

## THE THEORY OF THERMOLUMINESCENCE WITH AN ARBITRARY SPATIAL DISTRIBUTION OF TRAPS

A. Mandowski

Institute of Physics, Pedagogical University  
ul. Armii Krajowej 13/15, 42–200 Częstochowa, Poland

**Abstract**—There are two basic analytical models for thermoluminescence (TL). The first relates to the uniform distribution of traps. The second relates to the pairs of traps and recombination centres placed close to each other. In both cases, it was possible to formulate a set of differential equations describing charge carriers' kinetics. Some recent results, both experimental and theoretical, show that this simple picture may not be applicable, especially in dosimetric applications of TL. There are strong indications that many measured TL glow curves come from clusters of spatially associated traps and recombination centres. The kinetics of TL and some relevant processes in spatially correlated systems was studied numerically using Monte Carlo simulations. In this paper, new equations are presented for TL in a system with an arbitrary spatial distribution of traps and recombination centres. An analytical formulation allows easier comparison of the theory with experimentally observed data.

### INTRODUCTION

Physical parameters of trap states are investigated by a variety of methods. Many of them are based on the observation of thermally stimulated relaxation spectra. Among them, thermoluminescence (TL) and thermally stimulated conductivity (TSC) phenomena are one of the basic tools. While performing these experiments a sample is excited in a 'low' temperature  $T_0$  and then it is heated, usually with a constant rate  $\beta$ . During heating a fraction of charge carriers thermally released from traps recombines with opposite carriers trapped at recombination centres. The probability of thermal excitation of a carrier is assumed to be given by a Boltzmann factor. A series of peaks appearing on a TL or TSC spectrum may be attributed to trap levels having different activation energies  $E_i$ . A theoretical description of these non-equilibrium phenomena usually assumes uniform distribution of traps and recombination centres<sup>(1,2)</sup>. Another extreme case was the model of localised transitions by Halperin and Braner<sup>(3)</sup> regarding hole–electron pairs trapped close to each other. Only for the two cases was it possible to formulate differential equations describing charge carriers' kinetics. Using recently developed Monte Carlo techniques the kinetics of trapping and recombination may be studied in systems with a different kind of spatial correlation between traps and recombination centres<sup>(4,5)</sup>. This allows a variety of cases much closer to reality to be studied. In some situations the spatial correlation comes as a consequence of a structure of a solid, e.g. in polycrystalline samples. However, one can expect a similar distribution in every case, where a sample (semiconductor or insulator) is exposed to a high energy radiation, which produces large defects—traps and recombination

centres, most probably assembled into groups<sup>(6)</sup>. The latter case is especially important due to the dosimetric applications of TL.

In some recent papers<sup>(5–9)</sup> it was shown that TL coming from a system with a non-homogenous distribution of traps reveals certain features that cannot be properly described in terms of the standard kinetic models. The TL glow curve could be significantly distorted suggesting the existence of additional energy levels. Another interesting feature, recently discovered numerically in 1-D systems is the possibility of occurrence of additional 'displacement peaks' resulting from inter-cluster transitions<sup>(8,9)</sup>. All these peculiarities were discovered using Monte Carlo simulation. In this paper an analytical model is proposed to describe TL kinetic properties irrespective of spatial arrangement of traps and recombination centres. Initially, the model is formulated for monoenergetic traps, however some consequences could be easily generalised for more complex systems.

### THEORY

#### Two standard models

In dielectrics with randomly distributed traps and recombination centres, where all transitions go through the conduction band, the kinetics of trapping and recombination can be well described by the simple trap model (STM)<sup>(1)</sup>. Assuming that within a given temperature range only one trap level and one type of recombination centre are 'active', the charge carriers kinetics are described by the following set of equations:

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

$$-\dot{m} = Bmn_c \quad (1b)$$

$$m = n + n_c + M \quad (1c)$$

here  $E$  stands for the activation energy,  $N$ ,  $n$ , and  $m$

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Contact author E-mail: a.mandowski@wsp.czest.pl  
arkad@wsp.czest.pl

denote the concentrations of trap states, electrons trapped in ‘active’ traps and holes trapped in recombination centres (RC), respectively.  $M$  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  $\nu$  is the frequency factor.

Another situation was considered by Halperin and Braner<sup>(3)</sup> (modified later by Land<sup>(10)</sup>). They assumed that traps and recombination centres are closely correlated in space forming pairs that can be considered as independent units, i.e. all charge transfer takes place within groups of one kind, each having one trapping state, one excited state and one recombination centre. Following Land<sup>(10)</sup> the kinetic equations can be written as:

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

$$-\dot{m} = \bar{B}n_e \quad (2b)$$

$$m = n + n_e \quad (2c)$$

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 thermally stimulated conductivity. It is assumed that  $\bar{A}$  and  $\bar{B}$  are constants.

### Generalised equation

Let us consider a more general model presented in Figure 1. It represents a single cluster of traps having a common excited state, a number of traps, a set of recombination centres and some deeper traps. Although this figure represents a single cluster it will be assumed that the whole system has a sufficiently high number of the same clusters, to define the same concentrations as for the Equations 1a and 2. Instead of  $n_e$  the concentration of carriers in the excited state  $n_c$  will be used. Considering individual charge carriers’ transitions (that is the basis of the Monte Carlo simulation) the probabilities of each allowed transition, i.e. detrapping of a carrier to the conduction band  $D_i$ , trapping  $T_i$  from the conduction band to a given trap, and recombination  $R_s$  of a carrier from the conduction band directly to recombination centre are given by the following equations:

$$D_i = \nu_i \exp\left(\frac{-E_i}{kT}\right) \quad (3)$$

$$T_i = A_i(N_i - n_i) \quad (4)$$

$$R_s = B_s m_s \quad (5)$$

where the indices denote discrete trap levels and recombination centres. Additionally, the variable

$$\theta(t) = \int_0^t n_c(t') dt' \quad (6)$$

may be defined.

From simple probabilistic arguments<sup>(4)</sup> it is obvious that the total concentration of free holes should depend especially on  $\theta(t)$ , which 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:

$$m(t) = F_m[\theta(t), W_k] \quad (7)$$

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

$$\frac{dm}{dt} = \frac{\partial F_m}{\partial \theta} n_c \quad (8)$$

Using similar arguments, in a special case when transitions S2 and A (in Figure 1) do not occur that:

$$\frac{dn_c}{dt} = -\frac{dn}{dt} = \frac{\partial F_n}{\partial \theta} n_c \quad (9)$$

where  $F_n$  is another function. The equations allow transitions S1 and S2 to be characterised. Transition A is still described by Equation 3. The partial derivatives written above are not constant, but depend on the actual concentrations of carriers in a destination trap level. The following equations are therefore denoted as:

$$\Gamma_m(m) = -\frac{\partial F_m}{\partial \theta} \quad (10)$$

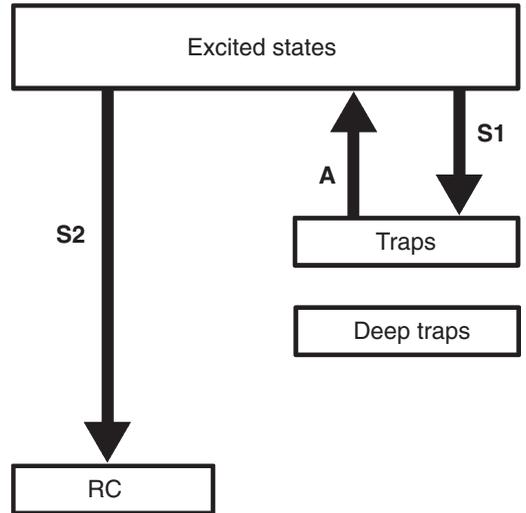


Figure 1. Schematic energy diagram for a single cluster consisting of a single trap level, one kind of recombination centre (RC) and a number of deeper traps. The system under consideration consists of a very large number of clusters having the same energy configuration. The number of traps and RC in each cluster may be different.

$$\Gamma_n(n) = \frac{\partial F_n}{\partial \theta} \quad (11)$$

The comparison with previous sets of the kinetic equa-

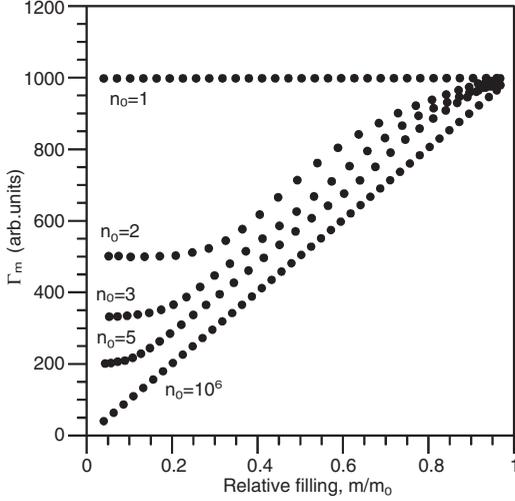


Figure 2. The function  $\Gamma_m(m)$  calculated for a system consisting of  $n_0$  traps in a single cluster and no ‘thermally disconnected’ traps, i.e.  $M = 0$ . The function was computed using Monte Carlo simulation. The shape of  $\Gamma_m(m)$  does not depend on the activation energy assumed, the heating rate and other trap parameters. The case  $n_0 = 1$  corresponds to the ‘localised transitions’ model given by Equation 2. The solutions for  $n_0 = 10^6$  coincides with the STM given by Equation 1.

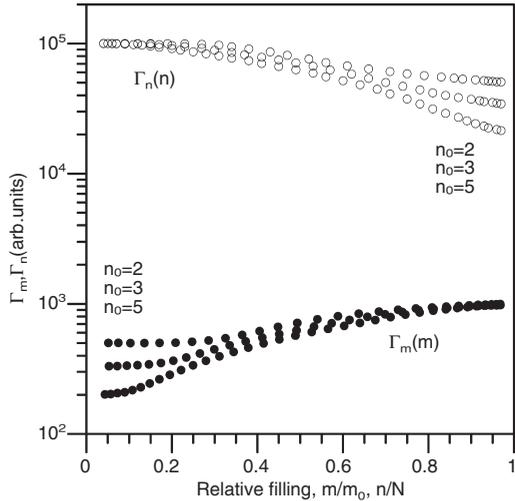


Figure 3.  $\Gamma_m(m)$  and  $\Gamma_n(n)$  calculated for  $n_0 = 2, 3$  and  $5$  traps in a single cluster and no ‘thermally disconnected’ traps, i.e.  $M = 0$ . The retrapping coefficient was  $r = 100$ . One may notice the symmetry:  $\Gamma_m(m) \propto \Gamma_n(N - n)$ .

tions allows the following equations to finally be written:

$$-\dot{n} = n\nu \exp\left(\frac{-E}{kT(t)}\right) - \Gamma_n(n)n_e \quad (12a)$$

$$-\dot{m} = \Gamma_m(m)n_e \quad (12b)$$

$$m = n + n_e + M \quad (12c)$$

Therefore it is postulated that the set of Equation 12 describes charge carriers’ kinetics (including TL:  $J_{TL} \propto -\dot{m}$ ) in an arbitrary system consisting of separate

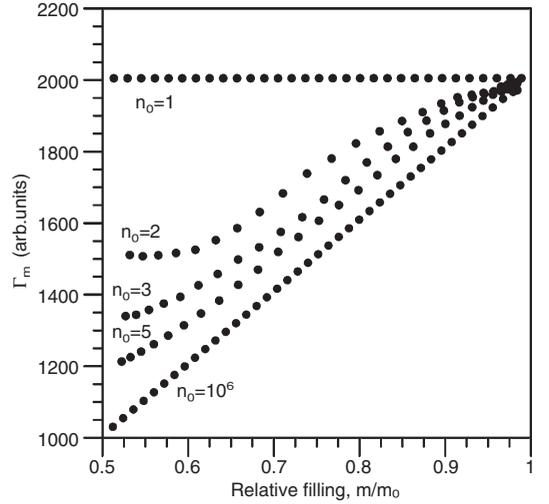


Figure 4. The function  $\Gamma_m(m)$  calculated for  $M = N$  and various occupancy of a single cluster  $n_0$ .

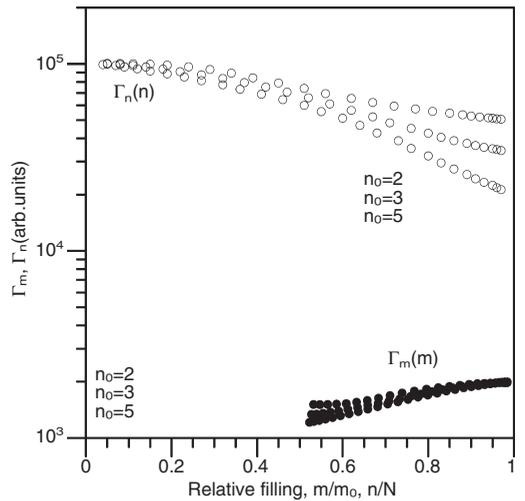


Figure 5. The functions  $\Gamma_m(m)$  and  $\Gamma_n(n)$  calculated for  $M = N$  and  $r = 100$ .

assemblies of traps and recombination centres, irrespective of its thermal history. The clusters may consist of various numbers of traps. Structural properties of such a system are unequivocally described by the functions  $\Gamma_m$  and  $\Gamma_n$ .

### Properties of structural functions

To show some basic properties of  $\Gamma_m$  and  $\Gamma_n$  the functions using the previously described Monte Carlo method are calculated. Typical behaviour of  $\Gamma_m$  in the case of no thermally disconnected traps ( $M = 0$ ) is shown in Figure 2. The cases  $n_0 = 1$  and  $n_0 = 10^6$  correspond to the localised transitions and the STM, respectively. Both  $\Gamma_m$  and  $\Gamma_n$  in this case are presented in Figure 3. The striking feature in this system is the symmetry between  $\Gamma_m$  and  $\Gamma_n$ . Namely  $\Gamma_m(m) \propto \Gamma_n(N - n)$ . Unfortunately, this nice property does not hold for  $M > 0$ , and for  $n_0 < N$ . The next example, for  $M = N$ , is presented for the function  $\Gamma_m$  alone, as well for both  $\Gamma_m$

and  $\Gamma_n$  on a log scale in Figures 4 and 5, respectively. It is clearly seen that in spite of the changes seen for  $\Gamma_m(m)$ , the second function,  $\Gamma_n(n)$ , remains unchanged. The reason is very simple—the ‘new’ system has modified only recombination centres while the ‘active’ traps remain unchanged. It clearly proves the ‘structural character’ of the functions  $\Gamma_m$  and  $\Gamma_n$ .

### 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. The aim of future studies will be focused on the possibility of experimental determination of  $\Gamma_m$  and  $\Gamma_n$ .

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