Numerical study of the dependence of thermally stimulated currents in disordered solids on initial trap occupancy

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Abstract. In the paper a numerical investigation of thermally stimulated currents (TSCs) in disordered solids, which are characterized by continuous energy distribution of trapping states, is presented. The set of stiff differential equations governing TSCs is solved with the use of Gear’s algorithm. The dependence of TSC curves on the initial trap occupancy as well as on the carrier recombination time is examined. It is concluded that the Fritzsche-Ibaraki method of TSC analysis, ameliorated by other authors, applies solely for almost complete trap filling and high carrier recombination rate. In the case of small trap filling the method of analysis the TSCs proposed by the present authors may be more adequate.

1. Introduction

The thermally stimulated current (TSC) method is potentially a powerful tool of investigating the energy distribution of trapping states in disordered solids. In the TSC measurements the sample is cooled down to a low temperature, illuminated to generate excess charge carriers and after some delay is heated in the dark, more frequently at a constant rate. The temperature dependence of resulting TSC intensity is determined by the kinetics of carrier thermal release, retrapping and recombination.

The TSC technique has been applied to many disordered solids, especially to amorphous hydrogenated silicon (a-Si:H), e.g. [1,2]. However, the interpretation of obtained results turned out to be difficult and controversial [3-5]. This was due to uncertainty about the underlying mechanism of carrier transport, multiple-trapping (MT) or hopping, and about the validity of some approximations used.

In recent years it has been demonstrated via numerical simulations that the MT model well reproduces the shape of TSC curves measured in a-Si:H, as well as their dependencies on the heating rate and the initial temperature [6,7]. It has been shown that the Fritzsche-Ibaraki method of TSC analysis [1], ameliorated by other authors [6], makes possible to determine the energy distribution of trapping states in a solid with good accuracy. The applicability of the method requires, among others, almost complete filling of traps by excess carriers at the onset of TSC experiment. The alternate theories of TSCs, based on the MT model and assuming negligibly small or fractional initial trap occupancy, have been developed in [8-10]. Therefore, it seems desirable to study the dependence of TSCs on the extent of initial trap filling and establish the range of validity of the mentioned theories. This is the aim of the present paper.

2. Formulas for determining trap distribution

Here, some formulas resulting from the MT model, which may be used in the analysis of measured TSCs, are recalled. The equilibration of charge carriers in the traps is characterized by the position
of demarcation energy level, $\varepsilon_0(T)$, in the energy gap, where $T$ denotes the sample temperature. In the following, the energy will be measured from the edge of allowed band. For the linear heating scheme, $T(t) = T_0 + \beta t$ (with $T_0$ – the initial temperature, $\beta$ - the heating rate, $t$ – the time), the limiting energy is given by [1]:

$$\varepsilon_0(T) \approx ki(c^* T - T^*),$$

$$c^* = 0.967 \ln(46K \cdot v / \beta), \quad T^* = 180K.$$

Here, $k$ is the Boltzmann constant and $v$ is the frequency factor.

Subject to the conditions that the carrier retrapping is negligible and the kinetics of carrier recombination has a monomolecular character, the trap density per energy unit, $N_t(\varepsilon_0)$, and the TSC conductivity, $\sigma_{TSC}(T)$, are interrelated by [10]:

$$N_t(\varepsilon_0) \approx \frac{\sigma_{TSC}(T)}{\delta_f} \cdot \mu \tau_{R},$$

$$\delta_f = 1 - (1 - n_0 / N_{tot}) \exp(-\tau_{R} C_t n_0) .$$

Here, $e$ is the elementary charge, $\mu$ - the microscopic carrier mobility, $\tau_{R}$ – the mean time of carrier recombination, $n_0$ – the density of generated carriers, $N_{tot}$ – the total trap density, $C_t$ – the carrier capture coefficient. Eq. (2) can be considered as the extension of the formula obtained by Fritzschke and Ibaraki [1] and re-derived in [6] to the case of an arbitrary trap occupancy. In [6] more elaborated formulas for $\varepsilon_0(T)$ and $N_t(\varepsilon_0)$ were given. It will be shown, however, that Eqs. (1)-(2) have usually sufficient accuracy.

In the case of negligibly small initial trap filling and monomolecular carrier recombination the relationship between $N_t(\varepsilon)$ and $\sigma_{TSC}(T)$ resulting from the formulas given in [9] has the form of:

$$N_t(\varepsilon_0) \approx \frac{a_n \sigma_{TSC}(T)}{k c^* \mu \tau_{R}},$$

$$a(T) = \int_{T_0}^{T} \sigma_{TSC}(T') \mu \tau_{R} \mu c^* \sigma_{TSC}(T'),$$

$$a_n \equiv a(x) = e \mu n_0 \tau_{R}.$$  

The $a(T)$ function corresponds to the area under TSC curve determined by the ordinates $T_0$ and $T$. Contrary to Eq. (2), Eq. (3) takes into account the carrier retrapping. It can be shown that for small trap filling and negligible carrier retrapping, when $a(T) \approx a_n$, Eqs. (2) and (3) became equivalent.

3. Numerical method

In general, the calculation method follows that of the paper [7]. The treatment concerns to electron-dominant conduction, monovalent trapping states and monomolecular carrier recombination. In distinction to [7], neither the time dependence of the carrier recombination rate nor the dark current contribution to TSC are taken into account. Then, the rate equations for free electron density, $n(t)$, and trapped electron densities per energy unit, $n_i(t, \varepsilon)$, are

$$\frac{d}{dt}[n(t) + n_i(t)] = G(t) - \frac{n(t)}{\tau_{R}},$$

$$\frac{dn_i(t, \varepsilon)}{dt} = C_i [N_i(\varepsilon) - n_i(t, \varepsilon)] n(t) - \frac{n_i(t, \varepsilon)}{\tau_{R}(\varepsilon, t)},$$

with

$$\tau_{R}(\varepsilon, t) = v^{-1} \exp[\varepsilon/kT(t)],$$

$$n_i(t) = \int_{0}^{\varepsilon} n_i(t, \varepsilon) d\varepsilon .$$

In the above equations $G(t)$ is the carrier generation rate, $\tau_{R}(\varepsilon, t)$ is the mean carrier dwell-time in the traps of depth $\varepsilon$ and $\varepsilon_0$ is the maximum trap depth. The TSC conductivity is proportional to the density of free carriers,
As in [6,7], the model distribution $N(ε)$ of electron traps consists of an exponential ‘tail’ of conduction band and a deep Gaussian ‘bump’. The distribution corresponds roughly to that established in $a$-Si:H. The basic calculation parameters are listed in Table 1. For given parameters the total density of traps $N_{tot} = 3 \cdot 10^{19}$ cm$^{-3}$ and the mean carrier capture time in empty traps $τ = 1/C_t N_{tot} ≈ 3.33 \cdot 10^{-12}$ s.

Table 1
Parameters used in the numerical calculations

| Parameter                                          | Value                      |
|----------------------------------------------------|----------------------------|
| Trap density of the exponential distribution at the band edge, $N_{tE}(0)$ | $10^{21}$ cm$^{-3}$ eV$^{-1}$ |
| Characteristic energy of the exponential distribution, $ε_{cE}$ | 0.03 eV                   |
| Maximum trap density of the Gaussian distribution, $N_{tG}(ε_{mG})$ | $10^{16}$ cm$^{-3}$ eV$^{-1}$ |
| Centre of the Gaussian distribution, $ε_{mG}$ | 0.6 eV                    |
| Half-width of the Gaussian distribution, $ε_{cG}$ | 0.2 eV                    |
| Maximum trap depth, $ε_t$ | 0.9 eV                    |
| Carrier capture coefficient, $C_t$ | $10^8$ cm$^3$ s$^{-1}$ |
| Frequency factor, $ν$ | $10^{12}$ s$^{-1}$ |
| Free electron mobility, $µ$ | $10$ cm$^2$ V$^{-1}$ s$^{-1}$ |

For the purpose of numerical calculations Eqs. (5) – (6) are discretized in energy. The resulting set of stiff differential equations is solved with the use of Gear’s subroutine DIFSUB [11]. The original procedure is slightly modified in order to take into account the sparse form of the Jacobian of considered equations. It is assumed that the time dependencies of the carrier generation rate and the sample temperature are given by:

$$G(t) = G_0, \quad t < t_{exc},$$
$$G(t) = 0, \quad t ≥ t_{exc},$$

(8)
The values of corresponding parameters are: $t_{exc} = 10 \text{ s}$, $T_0 = 20 \text{ K}$, $\beta = 0.05 \text{ K/s}$, $t_{rel} = 100 \text{ s}$.

Fig. 2. The TSC curves computed for intermediate value of the carrier recombination time, $\tau_R = 10^{-8} \text{ s}$, and three values of the carrier generation rate, $G_0 = 10^{14} \text{ cm}^3 \text{ s}^{-1}$ (curve 1), $10^{16} \text{ cm}^3 \text{ s}^{-1}$ (curve 2), $10^{18} \text{ cm}^3 \text{ s}^{-1}$ (curve 3).

Fig. 3. The TSC curves computed for high value of the carrier recombination time, $\tau_R = 10^{-6} \text{ s}$, and three values of the carrier generation rate, $G_0 = 10^{14} \text{ cm}^3 \text{ s}^{-1}$ (curve 1), $10^{16} \text{ cm}^3 \text{ s}^{-1}$ (curve 2), $10^{18} \text{ cm}^3 \text{ s}^{-1}$ (curve 3).

4. Results and discussion

Figs. 1, 2 and 3 show the TSC curves, corresponding to different values of the mean time of carrier recombination, $\tau_R = 10^{-10}$, $10^{-8}$ and $10^{-6} \text{ s}$, respectively. In each figure three TSC curves calculated for different values of the carrier generation rate, $G_0 = 10^{14}$, $10^{16}$, $10^{18} \text{ cm}^3 \text{ s}^{-1}$, are presented. For given values of $G_0$ the initial trap filling amounts to $n_0/N_{tot} = 3.33 \times 10^{-5}$, $3.33 \times 10^{-3}$, $3.33 \times 10^{-1}$, respectively.
It can be seen that for the smallest value of $\tau_R$ (cf. Fig. 1) the shape of TSC curves is almost independent of the carrier generation rate $G_0$ and follows almost exactly the trap distribution. This indicates that the carrier retrapping is practically negligible in the whole temperature region. In this case the energy distribution of traps may be determined from Eq. (2). One can notice that for the calculation of absolute trap density the value of $\mu \tau_R$ must be known. It is usually determined from the photoconductivity measurements [1]. In the case of partial trap filling ($\delta < 1$) the knowledge of the factors $n_0/N_{int}$ and $\tau_R C_{int}$ is also needed.

For larger values of $\tau_R$ (cf. Figs. 2 and 3) the form of TSC curves corresponding to higher carrier generation rate $G_0$ somewhat changes. This means that the Eq. (2) should reproduce the form of trap distribution only approximately. For intermediate and low values of $G_0$ the initial TSC intensities increase with temperature and are significantly lower compared to the previous case. This is due to the carrier retrapping. For sufficiently high temperatures the curves corresponding to different values of $G_0$ overlap. Thus, the Eq. (2) is applicable only in higher temperature region. For the lowest value of $G_0$ the intensity of TSC in Fig. 2 decreases in whole temperature range. This corresponds to the case of small trap filling. Then, the energetic trap distribution can be determined from Eq. (3). In this case the computation of absolute trap density requires the knowledge of the factor $\tau_R C_n$.

![Fig. 4. The output trap distributions (points) calculated from several TSCs given in previous figures compared with the input distribution (solid line). The distributions marked by (×) and (+) are obtained using Eq. (2) from the curves 3 in Figs. 1 and 3, respectively. The distribution indicated by (•) is obtained from the curve 1 in Fig. 2, making use of Eq. (3).](image)

Fig. 4 presents the comparison of the trap distributions (points) determined from the simulated TSC curves with the input trap distribution (continuous line). The distributions marked by (×) and (+) are obtained using Eq. (2) from the curves 3 in Figs. 1 and 3, respectively. It can be recognized that the accuracy of reconstruction worsens with the increase of carrier recombination time, i.e., with more intensive carrier retrapping. The distribution indicated by (•) is obtained from Eq. (3) and the curve 2 in Fig. 2. The accuracy of this reconstruction is comparable with that marked by (×).

The given study indicates the importance of experimental investigation of the TSC dependence on the carrier generation rate. The knowledge of the extent of trap filling is necessary for the correct interpretation of obtained results. It is worth to notice that the dependence of TSCs curves measured in a-Si:H [1] on the generation rate of carriers seems to be similar to that presented in Fig. 3.
5. Conclusion

We have demonstrated that the form of TSC curves in disordered solids strongly depend on the carrier generation rate and, therefore, on the initial trap occupancy. The Fritzsche-Ibaraki method of TSC analysis is applicable only for the case of almost complete trap filling and high carrier recombination rate. In the case of negligible trap occupancy the method of analysis the TSCs proposed by the present authors is more suitable.

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