J. Phys. D: Appl. Phys. 25 (1992) 1829–1833. Printed in the UK

A method for determining the density of deep traps by using the simultaneous TL/TSC measurement technique

A Mandowski and J Świątek

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

Received 19 May 1992

Abstract. A classical model describing the kinetics of trapping and recombination of carriers in insulating and semiconducting solids is considered. For the model some exact formulae for thermally stimulated conductivity (TSC) are derived. It is shown that the area under the TSC curve calculated for one type of recombination centre depends only on the ratio of the number of carriers which remain in thermally disconnected traps. Using this formula we demonstrate that by performing a series of simultaneous TSC/TL (thermoluminescence) experiments it is possible to estimate the relative density of the carriers remaining in deep traps. The basic formulae derived here are independent of the heating programme so they are also valid for the isothermal decay current IDC method.

1. Introduction

Thermally stimulated conductivity (TSC) and thermoluminescence (TL) are phenomena frequently observed in insulators and semiconductors during a heating period after excitation at a low temperature. The simplest and most often used model for the explanation of the phenomena is based on the traps concept. The excitation in an appropriately low temperature fills the traps with carriers. During heating the probability of detrapping increases and the carriers released from the traps to the conduction band give rise to conductivity (TSC) and luminescence (TL) according to the equations:

$$J_{\mathrm{TSC}} = n_c \mu e \tag{1}$$

$$J_{\mathrm{TL}}^{\lambda} = -\alpha \mathrm{d}m_{\lambda}/\mathrm{d}t \tag{2}$$

where n_c stands for the number of electrons in the conduction band, m_λ stands for the number of holes in recombination centres characterized by the wavelength λ of the emitted light, μ represents the mobility of electrons and α is the proportionality coefficient. For the sake of clarity, it is often assumed that only one type of charge carrier, i.e. electrons, is involved in the conduction mechanism—the restriction is explicitly included in equation (1).

Looking at the carrier kinetics mechanism, it is obvious that TL as well as TSC spectra must contain some information about trap parameters, which is why many methods have been developed for determining them from thermostimulated spectra. Special attention has been paid to the determination of trap depth (see e.g. the work of Nicholas and Woods (1964) or Kivits and Hagebeuk (1977)). All of the methods are based on simplified or approximated rate equations. This approach has led to a number of phenomenological models called 'monomolecular', 'bimolecular' or 'general order' kinetics, which have been extensively used by many authors (for a review see Chen and Kirsh (1981) and Lewandowski and McKeever (1991)). Because of their very approximate character, the above equations can take into account only the most significant trap parameters such as the activation energy of a trap and the capture cross section. The other parameters were usually neglected.

In this paper we derive, using the most common theoretical model, exact formulae for the area under the TSC curve. We demonstrate that by using the relationships it is possible to determine the density of thermally disconnected (deep) traps from simultaneous TL/TSC measurements.

2. Fundamental equations

Assuming a simple model consisting of p discrete trap levels and k types of recombination centre, one can write the following set of equations describing carrier kinetics (Chen and Kirsh 1981, McKeever 1985):

$$-\dot{n}_i = n_i D_i - n_c A_i (N_i - n_i) \qquad i = 1 \ldots p \tag{3a}$$

$$-\dot{m}_s = B_s m_s n_c \qquad s = 1 \ldots k \tag{3b}$$

0022-3727/92/121829+05$07.50

$$\sum_{s=1}^{k} m_s = \sum_{i=1}^{p} n_i + n_c + M \tag{3c}$$

where

$$D_i = \nu_i \exp\left(\frac{-E_i}{kT}\right) \tag{4}$$

represents the detrapping probability of an electron from the ith trap level, having the energy depth E_i and characterized by the frequency factor ν_i. The remaining symbols have the following meaning. n_i is the concentration of electrons in the ith trap level, N_i is the total number of trapping states in this level, A_i and B_s represent the trapping and recombination probabilities respectively, M stands for the number of electrons in the thermally disconnected traps (deep traps), i.e. traps which are not emptying during the experiment, k is the Boltzmann constant, and T is the temperature of the sample. For TL and TSC purposes a linear heating programme is usually applied to the sample, i.e. $T(t) = T_0 + \beta t$ where β stands for the heating rate, but in the following calculations no particular form of this relation will be assumed.

The set of equations (3) has no analytical solutions even in the case of $p = 1$ and $k = 1$ (Kelly and Braunlich 1970, Kelly *et al* 1971). However, it can be written in a different equivalent form. Equation (3*a*) can be solved with respect to n_i yielding:

$$n_i(t) = N_i \exp\left(-\int_0^t \left[D_i(t') + n_c(t')A_i\right] dt'\right) \times \left[\eta_{0i} + \int_0^t n_c(t')A_i \exp\left(\int_0^{t'} [D_i(t'') + n_c(t'')A_i]\, dt''\right) dt'\right]. \tag{5}$$

Similarly from equation (3*b*) results:

$$m_s = m_{0s} \exp\left(-B_s \int_0^t n_c(t')\, dt'\right). \tag{6}$$

In the above equations $N_i\eta_{0i}$ and m_{0s} stand respectively for the initial concentrations of electrons in traps and holes in recombination centres. The relative initial filling of ith trap level η_{0i} can vary between 0 and 1. Before substituting the equations into (3*a*), let us introduce a new variable $C(t)$ and a quantity S, defined by

$$C(t) = \int_0^t n_c(t')\, dt' \tag{7}$$

and

$$S = \lim_{t\to\infty} C(t). \tag{8}$$

Now, combining equation (5), (6) and (3*c*) gives the following integral equation:

$$\sum_{s=1}^{k} m_{0s} \exp(-B_s C) = \sum_{i=1}^{p} N_i \exp(-A_i C) \times \left[\eta_{0i} \exp\left(-\int_0^t D_i\, dt'\right) + \exp\left(-\int_0^t D_i\, dt'\right) \times \int_0^t A_i \dot{C} \exp(A_i C) \exp\left(\int_0^{t'} D_i\, dt''\right) dt'\right] + \dot{C} + M. \tag{9}$$

The possible solutions of equation (9) with respect to n_c (or C) should be the same as those resulting from the set of equations (3). In the following parts of the paper we will explore equation (9) for the investigation of TSC and its dependence on the initial filling of traps.

3. The simplest case: one kind of trap and recombination centre

Now we consider the simplest case of $p = 1$ and $k = 1$, where only one type of trap and one type of recombination centre is active. In this case, the analysis of the solutions of equation (9) is much more clear. The variable $C(t)$ in equation (7) is proportional to the integrated TSC current (equation (4)), so its asymptotic limit S (equation (8)) is proportional to the area under the TSC curve on the J_{TSC} against t plot, which is usually an easily measurable quantity. Let us consider equation (9) in the limit $t \to \infty$. For physical reasons it is clear that for there to be enough high values of t all the trapping states should be emptied, and that after some time the carriers should recombine into recombination centres (since $M \geqslant 0$). Mathematically this means that $n_c(t) \equiv \dot{C}(t) \underset{t\to\infty}{\longrightarrow} 0$. So, in this limit one comes to

$$m_0 \exp(-BS) = M. \tag{10}$$

A more rigorous mathematical proof of this formula, resulting from equation (9), is given in the appendix. Nevertheless, this result is quite evident from a physical point of view—looking at equation (3*c*) it means that

$$m(\infty) = M. \tag{11}$$

Of course, the 'infinity' should be understood in physical terms—it denotes such a long time that the trap is, in practice, empty, so that residual carriers do not contribute to the measured current.

Since from initial conditions $m_0 = n_0 + M$, the solution of equation (10) for S can be written as

$$S = \frac{1}{B} \ln\left(1 + \frac{n_0}{M}\right) \tag{12}$$

which gives the dependence of the area under the TSC curve on the initial population of trapped carriers. It is convenient to write formula (12) in the form:

$$S(\eta_0) = \frac{1}{B} \ln\left(1 + \frac{\eta_0}{\omega}\right) \tag{13}$$

where $\eta_0 = n_0/N$ represents the relative number of initially filled trapping states and $\omega = M/N$ stands for the

relative number of thermally disconnected traps. The dependence $S(\eta_0)$ for a few values of ω is schematically presented in figure 1. When a particular dependence $S(\eta_0)$ is established experimentally, the parameter ω can be estimated by fitting the curve represented by equation (13) to the experimental data. For this purpose one can use a variety of numerical methods. One of the simplest methods is the graphical one. It is obvious that for low values of η_0/ω the dependence (13) is linear:

$$S_{ext}(\eta_0) = \frac{1}{B}\frac{\eta_0}{\omega}. \tag{14}$$

Extrapolating this line up to $\eta_0 = 1$, one obtains the value $S_{ext}(1)$ (see figure 1). Hence

$$\frac{S(1)}{S_{ext}(1)} = \omega \ln\left(1 + \frac{1}{\omega}\right). \tag{15}$$

Since $S(1)$ and $S_{ext}(1)$ are known, equation (15) can be solved with respect to ω by using simple numerical algorithms. Another possibility of evaluating the ratio η_0/ω is to measure two areas S_1 and S_2 for the relative initial populations of carriers η_0 and $a\eta_0$ respectively. In the cases when the parameters a and $\chi = S_1/S_2$ are known, the ratio η_0/ω can be found numerically as a solution of the following nonlinear equation:

$$\left(1 + a\frac{\eta_0}{\omega}\right)^{\chi} = 1 + \frac{\eta_0}{\omega}. \tag{16}$$

We now discuss correspondences to previously published results. First, it should be noted that the approximate dependence of S on the initial filling of traps η_0 was first derived by Saunders (1969) under conditions of constant lifetime of the carriers in the conduction band, and the quasi-equilibrium between free and trapped carriers. He found the dependence to be linear, i.e. equivalent to the form of equation (14) which is valid, as was shown here, only for low values of η_0/ω. Another characteristic feature, which can be concluded from equation (12), is the result that in the limit $M = 0$ (i.e. 'no deeper traps') the area under the TSC curve approaches infinity, independent of the number of initially trapped charge carriers n_0. This is in accordance with exact numerical results obtained by Braunlich and Kelly (1970) and Kelly *et al* (1971). They stated, numerically solving the set of equations (3), that TSC spectra in the high-temperature region exhibit a very flat curve. It is also interesting to note that the property is characteristic only for systems with randomly distributed traps and recombination centres (this assumption is included in equations (3)). For different cases, i.e. when traps and recombination centres are spatially correlated, it was shown that the area under the TSC curve is finite even for $M = 0$ (Mandowski and Świątek 1992).

4. Series of traps and recombination centres

The simplest case considered here will consist of one recombination centre and a series of trapping levels.

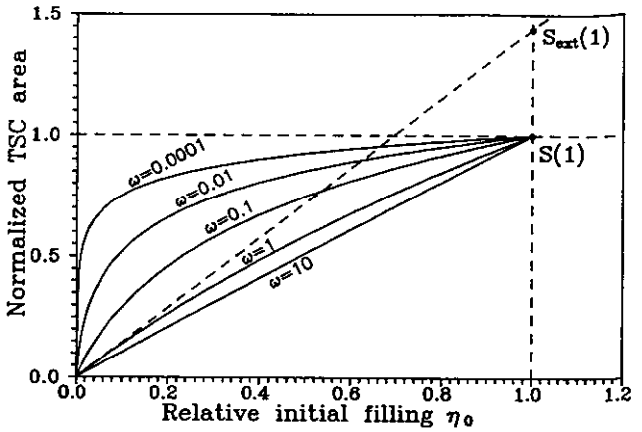

Figure 1. Plot of TSC area S against the relative initial filling of traps η_0 for different relative populations of carriers in thermally disconnected traps ω. Values $S(1)$ and $S_{ext}(1)$ denote respectively the TSC area for $\eta_0 = 1$ directly measured in the experiment and that extrapolated from the linear initial sector of the curve.

Equations (10) and (11) remain the same. Thus by solving equation (11) with respect to S one obtains

$$S = \frac{1}{B}\ln\left(1 + \frac{\sum_{i=1}^{p} n_{0i}}{M}\right). \tag{17}$$

Denoting the ratios $\sum_{i=1}^{p} n_{0i} / \sum_{i=1}^{p} N_i$ by η and $M / \sum_{i=1}^{p} N_i$ by ω, one comes to the equation, analogous to (13):

$$S(\eta) = \frac{1}{B}\ln\left(1 + \frac{\eta}{\omega}\right). \tag{18}$$

This means that the area under the TSC curve does not depend on the populations of carriers in particular trap levels, but depends on the total number of trapped carriers in 'active' and 'thermally disconnected' levels. Since the equations have the same form, the methods of evaluating ω developed for the single trapping level may also be the same.

It is also interesting to study a simple case of two non-interacting trapping levels, i.e. trapping states which are active in different ranges of temperature. The areas S_1 and S_2 under each peak can be determined separately. Assuming that the concentrations of carriers in the respective levels were n_{01} and n_{02}, the formulae for S_1 and S_2 are:

$$S_1 = \frac{1}{B}\ln\left(1 + \frac{n_{01}}{M + n_{02}}\right) \tag{19}$$

$$S_2 = \frac{1}{B}\ln\left(1 + \frac{n_{02}}{M}\right). \tag{20}$$

One can see that even for $n_{01} = n_{02}$, $S_1 < S_2$. Generally, for a series of TSC peaks originating from a series of trap levels in a system with one type of recombination centre, for the generation of peaks having the same area, many more carriers are needed at low temperatures than at higher ones.

Let us now discuss the more general case: a system consisting of a series of recombination centres and

a series of trapping levels. Here, at the end of the thermostimulated process, equation (3c) reads:

$$\sum_{s=1}^{k} m_s(\infty) = M. \tag{21}$$

Substituting into equation (6) one comes to the equation

$$\sum_{s=1}^{k} m_{0s} \exp(-B_s S) = M \tag{22}$$

with the initial condition

$$\sum_{s=1}^{k} m_{0s} = \sum_{i=1}^{p} n_{0i} + M. \tag{23}$$

This can also be written in the form:

$$\sum_{s=1}^{k} m_{0s} [1 - \exp(-B_s S)] = \sum_{i=1}^{p} n_{0i}. \tag{24}$$

The above equation can be analytically solved with respect to S only in the limit $B_s S \ll 1$ (it can be concluded from (6) that this is equivalent to a small filling of each centre), but since it depends on many parameters, its usefulness is rather limited.

5. Limited heating cycles

The above results can be easily generalized to cases where not all the trapping states are emptied at the end of the thermostimulated process. For example, this occurs in the case when a sample is heated up to certain temperature T_e and then cooled to T_0 again. It is a quite common method known as the 'fractional glow technique' (Gobrecht and Hofmann 1966). Obviously, after some time the situation returns to the quasi-equilibrium state and all transitions between trapping states disappear. In this way the TSC current and TL come to zero. As soon as the quasi-equilibrium state is reached, the following relation must be satisfied:

$$\sum_{s=1}^{k} m_{0s} = \sum_{i=1}^{p} n_{0i}^{(e)} + M \tag{25}$$

where $n_{0i}^{(e)}$ denotes the concentration of carriers remaining in traps at the end of the process (i.e. at low temperature). Under the assumption that one deals with one type of recombination centre only, the following equation is obtained

$$S(\xi) = \frac{1}{B} \ln\left(1 + \frac{\xi}{\omega + \eta - \xi}\right). \tag{26}$$

where the symbols used have the same meaning as in equation (18); ξ denotes the relative number of carriers which have left the trapping states, i.e.

$$\xi = \left(\sum_{i=1}^{p} n_{0i} - \sum_{i=1}^{p} n_{0i}^{(e)}\right) \Big/ \sum_{i=1}^{p} N_i. \tag{27}$$

From equation (26) it is clearly seen that the carriers remaining in traps effectively act on S as charge carriers occupying thermally disconnected states.

6. Discussion

From the analytical formulae for the area under the TSC curve derived here it appears that for a system consisting of one type of recombination centre the quantity depends only on the ratio of the number of carriers which have left the trapping states at the end of the thermostimulated process to the number of carriers remaining in traps (equation (26)). This gives the possibility of determining certain trapping parameters, such as the relative density of thermally disconnected traps ω and the relative initial filling ratio η_0/ω. All the methods require determination of the dependence $S(\eta_0)$. For this purpose one has to measure the areas of TSC for various initial fillings without changing the remaining parameters—especially the number of carriers in thermally disconnected traps M. The problem cannot be solved by simply changing the dose of excitation before thermal heating, because the excitation can also change M. A possible way out of this problem can be found, for example, by excitation of the sample each time up to saturation. Thus, the filling ratio η_0 (or η) can be controlled by heating and cooling the sample (the 'limited heating cycle') before the main thermostimulated process. Because the sample was previously excited up to saturation, the thermal emptying of shallow traps should not change the concentration of carriers in deep traps M.

All the considerations presented here are independent of the method of determining η_0. The only condition is to do this simultaneously to appropriate TSC measurements. The well known method is a correlated TL/TSC measurement (Chen 1971). From equation (2) the area under the TL spectrum is proportional to the decrease of holes in recombination centres:

$$\int_{t_1}^{t_2} J_{TL}\, dt = -\sum_{\lambda} \alpha_\lambda \Delta m_\lambda. \tag{28}$$

Since the number of electrons in thermally disconnected traps M remains the same and $n_c = 0$ (at the end and at the beginning of the process), the charge conservation law (3c) implies that the right-hand side of equation (28) should be proportional to the number of carriers which have left their trapping states during the thermostimulated process. It has a simple linear form for a system consisting of only one active recombination centre. An important feature of the formula presented here is its independence of the heating programme $T(t)$. This property can be used to verify the validity of the model determined by equations (3) and (1).

It should be stressed that the basic equation defining TL (2) was questioned by some authors—e.g. Gasiot and Fillard (1977) and Fillard *et al* (1978), who performed correlated TL/TSC experiments. Different models for carrier kinetics were also proposed by Fields and Moran (1974) and Land (1969) who took into consideration spatial correlation between trapped carriers and optically active recombination centres. A similar model was recently studied numerically by Mandowski

and Świątek (1992). For such cases the above method of determining M does not apply or more sophisticated techniques should be used to determine Δm (see Fillard *et al* (1978)).

Appendix

To prove mathematically the validity of equation (10), irrespective of its physical meaning, let us consider two components in the square brackets on the right-hand side of equation (9). It is enough to assume that the temperature dependence obeys the condition:

$$T(t) \geqslant T_{\min} > 0 \tag{A.1}$$

which is equivalent to

$$D_i(t) \geqslant \Delta_i > 0 \tag{A.2}$$

where $T_{\min}$ and Δ_i are constants. Taking into account this property it is evident that the first term in brackets in equation (9) approaches zero in the limit $t \to \infty$. The second term can be written as:

$$F(t) = \int_0^t \frac{\mathrm{d}}{\mathrm{d}t'} [\exp(A_i C)] \exp\left(-\int_{t'}^t D_i \,\mathrm{d}t\right) \mathrm{d}t'. \tag{A.3}$$

Now, taking into account equations (29) and (8), one can approximate $F(t)$ in the following way:

$$F(t) \leqslant \int_0^t \frac{\mathrm{d}}{\mathrm{d}t'} [\exp(A_i C)] \exp\left[-(t-t')\Delta_i\right] \mathrm{d}t'$$

$$\leqslant K \int_0^t \exp[-(t-t')\Delta_i] \,\mathrm{d}t'$$

$$= \frac{K}{\Delta_i}[1 - \exp(-t\Delta_i)] \underset{t\to\infty}{\longrightarrow} 0 \tag{A.4}$$

where

$$K = \max\{\mathrm{d}[\exp(A_i C]/\mathrm{d}t\} < A_i n_c^{\max} \exp(A_i S). \tag{A.5}$$

Since for physical reasons $F(t) \geqslant 0$, the result is $F(t) \underset{t\to\infty}{\longrightarrow} 0$.

References

Chen R 1971 *J. Appl. Phys.* **42** 5899

Chen R and Kirsch Y 1981 *Analysis of Thermally Stimulated Processes* (Oxford: Pergamon)

Braunlich P and Kelly P 1970 *Phys. Rev.* B **1** 1596

Fields D E and Moran PR 1974 *Phys. Rev.* B **9** 1836

Fillard J P, Gasiot J and Manifacier J C 1978 *Phys. Rev.* B **18** 4497

Gasiot J and Fillard J P 1977 *J. Appl. Phys.* **48** 3171

Gobrecht H and Hofmann D 1966 *J. Phys. Chem. Solids* **27** 509

Kelly P and Braunlich P 1970 *Phys. Rev.* B **1** 1587

Kelly P, Laubitz M J and Braunlich P 1971 *Phys. Rev.* B **4** 1960

Kivits P and Hagebeuk H J L 1977 *J. Lumin.* **15** 1

Land P L 1969 *J. Phys. Chem. Solids* **30** 1693

Lewandowski A C and McKeever S W S 1991 *Phys. Rev.* B **43** 8163

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

Mandowski A and Świątek J 1992 *Phil. Mag.* B **65** 729

Nicholas K H and Woods J 1964 *Br. J. Appl. Phys.* **15** 783

Saunders I J 1969 *J. Phys. C: Solid State Phys.* **2** 2181