

The kinetics of trapping and recombination in low dimensional structures

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Received 26 June 1999; accepted 10 September 1999

Abstract

A one-dimensional structure consisting of traps and recombination centres is considered. Kinetics of trapping and recombination of charge carriers in this system is studied numerically by means of the Monte Carlo method. It is shown that such a system may exhibit some interesting properties that are not predicted by classical theories. Particularly, an additional peak could be observed relating to charge carriers' transport along the chain. These properties could be observed on thermoluminescence (TL) as well as thermally stimulated conductivity (TSC) curves. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Trap levels; Recombination of charge carriers; Monte Carlo methods; Thermoluminescence (TL); Thermally stimulated conductivity (TSC)

1. Introduction

Physical properties of charge carriers' traps are usually studied by thermally stimulated relaxation (TSR) techniques. Among them, the most popular are thermally stimulated conductivity (TSC) and thermoluminescence (TL). During initial stage of these processes, at appropriate "low" temperature T_0 , a sample under study is excited in any way — e.g., by high energy radiation. The excitation fills charge carriers' traps with electrons and holes. Then, increasing temperature, one increases the probability of detrapping and charge carriers (here, we assume electrons) are released from traps. The free carriers may be recaptured by empty traps or may recombine with opposite charge carriers. Measuring conductivity of the sample or luminescence one calls the processes TSC or TL, respectively. A series of peaks appearing on TL or TSC spectrum may be attributed to trap levels characterised by different activation energies E_i and frequency factors v_i . Theoretical description of these non-equilibrium phenomena usually assumes uniform distribution of traps and recombination centres (the simple model [1]). For the sake of simplicity, it is assumed that only one type of charge carriers — i.e., electrons may be released from traps. Analysing the

kinetics, it is possible to write the following set of differential equations:

$$-\dot{n}_i = n_i v_i \exp\left(\frac{-E_i}{kT}\right) - n_c A_i (N_i - n_i), \quad i = 1 \dots p, \quad (1a)$$

$$-\dot{m}_s = B_s m_s n_c, \quad s = 1 \dots k, \quad (1b)$$

$$\sum_{s=1}^k m_s = \sum_{i=1}^p n_i + n_c + M, \quad (1c)$$

where N_i , n_i , and m_s denote the concentrations of trap states, electrons trapped in "active" traps and holes trapped in recombination centres. M stands for the number of electrons in the thermally disconnected traps (deep traps), i.e., traps that are not emptied during the experiment. A_i and B_s stand for the trapping and recombination probabilities, respectively. Luminescence intensity is proportional to $(-m)$. The set of Eqs. (1a), (1b) and (1c) is strongly nonlinear and it has no analytical solutions. Hence, only numerical solutions are possible. Approximate solutions are known as first- and second- order kinetics [1]. Another extreme case is the model of localised transitions by Halperin and Braner [2] regarding hole–electron pairs trapped close to each other. For this case, it was also possible to formulate differential equations describing charge carriers' kinetics. Straightforward approximation usually leads to a simple first-order kinetics.

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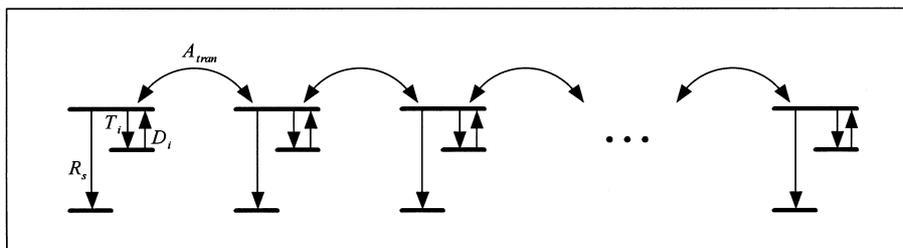


Fig. 1. Allowed transitions between localized energy states in one-dimensional system. (R_s) Denotes recombination; (T_i) trapping; (D_i) detrapping (thermal activation); and (A_{tran}) transition between neighbouring trap clusters.

Recently, it was also shown [3,4] that other spatial arrangement of traps could have an effect on TSR properties. Taking into account spatial correlation between traps and recombination centres, one can get unusual TL and TSC spectra that cannot be described in terms of the above standard models. For example, in some cases, one can easily identify false peaks that could not be attributed to any real trap level in a solid [4]. This case can be found in solids containing small clusters of traps. In this paper, a new Monte Carlo algorithm is applied for the calculation of trapping and recombination properties in one-dimensional systems. Assuming that charge traps are aligned along a chain (e.g., a polymer) where charge carriers' transport is possible, we study properties of TL and TSC. It will be shown that in such structure an additional TL (or TSC) peak can be observed that relates to the transport of charge carriers along the chain. Nevertheless, the peak could not be described (and analysed) in terms of standard kinetic models.

2. The model

To perform Monte Carlo calculations, a simple one-dimensional structure is proposed as shown in Fig. 1. It is assumed that only one type of charge carriers (here, elec-

trons) can move between excited states. Holes are trapped in recombination centres. Instead of solving the set of differential Eqs. (1a), (1b) and (1c), we have to consider elementary charge carrier transitions. In a solid having discrete trapping and recombination levels, the following transitions are allowed: detrapping of a carrier to a local excited level D_i , trapping T_i from the excited state to a given trap, and recombination R_s of a carrier from the excited state to a recombination centre. These transitions are given by the following equations:

$$D_i = v_i \exp\left(\frac{-E_i}{kT}\right) \quad (2)$$

$$T_i = A_i (N_i - n_i), \quad (3)$$

$$R_s = B_s m_s. \quad (4)$$

In general, we can assume that traps and recombination centres form clusters (groups of traps) having common excited state. It is assumed that the transition probability between neighbouring clusters A_{tran} is also thermally activated, so it is given by the following equation:

$$A_{\text{tran}} = v_{\text{tr}} \exp\left(\frac{-E_{\text{tr}}}{kT}\right) \quad (5)$$

where E_{tr} is the effective activation energy and v_{tr} is the pre-exponential factor. The temperature T may be an

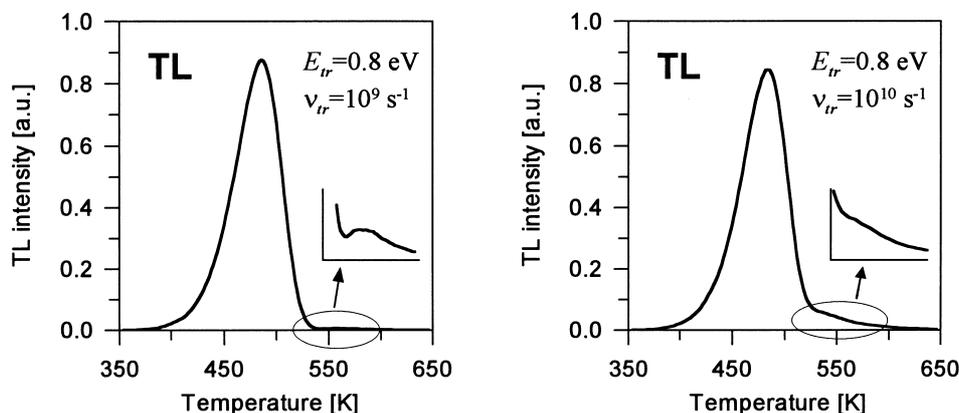


Fig. 2. Thermoluminescence glow curves ($-dm/dt$) calculated for $E_{\text{tr}} = 0.8$ eV and two values of the pre-exponential factors $v_{\text{tr}} = 10^9$ s $^{-1}$ and $v_{\text{tr}} = 10^{10}$ s $^{-1}$.

Table 1

Results of glow curve deconvolution of simulated TL glow curve according to first- and second-order kinetics

	Input parameters				Fitted parameters					
	E_1 (eV)	ν_1 (s ⁻¹)	E_{tr} (eV)	ν_{tr} (s ⁻¹)	E_1 (eV)	ν_1 (s ⁻¹)	b_1	E_{tr} (eV)	ν_{tr} (s ⁻¹)	b_{tr}
Curve 1 (Fig. 2)	0.9	10 ¹⁰	0.8	10 ⁹	0.907	1.1 × 10 ⁸	1.0	1.51	3.2 × 10 ¹⁰	2.0
Curve 2 (Fig. 2)	0.9	10 ¹⁰	0.8	10 ¹⁰	0.976	7.5 × 10 ⁸	1.0	0.658	1.2 × 10 ²	2.0

arbitrary increasing function of time, however, in TL and TSC measurements it is usually a linear function of time: $T(t) = T_0 + \beta t$, where β is the heating rate. In order to perform each step of the simulation, the times of each allowed transition were generated on a computer for all carriers in the system. Since the probability distribution of the transition times t_i has the form

$$p(t_i) = \lambda(t_i) \exp\left(-\int_0^{t_i} \lambda(t') dt'\right) \quad (6)$$

it can be proven that t_i can be determined by solving the following integral equation:

$$\int_0^{t_i} \lambda(t') dt' = -\ln(\alpha_i) \quad (7)$$

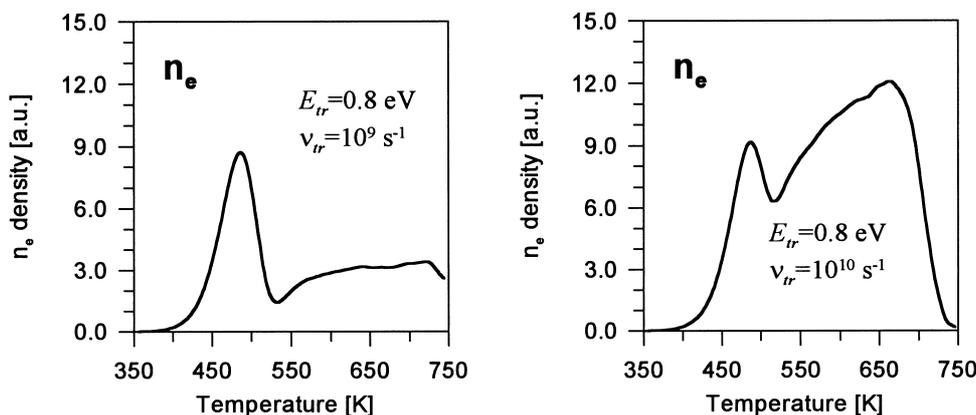
where α_i is a homogeneous random variable from the interval (0, 1) and λ denotes the probability of allowed transition defined by Eqs. (2)–(5).

3. Results

The calculations were performed for a system consisting of hole–electron pairs. For the sake of clarity, it was assumed that trap levels are characterised by the same discrete activation energy $E = 0.9$ eV, the frequency factor $\nu = 10^{10}$ s⁻¹ and the retrapping coefficient $r \equiv A/B = 10^2$.

Transitions between clusters (here hole–electron pairs) were characterised by different values of activation energies E_{tr} and pre-exponential factors ν_{tr} . One-dimensional chains had variable length as well as variable number of hole–electron pairs. To simulate a very long chain periodic boundary conditions were applied. Heating rate was assumed to be $\beta = 1$ K/s. During the simulation, the concentration of charge carriers in excited state n_e and TL intensity, defined as $(-dm/dt)$ were recorded. In Fig. 2, TL intensities (glow curves) are calculated for $E_{tr} = 0.8$ eV and two exemplary values of the pre-exponential factor $\nu_{tr} = 10^9$ s⁻¹ for the first diagram and $\nu_{tr} = 10^{10}$ s⁻¹ for the second one. It is clearly seen that for a certain range of transition probabilities A_{tran} a small additional TL peak is formed in the high-temperature region. It corresponds to the transport of charge carriers along the chains. Applying standard non-linear deconvolution methods we get highly inaccurate results shown in Table 1. It shows inapplicability of these models, however, the shape of fitted glow curve is acceptable. It should be noted that the best fit was obtained assuming first-order kinetics for inter-pair transitions and second-order for the additional transport peak.

As the transition probability increases (in Figs. 2 and 3, this is achieved by increasing the pre-exponential factor ν_{tr}), the transport peak shifts toward the main TL peak. On the other hand, for very low transition probabilities A_{tran} (e.g., assuming the energy $E_{tr} > 1.0$ eV) only one first-order TL peak can be observed, that is in good agreement with

Fig. 3. Temperature dependencies of the total concentration of electrons in excited states n_e .

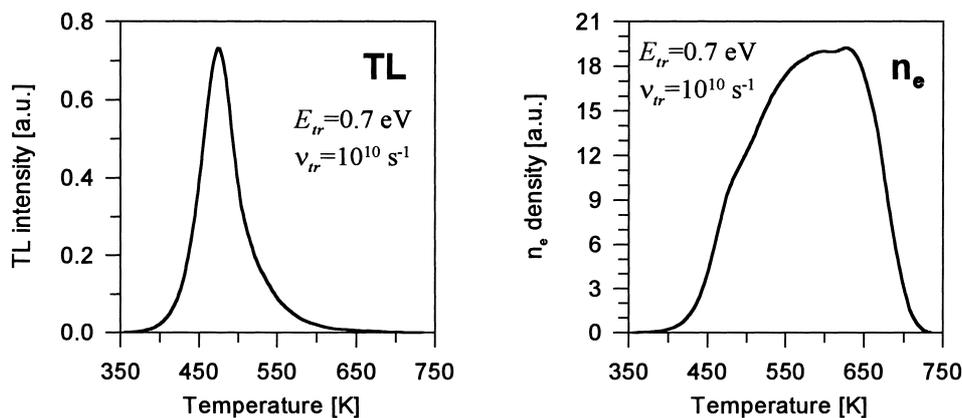


Fig. 4. Thermoluminescence intensity and the concentration of charge carriers in excited states n_e calculated for $E_{tr} = 0.7 \text{ eV}$ and $v_{tr} = 10^{10} \text{ s}^{-1}$.

classical theory [1]. Calculating the total concentration of electrons in excited states n_e (Fig. 3) one could notice a similar behaviour. However, the n_e peak related to inter-group transitions is much more higher and broader. It should be noted that for weak electrical fields applied this concentration should be proportional to the measured current during TSC experiment. In Fig. 4, TL and n_e curves are presented calculated for $E_{tr} = 0.7 \text{ eV}$ and $v_{tr} = 10^{10} \text{ s}^{-1}$. Therefore, in this case the transition probability is much higher as compared to the previous cases. Both TL and n_e curves appear to consist of a single peak. It means that the main peaks and inter-group transition-related peaks occupy nearly the same position. Therefore, it is difficult to identify and separate them.

4. Conclusions

In this paper, one-dimensional properties of trapping and recombination kinetics were presented. Numerical simulations were performed for a system of closely positioned hole–electron pairs, arranged as a chain. It was allowed that the electrons in the excited state may shift between neighbouring groups. To assure enough length of the chain periodic boundary conditions were applied. The transport was assumed to be thermally activated (Eq. (5)). Exemplary calculations show that even for such a simple

system with a monoenergetic trap level for electrons, TL and TSC curves may exhibit complex structure. An additional peak can be observed due to transitions of charge carriers between groups of traps. For very high transition probabilities A_{tran} as compared to the recombination probability (Eq. (3)) the transitions-related peak increases and it mingles with the main TL or TSC peak. In this case the main peak seems to be distorted. These properties are characteristic especially for the high-temperature region of the TSR phenomena and could be more distinctly seen on TSC (i.e., n_e) diagrams. For experimental work, it is necessary to distinguish between these two kind of peaks. In real organic solids, the simple model presented here seems to be oversimplified, since it does not take into account, e.g., energy distribution of trapping states. However, qualitative consequences are still valid. Considering that no analytical model for this type of kinetics has been constructed yet, further numerical studies on this subject are still required.

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