ON THE ANALYSIS OF TL GLOW CURVES IN SPATIALLY CORRELATED SYSTEMS

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Abstract — In the presence of spatial correlation between traps and recombination centres, some thermoluminescence (TL) curves reveal unusual properties that cannot be described in terms of standard kinetic models. In these cases the application of typical theoretical methods for the analysis of TL curves may lead to erroneous results. Using a novel, generalised version of the Monte Carlo algorithm the kinetics of TL is studied for a variety of spatial trap correlations. The algorithm allows calculation of TL with an arbitrary heating function applied that gives the possibility of simulating the use of initial rise methods as well as the fractional glow technique (FGT). It was found that these methods, as well as the various heating rate methods, can also be applied for determination of the activation energy from TL curves in cases when spatial correlation plays an important role. The influence of another experimentally controllable parameter — the initial filling ratio — is also taken into account. Some practical indications are suggested for theoretical analysis of TL glow curves in spatially correlated systems.

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. Theoretical descriptions of these phenomena, including thermoluminescence (TL) and thermally stimulated conductivity (TSC), assume a simple energy model consisting of localised electron and hole states within a band gap of a dielectric or semiconductor[1,2]. Only two limiting cases are described by analytical equations: the model of trap recombination centre pairs (known as the localised transitions model) of Halperin and Braner[3] and the simple model that assumes homogeneous distribution of charge carriers[2]. More precisely, the simple model assumes that a charge carrier released to the conduction band has an equal chance of recombining with every recombination centre in a solid. On the other hand, within the framework of the localised transitions model the carrier in an excited state can recombine with only one recombination centre. The latter case leads to a very simple first order kinetics process[1,3,4]. A few years ago Mandowski and Świątek[5] proposed an algorithm that allows numerical simulation of thermally stimulated processes without limitations imposed on spatial distribution of traps. It was found that some TL curves reveal unusual properties that were not predicted by the standard models. In some cases the occurrence of spatial correlation may produce additional peaks that may be erroneously attributed to different energy levels[6]. This illustrates the importance of applying credible methods for the analysis of thermally stimulated relaxation spectra.

The influence of experimentally controllable parameters like the heating rate and initial filling ratio is here analysed. The novel version of the Monte Carlo algorithm allows simulation of the use of complex heating profiles such as those used in the fractional glow technique (FGT). Some practical indications are also suggested for theoretical analysis of TL glow curves using peak fit methods.

NUMERICAL SIMULATION

The details of the Monte Carlo method were described in earlier papers[5,7]. Below, only the basic points are presented. It is assumed that the solid consists of a number of separate groups having the same configuration of energy levels — i.e. (1) 'active' trap levels, (2) 'thermally disconnected traps' (deep traps) and (3) recombination centres. It is possible to allow a charge carrier to move between groups assuming a 3-D cubic network of cells with periodic boundary conditions[7]; however, in all the calculations presented here it is assumed that the probability of a carrier moving between groups is considerably smaller compared with trapping and recombination probabilities. In the opposite case, when the probability is very high, the kinetics are well described by the simple model. Usually it is assumed that the temperature is a linearly rising function. A novel version of the Monte Carlo program that is used in the present calculations allows one to simulate TL kinetics with an arbitrary heating function T(t) applied. Some exemplary cases are presented illustrating the influence of experimentally controllable parameters on the character of TL glow curves.

RESULTS

The dependence on the heating rate

It was reported in previous papers that the influence of spatial correlation on TL is noteworthy in the region of high retrapping coefficients and low relative density of thermally disconnected traps. An exemplary set of parameters of that kind was chosen to illustrate the effect of the heating rate β on TL (Figure 1). Applying different heating rates from $\beta = 10^{-2}$ K.s^{-1} to 10^2 K.s^{-1}

one is not able to observe any differences in relative positions and shapes of the family of curves simulated for different spatial correlations. This remarkable property suggests the possibility of applying various heating rates methods for evaluating activation energy in any systems independently of spatial correlation. To check this hypothesis the method of Hoogenstraaten[8] was applied. This method uses values of the temperatures of maxima T_m measured for several heating rates β. A plot of $\ln(T_m^2/\beta)$ against $1/T_m$ gives a straight line of slope E/k from which the activation energy can be calculated. Recently it was found that the method as applied to the simple model is much more accurate than Chen's peak shape analysis[9]. The application of Hoogenstraaten's method to all of the curves presented in Figure 1 gave encouraging results. The calculated acti-

vation energies were very close to those assumed in the simulation value $E = 0.9$ eV. For all the cases the error was less than 3%. The result means that the various heating rates method is weakly sensitive to the spatial correlation of traps.

Initial rise analysis

The curve C from Figure 1 that appears to have a complex structure was also analysed by applying a more involved heating profile. The heating was chosen in the form of a saw-tooth curve with the increasing part of 20 K and decreasing 10 K. The increasing regions were then analysed in terms of initial rise dependence, i.e.

$$J(T) = \text{const} \times \exp\left(\frac{-E}{kT}\right) \qquad (1)$$

Calculated activation energies are plotted in the bottom diagram of Figure 2. Some deviations observed, mostly in the first part of the diagram, are chiefly due to statistical fluctuations of the Monte Carlo method. However the tendency is obvious. In the small initial region of the TL curve we find too low values of the determined activation energy. This effect is due to a high retrapping coefficient and full initial filling of traps. This drawback of the initial rise method was pointed out by Bräunlich[10]. Performing some heating and cooling
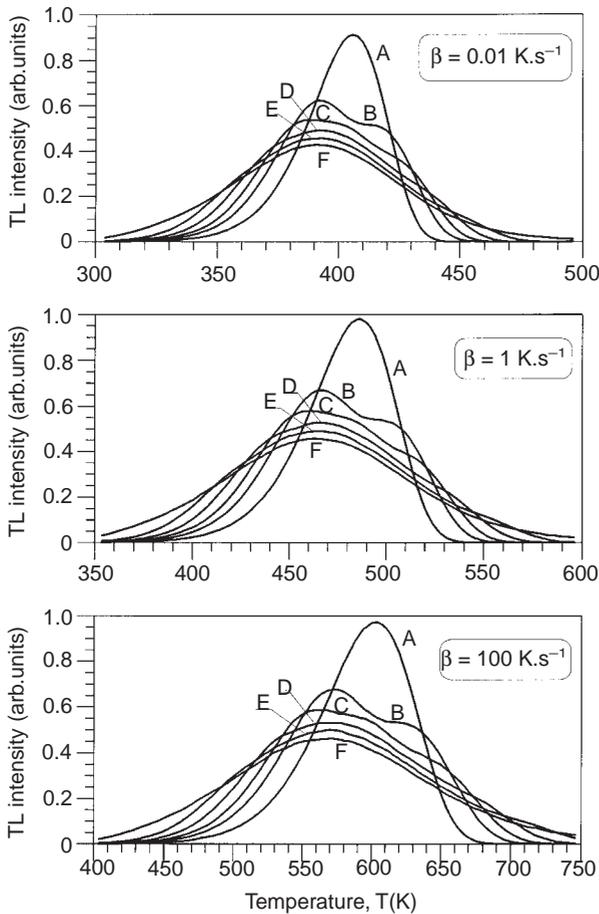

Figure 1. The dependence of TL on the heating rate. The three sets of curves were calculated for various heating rates: $\beta = 10^{-2}$ K.s^{-1}, $\beta = 1$ and $\beta = 10^{-2}$ K.s^{-1}. The parameters used for the simulation are the following: retrapping coefficient r = 100, $\omega \equiv M/N = 0$, $E = 0.9$ eV, $v = 10^{10}$ s^{-1} and initial filling ratio, $\eta_0 = 1$. The curves were calculated for the following values of the absolute number of initially trapped charge carriers in a single separate group: A, $n_0 = 1$ (this case corresponds to the localised 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.
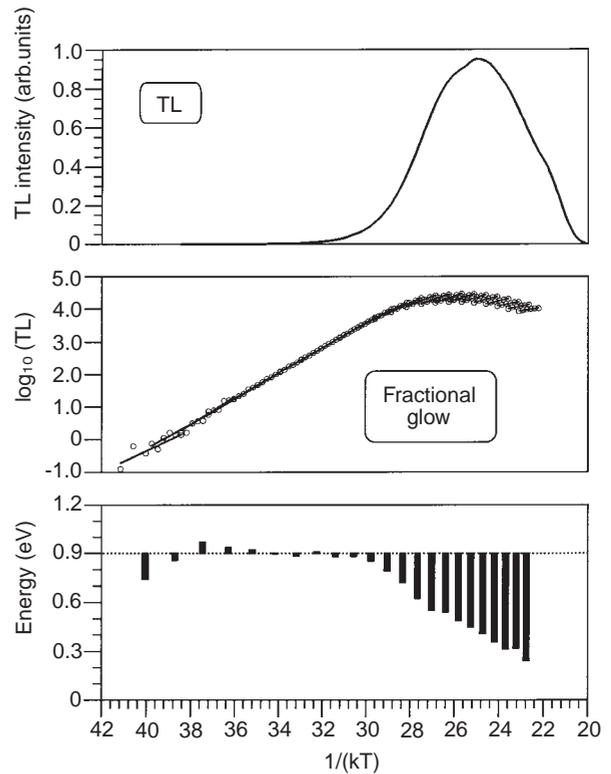

Figure 2. Illustration of the use of FGT. Parameters used for simulation are the same as for the curve D in Figure 1. The 'true' energy is 0.9.

cycles one decreases the number of carriers in traps and calculated activation energies become more accurate. This is true even for TL peaks that are very strongly affected by spatial correlation. From Figure 2 one concludes that initial rise method (and FGT) has approximately the same range of applicability as in classical models — i.e. when applied to the initial part of the peak (up to 10–15% of the peak maximum) it gives a reasonable estimation of the activation energy except for the limitation noted by Bräunlich.

Initial filling of traps

The range of applicability of the standard kinetic models for full initial filling of traps $\eta_0 = 1$ was estimated in a previous paper[11]. Performing similar calculations for $\eta_0 = 0.1$ and lower concentrations one concludes that the discrepancy between the two standard models increases. Nevertheless this difference does not necessarily mean inability to obtain reliable results by using for example, fitting algorithms. An interesting example is presented in Figure 3. The curve C shown in the middle plot of Figure 1 was analysed by fitting to a general order kinetics model[1]. The first fit obtained for $\eta_0 = 1$ is very wrong. Also, the estimation of the activation energy is highly inaccurate. The result indicates inapplicability of peak shape methods in this case. However, by decreasing the initial trap occupancy η_0 we get a quite different curve that can be successfully fitted to first order kinetics giving a very precise estimation of the activation energy. This result may be easily explained. The curve C represents the case of trap clusters consisting of five traps and five recombination centres. In Figure 4 the relative population of the clusters calculated for $\eta_0 = 0.1$ and $\eta_0 = 0.01$ is shown. With decreasing η_0 most of the clusters are occupied only by a single carrier. In this case the kinetics can be described by the same set of differential equations as for the localised transitions (e.g. see Land[4] and Chen[1] p. 36). Hence the mathematical consequences are the same.

Assuming typical quasi-equilibrium conditions: $n_e \ll n$ and $|\dot{n}_e| \ll |\dot{n}|$ one gets the following equation:

$$J = -\frac{dm}{dt} = -\frac{d(m - M)}{dt} = \frac{(m - M)v}{1 + \overline{A}/\overline{B}} \exp\left(\frac{-E}{kT}\right) \qquad (2)$$

which leads to simple first order kinetics with v replaced by $v' = v/(1 + \overline{A}/\overline{B})$. Therefore a fit to a first order curve yields a correct value of E. In the above equation n, M and m denote the concentrations of electrons trapped in 'active' traps, electrons trapped in deep traps and holes trapped in recombination centres, respectively, n_e denote the concentration of electrons in the excited state, $\overline{A}$ and $\overline{B}$ stand for the trapping and recombination probabilities, respectively.

DISCUSSION

Measuring TL glow curves one usually does not know *a priori* whether the spectra may be analysed in terms of standard kinetic models. There is no definite
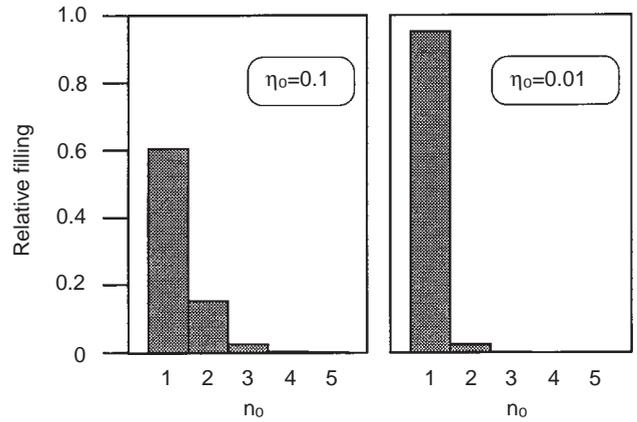

Figure 4. Results of preliminary Monte Carlo calculations — relative initial population of charge carriers in a system of clusters containing five traps computed for $\eta_0 = 0.1$ and $\eta_0 = 0.01$. These populations correspond to TL peaks shown in Figure 3.
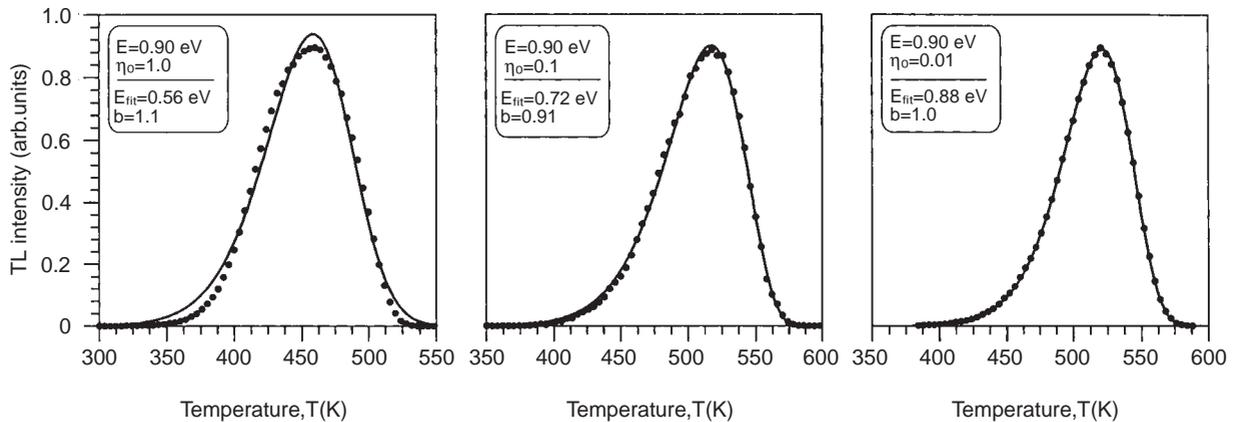

Figure 3. Numerical fit of general order kinetics to curve D (taken from Figure 1) performed for different initial populations: $\eta_0 = 1$, $\eta_0 = 0.1$ and $\eta_0 = 0.01$.

answer to this problem; however, we can formulate some indications that may help to analyse specific cases. Analysing hundreds of TL curves calculated for various sets of parameters it was found that fitting of the spectra with general order kinetics gives reliable results only in two cases: when the curves are perfectly of first or second order kinetics. The dependence of TL on the initial filling ratio led to the following conclusions: (1) if the system under study is suspected to consist of rather large trap clusters (>10) it is suggested that TL be measured with full initial filling $\eta_0 = 1$ to bring it near to the simple model; (2) if the system is thought to consist of rather small trap clusters (<10) it is suggested that TL be measured for very low carrier concentrations to bring it near to simple first order kinetics. Consequently in these cases peak shape analysis can be applied (e.g. using first order kinetics or quasi-equilibrium conditions[12]). Any other cases should be studied very carefully. For this purpose one can use, for example, the initial rise method. It was shown that this method has the same advantages (and limitations) in either correlated and non-correlated cases. The results of calculations performed for various heating rates also confirm the usefulness of heating rate methods, as was demonstrated for the case of the Hoogenstraaten method. These methods can be applied for any TL peaks, even those that are strongly affected by spatial correlation.

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