Numerical study of dependence of thermally stimulated currents in disordered solids at step heating regime on initial trap occupancy

W Tomaszewicz, P Grygiel
Department of Physics of Electronic Phenomena, Gdansk University of Technology, 11/12 Narutowicza Str., 80-233 Gdansk, Poland
E-mail: wtomasze@sunrise.pg.gda.pl

Abstract. In the present paper numerical investigation of thermally stimulated currents (TSCs) in disordered solids, measured at step heating regime, is performed. The utilized energy distribution of trapping states is the superposition of exponential and Gaussian distributions. The monomolecular carrier recombination regime is assumed. The resulting set of stiff differential equations governing TSCs is solved with the use of Gear's procedure. The calculations are made for several carrier generation and recombination rates. The TSC curves are next analyzed by the methods developed in previous papers and the calculated trap distributions are compared with the input distributions. It is concluded that the methods have satisfactory accuracy solely in the cases of week carrier retrapping or small trap occupancy.

1. Introduction
The measurements of thermally stimulated currents (TSCs) are widely applied technique of the determination of energy distribution of trapping states in disordered solids. The method consists in the photogeneration of excess carriers in the sample at low temperature and the subsequent sample heating, most frequently with a constant rate. The resulting dependence of TSC intensity on temperature is determined by the kinetics of carrier thermal release, retrapping and recombination.

In general, the interpretation of TSCs in disordered solids constitutes difficult and not fully resolved problem. This is due to uncertainty about the dominant mechanisms of carrier transport (multiple trapping (MT) or hopping) and recombination, as well as about the validity of approximations used for solving the corresponding equations. In recent years it has been established via numerical calculations that the MT model, assuming monomolecular carrier recombination, satisfactorily describes the TSCs measured in hydrogenated amorphous silicon (a-Si:H) [1, 2]. One of the factors complicating the TSC interpretation is the carrier retrapping, which results in gradual redistribution of captured carriers towards deeper traps. The reliable determination of energy distribution of trapping states is possible either in the case of sufficiently slow carrier retrapping [1, 2] or in the case of negligible trap occupancy [3]. The range of validity of the mentioned methods has been studied in [3] basing on the numerical calculations of TSCs for several values of carrier generation and recombination rates.

In some TSC measurements the complex heating schemes, consisting of several heating-cooling cycles, are also utilized. These measurements make possible to determine the charge released from the traps during sequential cycles as well as the corresponding trap depths (e.g., [4, 5]). However, the
determination of the energetic trap distribution is subject to the same limitations as indicated above. One can state that the methods described in [4, 5] apply in the case of very slow carrier retrapping. The methods taking into account the carrier retrapping, developed in [6 - 8], are valid only in the case of small trap filling. In the present paper the numerical study of TSCs registered at step heating regime is performed and the range of applicability of these methods is investigated. The investigation is the continuation of that presented in [3], which concerns the TSCs at linear sample heating.

2. Formulas for determining trap distribution

In the step heating regime the sample temperature \( T(t) \) is increased with the time \( t \) from initial temperature \( T_0 \) to higher and higher temperatures \( T_m \) (\( m \) – the cycle number) and then decreased to initial temperature, as shown in Fig. 1. The sample heating and cooling rates, \( \beta_h = dT(t)/dt \) and \( \beta_c = -dT(t)/dt \), are usually constant.

For complex heating schemes the initial rise of thermally stimulated conductivity, \( \sigma(T) \), has approximately an activated character [4 - 8]. When the trapping states are continuously distributed in a wide energy region, the activation energy is approximately equal to demarcation energy \( \varepsilon_m \), corresponding to the maximum temperature \( T_m \) of preceding heating cycle. The energy \( \varepsilon_m \) separates the traps with equilibrium \( (\varepsilon < \varepsilon_m) \) and non-equilibrium \( (\varepsilon \geq \varepsilon_m) \) occupancies. For the step heating regime the demarcation energy is given by the formula [6 - 8]

\[
\varepsilon_m \approx k \left( c^* T_m - T^* \right),
\]

(1)

Where

\[
c^* = 0.967 \ln(46 \text{ K} \cdot \nu / \beta), \quad T^* = 180 \text{ K},
\]

\[
\beta = \beta_h \beta_c / (\beta_h + \beta_c)
\]

and \( \nu \) is the frequency factor. Therefore, the rise of TSC conductivity at the onset of \((m+1)\)-th cycle is described by the formula

\[
\sigma(T) \propto \exp\left( -\varepsilon_m / kT \right),
\]

(2)

where \( k \) is the Boltzmann constant.

In the following it is assumed that the kinetics of carrier recombination has monomolecular character. When the carrier retrapping is negligible, the formula relating the trap density per energy unit, \( N(\varepsilon) \), and the charge, \( \Delta Q_m \), collected during \( m \)-th heating-cooling cycle may be derived from that given in [9]. It has the form of
Where
\[ \delta_f = 1 - (1 - \delta) \exp(-\tau RC_t n_0) , \]
\[ \varepsilon_m^* = \left( \varepsilon_{m-1} + \varepsilon_m \right) / 2 , \]
\[ \Delta \varepsilon_m = \varepsilon_m - \varepsilon_{m-1} . \]

In the equations \( n_0 \) is the initial density of carriers in the sample, \( \delta \) is the final relative occupancy of traps having depth \( \varepsilon \geq \varepsilon_{mi} \), \( Q_\infty \) is the total collected charge corresponding to the whole area under TSC curve, \( \delta = n_0/N_{tot} \) is the initial relative trap occupancy (with \( N_{tot} \) – the total trap density), \( \tau_R \) is the mean time of carrier recombination and \( C_t \) is the carrier capture coefficient. It is seen that for the determination of absolute trap density, \( N_t(\varepsilon) \), the value of initial carrier density \( n_0 \) and, in the case of final partial filling of the traps (\( \delta_f < 1 \)), the values of \( \delta \) and \( \tau_RC_t n_0 \) must be known.

When the initial trap occupancy is negligibly small, the relationship between \( N_t(\varepsilon) \) and the charge \( Q_m \), collected after \( m \) heating cycles has the following form [8]:
\[ N_t(\varepsilon_m^*) \approx \frac{Q_\infty}{\tau_R C_t} \frac{\Delta Q_{m-1}}{\Delta \varepsilon_m} , \]
where
\[ \Delta Q_{m-1} = Q_{m-1}^{-1} - Q_m^{-1} . \]

In this case the computation of absolute trap density requires the knowledge of \( \tau_RC_t \) value. The above equation takes into account the carrier retrapping, contrary to Eq. (3). One can check that for small initial trap filling and negligible carrier retrapping, when \( \delta \ll C_t n_0 \tau_R \ll 1 \) and \( \Delta Q_m \ll Q_m \) for arbitrary \( m \), Eqs. (3) and (5) become identical.

3. Numerical method
The calculation method follows closely that of the paper [3], except for the sample heating scheme. It is assumed that the dominant contribution to the TSC is due to electrons. The kinetic equations for free electron density, \( n(t) \), and trapped electron densities per energy unit, \( n_t'(t,\varepsilon) \), are
\[ \frac{d}{dt} \left[ n(t) + n_t'(t) \right] = G(t) - \frac{n(t)}{\tau_R} , \]
\[ \frac{d}{dt} n_t'(t,\varepsilon) = C_t \left[ N_t(\varepsilon) - n_t'(t,\varepsilon) \right] n(t) - \frac{n_t'(t,\varepsilon)}{\tau_R(\varepsilon,t)} , \]
\[ n_t(t) = \int_{0}^{\varepsilon_t} n_t'(t,\varepsilon) d\varepsilon . \]
with

$$\tau_r(\varepsilon, t) = v^{-1} \exp\left[\varepsilon/kT(t)\right].$$

Here, \(G(t)\) is the carrier generation rate, \(\tau_r(\varepsilon, t)\) is the mean carrier dwell-time in the traps of depth \(\varepsilon\) and \(\varepsilon_t\) is the maximum trap depth. The TSC conductivity is given by the formula,

$$\sigma_{\text{TSC}}(t) = e\mu n(t),$$

(9)

where \(e\) is the elementary charge and \(\mu\) is the free electron mobility.

As in [1 - 3], the model distribution \(N(\varepsilon)\) of electron traps is the superposition of the exponential and Gaussian distributions. The chosen distribution corresponds approximately to that established in a-Si:H. The main calculation parameters are listed in Table 1. For given parameters the total density of traps \(N_{\text{tot}} = 3\times10^{19} \text{ cm}^{-3}\) and the mean carrier capture time in empty traps \(\tau = 1/C_t N_{\text{tot}} \approx 3.33\times10^{-12} \text{ s}\).

| Parameter                                      | Value                      |
|-----------------------------------------------|----------------------------|
| Trap density of the exponential distribution at the band edge, \(N_{\text{te}}(0)\) | \(10^{17} \text{ cm}^{-3} \text{ eV}^{-1}\) |
| Characteristic energy of the exponential distribution, \(\varepsilon_{\text{ce}}\) | 0.03 eV                    |
| Maximum trap density of the Gaussian distribution, \(N_{\text{tg}}(\varepsilon_{\text{mG}})\) | \(10^{16} \text{ cm}^{-3} \text{ eV}^{-1}\) |
| Centre of the Gaussian distribution, \(\varepsilon_{\text{mG}}\) | 0.6 eV                     |
| Half-width of the Gaussian distribution, \(\varepsilon_{\text{cG}}\) | 0.2 eV                     |
| Maximum trap depth, \(\varepsilon_t\) | 0.9 eV                     |
| Carrier capture coefficient, \(C_t\) | \(10^{8} \text{ cm}^3 \text{ s}^{-1}\) |
| Frequency factor, \(\nu\) | \(10^{12} \text{ s}^{-1}\) |
| Free electron mobility, \(\mu\) | \(10 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}\) |

For the purpose of numerical calculations the model trap distribution is approximated by the 6000 discrete trap levels. The obtained set of stiff differential equations is solved with the use of modified Gear’s subroutine DIFSUB [10]. In program the TSC conductivity \(\sigma(t)\) is computed and next the relative collected charges \(\Delta Q_m/Q_\infty\) and \(Q_m/Q_\infty\) are calculated.

It is assumed that the carrier generation rate is given by:

$$G(t) = G_0, \quad t < t_{\text{exc}},$$

$$G(t) = 0, \quad t \geq t_{\text{exc}},$$

(10)

with the sample excitation time \(t_{\text{exc}} = 10 \text{ s}\). The maximum temperatures of sequential heating-cooling cycles (cf. Fig. 1) are determined by

$$T_m = T_0 + m\Delta T,$$

(11)

with \(T_0 = 20 \text{ K}\) and \(\Delta T = 25 \text{ K}\). The heating and cooling rates are \(\beta_h = 0.05 \text{ K/s}\) and \(\beta_c = 0.1 \text{ K/s}\), the onset of first cycle is \(t_{s1} = 100 \text{ s}\), and the number of cycles equals to 12.
4. Results and discussion

Figure 2. The TSC curves computed for low value of the carrier recombination time, \( \tau_R = 10^{-10} \) s, and two values of the carrier generation rate, \( G_0 = 10^{14} \) cm\(^{-3}\) s\(^{-1}\) (a) and \( 10^{18} \) cm\(^{-3}\) s\(^{-1}\) (b). The calculated TSC curves corresponding to the values \( \tau_R = 10^{-10}, 10^{-8} \) and \( 10^{-6} \) s of the mean time of carrier recombination are presented, respectively, in Figs. 2, 3 and 4. In each figure two curves calculated for the values \( G_0 = 10^{14} \) and \( 10^{18} \) cm\(^{-3}\) s\(^{-1}\) of the carrier generation rate are shown. The curves are marked by a) and b), respectively. Since \( \tau_i \ll \tau_R \), the initial carrier density in the sample equals to \( n_0 = G_0 t_{\text{exc}} \). Therefore, for given values of \( G_0 \) the initial trap filling amounts, respectively, to \( \delta = 3.33 \times 10^{-5} \) and \( 3.33 \times 10^{-1} \). The curve envelopes are almost identical with the corresponding TSC curves computed in [3] for linear sample heating.

Figure 3. The TSC curves computed for intermediate value of the carrier recombination time, \( \tau_R = 10^{-8} \) s, and two values of the carrier generation rate, \( G_0 = 10^{14} \) cm\(^{-3}\) s\(^{-1}\) (a) and \( 10^{18} \) cm\(^{-3}\) s\(^{-1}\) (b).
Figure 4. The TSC curves computed for high value of the carrier recombination time, $\tau_R = 10^{-6}$ s, and two values of the carrier generation rate, $G_0 = 10^{14}$ cm$^{-3}$ s$^{-1}$ (a) and $10^{18}$ cm$^{-3}$ s$^{-1}$ (b).

Figs. 2 - 4 illustrate the growing influence of carrier retrapping on the TSCs with the increase of carrier recombination time, $\tau_R$. The shape of TSC curves in Figs. 2a and 2b corresponding to different values of $G_0$ is almost identical and their envelopes have the form similar to that of the trap distribution. This indicates that the carrier retrapping is practically negligible. The shape of TSC curves in Figs. 3a and 4a corresponding to lower generation rate $G_0$ significantly changes which shows the increasing influence of the carrier retrapping. Making use of Eq. (4) one can prove that the final trap occupancy is negligibly small for the curves from Figs. 2a and 3a and is almost complete for the curve from Fig. 4a. On the other hand, the form of TSC curves in Figs. 3b and 4b, which correspond to higher value of $G_0$, changes only slightly due to significant trap occupancy.

The obtained TSC curves are analyzed as follows. The activation energies $\varepsilon_m$ of the initial TSC rise for sequential heating-cooling cycles are calculated from the plots of $\ln \sigma_{TSC}(t)$ versus $1/T$. Since the initial rise of TSC is slightly faster than predicted by Eq. (2), the calculation of $\varepsilon_m$ is somewhat arbitrary. The exemplary plot of the dependence of $\varepsilon_m$ on the maximum temperature $T_m$ is shown in Fig. 5. As is seen, there is rather good agreement with Eq. (1).

According to above discussion, for the TSC curves in Figs. 2a and 3a
the energetic trap distribution may be determined from Eq. (5) and for the curves in Figs. 2b and 4b - from Eq. (3). The comparison of the calculated trap distributions (points) with the input trap distribution (continuous line) is presented, respectively, in Figs. 6a and 6b. For sufficiently small carrier recombination times the accuracy of reconstruction in both figures is quite satisfactory. However, the accuracy of reconstruction in Fig. 6b worsens with increasing recombination time of the carriers, i.e., with more intensive carrier retrapping. The present study shows that the correct interpretation of TSC measurements requires the knowledge of the extent of trap filling. This emphasizes the importance of the experimental investigations of TSC dependence on the carrier generation rate.

![Graph](image)

**Figure 6.** The output trap distributions (points) calculated from several TSCs given in Figs. 2 – 4, compared with the input distribution (solid line). The distributions in (a) indicated by (×) and (●) are obtained, respectively, from the curves in Figs. 2a and 3a making use of Eq. (5). The distributions in (b) marked by (×) and (●) are obtained using Eq. (3) from the curves in Figs. 2b and 4b, respectively.

It is worth to notice that very similar results were obtained in [3] for the linear sample heating. Although the TSC measurements at complex heating schemes are more complicated, they enable us to determine the dependence of demarcation energy on temperature in straightforward manner. On this basis one can distinguish between the cases of discrete trap levels and continuous trap distribution [4, 5].

5. Conclusion

We have demonstrated that the form of TSC curves in disordered solids strongly depends on the carrier generation and recombination rates. Subject to the monomolecular recombination kinetics, the reliable determination of the energetic trap distribution is possible either in the case of very week carrier retrapping or in the case of negligibly small trap occupancy.

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