the main parameter for charge relaxation is its radiation-induced conductivity. This work is devoted to the study of the radiation-induced conductivity of PET. The general properties of the radiation-induced conductivity of industrial polymers, such as PS, LDPE, PTFE, and mineral-filled foam polymers, are considered in monograph [1]. The radiative-induced conductivity of PET was studied in [2–7]. It was shown that the radiation-induced conductivity in this polymer has a number of features that distinguish it from other polymers.

Radiation-induced conductivity, as is well known, is used as the main method for studying the transport of the main charge carriers in polymers. The radiation-induced conductivity of PET is in many respects similar to the conductivity of the above technically important polymers [1]. But a number of features distinguish this polymer from the others. The mobile charge carriers in PET are electrons rather than holes as in the polymers mentioned above. The decay of current after the end of the irradiation pulse follows a power law $j(t) \propto t^{-1.5}$ (usually the exponent does not exceed unity). In addition, under continuous irradiation at a constant dose rate, a situation is easily realized in which radiation-induced conductivity is simply constant throughout the exposure time, reaching several hundred seconds [8]. The authors of [8] explained the last two features in terms of a semiquantitative theory based on the effect of electron extraction from the polymer film in the applied electric field. Assuming the dispersion parameter α for electrons to be 0.5, the authors of the cited work were able to explain both of the above features of the radiation-induced conductivity of PET.

However, everything is not so clear. As was shown in [9], despite the fact that the noted features of the radiation-induced conductivity of PET actually take place, the description proposed in [8] is quantitatively contradictory. We proposed an alternative approach to solving the problem under consideration which is based on the concept of monomolecular electron capture in the dispersive transport regime. However, this approach has not yet received detailed experimental confirmation.

The objective of this work is to conduct additional experimental and theoretical studies confirming our point of view.

THEORETICAL CONSIDERATION

The radiation-induced conductivity of polymers is described using the multiple trapping concept which is based on the quasi-band mechanism of mobility of radiation-generated charge carriers [1]. The fact that

the hopping transport is realized in a number of polymers should not lead to misunderstanding, since the transport level concept makes it possible to solve this problem [10, 11].

The basic equations of this model have the following form and do not depend on the specific type of problem under consideration [1]:

$$\partial\rho/\partial t = (N_0/\tau_0)[M(E) - \rho]/M_0 - \rho\nu_0\exp\left(-\frac{E}{kT}\right). \quad (1)$$

$$N = N_0 + \int_0^\infty \rho dE, \quad (2)$$

where N is the total concentration of electrons, N_0 is their concentration in the conducting state with mobility μ_0 and lifetime τ_0. The density of trapped electron distribution is described by function $\rho(E)$ and $M(E)$ is the trap density distribution $E \geq 0$ (their full concentration is M_0). The frequency factor is ν_0, and, finally, T is the temperature and k is the Boltzmann constant. In accordance with the main provisions of the multiple trapping model parameters, τ_0 and ν_0 are considered constant values independent of the trap energy E.

The exponential energy trap distribution is considered

$$M(E) = \frac{M_0}{E_0}\exp(-E/E_0), \quad (3)$$

where E_0 is the distribution parameter. The dispersion parameter important for the theory is $\alpha = kT/E_0$.

The one-dimensional approximation is traditionally used (coordinate x is counted from the irradiated electrode and directed deep into the polymer layer normally to its surface). The low-signal irradiation mode makes it possible not to take into account the volume recombination of charge carriers and to consider the electric field in the sample as constant and uniform. Thus, the system of Eqs. (1) and (2) is linearized. In moderately strong electric fields ($\geq 10^6$ V/m), the contribution the diffusion component of the conduction current to the total current can be neglected. Thus, in the general case, quantities N and N_0 depend on the coordinate and time and ρ additionally depends on the energy of the traps.

Current density $j(t)$measured in the external circuit is (e is the elemental electric charge)

$$j(t) = \frac{e\mu_0 F_0}{L}\int_0^L dx N_0(x,t). \quad (4)$$

In this paper, we consider the two most common formulations of the radiation experiment. In the first, the carrier generation rate g_0 is homogeneous and constant, so that the concentration of electrons is also independent of the coordinate. The continuity equation is used in the following form:

$$dN/dt = g_0 - k_{rec}N_0N, \quad (5)$$

where k_{rec} is the coefficient of volume recombination of quasi-free electrons with fixed holes (the condition of quasi-neutrality requires equality of the total concentrations of electrons and holes). Expression (4) is simplified and takes the form $j(t) = N_0(t)\mu_0F_0e$.

The second formulation of the problem assumes the extraction of electrons to the pulling electrode (time-of-flight experiment) and, accordingly, the continuity equation is modified:

$$\partial N(x,t)/\partial t + \mu_0F_0\partial N_0(x,t)/\partial x = g_0. \quad (6)$$

In this equation, the recombination loss of electrons (the low-signal irradiation regime) is neglected.

Approximate analytical formulas were developed for the case of pulsed low-signal irradiation with a constant dose rate ($g_0 = \text{const}$) [1]. Unfortunately, a program for the numerical counting of the transient current which simultaneously takes into account the time of flight and recombination effects has to be developed. In this work, the Rose–Fowler–Vaisberg model with the continuity equation in the form of expression (5) was used to evaluate the recombination effects. When analyzing the flight and monomolecular capture effects, the analytical formulas proposed in [12] were applied. Unfortunately, an inaccuracy crept into the formulas; therefore, below they are given in the corrected form:

$$j(t) = \begin{cases} eg_0Lp(t), & t < t_p \\ eg_0L[p(t) - p(t - t_p)], & t \geq t_p, \end{cases} \quad (7)$$

where $p(t) = l^2(t)\,[l^{-1}(t) + \exp(-l^{-1}(t)) - 1]$, $l(t) = \mu_0F_0\tau(t)/L$, $\tau(t) = \alpha^{-1}\tau_0(\nu_0t)^\alpha\gamma(\alpha, \nu_0t)^{-1}$, and $\gamma(\alpha, x) = \int_0^x \exp(-z)z^{\alpha-1}dz$ is the incomplete gamma function (t_p is the irradiation time). At large times ($\nu_0t \gg 1$), $\tau(t) \approx \frac{\tau_0(\nu_0t)^\alpha}{\Gamma(1+\alpha)}$. Formulas (7) are simplified in limiting cases $l(t) \ll 1$ and $l(t) \gg 1$ (it is assumed that the ratio $\nu_0t \gg 1$ is satisfied). At $t < t_p$, in the first case, $j(t) = g_0\mu_0eF_0\tau(t) \propto (\nu_0t)^\alpha$, and in the second case, $j(t) \to (1/2)g_0Le$ (complete collection of generated electrons, holes are immobile; hence, a factor of 1/2 is present). At the stage of current decay ($t \gg t_p$), we have $j(t) \propto t^{-1-\alpha}$.

In the presence of monomolecular capture with time constant τ_c, formulas (7) are still valid, but the form of the τ function changes: $\tau_\Sigma(t) = \tau(t)\tau_c/[\tau(t) + \tau_c]$ [12]. Now the current during irradiation at $l(t) \gg 1.0$ (i.e., in a moderately strong electric field)

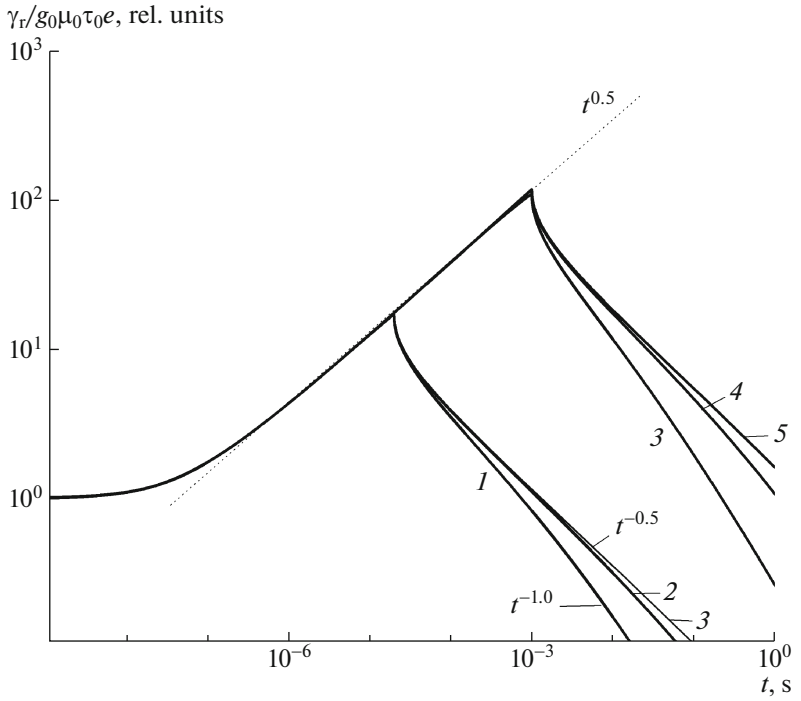

Fig. 1. Transient current curves calculated using the Rose–Fowler–Vaisberg model with dielectric parameters given in the text. All curves are normalized to $\hat{\gamma}_p$ (see text). g_0 = (*1*) 10^{26}, (*2*) 10^{25}, (*3*) 10^{24}, (*4*) 10^{23}, and (*5*) 10^{22} m^{-3} s^{-1}. Deep trapping is not taken into account (τ_c = 5.4 s).

$j(t) \to g_0\mu_0\tau_c eF_0$, but in extremely strong fields, $F_0 \to \infty$ $j(t) \to 0.5g_0Le$ (and again the full collection mode of generated electrons is realized). Note that, at all observation times, the density of the recorded current is proportional to the volume generation rate (a direct consequence of the low-signal irradiation regime). To carry out approximate calculations, we use the values of the model parameters of the radiation-induced conductivity of PET proposed in [9]: $\mu_0 = 10^{-5}$ $m^2/(V\,s)$, $\tau_0 = 2 \times 10^{-11}$ s, $\tau_c = 5.4 \times 10^{-10}$ s, $\nu_0 = 3 \times 10^7$ s^{-1}, $k_{rec} = 5.8 \times 10^{-14}$ m^3/s, and $\alpha = 0.5$. Next, the radiation yield of free electrons in a field of 4×10^7 V/m is assumed to be 0.7 per 100 eV of absorbed energy, which at a polymer density of 1.4 g/cm^3 corresponds to the rate of the volume generation of electrons $g_0 = 1.2 \times 10^{24}$ m^{-3} s^{-1} for the dose rate $R_0 = 1.9 \times 10^4$ Gy/s.

EXPERIMENTAL

Experiments used an ELA-50/5 electron-beam installation, which makes it possible to irradiate polymer samples with accelerated electrons with an energy of 50 keV in both the pulsed and continuous regimes [1]. Basic information regarding the buildup and decay of transient current curves was obtained when working with rectangular electron pulses with a duration of 20 μs and 1 ms. The instantaneous component of the radiation current was measured using a short (3 μs base) triangular pulse.

If in the first case the computer recording of transient current curves was used, then in the latter case the data were read from the oscilloscope screen with a bandwidth of 20 MHz. The methodology for conducting experiments and processing the obtained data was examined in detail in [1, 9].

The transient current in the polymer sample under voltage was measured in the current mode when the measurement time constant *RC* was much less than the characteristic time of observation. Electron pulses with an energy of 50 keV, which provide a fairly uniform irradiation of polymer films up to 25 μm thick, were used. Beam dosimetry was performed using a Faraday cup. The diameter of a collimator arranged directly at the entrance to the measuring cell was 20 mm.

The tests were carried out using disk PET films (PET-E polyethyleneterephthalate film, OAO Vladimir Chemical Plant) with a diameter of 38 mm cut from industrial polymer films up to 20 μm thick. Electrodes with a diameter of 32 mm were applied by thermal spraying of aluminum in vacuum. The thickness of the aluminum layer did not exceed 50 nm.

When planning the control experiments, it was necessary to evaluate the role of each of the three factors determining the nonstandard behavior of the radi-

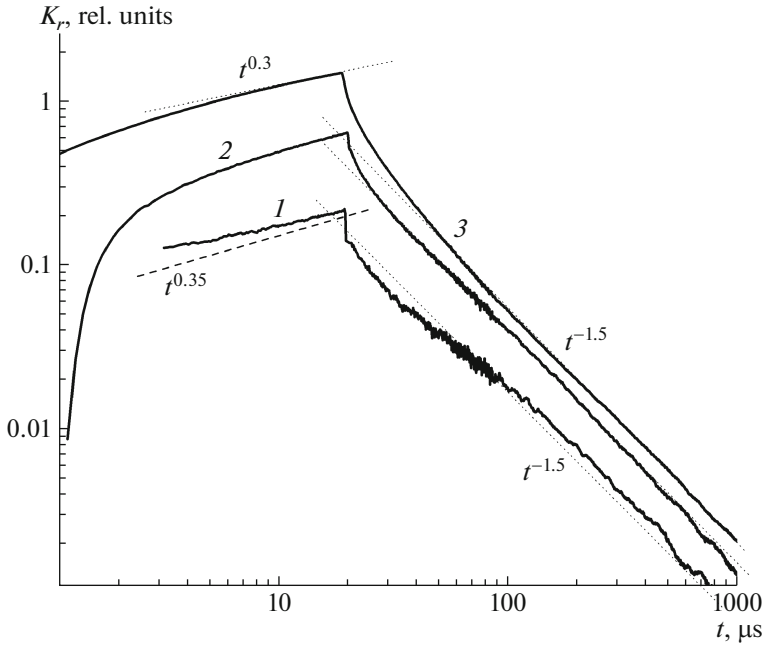

Fig. 2. Experimental transient current curves measured at a radiation pulse duration of 20 μs in the small-signal regime with electric field values of (*1*) 10^7, (*2*) 4×10^7, and (*3*) 8×10^7 V/m. $K_{rm} \times 10^{14}$ = (*1*) 0.8, (*2*) 2.4, and (*3*) 5.6 Ω^{-1} m^{-1} Gy^{-1} s. The dashed curve characterizes growth of the delayed component in time. See text for explanations.

ation-induced conductivity of PET. This is the extraction of electrons to the electrodes already at the irradiation stage, their capture by a few deep traps of biographic origin in the dispersion transport regime, and, finally, bimolecular recombination distorting the shape of the curves at the decay stage, even if it does not significantly affect the shape of the curves recorded during the irradiation process.

RESULTS AND DISCUSSION

The most unambiguous data were obtained when working with electron pulses with a duration of 20 μs. Just in this irradiation regime, the optimum time resolution is achieved with a minimum of recombination losses. In a typical experiment (electric field, 4×10^7 V/m), the dose rate is 3.8×10^4 Gy/s (dose, 0.76 Gy), which corresponds to the electron generation rate $g_0 = 2.4 \times 10^{24}$ m^{-3}/s. Calculations performed using the Rose–Fowler–Vaisberg model show that the effect of recombination is absent at observation times not exceeding 10 ms even at $g_0 = 10^{25}$ m^{-3}/s, covering the entire range of the dose rates used (Fig. 1). In the case of 1-ms pulses, it is necessary to reduce the volume generation rate to 10^{23} m^{-3}/s. But even at $g_0 = 10^{24}$ m^{-3}/s, the current buildup curve is still not distorted, although the current decay curve undergoes significant changes. Thus, in the indicated time range, the low-signal irradiation regime is reliably realized, when the influence of recombination can be neglected, but at the same time, experiments with the necessary time resolution can be performed. The instantaneous component of the radiation-induced conductivity in the studied polymer per unit dose rate K_p turned out to be close to 10^{-15} Ω^{-1} m^{-1} Gy^{-1} s. This value is known to be proportional to the dose rate and hardly depends either on the field or on the temperature. The multiple trapping model uses its respective expression $\hat{\gamma}_p = g_0\mu_0\tau_0 e$, which may differ significantly from the original.

Figure 2 shows the transient current curves for several values of the electric field. It is seen that the shape of the curves hardly changes and only an increase in the values of the radiation-induced conductivity reduced to the unit dose rate K_r is observed at the end of the radiation pulse $K_{rm} = \gamma_{rm}/R_0$ owing to an increase in the radiation yield of free charges according to the Onsager theory [1]. If the current decay according to the law $j \propto t^{-1.5}$ could be related to the time-of-flight effect, one would expect a noticeable shift in the decay curve to longer times with a decrease in the electric field, which actually does not happen. The dashed curve represents the growth of the delayed component by the law $j \propto t^{0.35}$ obtained by subtracting the prompt component from curve *1* measured at the stage of radiation-induced conductivity build-up. In this case, the pattern of the delayed component reproduces its course in a strong field, as in curve *3*, in which this component already dominates.

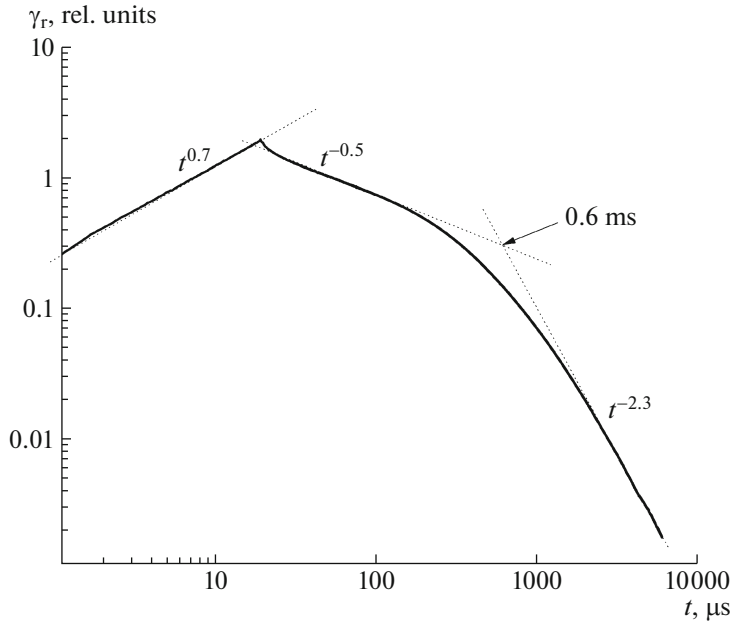

Fig. 3. Transient current curve measured in the DEH sample. Electric field, 10^8 V/m; pulse duration, 20 μs; and film thickness, 9 μm. $K_{rm} = 1.1 \times 10^{-13}$ Ω^{-1} m^{-1} Gy^{-1} s. The arrow indicates the time of flight.

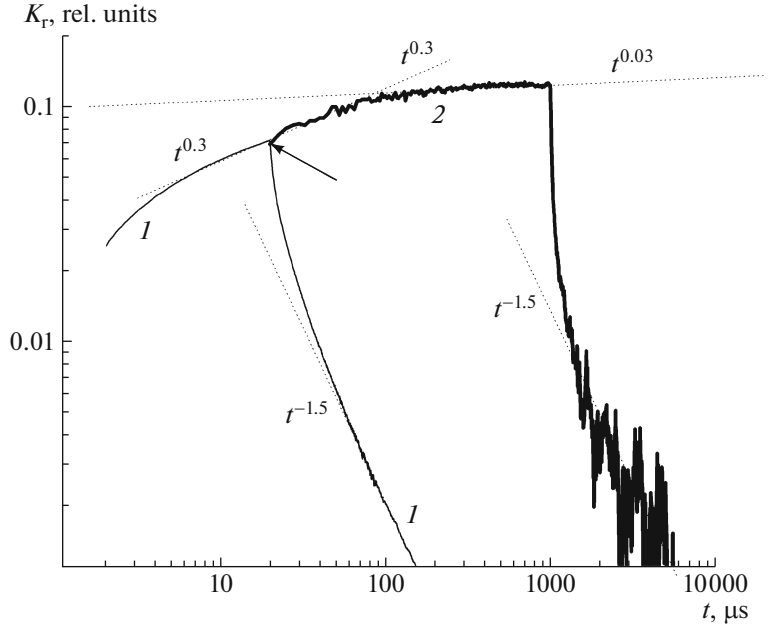

Fig. 4. Transient current curves measured for radiation pulses with duration (*1*) 20 μs and (*2*) 1 ms in an electric field of 8×10^7 V/m at a dose rate of (*1*) 3.8×10^3 and (*2*) 190 Gy/s. *RC* = (*1*) 0.2 and (*2*) 2 μs. The arrow indicates the stitching time of two curves (20 μs). K_{rm} in the end of pulse is (*1*) 7×10^{-14} and (*2*) 1.2×10^{-13} Ω^{-1} m^{-1} Gy^{-1} s, respectively.

In addition, note that in the experiment only the postflight branch of the curve is seen, while the preflight branch is simply absent. This seems strange, and to clarify this issue, a special experiment was conducted under the same conditions using PC molecularly doped with 30 wt % *p*-diethylaminobenzaldehyde diphenylhydrazone (**DEH**), the hole transport in which was studied in detail [13]. Its results are shown in Fig. 3. It is noteworthy that the mobility of holes in DEH is somewhat higher than that of electrons in

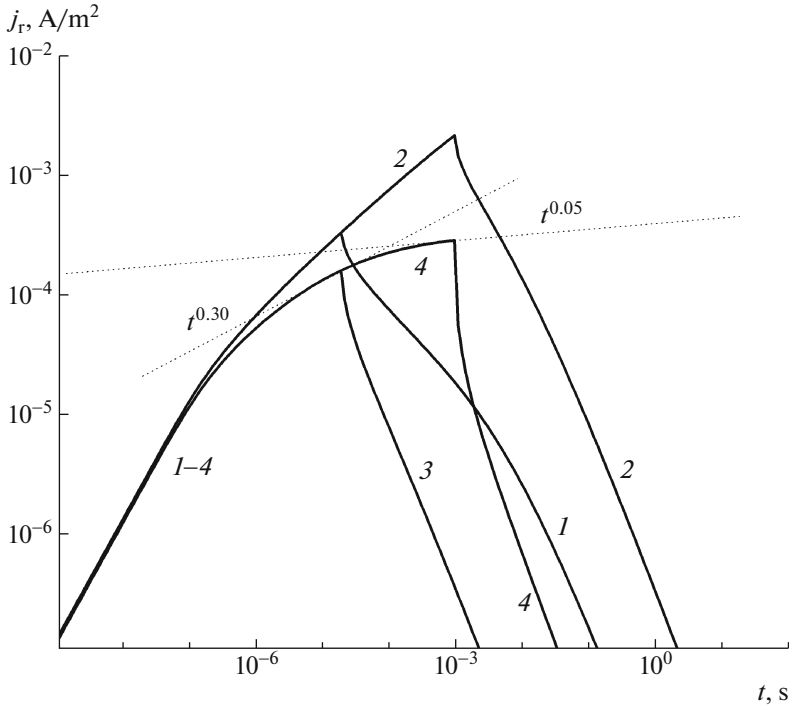

Fig. 5. Transient current curves calculated using Eqs. (7) for the dielectric parameters given in the text. $g_0 = 10^{22}$ m^{-3}/s. Pulse duration is (*1*, *3*) 20 μs and (*2*, *4*) 1 ms. τ_c = (*1*, *2*) 5.4 and (*3*, *4*) 5.4×10^{-10} s. The electric field is 4×10^7 V/m.

PET, but its time-of-flight curve has clearly defined preflight $j \propto t^{-0.5}$ and postflight $j \propto t^{-2.3}$ branches even in an extremely strong field (10^8 V/m) in the polymer film with a thickness of only 9 μm. Also note that the transit time is fairly large (0.6 ms).

As the pulse duration was increased to 1 ms, the transient current curves achieved a quasi-stationary value (Fig. 4). Stitching two curves at $t = 20$ μs occurs quite smoothly, and the general tangent at this point is described by the expression $j \propto t^{0.3}$. Subsequently, the exponent $\beta = d\log j/d\log t$ only decreases, reaching a value of 0.03 by 1 ms. In the framework of the concept of charge carrier extraction to the electrodes [8], such a behavior of the shape of the transient current curves should be associated with the complete collection of generated charges. This assumption is not true. Even in a field of 8×10^7 V/m, the current density at 1 ms (1.6×10^{-3} A/m^2) is more than 15 times less than the expected value when the generated charge is fully collected (44×10^{-3} A/m^2). This is also evidenced by theoretical estimates (Fig. 5). The current density of electrons at their complete collection (10^{-2} A/m^2) is almost 35 times higher (2.87×10^{-4} A/m^2) than the calculated value for curve *4* at 1 ms.

A more plausible explanation [9] relates this behavior to deep trapping, which does not require a strong electric field. Numerical calculations fully confirm the correctness of such an approach (Fig. 5). It is seen that taking deep electron trapping into account leads to limitation of the growth of the delayed component with an increase in the duration of pulsed irradiation. Moreover, at $t = 20$ μs, slope β has a required value of 0.3, as in Fig. 4.

CONCLUSIONS

Thus, it can be inferred that the electron transport in PET takes place in the dispersive mode, but in the presence of deep traps, the extraction of electrons from which can be neglected. This circumstance explains the unusual behavior of its radiation-induced conductivity during pulsed and continuous irradiation in the small-signal regime. This phenomenon can be described using analytical results reported in [12].

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