

ELECTRICAL RELAXATION RESPONSE OF MISM STRUCTURE MONITORED BY DLTS AND TSD METHOD

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Detailed analysis of the thermally stimulated depolarization (TSD) and charge deep level transient (QDLTS) responses of the metal—ideal insulator—high resistivity semiconductor—metal structure is performed. The possible presence of the frequency dependence of electrical conductivity which appears in connection with the hopping of carriers through localized states is considered. Our computer simulations show that the frequency dependent conductivity together with usual dc-conductivity leads to non-exponential responses in both TSD and QDLTS, formally to a time dependent relaxation time constant. Standard methods for evaluating the activation energy of the relaxation processes in such a case provide an erroneous result. We find a process which detects the presence of frequency dependent conductivity in the case of TSD. The QDLTS does not provide such a relatively simple method and the detection of the presence of frequency dependent conductivity is more complicated.

Key words: thermally stimulated depolarization, ideal insulator, high resistivity semiconductor

1 INTRODUCTION

There are various known methods for determining the electric conductivity of semiconductors. Using a two electrode system with large area contacts, relatively large currents can be obtained, however, the experimental results may be influenced or even dominated by the properties of the contact region. Usually blocking effects are observed which are caused by band bending in electronic contacts and resulting from polarization of the electrodes in ionic conductors. The way how to circumvent these difficulties is inserting a perfectly insulating plane layer (also an air gap) between the sample and the electrode in order to form an ideal blocking contact. Consequently, MISM or MISIM structure (M — metal, I — perfect insulator, S — semiconductor sample to be investigated) was suggested for the determination of the electrical conductivity of semi-insulators from the kinetics of discharging currents flowing after step voltage excitation. Müller's method [1] could be successfully used when only equilibrium electrical charge carriers would move over the mean free path while obtaining the energy corresponding to the higher energy levels in the conduction band. Doubt arises as to the interpretation of experimental results namely the frequency dependent transport via hopping through localized states in the forbidden gap occurs. Such a type of conductivity was widely observed in semiconducting chalcogenides [2], oxide glasses [3] and in some types of ceramics [4]. If the frequency dependent conduction is comparable with dc-conductivity, the electrical response of the system becomes non-exponential, consequently the interpretation of experimental results using a standard approach is misleading.

The present paper contains the analysis of the non-exponential response obtained by means of thermally stimulated depolarization (*eg*, in non-isothermal mode) — TSD or in isothermal regime using deep level transient spectroscopy — DLTS. Some experimental proofs of the presence of the non-exponential response are suggested.

2 THERMALLY STIMULATED DEPOLARIZATION

The well-defined arrangement consisting of a sample that is fully insulated from the metallic electrode by a foil of non-conducting polymer, presented in Fig. 1, is chosen for further considerations. Electrical relaxation by the movement of equilibrium charge carriers was investigated by Müller [1, 5]. Immediately after applying a voltage on the MISM structure the free carriers move and concentrate in a narrow layer close to the electrode — the initial polarization $P_0 = Q_0/S$ is established, with Q_0 being the charge on the electrode and S the cross section of the sample. The time variation of the polarization in the short-circuited sample can be written as

$$-\frac{dP(t, T)}{dt} = i(t, T) = \sigma(T)F(t) = \sigma(T)\frac{P(t, T)}{\varepsilon_0\varepsilon_1}, \quad (1)$$

where ε_1 is the relative permittivity of the sample, $\sigma(T)$ is the conductivity

$$\sigma(T) = \sigma_0 \exp\left(-\frac{E_C}{kT}\right), \quad (2)$$

here σ_0 , E_C , k , and T have the usual meaning, and $F(t)$ is the electric field in the sample. Equation (1) was derived [1] assuming that the spatial extension of the separated charge is small compared with the thickness of

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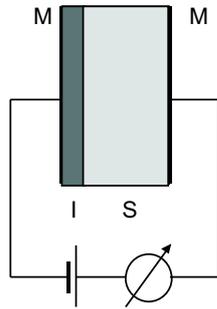


Fig. 1. Schematic representation of a MISIM structure as used for numerical simulations of electric relaxation currents (TSD) and charges (QDLTS) (M — metallic electrodes, S — high resistivity semiconductor, I — perfect insulator).

the sample, that the sample is a semiconducting insulator with higher resistance than that of classical semiconductors. The geometrical factor f which includes the thickness and the relative permittivities of both the sample and the foil, d_1 , d_2 and ε_1 , ε_2 , respectively [1] is set equal one, $f = 1$.

In order to measure the TSD spectrum, the fully charged MISIM structure is cooled down with the voltage applied to a low temperature where all carriers are fixed. Then the voltage is switched off and the system is heated up without any external field. After switching off the voltage and short-circuiting the sample, the inner field F is built up inducing the relaxation process. When during heating the sample becomes conducting, a discharging current will be measured corresponding to the disappearance of the induced charge on the insulated electrode. Using a linear heating regime

$$\frac{dT}{dt} = v \quad \text{or} \quad T = T_0 + vt, \quad (3)$$

the polarization is given by

$$P(T) = P_0 \exp\left(-\int_{T_0}^T \frac{\sigma(T)}{v\varepsilon_0\varepsilon_S} dT\right), \quad (4)$$

where v ($v = \text{const}$) is the heating rate and T_0 is the temperature of switching off the voltage. If the temperature of the sample is given by (3), one obtains the current density

$$i(T) = \frac{\sigma_0 P_0}{\varepsilon_0 \varepsilon_S} \exp\left[-\frac{E_C}{kT} - \frac{\sigma_0}{v\varepsilon_0\varepsilon_S} \int_{T_0}^T \exp\left(-\frac{E_C}{kT}\right) dT\right]. \quad (5)$$

Introducing the relaxation time constant

$$\tau(T) = \tau_0 \exp\left(\frac{E_C}{kT}\right) = \frac{\varepsilon_0 \varepsilon_S}{\sigma_0} \exp\left(\frac{E_C}{kT}\right), \quad (6)$$

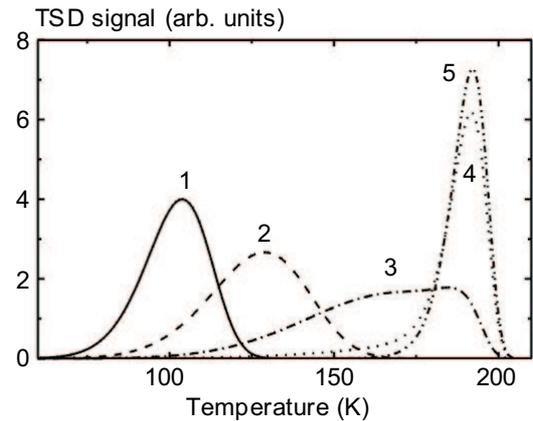


Fig. 2. Calculated TSD curves for linear heating, $v = 0.15 \text{ Ks}^{-1}$. In the case (1) ac-conductivity dominates contrary to the case (5) when dc-conductivity is prevailing. Other parameters: $b = \sigma_{0a}/\sigma_{0d} = 10^{-8}$ (1), 10^{-9} (2), 10^{-10} (3), 10^{-11} (4), and 10^{-12} (5), $s = 0.8$, $E_d = 0.6 \text{ eV}$, $E_a = 0.1 \text{ eV}$.

(assuming that ε_S is not temperature dependent) Eq. (5) can be rewritten into

$$i(T) = \frac{P_0}{\tau} \exp\left[-\int_{T_0}^T \frac{1}{v\tau(T)} dT\right], \quad (7)$$

which is equivalent to the Bucci-Fieschi equation [6, 7] for the ionic termocurrent (ITC) method. The standard approach to the interpretation of ITC response can be used in our consideration:

- 1) For the low temperature part of the TSD glow curve one can obtain

$$\ln i(T) = \text{const} - \frac{E_C}{kT}, \quad (8)$$

which allows the determination of the value of the activation energy E_C .

- 2) The activation energy can be obtained by using two different heating rates v_1 and v_2 . Using the temperatures of the maxima of the corresponding TSD curves T_{m1} and T_{m2} one can write the equation

$$E_C = k \frac{T_{m1} T_{m2}}{T_{m1} - T_{m2}} \ln \left[\frac{v_1}{v_2} \left(\frac{T_{m1}}{T_{m2}} \right)^2 \right]. \quad (9)$$

According to Müller's theory the parameters of the electric conductivity are available from the TSD measurements on a MISIM (or MISIM) structure.

Let us consider that the parameters of the electric conductivity of a semiconductor sample can be generally expressed as a sum of two parts

$$\sigma = \sigma_d + \sigma_a, \quad (10)$$

where σ_d stands for dc-conductivity and σ_a is the frequency dependent part

$$\sigma_a = A\omega^s. \quad (11)$$

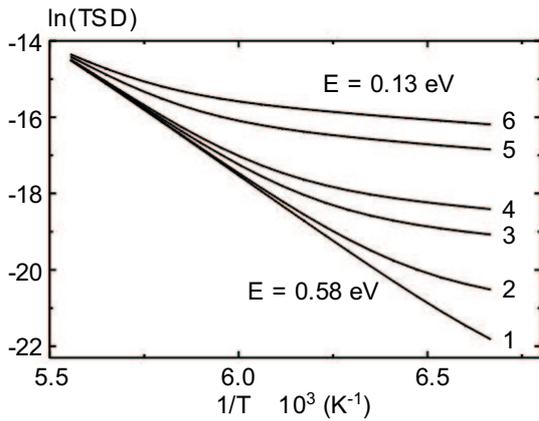


Fig. 3. Logarithm of the low-temperature part of the TDS signal. $b = 10^{-12}$ (1), 10^{-11} (2), 10^{-10} (3), 5×10^{-10} (4), 10^{-9} (5), and 10^{-8} (6). Other parameters are the same as in Fig. 2.

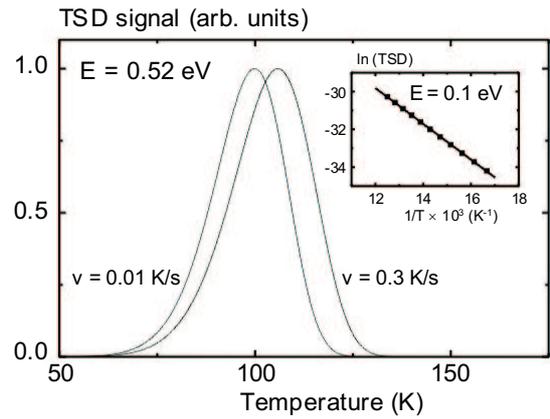


Fig. 4. TSD currents calculated for linear heating at two different velocities. The activation energy, as determined using Eq. (9) is $E = 0.52$ eV. The inset presents the logarithm of the low-temperature part of the TSD signal obtained for $v = 0.01$ Ks $^{-1}$. The slope corresponds to the effective activation energy $E = 0.1$ eV. Other parameters: $b = 10^{-8}$, $s = 0.8$, $E_d = 0.6$ eV, $E = 0.1$ eV.

Here A is a frequency independent constant, ω is the frequency, and $0 < s < 1$.

The time dependence of ω_a can be obtained by means of the reverse Fourier transform

$$\sigma_a(t) \propto \int_0^\infty \varepsilon \sin(\omega t) d\omega.$$

Entering the expression for the imaginary part of permittivity

$$\varepsilon'' = \frac{\sigma}{\omega} \propto \omega^{s-1}.$$

The alternative form for $\sigma_a(t)$ is

$$\sigma_a(t) \propto \int_0^\infty \omega^{s-1} \sin(\omega t) d\omega.$$

Solving this integral one can obtain the conductivity in the time domain

$$\sigma_a(t) \propto t^{-s}. \quad (11a)$$

The effect of the time dependence of conductivity can be manifested during the TSD measurement starting at the moment when after switching off the voltage (at low temperature T_0 the inner electrical field is abruptly increased).

The following analyses are performed by numerical calculation of both parts of conductivity

$$\sigma = \sigma_{0d} \exp\left(-\frac{E_d}{kT}\right) + \sigma_{0a} \left(\frac{t}{\Theta}\right)^{-s} \exp\left(-\frac{E_a}{kT}\right). \quad (10a)$$

Constant Θ has a dimension of time and we set $\Theta = 1$ s.

In this case the TSD response has the form

$$i(t) \propto \left[\exp\left(-\frac{E_d}{kT}\right) + b \left(\frac{T - T_0}{v}\right)^{-s} \exp\left(-\frac{E_a}{kT}\right) \right] \times \exp\left\{ -\frac{\sigma_{0d}}{v} \int_{T_0}^T \left[\exp\left(-\frac{E_d}{kT}\right) + b \left(\frac{T - T_0}{v}\right)^{-s} \exp\left(-\frac{E_a}{kT}\right) \right] dT \right\}. \quad (12)$$

The TSD signal was calculated for various values of $b = \sigma_{0a}/\sigma_{0d}$ reflecting various representations of the single parts of conductivity.

The TSD currents calculated for the following set of parameters: $E_a = 0.1$ eV; $E_d = 0.6$ eV; $s = 0.8$; $v = 0.15$ Ks $^{-1}$ are shown in Fig. 2. The ratio b varies from 10^{-9} to 10^{-15} . Curve 5 in Fig. 2 represents the case when σ_d is dominant and the expression for the TSD current (12) reduces to Eq. (5). The logarithm of the low temperature part of the response gives a nearly straight line (Fig. 3 curve 1) with the slope providing the value of the activation energy $E_C \sim E_d$. The same procedure of evaluating the activation energy in the cases $b > 10^{-15}$ (the role of σ_a raises) gives neither activation energy E_d nor E_a (Fig. 3).

Another determination of the activation energy consists in the measurement of the TSD curves at various heating rates. Such measurements are numerically simulated in Fig. 4. If only σ_d is present, using Eq. (9) one obtains an evident result: the activation energy evaluated using temperature positions of the maxima is the same as that calculated using the logarithm of the low temperature part. On the other hand, the procedure with various heating rates in the case of the presence of the frequency dependent conductivity σ_a gives a value of the activation energy different from that one obtained by a logarithm of the low temperature part. Moreover, this value is neither E_d nor E_a .

So we can say that the evaluating of the activation energy using these different methods is a simple test for the presence of the frequency dependent part of conductivity in the investigated sample.

The temperature position of the maxima of the TSD response, calculated using Eq. (5) (only σ_d is present), does not depend on the starting temperature T_0 as far as polarization is sufficiently frozen (Fig. 5). When the

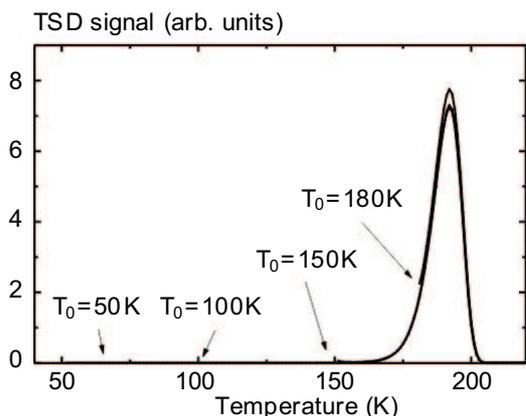


Fig. 5. Demonstration of the trivial fact that the TSD signal does not depend on the starting temperature T_0 , when the dc conductivity is dominant ($\sigma_{0a} = 0$ for these calculations).

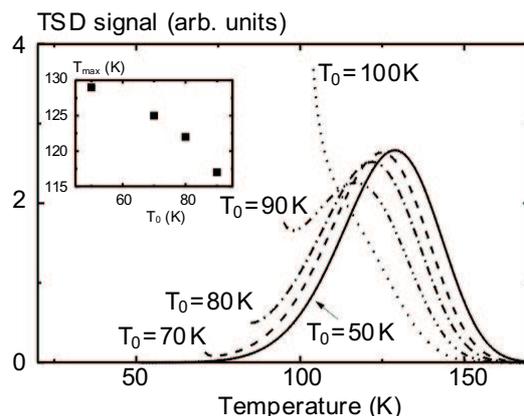


Fig. 6. TDS responses calculated for various starting temperatures T_0 . The dramatic drop in the temperature of the TSD maximum T_{max} is documented in the inset. The responses were calculated for $b = 10^{-6}$, $s = 0.8$, $E_d = 0.6$ eV, $E_a = 0.1$ eV, and $v = 0.15$ Ks $^{-1}$.

frequency dependent conductivity is present, the choice of T_0 influences the position of the TSD signal as is illustrated in Fig. 6 as well as the height of its maximum.

3 DEEP LEVEL TRANSIENT SPECTROSCOPY

The following analysis is focused on DLTS originally presented by Lang [8] in its modified version [9, 10] which is known as charge transient spectroscopy (QDLTS).

If a single exponential response to a voltage pulse excitation applied to the sample is assumed, the recorded signal can be expressed as follows:

$$\Delta Q = Q_0 \left[\exp\left(-\frac{t_2}{\tau}\right) - \exp\left(-\frac{t_1}{\tau}\right) \right]. \quad (13)$$

Here τ is the time constant (6) of the thermally activated relaxation, t_1 and t_2 are time instants of sampling. The maximum ΔQ_m of the QDLTS signal appears for

$$\tau(T_m) = \frac{t_2 - t_1}{\ln(t_2/t_1)}. \quad (14)$$

By changing the time t_1 (usually the ratio t_2/t_1 remains equal to 2 for all settings) the maxima of the signal are shifted to different temperatures T_m . This procedure allows to calculate the values of the decay time constant τ at different temperatures and, consequently, to construct the Arrhenius plot which provides information on the value of the activation energy.

Let us formally introduce the time constant as

$$\tau_a = \frac{\varepsilon}{\sigma_a} = \tau_{0a} \left(\frac{t}{\Theta}\right)^s \exp\left(\frac{E_a}{kT}\right) = \frac{\varepsilon}{\sigma_{0a}} \left(\frac{t}{\Theta}\right)^s \exp\left(\frac{E_a}{kT}\right), \quad (15)$$

with a comment that it follows from the expression of the time dependence of conductivity (11) and can represent

one type of non-exponentiality of the relaxation response. Solving the differential equation

$$\frac{dP}{dt} = -\frac{P}{\tau_a}, \quad (16)$$

the time dependence of the polarisation P is obtained

$$P = P_0 \exp\left[-\frac{\Theta^s}{\tau'_a(1-s)} t^{1-s}\right], \quad (17)$$

where τ'_a is the time independent part of the time constant $\tau'_a = \tau_{0a} \exp(E_a/kT)$. Consequently, for the QDLTS signal we have the expression

$$\Delta Q = Q_0 \left\{ \exp\left[-\frac{\Theta^s}{\tau'_a(1-s)} t_2^{1-s}\right] - \exp\left[-\frac{\Theta^s}{\tau'_a(1-s)} t_1^{1-s}\right] \right\}. \quad (18)$$

For its maximum we can write

$$\tau_a(T_m) = \frac{1}{(1-s)^2} \frac{t_2^{1-s} - t_1^{1-s}}{\ln(t_2/t_1)}. \quad (19)$$

If $s \rightarrow 0$, Eqs. (18) and (19) turn to Lang's formulas (13) and (14).

In the situation when both mechanisms of conductivity are present (σ_a as well as σ_d) the QDLTS signal is expressed as

$$\Delta Q = Q_0 \left\{ \exp\left[-\left(\frac{\Theta^s}{\tau_a(1-s)} t_2^{1-s} + \frac{t_2}{\tau_j}\right)\right] - \exp\left[-\left(\frac{\Theta^s}{\tau_a(1-s)} t_1^{1-s} + \frac{t_1}{\tau_j}\right)\right] \right\}. \quad (20)$$

For the time constant of the dc-conductivity τ_j we have the expression

$$\tau_j = \tau_{0j} \exp\left(\frac{E_j}{kT}\right) = \frac{\varepsilon}{\sigma_{0d}} \exp\left(\frac{E_j}{kT}\right). \quad (21)$$

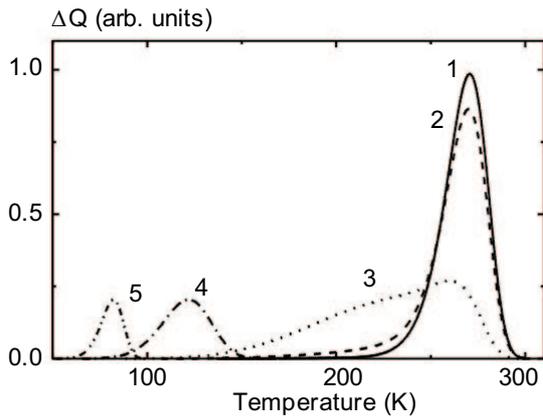


Fig. 7. QDLTS signals calculated for different values of $b = 10^{-14}$ (1), 10^{-13} (2), 10^{-12} (3), 10^{-10} (4), and 10^{-8} (5). Other parameters: $E_d = 0.6$ eV, $E_a = 0.1$ eV, $s = 0.8$, $t_1 = 10^{-3}$ s, $t_2 = 2t_1$.

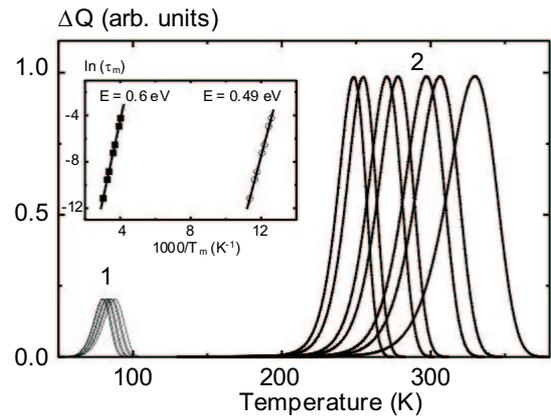


Fig. 8. Two families of QDLTS responses calculated for $b = 10^{-8}$ (1) and $b = 10^{-14}$ (2). For each value b , QDLTS signals were calculated for various time constants $t_1 = 10^{-5}$, 5×10^{-5} , 10^{-4} , 5×10^{-4} , 10^{-3} , 5×10^{-3} , 10^{-2} s. The subsequent evaluation of the activation energy according to standard Lang's approach is shown in the inset.

The family of QDLTS signals as a function of temperature T calculated using Eq. (20) is depicted in Fig. 7. Varying the ratio b a fatal shift along the temperature scale and a change of the shape of the response can be observed. For the purpose of a further analysis, the QDLTS responses for various time instants t_1 ($t_2 = 2t_1$) were calculated. Two families of curves in Fig. 8 correspond to the case when frequency dependent conductivity is present (curves 1) and to the case when it is omitted (curves 2). The numerically obtained QDLTS signals in Fig. 8 are further considered as an “experimental” result and according to standard Lang's approach Eq. (14) we construct Arrhenius' plots, which are straight lines in both cases. In the case of the presence of the frequency dependent conductivity (curves 1) the apparent value of activation energy $E_C = 0.49$ eV represents neither dc-conductivity nor the frequency dependent one. The slope of Arrhenius' plot (2) gives exactly the same value $E_C = E_d = 0.6$ eV as was chosen at the beginning of the calculation.

4 DISCUSSION

In our proposed model of MIS structure the frequency dependent ac-conductivity of a semiconductor sample is included into the electrical transport mechanism. The numerical simulations show that both TSD and QDLTS spectra differ significantly from those calculated for the model which considers solely dc-conductivity. In general, the analysis of the spectra according to the standard approach gives erroneous parameters of relaxation processes.

The electrical transport through localized states in the forbidden gap in a semiconductor is dominant at low temperatures. On the other hand the transport in the conduction band prevails at higher temperatures. These facts

correspond with the calculated TSD responses in Fig. 2. The signal in the case of dominant dc-conductivity is positioned at a higher temperature. Its low temperature tail gives, using (8), an approximate value of the activation energy $E_C = E_d$. With increasing the contribution of ac-conductivity, the TSD signals are shifted to lower temperatures while the area under the curves, *ie*, the relaxed charge, is preserved. By replotting the low temperature tails one obtains the apparent energies between $E_C = 0.6$ eV and the inherent value for ac-conductivity $E_a = 0.1$ eV.

Using two different heating rates, the TSD curves were calculated and with the aid of Eq. (9) the apparent activation energy $E_C = 0.52$ eV was obtained. Arrhenius' plot of the low temperature part of the peak obtained with the heating rate $v_1 = 0.01$ Ks $^{-1}$ gives the correct energy $E_C = E_a = 0.1$ eV.

The calculation of the TSD responses for various starting temperatures T_0 revealed the dependence of the temperature T_{\max} (T_{\max} is the temperature of TSD maximum) on temperature T_0 when ac-conductivity is dominant (Figs. 5,6). Then the experiment with varying T_0 is proposed as a test of the presence of ac-conductivity. The decrease of T_{\max} while increasing T_0 seems to be an unambiguous proof.

The family of QDLTS signals as functions of T calculated using (18) for various contributions of ac-conductivity (Fig. 7) show the same features as the TSD spectra. Using Lang's approach (14) the apparent activation energy can be obtained. The set of high temperature curves (Fig. 8) gives $E_C = E_d = 0.6$ eV while the set positioned at a low temperature provides the apparent energy which represents neither dc nor ac-conductivity.

The simple test to decide if the standard Lang's approach is justified was suggested in [11]. The experimental data are analysed using Lang's approach. The values of

the preexponential factor τ_0 and the activation energy are determined. Using these parameters, the QDLTS signal is numerically reconstructed. In the case of an exponential response (only dc-conductivity is present) one achieves a satisfactory agreement with experiment. On the other hand, when one deals with a non-exponential response (ac-conductivity is present), the reconstructed signal is narrower than the experimental signal. Another useful indicator of the presence of the non-exponential response is an unrealistically low value of the preexponential factor (as low as 10^{-18} s.)

Finally, let us turn our attention to the question whether there are possibilities for determining the parameters (namely activation energy) for dc and ac-conductivity separately. The two mechanisms of charge transport contribute simultaneously to the TSD or QDLTS response. The measure of individual contribution depends on temperature at which the signal appears. Consequently, only the apparent activation energy can be estimated from a measurement performed at medium temperatures. However, the apparent energy can reach the value characteristic for dc-conductivity if the measurement is situated to higher temperatures. This requirement is fulfilled by setting a high heating rate for the TSD or small values of time t_1 for QDLTS. Poor thermal stability of the measured material, the non-homogeneous temperature field in the volume of the sample owing to the high heating rate can make the high temperature measurement impossible. Low temperature measurement would lead to an approximate determination of parameters of ac-conductivity. However, TSD signal obtained at a low temperature using a slow heating rate is very broad with its maximum being comparable with the noise.

5 CONCLUSION

To investigate whether the standard interpretation of TSD and DLTS experiment with a nonexponential response is justified, TSD current and DLTS charge were calculated. As the model, MIS structure with frequency dependent conductivity of semiconductor built in the structure was considered.

The calculated spectra were considered as "experimental" results. It was shown that their interpretation following the standard approach leads to erroneous results. The experimental procedure which allows to decide if one

deals with either exponential or nonexponential response of relaxation process was described. Possible experiment for the determination of the approximate individual parameters of both dc- and ac-conductivity was suggested.

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