Recombination in Complex Systems – An Analytical Approach

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Summary: A new analytical model is proposed to describe the kinetics of trapping and recombination of charge carriers in complex systems with an arbitrary spatial distribution of traps and recombination centres. The structural properties of a material are described by two functions Γ_m and Γ_n irrespective of the thermal history of the sample. A simple method is proposed to determine the function Γ_m from simultaneous thermoluminescence (TL) and thermally stimulated conductivity (TSC) measurements.

Keywords: Monte Carlo simulation; recombination; thermoluminescence; thermally stimulated conductivity; traps

Introduction

Classic theories of trapping and recombination of charge carriers in dielectrics relate to the two analytically described cases. The first relates to uniform distribution of traps.[1] The second relates to pairs of traps and recombination centres placed close to each other.[2] None of the cases is likely to prevail in complex organic solids. Under such circumstances it is usually not possible to formulate a set of analytical equations describing charge carriers kinetics in such processes as phosphorescence, thermoluminescence (TL), thermally stimulated conductivity (TSC) and others. So far, no theory has been constructed that takes into account arbitrary spatial distribution of traps and recombination centres. Some peculiarities of the kinetics that may take place in non-homogeneous systems (e.g. 1-D structures or clusters) were shown in a number of papers in last few years.[3-5] Examples include apparently composite structures of monoenergetic peaks[4] and additional 'displacement' peaks.[6-8] The results were obtained numerically using Monte Carlo algorithms.[3] The numerical results were hardly compared with the experiment due to the lack of an appropriate analytical theory. In this paper new equations are presented for charge carrier trapping in a system with an arbitrary spatial distribution of traps and recombination centres. It is shown that the distribution could be characterised by two functions Γ_n and Γ_m.

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These functions depend only on structural properties (e.g. spatial distribution, energy barriers, etc.) of metastable states in a solid. The Γ function has to be determined separately for traps and recombination centres (RC). However, in most cases this process could be significantly improved by utilizing special symmetry properties. Examples of Γ functions and a method of determining Γ's from experimental data are presented.

Theory - two standard models

Commonly accepted explanation of long-lasting phosphorescence and thermoluminescence phenomena is based on the assumption of metastable levels (traps and recombination centres) situated within the energy gap. Although direct transition from trap to a recombination centre is possible, most of the transitions take place through excited states. This is shown schematically in the case of 'active' electron traps in Figure 1.

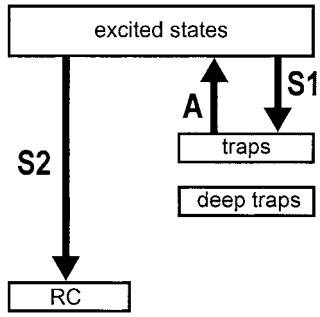

Figure 1. Energy diagram for a system consisting of trap levels, one kind of recombination centres (RC) and a number of deeper traps. **A** denotes thermally activated transitions (detrapping). **S1** and **S2** denote trapping and recombination, respectively. These are structural transitions depending on spatial configuration of traps and RC.

The diagram comprises several cases, including the model where electrons are excited to the conduction band, and the model of localized transitions. Only for these two cases it is possible to formulate a set of kinetic equations describing charge carriers kinetics. To simplify the following equations, we will assume that, within a given temperature range, only one trap level and one type of recombination centres are 'active'. All transitions to a set of deeper (thermally disconnected) traps are neglected. Thus, in the framework of the conduction model, the charge carrier kinetics obeys the following set of equations:

$$-\dot{n} = n\nu \exp\left(\frac{-E}{kT}\right) - n_c A(N-n), \tag{1a}$$

$$-\dot{m} = Bmn_c, \tag{1b}$$

$$m = n + n_c + M, \tag{1c}$$

here E stands for the activation energy, N, n, and m denote the concentrations of trap states, electrons trapped in 'active' traps and holes trapped in recombination centres, respectively. n_c denotes the concentration of electrons in the conduction band. 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 and B stand for the trapping and recombination probabilities, respectively, and ν is the frequency factor.

Another situation was considered by Halperin and Braner[2]. They assumed that traps and recombination centres are closely correlated in space, forming pairs that can be considered as independent units - i.e., the whole charge transfer takes place within groups of one kind, each having one trapping state, one excited state and one recombination centre. In this case the kinetic equations are the following (in a slightly modified form with respect to[2]):

$$-\dot{n} = n\nu \exp\left(\frac{-E}{kT}\right) - \bar{A}n_e, \tag{2a}$$

$$-\dot{m} = \bar{B}n_e, \tag{2b}$$

$$m = n + n_e, \tag{2c}$$

where n_e denotes the concentration of electrons in the excited state. Because the transport of charge carriers does not take place through the conduction band, the TL peak should not be accompanied by TSC. It is assumed that $\bar{A}$ and $\bar{B}$ are constants.

Theory - generalized equations

The simple energy configuration shown in Figure 1 comprises many more systems than those conceived by Eqs (1 and 2). Typical examples of this kind are presented in Figs 2 and 3. Figure 2 shows a set of clusters of traps and RC's. The clusters are separated by a distance and/or energy barriers. Each cluster has the energy configuration shown in Fig. 1. Figure 3 illustrates two one-dimensional systems of traps. It is assumed that charge carriers thermally released from traps are able to move along the chain. These exemplary arrangements are much closer to what one can find in such complex structures as molecular crystals or polymers. Properties of thermally stimulated relaxation processes in such systems were studied numerically using the Monte Carlo technique. Many new interesting features of this 'unusual type of kinetics' were discovered. Unfortunately, the results were hardly compared

with experiment due to the lack of an appropriate analytical model of the phenomena. It will be shown that such a theory is possible to construct.

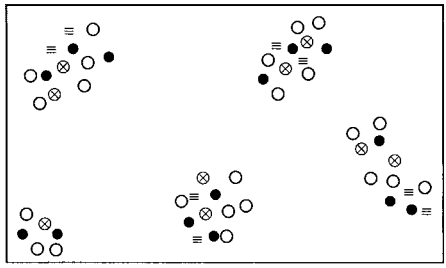

Figure 2. Groups of spatially correlated traps and recombination centres. ● - filled traps, ⊗ - empty traps, ≡ - thermally disconnected (deep) traps, O - recombination centres.

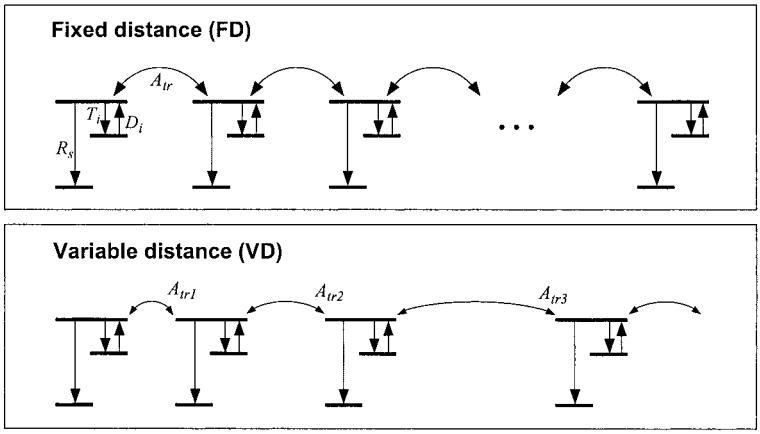

Figure 3. Exemplary one-dimensional models of a system of traps and RC. A carrier released from a trap can move along the chain. A_{tr}, A_{tr1}, ... A_{tr3} denote transitions between excited states. T_i, D_i and R_s denote trapping, detrapping and recombination, respectively.

Let us define the variable

$$\theta(t) = \int_0^t n_c(t')dt' \tag{3}$$

From simple probabilistic arguments[3,5] it is obvious that the total concentration of free holes should depend especially on $\theta(t)$ that is proportional to the total time spent by electrons in the excited state, and also on some other parameters W_k - dependent, e.g., on the initial occupation of traps. Therefore:

$$m(t) = F_m[\theta(t), W_k] \tag{4}$$

where F_m is an unknown function. As W_k does not depend on time it is obvious that

$$\frac{dm}{dt} = \frac{\partial F_m}{\partial \theta} n_e \tag{5}$$

Using similar arguments, in a special case when transitions S2 and A (Fig. 1) do not occur,

$$\frac{\mathrm{d}n_c}{\mathrm{d}t} = -\frac{dn}{dt} = \frac{\partial F_n}{\partial \theta} n_e \tag{6}$$

where F_n is another function. The equations allow to characterise transitions S1 and S2. The above partial derivatives are not constant, but depend on the actual concentrations of carriers in a destination trap level. Therefore we denote:

$$\Gamma_m(m) = -\frac{\partial F_m}{\partial \theta} \tag{7}$$

$$\Gamma_n(n) = -\frac{\partial F_n}{\partial \theta} \tag{8}$$

A comparison with previous sets of the kinetic equations allows to write finally:

$$-\dot{n} = n\nu \exp\left(\frac{-E}{kT(t)}\right) - \Gamma_n(n) n_e, \tag{9a}$$

$$-\dot{m} = \Gamma_m(m) n_e, \tag{9b}$$

$$m = n + n_e + M, \tag{9c}$$

Therefore we claim that the set of Eqs (9) describes the charge carrier kinetics in an arbitrary system consisting of traps and RC's, irrespective of its thermal history. As the shape of the Γ's depends solely on spatial distribution of traps and RC's, we conclude that the functions Γ_m and Γ_n describe structural properties of the system.

Properties of Γ functions

To show some basic properties of Γ_m and Γ_n, we calculate the functions using the previously described Monte Carlo method. Γ_m in the case of M=N is shown in Fig. 4. The cases n_0=1 and n_0=10^6 correspond to the localised transitions and the conduction band model, respectively. In these cases Γ_m is represented by a straight line. The same result was obtained for Γ_n. Both Γ_m and Γ_n for the same case M=N are presented in Fig. 5. Only for two standard cases (localised transitions and STM) the Γ's are linear. In all other cases the Γ's are nonlinear monotonic functions. The nonlinearity results in distorted (apparently composite[4,5]) TL peaks. However, the striking feature is the symmetry between Γ_m and Γ_n. This property may facilitate experimental determination of Γ functions.

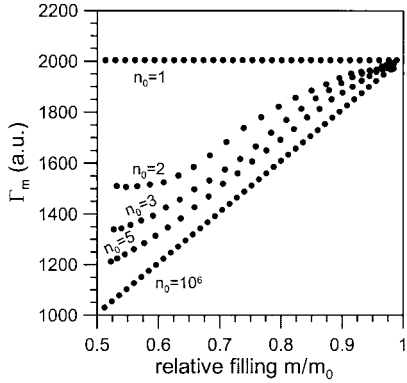

Figure 4. The function $\Gamma_m(m)$ calculated for M=N and various occupancy of a single cluster n_0.

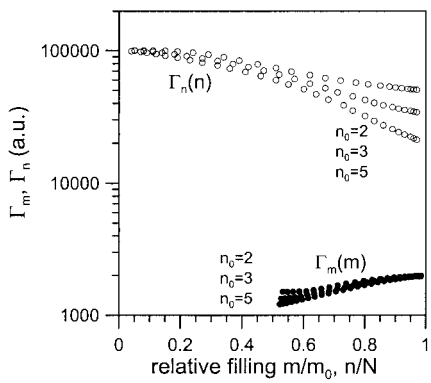

Figure 5. The functions $\Gamma_m(m)$ and $\Gamma_n(n)$ calculated for M=N and r=A/B=100. n_0 and m_0 denote initial concentrations of trapped electrons and holes, respectively.

Conclusions

A new analytical model is proposed to describe TL kinetic properties for an arbitrary spatial distribution of traps and recombination centres. The structural properties of a material are described by two functions $\Gamma_m(m)$ and $\Gamma_n(n)$ irrespective of the thermal history of the sample measured. Any modification of the spatial arrangement or traps does not influence the structural function for recombination centres and *vice versa*. Thus the basic question concerns the possibility of determining Γ's from experimental data. Surprisingly, the answer is very simple, at least in the straightforward case, when TL and TSC intensities are characterized by common definitions: $J_{TL} \propto -\dot{m}$ and $J_{TSC} \propto n_e$. Applying the relations to Eq. (9b), one gets

$$\Gamma_m\left(m_0 - \alpha \int_0^t J_{TL}(t')\mathrm{d}t'\right) \propto J_{TL}/J_{TSC} \tag{10}$$

Therefore, the information on Γ_m could be achieved from simultaneous TL/TSC measurements. Any assumptions with respect to Γ_n can be made using symmetry arguments.

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