RELATED FEATURES OF TSD AND QDLTS METHODS

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Two standard methods for investigating relaxation processes in solids — deep level transient spectroscopy (DLTS) and thermostimulated depolarization method (TSD) are analyzed. A complex formalism is introduced and numerically analyzed. Related features were revealed including a direct reflection of the shape of an arbitrary distribution of relaxation times by the DLTS/TSD response. The extraordinary resolution ability of the so-called step heating TSD is numerically demonstrated. A discussion is given of a new approach to the analysis of the DLTS spectra as well as TSD currents due to different relaxation mechanisms, namely in the case of a distribution of the activation energy.

K e y w o r d s: deep level transient spectroscopy, thermally stimulated depolarization, relaxation process

1 INTRODUCTION

The deep-level transient spectroscopy (DLTS) developed originally by Lang [1] occurs in many versions. One of them referred to as charge transient spectroscopy (QDLTS, abbreviation QTS is also used) was suggested in [2, 3]. All the modifications of DLTS are widely used for the investigation of deep energy levels in semiconductor structures. There are also possibilities to expand QDLTS utilization to other materials or to relaxation processes of different origins. The possibilities to expand QDLTS to ionic crystals, ceramics and fullerenes were pointed out in [4–7]. In this paper we concentrate on dielectric polarization phenomena in insulators containing dielectric dipoles. The QDLTS can serve as an alternative for the thermally stimulated depolarization (TSD method) [8] of a dielectric. Dielectric usually contains several kinds of dipoles, even in some cases distributed spectra of relaxation times are expected. This article concerns a comparison between QDLTS and TSD abilities to resolve the contributions of different dipoles to the overall response and to the question how trustworthy the QDLTS as well as TSD spectra reflect the shape of the distribution function $G(E)$.
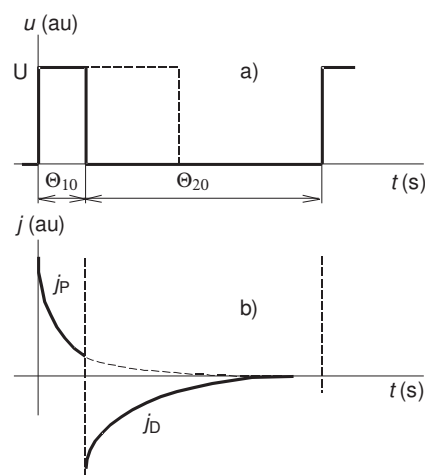
2 PARTIAL EXCITATION MODE (PEM)

2.1 Consequence of PEM for QDLTS

We will assume that the duration of the charging pulse U is Θ_1 and the rest of the interval between subsequent pulses is Θ_2 (Fig. 1), *ie* the repetition frequency is $f_r = (\Theta_1 + \Theta_2)^{-1}$. At the end of the charging pulse a value

of the polarization P reaches a fraction of steady-state (saturated) polarization P_s

$$P_1 = \left[1 - \exp\left(-\frac{\Theta_1}{\tau}\right)\right] P_S \qquad (1)$$

Fig. 1. Schematic drawing of transient current processing a) excitation voltage waveform (the dashed line represents the standard regime of excitation), b) transient current due to partial charging (j_P) and complex discharging (j_D) of the dielectric.

(if we assume that at $t = \Theta_2$, $P = 0$). The symbol $\tau = \tau_0 \exp\left(E/k_B T\right)$ stands for the relaxation time of Debye-type dielectric polarization. After the charging pulse the saturated polarization P_S is reached only if $\Theta_1 \gg \tau$. In other cases P_1 is less than P_S. For the discharging current $j_D(t)$ one can write

$$j_D = -\frac{P_S(T)}{\tau} \frac{1 - \exp\left(-\frac{\Theta_1}{\tau}\right)}{1 - \exp\left(-\frac{\Theta_1 + \Theta_2}{\tau}\right)} \exp\left(-\frac{t}{\tau}\right). \qquad (2)$$

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The charge response during the discharging period Θ_2 is

$$Q(t) = \int j_D \mathrm{d}t. \tag{3}$$

The principal QDLTS method consists in measuring the differential charge

$$\Delta Q = Q(t_2) - Q(t_1) = P_S \left[\exp\left(-\frac{t_1}{\tau}\right) - \exp\left(-\frac{t_2}{\tau}\right) \right]$$
$$\times \frac{1 - \exp\left(-\frac{\Theta_1}{\tau}\right)}{1 - \exp\left(-\frac{\Theta_1 + \Theta_2}{\tau}\right)}, \tag{4}$$

where t_1 and t_2 are time instants at which the charge response is recorded. If both Θ_1 and Θ_2 are much larger than τ, the analysis of the signal ΔQ (4) is identical with the standard approach introduced by Lang [1]. The numerical calculation of (4) for one type of dipoles and for partial charging (*eg* when $\Theta_1 \ll \tau$ — or sufficiently high repetition frequency is assumed) [9] showed that (i) the QDLTS peak magnitude is reduced (mainly at its low temperature side), (ii) the full width at half maximum (FWHM) is significantly reduced. The last effect results in improving the selectivity which is important in the case when a dielectric contains several kinds of dipoles. The evolution of such a signal originating from three dipole species differing in the activation energy ($E_a = 0.4$ eV, $E_b = 0.45$ eV and $E_c = 0.5$ eV) is envisaged in Fig. 2. It is evident that the separation between the peaks increases. The third peak can be reliably resolved only at the higher frequency.
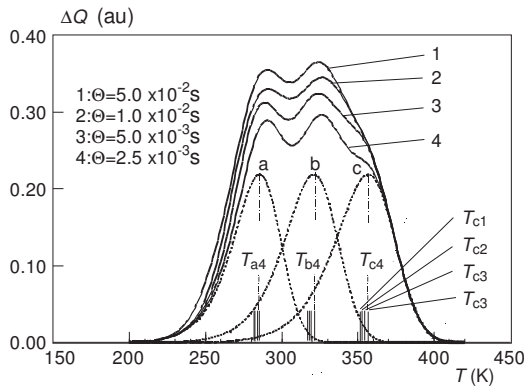
Fig. 2. Enhanced peak resolution at higher repetition frequencies $f = (\Theta_1 + \Theta_2)^{-1}$, ($\Theta = \Theta_1$) (is visible mainly for peak (c) at about 350 K). Individual QDLTS peaks a, b and c correspond to activation energies $E = 0.4$, 0.45 and 0.5 eV, respectively. T_{ij} denotes the position of individual TSD maximum.

Let us turn our attention to the case when QDLTS signal reflects a continuously distributed spectrum of relaxation times. The complete expression for QDLTS signal has the form

$$\Delta Q = P_S \int_{-\infty}^{\infty} \left[\exp\left(-\frac{t_1}{\tau}\right) - \exp\left(-\frac{t_2}{\tau}\right) \right]$$
$$\times \frac{1 - \exp\left(-\frac{\Theta_1}{\tau}\right)}{1 - \exp\left(-\frac{\Theta_1 + \Theta_2}{\tau}\right)} G(E) \mathrm{d}E, \tag{5}$$

where the distribution function $G(E)$ was considered for the distribution in activation energies E. For our analysis we have chosen the widely used Gauss distribution function

$$G(E) = \frac{1}{\sqrt{\pi}\,\sigma} \exp\left[-\frac{(E - E_0)^2}{2\sigma^2} \right]. \tag{6}$$

The numerical calculation of (6) with decreasing duration of the polarization charging pulse, Θ_1, has been made for both cases of narrow and broad distribution. The calculation shown in Fig. 3a has been made for $\sigma = 0.01$. One deals, in such a case, with a very narrow distribution that is representative for the case of a discrete value of the activation energy. When decreasing Θ_1, the "single energy" QDLTS peak is reduced at its low-temperature side only (similarly as in [8]) and, simultaneously, the position of its maximum shifts apparently to higher temperatures.
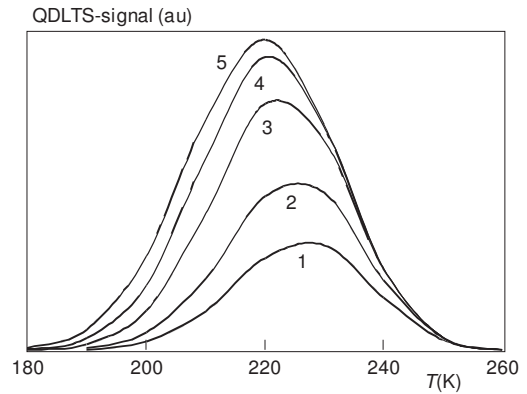
Fig. 3a The family of QDLTS signals calculated using Eq. (4) for a discrete energy level $E = 0.36$ eV. The curves 1 to 5 correspond to different values of duration Θ_1 from bottom to top): 5×10^{-4}, 10^{-3}, 3×10^{-3}, 5×10^{-3}, 10^{-2} s. Pre-exponential factor $\tau_0 = 10^{-12}$ s, $t_1 = 10^{-3}$ s and $\Theta_2 = 10^{-1}$ s were taken in all cases.
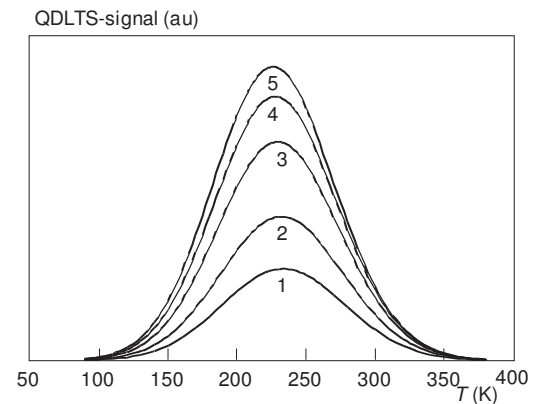
Fig. 3b The family of QDLTS curves calculated for a distribution of relaxation times. The Gauss distribution function (6) with parameters $\sigma = 0.07$ eV and $E_0 = 0.36$ eV was used. The curves 1 — 5 correspond to values of charging time Θ_1 (from bottom to top): 10^{-3}, 3×10^{-3}, 5×10^{-3}, 10^{-2}, 10^{-1} s. Pre-exponential factor $\tau_0 = 10^{-12}$ s and $\Theta_2 = 10^{-1}$ s were used in calculation.

For the distributed QDLTS spectra (the calculation was made for $\sigma = 0.07$ eV — see Fig. 3b) with reducing Θ_1 the signal reduces simultaneously within the whole temperature range in which the signal is situated. The position of the maximum is the same for all Θ_1.

2.2 Influence of PEM on TSD spectra

The thermally stimulated depolarization experiment starts with polarization of the sample placed between two electrodes at temperature T_i. The electrical field is maintained while cooling the sample to the temperature T_0 sufficiently low to freeze up the electrical configuration. The frozen polarization P depends on time and the temperature

$$P_1 = \left[1 - \exp\left(-\frac{t}{\tau}\right)\right]P_S. \qquad (7)$$

This is equation (1) in its general form. By heating the polarized sample (field is switched off) the discharge becomes measurable and gives rise to a current in the external circuit. In the simple case characterized by a single relaxation time τ the following formula for the non-isothermal discharging current can be derived [10]

$$j(T) = \frac{P}{\tau}\exp\left(-\int_{T_0}^{T}\frac{\mathrm{d}T'}{b\tau}\right). \qquad (8)$$

Here b is the rate of linear heating, $b = \mathrm{d}T/\mathrm{d}t$, which starts at temperature T_0. The TSD glow curve (8) shows a pronounced maximum at a certain temperature T_m given by the transcendental equation

$$T_m^2 = \frac{b\tau_0 E}{k_B}\exp\left(\frac{E}{k_B T_m}\right). \qquad (9)$$

For our further analysis it is important that the low-temperature tail of the TSD curve (8) is such that

$$\ln j(T) = \mathrm{const} - \frac{E}{k_B T}. \qquad (10)$$

In the case of several types of dipoles with different activation energies being present we suppose the measured signal to be a simple sum of partial responses

$$j(T) = \sum_i \frac{P_i}{\tau_i}\exp\left(-\int_{T_0}^{T}\frac{\mathrm{d}T'}{b\tau_i}\right), \qquad (11)$$

where $\tau_i = \tau_0 \exp\left(E_i/k_B T\right)$, $i = 1, \ldots, n$.
Finally, in the case of continuous spectra of energies the sum (11) will change to an integral

$$j(T) = \int_{-\infty}^{\infty}\frac{P(E)}{\tau(E)}\exp\left(-\int_{T_0}^{T}\frac{\mathrm{d}T'}{b\tau(E)}\right)G(E)\mathrm{d}E, \qquad (12)$$

where $G(E)$ is the Gauss distribution function, which has a sound physical basis. It seems to be plausible that the activation energy E is distributed around the most probable value E_0.

The partial polarization regime can be realized by shortening the charging time t_0 (the way used in Sect. 2.1) or lowering temperature T_i while t_p is kept constant (see scheme in Fig. 4). For a nondistributed polarization such regime will only change the initially frozen-in polarization and as a result the TSD signal is displaced by a constant factor over the whole temperature range (Fig. 5a). This is not the case for a distributed polarization for which the filling of the various subpolarizations will be affected in different ways. The fast subpolarizations will always react first, so these are first filled, and also first discharged. Consequently the height as well as the shape of the TSD thermograms will change (Fig. 6). In the case of the distribution of more discrete energy levels, the individual parts of polarization can be separated (Fig. 5b) step by step. Using such a procedure the details of distribution shape can be recognized
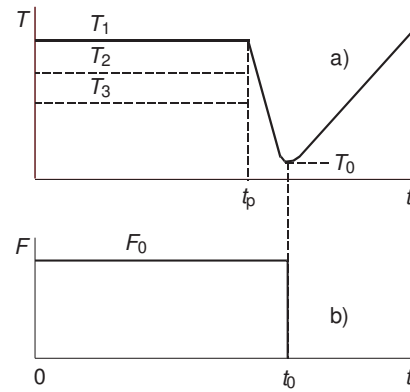
Fig. 4. Illustrative scheme of TSD regime: (a) Polarization at various temperatures keeping time t_p constant, subsequent cooling to low temperature T_0 and linear heating. (b) Electrical field F is switched at the starting moment of heating.

3 THE DIRECT IMAGE OF DISTRIBUTION FUNCTION

The signal measured by QDLTS or by TSD technique is in general given

$$S \approx \int_{-\infty}^{\infty}F(E,T)G(E)\mathrm{d}E. \qquad (13)$$
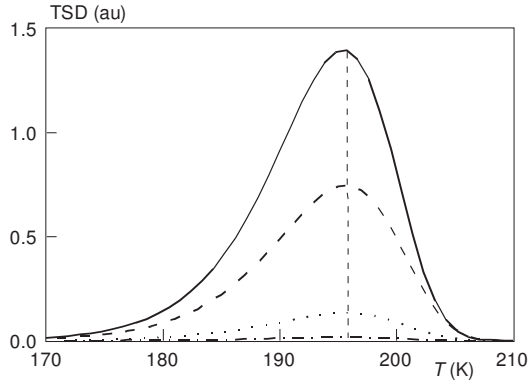
In the case of QDLTS the function $F(E,T)$ has a form

$$F(E,T) = \exp\left[-\frac{t_1}{\tau(E,T)}\right] - \exp\left[-\frac{t_2}{\tau(E,T)}\right] \qquad (14)$$

and for TSD

$$F(E,T) = \frac{1}{\tau(E,T)}\exp\left[-\int_{T_0}^{T}\frac{\mathrm{d}T'}{b\tau(E,T')}\right]. \qquad (15)$$

The resulting signal (13) would have the same shape as the distribution function G(E) only if the unrealistic case

$$S \approx \int_{-\infty}^{\infty}\delta(E - E_x)G(E)\mathrm{d}E \qquad (16)$$

Fig. 5a. The calculated TSD discharging currents for the case of discrete energy level, $E = 0.6$ eV event. As a temperature of polarization was taken (curves from bottom to top): $T_p = 170$ (dot-and-dashed), 180 (dot), 190 (dashed) and 200 K (full line). When calculating Eq. (8) the heating rate $b = 0.1\,\text{Ks}^{-1}$, $T_0 = 150$ K were set.
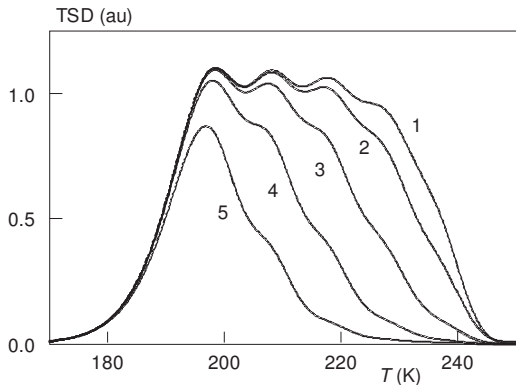

Fig. 5b. The family of TSD signals calculated for dielectric containing five types of dipoles. Activation energy of individual relaxation times are: $E = 0.6$, 0.625, 0.65, 0.675 and 0.7 eV. The temperatures of polarization $T_p = 240$ K (curve 1), 230 (2), 220 (3), 210 (4) and 200 K (curve 5).
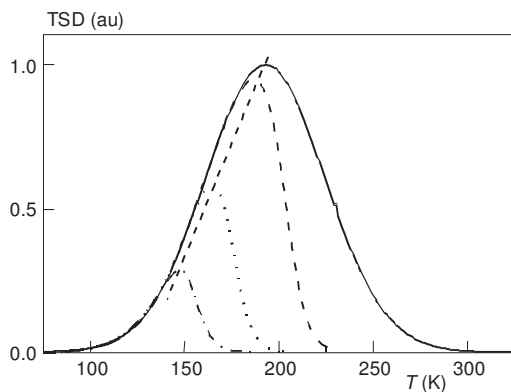

Fig. 6. Evolution of TSD signals with increasing temperature of polarization (from bottom to top): $T_p = 150$ (dot-and-dashed), 170 (dot), 200 (dashed) and 300 K (full line). The TSD curves were calculated for Gauss distribution of activation energies (6), $E_0 = 0.6$ eV and $\sigma = 0.1$ eV.

occurs. The delta function $\delta(E - E_0)$ is placed instead of a complex response $F(E, T)$. However, the $F(E, T)$

as a function of E with the parameter T_m has a finite FWHM. The narrower is the $F(E, T_m)$, the more immediate reflection of $G(E)$ is obtained.
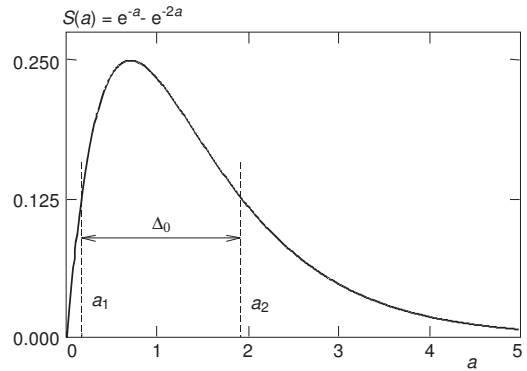
Fig. 7a. Generalized function $f(a)$. The generalized halfwidth Δ_0 is pointed out.
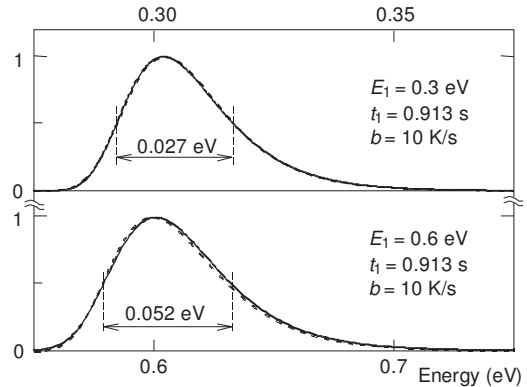
Fig. 7b. Function $F(E, T)$ for different energies: **Top**: $E_1 = 0.3$ eV, corresponding parameters $T_{m1}(E_1) = 124.6$ K (QDLTS), $T_{m2}(E_1) = 129.3$ K (TSD). Two $F(E, T)$ curves (for the both QDLTS and TSD) are identical. **Bottom**: $E_2 = 0.6$ eV, corresponding parameters $T_{m1}(E_2) = 249.4$ K (QDLTS — solid line), $T_{m2}(E_2) = 252.6$ K (TSD — dotted line).

3.1 FWHM of $F(E, T_m)$ for QDLTS

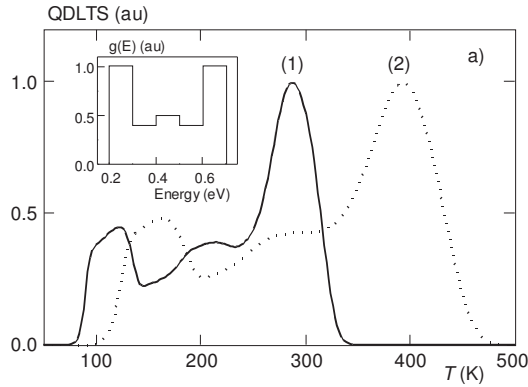The $F(E, T_m)$ (14) can be rewritten into

$$f(a) = \exp(-a) - \exp(-ka) \qquad (17)$$

where $k = t_2/t_1$ and a reaches a value $a = \ln k/(k - 1)$ for a maximum of $f(a)$. The generalized function $f(a)$ is depicted in Fig. 7a. For the generalized halfwidth Δ_0 one can derive the expression
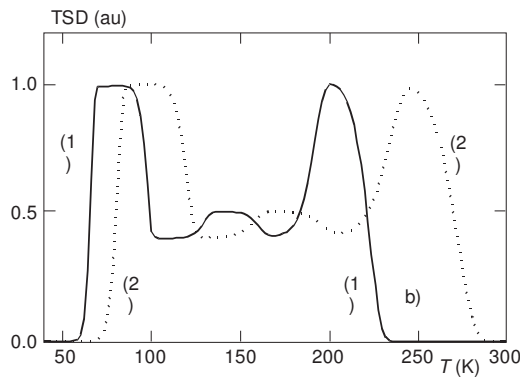
$$\Delta_0 = \ln(a_2/a_1)k_B T_m . \qquad (18)$$

In a wide range of k and consequently a wide range of both a_1 and a_2, Δ_0 changes only a little (from $2.4 \times k_B T_m$ to $2.6 \times k_B T_m$) so the average value $2.5 \times k_B T$ can be taken as a representative. This value, lesser than $3 \times k_B T$, points the fact that only species (*eg* dipoles) from

Fig. 8a. The calculated QDLTS response for distribution function shown in inset

Fig. 8b. The calculated TSD glow discharge for distribution function shown inset in Fig. 8a

a very narrow interval of energies around E_x contribute to the QDLTS at temperature $T_m(E_x)$. All this indicates that the shape of a QDLTS curve represents an immediate reflection of the shape of the distribution function G(E). According to (18), the reflection is better when the signal is positioned at lower temperatures. The resolution ability decreases with increasing temperature.

3.2 FWHM of $F(E, T_m)$ for TSD

The dipoles with the activation energy E_x contribute to the TSD signal with the maximum at temperature $T_m(E_x)$ which is given by the transcendental equation (9). The function $F(E, T)$ (15) is calculated as a function of E, $T_m(E_x)$ being the parameter, for two different energies $E_1 = 0.3$ eV and $E_2 = 0.6$ eV (see Fig. 7b). The narrow peaks with a halfwidth of $2.5 \times k_B T_m$ and $2.4 \times k_B T_m$ show the same property as the QDLTS does. Finally, it is confirmed by the calculation of the function (14). The $F(E, T)$ curves depicted in Fig. 7b slightly differ only for higher energies.

The illustration of this conclusion is presented in Figs. 8a and 8b. The hypothetical distribution function

$G(E)$ with an expressive shape was chosen (see insert in Fig. 8a).

4 THE STEP–HEATING TECHNIQUE

The step-heating TSD (also multi-stage TSD) is used. This regime consists of partial depolarization following one by one without additional polarization (Fig. 9). The first run is stopped before the TSD signal reached its maximum value. Then the sample is rapidly cooled to the temperature T_0 and consequently it is heated.
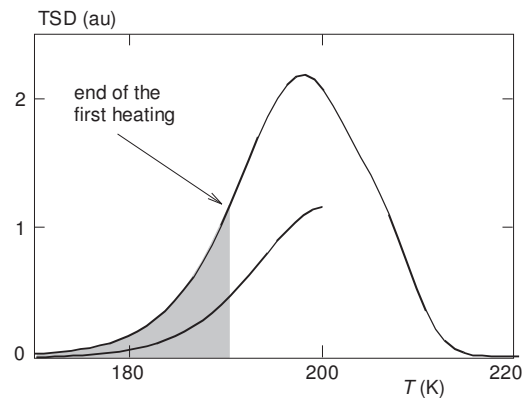
Fig. 9. Scheme of the procedure of step-heating experiment. The cross-hatched plane represents the polarization discharged during the first step the solid tail is obtained during the second step, which started with diminished polarization.
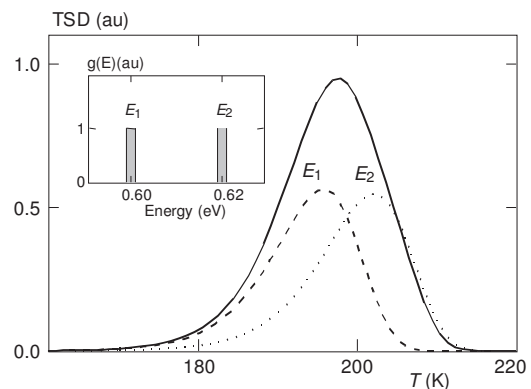
Fig. 10. TSD signals calculated for a sample containing two types of dipoles ($E_1 = 0.6$ eV — dashed line, $E_2 = 0.62$ eV — dot line). The resulting signal is denoted by solid line.

Note that the starting polarization in the second run P_0 is smaller than the original polarization P_S. The process of partial depolarization is repeated so as to obtain a number of low-temperature tails of the TSD curves. In case of a single relaxation time the tails give (replotted as (10)) the same value of activation energy E. On the other hand case if various types of dipoles enter the relaxation process a spectrum of values reflecting the distribution in activation energies is obtained.

Let us turn attention to Fig. 10. The existence of two types of dipoles with close activation energies $E_1 =$

0.6 eV, $E_2 = 0.62$ eV results in a narrow TSD thermogram which deceptively indicates a single relaxation process. The results of repeated calculations of the low-temperature tails (simulating multi-stage TSD) are presented in Fig. 11 and consequently replotted in Fig. 12 as the Arrhenius graphs (according equation (10)). The slope of straight lines indicates the activation energies $E_1 = 0.6$ eV and $E_2 = 0.62$ eV for the first and the last heating, respectively.

The presented calculation demonstrates the extraordinary resolution ability of the step- heating technique whose application is possible only in the TSD experiments.
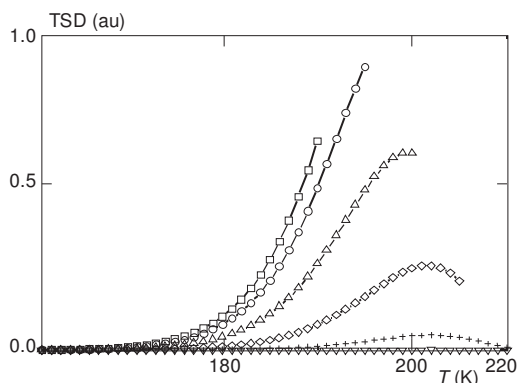

Fig. 11. Low-temperature tails of the resulting TSD signal (solid in Fig. 11) as a result of the numerically simulated step-heating experiment.
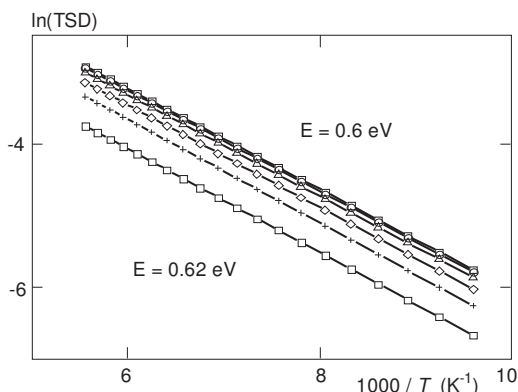

Fig. 12. The Arrhenius graphs obtained replotting low-temperature tails from Fig. 12 making use the expression (6).

5 SUMMARY

The DLTS and TSD methods are two of the most frequently used for the study of thermally activated relaxation processes such as dielectric polarization, migration polarization, trapping and emission of carriers at deep energy levels which are located at PN junction or Schottky barrier thermostimulated conductivity in insulators etc. The DLTS and TSD essentially create two large groups characterized by numerous modifications. The first group is isothermal in nature and the second one non-isothermal. Despite of the great diversity of individual methods there are common features which lead to nearly same advantages. Our analysis was performed for one type of relaxation process — dielectric polarization (depolarization) in solids. However, our conclusions can be extended to the area of various processes mentioned above.

Partial excitation mode can be realized by two regimes depicted in Figs. 1 and 4. The first fashion is easily applied for the DLTS method, on the other hand the second regime may be suitable for the TSD technique. Our analysis showed that for both methods the PEM leads to improved selectivity and possesses enhanced ability to resolve the contribution of different relaxation mechanisms to the overall response. A general exact criterion for resolution cannot be derived. Fig. 2 illustrates the evolution of QDLTS signal with increasing repetition frequency f_r, *ie* with decreasing charging time Θ_1. The tendency is evident — the separation between the peaks increases. Even the third peak can reliably be resolved only in the case when Θ_1 is much smaller than the relaxation time at actual temperature. However, this experimental approach brings also a disadvantage: The standard Lang formalism to the analysis of such spectra should lead to erroneous results mainly on activation energy [10]. This error is minimized by using the full expression (4) for the transient charge. The PEM used in TSD possesses excellent possibility to "cleaning" the complex spectra of relaxation time distribution, further standard approach being used without additional arrangement

When reducing Θ_1, the signal for a discrete energy level is reduced at its low-temperature side in the case of QDLTS and at its high-temperature side in the case of TSD. The shift of the maximum is rather pronounced. On the other hand, when reducing the duration of the charging pulses in the case of the broad distribution, the overall both QDLTS and TSD signal is reduced while the position of its maximum remaining the same for either Θ_1. The principal difference in the behavior of QDLTS and TSD responses related either to the discrete or the distributed energy cases, while using the partial excitation mode, may be regarded as a simple test for the presence of either of the two.

A numerical calculation showed that the shape of QDLTS as well as TSD curves is a direct reflection of shape of arbitrary shape of distribution function. The very narrow function $F(E, T)$ which gives a reason to such a phenomenon has generalized halfwidth of about $2.5 \times k_B T$ for both methods. Consequently, the QDLTS and TSD possesses the same resolution ability namely when the signal is positioned at lower temperatures. The amplitude reflection of the $G(E)$ seems to be better in the case of the TSD method.

Let us finally turn our attention to multistage TSD. The calculation presented above demonstrates the extraordinarily resolution ability of this experimental approach. In our calculations we considered the presence only distribution of activation energies. In some cases of

complex electrets also the distribution in pre-exponential factor τ_0 (*ie* in natural frequencies, $\nu_0 = 1/\tau_0$) are actual. The multistage TSD can be advocated to distinguish between a distribution in natural frequencies and one on activation energies. The multistage technique cannot be applied in the QDLTS method.

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