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THERMOLUMINESCENCE AND TRAP ASSEMBLIES—RESULTS OF MONTE CARLO CALCULATIONS

ARKADIUSZ MANDOWSKI and JÓZEF ŚWIĄTEK
Institute of Physics, Pedagogical University, ul. Armii Krajowej 13/15, PL-42200 Częstochowa, Poland

Abstract—Thermoluminesence (TL) glow curves depend on the spatial distribution of traps and recombination centres. Only two limiting cases are described by analytical theories: the model of trap-recombination centre pairs (known as the localized transitions model) and the simple model, that assumes homogeneous (or random) distribution of traps and recombination centres. Applying Monte Carlo methods we present some properties of TL in the intermediate cases of spatial correlation. The calculations were performed for monenergetic trap level and two-level system. The range of applicability of standard theoretical models is estimated. © 1998 Elsevier Science Ltd. All rights reserved

1. INTRODUCTION

Optical and electrical properties of semiconductors and insulators are significantly affected by defects and impurities in a solid. These imperfections produce additional energy levels lying in the band gap. The knowledge of the mechanisms of trapping and recombination of charge carriers taking place through these localized states is essential to the understanding of optical and electrical phenomena in solids. Physical parameters of the trap states are investigated by a variety of methods. Many of them are based on the observation of photoluminescence spectra. During thermoluminescence (TL) experiment a sample is excited at appropriately low temperature T_0 and then it is heated usually with a constant rate β. A series of peaks appearing on TL glow curve is attributed to trap levels having different activation energies.

The most frequently used theoretical model for the description of TL, the simple model, assumes that traps and recombination centres are uniformly distributed in space (or distributed in random) and displacement of a carrier takes place via the conduction band (for review see Chen and Kirsh, 1981; McKeever, 1985). Another extreme case is the model of localized transitions by Halperin and Braner (1960) regarding hole-electron pairs trapped close to each other. For the two cases it was possible to formulate differential equations describing charge carriers' kinetics. Until now, it is not possible to model the intermediate cases in terms of differential equations. Nevertheless, 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 (Mandowski and Świątek, 1992). First suggestions on the influence of spatial correlation on the kinetics of thermally stimulated relaxation processes were pointed out by Fields and Moran (1974). They used the model to explain results of simultaneous measurements of TL and TSC (thermally stimulated conductivity). Later, Faïn and Monnin (1977) used the same arguments to explain supralinearity and sensitization phenomena observed in TL. Exact numerical calculations on the influence of spatial correlation on the shape of TL and TSC curves were performed by Mandowski and Świątek (1992, 1994, 1995). The question of "how often the classical (i.e. randomly distributed) or spatially correlated case occurs in reality?" is of great importance. Certainly there are some cases where the spatial correlation comes as a consequence of a structure of a solid, e.g. in polycrystalline samples. However, one can expect a similar effect 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. The latter case is especially important due to dosimetric applications of TL (Faïn and Monnin, 1977; Horowitz *et al.*, 1996).

In this paper we present new features of TL calculated numerically for various spatial correlations between traps, particularly in comparison with two limiting cases that are described by analytical equations: the model of trap-recombination centre pairs (known as the localized transitions model) of Halperin and Braner (1960) and the simple model. We discuss the range of applicability of these standard theoretical models with respect to the basic trap parameters and spatial distribution of traps and recombination centres.

2. THEORY

2.1. *The simple trap model*

The most acceptable model for TL kinetics in crystalline semiconductors and insulators assumes

discrete distribution of trap levels on the energy scale. 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 of charge carriers' trapping and recombination one can write the following set of differential equations (Kelly *et al.*, 1971):

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

$$-\dot{m}_s = B_s m_s n_c, \qquad s = 1..l, \quad \text{(1b)}$$

$$\sum_{s=1}^{l} m_s = \sum_{i=1}^{p} n_i + n_c + M \qquad \text{(1c)}$$

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, respectively. M is the concentration of electrons in deep traps. A_i and B_s stand for the trapping and recombination probabilities, respectively. E_i and ν_i denote activation energies and frequency factors of active energy levels, respectively. To deal with this type of kinetics one has to assume uniform distribution of trapping states and trapped carriers within the bulk of solids. Unfortunately the set of [1] is strongly nonlinear and it has no analytical solutions even for the simplest case of $p = 1$ and $l = 1$.

2.2. *Localized transitions*

Another extreme situation was considered by Halperin and Braner (1960) and later modified by Land (1969) and Chen (1976). 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 (1969) we can write the kinetic equations:

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

$$-\dot{m} = \bar{B} n_e, \qquad \text{(2b)}$$

$$m = n + n_e \qquad \text{(2c)}$$

Where n_e denotes the concentration of electrons in the excited state. Because the displacement of charge carriers does not take place through the conduction band, the TL peak should not be accompanied by thermally stimulated conductivity. $\bar{A}$ and $\bar{B}$ have a similar meaning as A_i and B_s in [1] but they have different units. The difference is that $\bar{A}$ and $\bar{B}$ in [2] describe the transition probabilities of a given electron in the excited state to a trap or recombination centre, respectively, whereas the same probabilities in [1] are given by $A_i(N_i - n_i)$ and $B_s m_s$ respectively.

2.3. *Approximate solutions—the general order kinetics*

Since the basic model describing TL and phosphorescence kinetics is nonlinear ([1]), there were many attempts to find simple analytical approximations of the model. Fundamental results of Randall and Wilkins (1945) and Garlick and Gibson (1948) derived for weak and strong retrapping, respectively, were later generalized by May and Partridge (1964) in the form of so-called "general order kinetics" model (Chen, 1969). This approximate approach to TL kinetics was criticised by many authors (e.g. Moharil 1981, 1982; Opanowicz 1987, 1989). Lewandowski and McKeever (1991) and Lewandowski *et al.* (1994) suggested use of a kinetic order function instead of the kinetic order constant.

3. NUMERICAL CALCULATIONS

To study the influence of spatial correlation on trapping and recombination kinetics we studied TL kinetics by means of Monte Carlo simulation. Details of the algorithm were presented in our previous papers (Mandowski and Świątek, 1992, 1995). Below, we present only the most important points. The trap energy configuration used for the calculation is the same as for the simple model. However, it relates to each group of traps and recombination centres separately. To perform Monte Carlo calculations one has to deal with an absolute number of carriers instead of concentrations. If the initial absolute number of "active" charge carriers n_0 in a single separate group of traps is chosen as $n_0 = 1$ this corresponds to the localized transitions model. It can be proved that the homogeneous simple model corresponds mathematically to $n_0 = \infty$. Naturally, no infinities can be handled by any computer. However, it was found that for $n_0 > 10^3$ all simulated curves almost exactly coincide with the solutions of the simple model given by [1]. In each step of Monte Carlo calculations the times of all allowed transitions t_i were calculated and only one transition, characterized by the lowest value of t_i, was executed. 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:

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

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

$$R_s = B_s m_s. \qquad (5)$$

To decrease statistical fluctuations the calculations

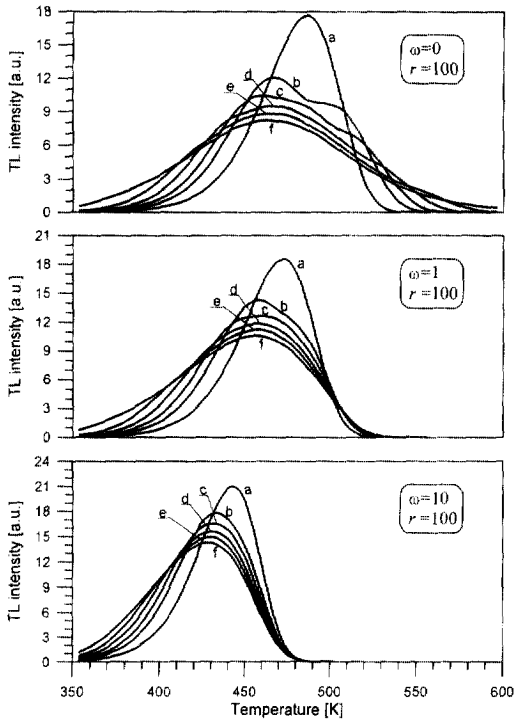

Fig. 1. The dependence of the shape of TL on the number of carriers n_0 in a single separate group of traps. The three sets of curves were calculated for various concentrations of thermally disconnected traps: $\omega \equiv M/N = 0$, $\omega = 1$ and $\omega = 10$. Other parameters: retrapping coefficient $r = 100$, $E = 0.9$ eV, $\nu = 10^{10}\text{s}^{-1}$ and initial filling ratio: $\eta_0 = 1$. The curves were calculated for (a) $n_0 = 1$ (this case corresponds to the localized transitions model), (b) $n_0 = 2$, (c) $n_0 = 3$, (d) $n_0 = 5$, (e) $n_0 = 10$, (f) $n_0 = 100$. For $n_0 > 100$ all curves coincide with (f) as well as with the solution of the simple model ([1]).

were repeated many times with the same initial conditions. To calculate TL response with trap levels that are initially not fully saturated with carriers, first one has to calculate the distribution of charge carriers in the system. The process of filling the traps can be easily simulated using Monte Carlo technique (Mandowski and Świątek, 1994). The results of the preliminary Monte Carlo simulations are the input data for the main simulation program.

4. RESULTS

4.0.1. *A single trap level.* The Monte Carlo calculations were performed for the total number of carriers 10^6 (i.e. population of all groups of traps). In Fig. 1 TL curves are calculated for a different number of carriers n_0 in a single separate group of traps. The model used allows calculation of localized transitions while choosing $n_0 = 1$ (i.e. a single electron in a group) as well as delocalized ones while choosing appropriate high n_0. It was found that for $n_0 > 10^3$ all the curves coincide with the simple trap model (1). The method of calculations allows consideration of intermediate cases also. The three sets of curves were calculated for various concentrations of thermally disconnected traps: $\omega \equiv M/N = 0$, $\omega = 1$ and $\omega = 10$. Other parameters used in the simulations are: $r \equiv A/B = 100$, $E = 0.9$ eV, $\nu = 10^{10}\text{s}^{-1}$ and the initial filling ratio: $\eta_0 \equiv n_0/N = 1$. It was shown in our previous papers (Mandowski and Świątek 1994, 1995) that spatial correlation affects TL especially in the case of low values of thermally disconnected traps $\omega \ll 1$ and high values of the retrapping coefficients $r \gg 1$. To describe this effect quantitatively we calculated the deviation of TL kinetics from standard theoretical models. The deviation is defined as:

$$\varepsilon_i = \left[\int_{T_0}^{\infty} J(T)\,\mathrm{d}T\right]^{-1} \int_{T_0}^{\infty} \left|J_i(T) - J(T)\right| \mathrm{d}T \qquad (6)$$

where $J_i(T)$ is the TL intensity as predicted by a standard model and $J(T)$ is the TL intensity calculated for a given spatial configuration of traps. In Figs 2 and 3 the effective deviation ε is plotted in the form of contour map. These figures show the dependence of ε on the recombination coefficient r and the initial number of "active" charge carriers in a single separate group of traps. The effective deviation is defined as $\varepsilon = \min(\varepsilon_1, \varepsilon_2)$, where ε_1, ε_2 denote relative deviations, defined by [6] for the localized transitions model and the simple model respectively. Figures 2 and 3 were plotted for $\omega = 0$ and $\omega = 1$ respectively. It is shown that the regions of huge divergence ($> 20\%$) are greater for low ω. The areas start from $r \approx 0.2$ and $r \approx 8$ for $\omega = 0$ and $\omega = 1$ respectively. The regions with $\varepsilon < 1\%$ are well described by standard kinetic models. In regions where $1\% < \varepsilon < 5\%$ the models are accep-

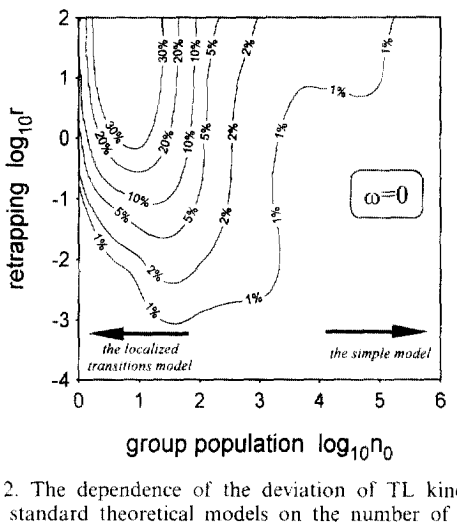

Fig. 2. The dependence of the deviation of TL kinetics from standard theoretical models on the number of carriers n_0 in a single separate group of traps and the retrapping coefficient r. The deviation was calculated as $\varepsilon = \min(\varepsilon_1, \varepsilon_2)$, where ε_1, ε_2 denote relative deviations, defined by [6], from the localized transitions model and the simple model respectively. The calculations were performed for $\omega = 0$. For other parameters see Fig. 1 caption.

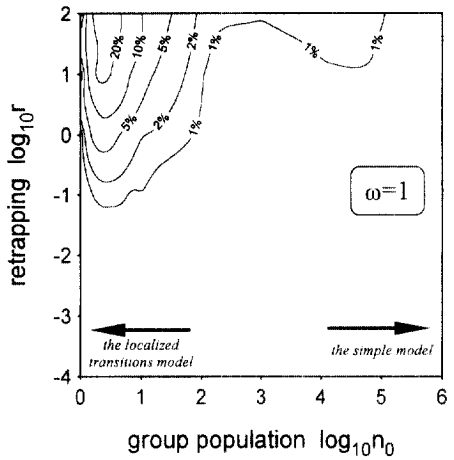

Fig. 3. The same as Fig. 2, but calculated for $\omega = 1$.

table. In regions of $\varepsilon > 20\%$ one can observe some peculiarities of TL curves. It appears that the curves, calculated for monoenergetic trap level, have a complex structure. Moreover, applying typical curve fitting techniques one can easily deconvolute the whole curve for individual first-order ($b = 1$) peaks. The number of peaks equal to the number of carriers in a single separate group of traps. Typical examples for $n_0 = 2$ and $n_0 = 3$ are shown in Figs 4 and 5 respectively.

4.0.2. *Two trap levels.* Even a more difficult case is shown in Fig. 6. TL curves were calculated for two-level system having trap levels at $E_1 = 0.9$ eV and $E_2 = 1.0$ eV. Thus each group calculated for "no thermally disconnected traps" ($\omega = 0$) and full initial filling ($\eta_0 = 1$) consists of $2n_0$ trapped electrons and $2n_0$ holes in recombination centres. Due to high retrapping coefficient ($r = 100$) "classical"

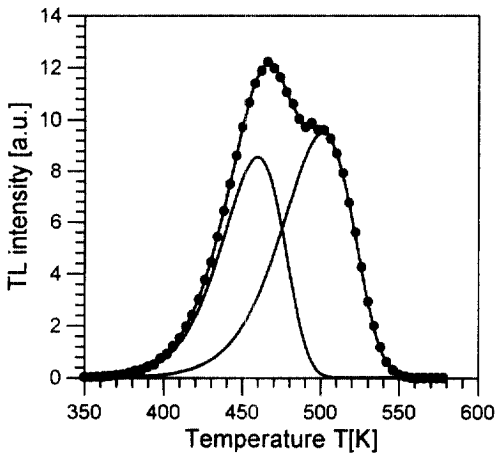

Fig. 4. Results of glow curve deconvolution performed for a single "spatially correlated" TL peak calculated for $E = 0.9$ eV, $\omega = 0$, $n_0 = 2$ and $r = 100$. The curve can be perfectly deconvoluted for two first-order peaks ($b = 1$) having "energies" $E_1 = 0.896$ eV and $E_2 = 0.907$ eV.

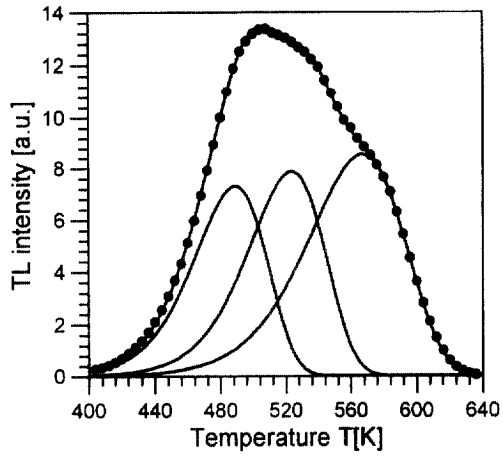

Fig. 5. Results of glow curve deconvolution performed for a single "spatially correlated" TL peak calculated for $E = 0.9$ eV, $\omega = 0$, $n_0 = 3$ and $r = 1000$. The curve can be perfectly deconvoluted for three first-order peaks ($b = 1$) having "energies" $E_1 = 0.893$ eV, $E_2 = 0.911$ eV and $E_3 = 0.932$ eV.

TL glow curve (i.e. calculated in the framework of the simple model—curve *d*) does not reveal its complex structure. Along with decreasing the number of charge carriers in a single group TL curve changes giving for purely localized transitions two well separated peaks. Thus, strong spatial correlation helps identify closely positioned energy levels. The result is also in good agreement with theoretical considerations of Chen and Kirsh (1981) who pointed out that the model of localized transitions leads to first-order kinetics. The intermediate cases (e.g. curves *b* and *c* in Fig. 6 calculated for $n_0 = 2$ and $n_0 = 5$, respectively) are very difficult to analyse. It appears that the number of individual peaks is greater than the number of trap levels. It is similar to the situation found in a single-trap level system.

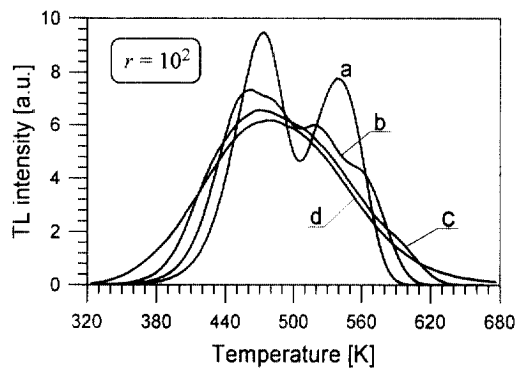

Fig. 6. The dependence of the shape of TL on the number of carriers n_0 in a single separate group of traps in a two-level system characterized by the following parameters: $E_1 = 0.9$ eV, $E_2 = 1.0$ eV, $\nu_1 = \nu_2 = 10^{10}\text{s}^{-1}$, $A_1 = A_2$, $\omega = 0$ and $r = 100$. The curves are calculated for (a) $n_0 = 1$, (b) $n_0 = 2$, (c) $n_0 = 5$, (d) $n_0 = 10^6$. Here n_0 denotes initial population of each trap level.

5. CONCLUSIONS

Calculations presented here clearly show the importance of the spatial correlation effects in the analysis of charge carriers' relaxation kinetics. The regions of high deviation from standard models were described. These are characterized especially by high values of the retrapping coefficient r and low concentrations of deep traps ω. The unusual shape of TL for small trap clusters could not be described in terms of standard kinetic models. This problem goes beyond the simple trap model and the model of localized transitions, through it could not be neglected. The lack of an appropriate kinetic model may lead to erroneous analysis of the obtained results and misleading interpretations. Spatial correlation significantly complicates the analysis of TL curves; nevertheless, in some multilevel systems it may increase resolution of TL measurements.

REFERENCES

Chen, R. (1969) Glow curves with general order kinetics. *Journal of the Electrochemical Society* **116**, 1254–1257.

Chen, R. (1976) Review: methods of kinetic analysis of thermally stimulated processes. *Journal of Material Science* **11**, 1521–1541.

Chen, R. and Kirsh, Y. (1981) *Analysis of Thermally Stimulated Processes*. Pergamon Press, Oxford.

Faïn, J. and Monnin, M. (1977) A model for the explanation of non-linear effects in thermoluminescence yields. In *Thermally Stimulated Processes in Solids: New Prospects*, ed. J. P. Fillard and J. van Turnhout, pp. 289–296. Elsevier, Amsterdam.

Fields, D. E. and Moran, P. R. (1974) Analytical and experimental check of a model for correlated. TL and TSC. *Physical Review* **B9**, 1836–1840.

Garlick, G. F. and Gibson, A. F. (1948) The electron trap mechanism of luminescence in sulphide and silicate phosphors. *Proceedings of the Physical Society* **60**(6), 574–590.

Halperin, A. and Braner, A. A. (1960) Evaluation of thermal activation energies from glow curves. *Physical Review* **117**, 408–415.

Horowitz, Y. S., Mahagna, S., Rosenkrantz, M. and Yossian, D. (1996) Unified theory of gamma and heavy charged particle TL supralinearity: the track/defect interaction model. *Radiaton. Protection Dosimetry* **65**, 7–12.

Kelly, P., Laubitz, M. J. and Bräunlich, P. (1971) Exact solutions of the kinetic equations governing thermally stimulated luminescence and conductivity. *Physical Review* **B4**, 1960–1968.

Land, P. L. (1969) Equations for thermoluminescence and thermally stimulated current as derived from simple models. *Journal of Physics and Chemistry of Solids* **30**, 1693–1708.

Lewandowski, A. C., Markey, B. G. and McKeever, S. W. S. (1994) Analytical description of thermally stimulated luminescence and conductivity without the quasiequilibrium approximation. *Physical Review* **B 49**, 8029–8047.

Lewandowski, A. C. and McKeever, S. W. S. (1991) Generalised description of thermally stimulated processes without the quasiequilibrium approximation. *Physical Review* **B43**, 8163–8178.

Mandowski, A. and Świątek, J. (1992) Monte Carlo simulation of thermally stimulated relaxation kinetics of carriers trapping in microcrystalline and two-dimensional solids. *Philosophical Magazine* **B65**, 729–732.

Mandowski, A. and Świątek, J. (1994) Properties of TL and TSC in polycrystalline materials—numerical studies. In *Polycrystalline Semiconductors III—Physics and Technology*, ed. H. P. Strunk, J. H. Werner, B. Fortin and O. Bonnaud, 37, pp. 249–254. Solid State Phenomena, Scitec Publications Ltd. Switzerland.

Mandowski, A. and Świątek, J. (1995) TSC and TL in spatially correlated systems. In *Solid State Crystals: Materials Science and Applications*, ed. J. Zmija, A. Rogalski and J. Zieliński, 2373, pp. 231–235. Proc. SPIE.

May, C. E. and Patridge, J. A. (1964) Thermoluminescence kinetics of alpha-irradiated halides. *Journal of Chemical Physics* **40**, 1401–1409.

McKeever, S. W. S. (1985) *Thermoluminescence of Solids*. Cambridge University Press, Cambridge.

Moharil, S. V. (1981) On the variation of order of kinetics during thermoluminescence. *Physica Status Solidi (a)* **68**, 413–418.

Moharil, S. V. (1982) On the general-order kinetics in thermoluminescence. *Physica Status Solida (a)* **73**, 509–514.

Opanowicz, A. (1987) On the kinetics of thermoluminescence processes. *Physica Status Solida (a)* **101**, 589–601.

Opanowicz, A. (1989) On the kinetics order of thermoluminescence in insulating crystals. *Physica Status Solida (a)* **116**, 343–348.

Randall, J. T. and Wilkins, M. H. F. (1945) Phosphorescence and electron traps: I. The study of trap distributions. *Proceedings of the Royal Society* **A184**, 366–389.