NUMERICAL ANALYSIS OF SIMULTANEOUS TL/TSC MEASUREMENTS

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Abstract — Thermoluminescence (TL) and thermally stimulated conductivity (TSC) are closely related phenomena. Simultaneous detection of luminescence and conductivity allows one to acquire more information concerning the basic trapping processes occurring during heating of a sample. In this paper a new formula for simultaneous TL/TSC measurement is derived under quasi-equilibrium (QE) conditions. Numerical analysis of the obtained experimental data requires fitting of only two unknown parameters. The new method of analysis was verified for computer generated TL/TSC curves. The practical usefulness of this method is demonstrated in application to the measurements performed for the α-alumina single crystal. The analysis, in general, confirms earlier results for the peak B′. The results obtained for the peak D′ are not so clear. Most likely they reveal some complex factors that are not taken into account.

INTRODUCTION

Thermally stimulated relaxation (TSR) phenomena are important tools in characterising high-resistivity materials (for a review see Chen and McKeever[1]). Using thermoluminescence (TL), thermally stimulated conductivity (TSC) or other methods one is able to get information concerning trap structure of the dielectrics under study. Unfortunately, the kinetics of the TSR processes are complex. This makes the analysis of the experimental data very difficult. Recently, it was shown by many authors[2–4] that some classical approximations of TL (e.g. general order kinetics — GOK[5,6]) are not so accurate as was believed earlier. For example — the GOK model would give very inaccurate results when applied to numerical fitting of experimental data. In some cases the error in estimation of the activation energy would be greater than 50%[2]. In crystalline solids, it is assumed that trap levels have a discrete distribution within the band gap. Usually, it is also assumed, that within a given temperature range only one trap level and one type of recombination centre is 'active'. In this case, termed the simple trap model (STM), the charge carriers kinetics during thermal stimulation are governed by the following set of equations:

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

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

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

where 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 (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 ν is the frequency factor. The set of Equations 1 has no analytical solutions in the general case. However, some exact analytical relations were found when considering simultaneous TL/TSC measurement[7–10]. Attempts were also made to model more complex simultaneous measurements[11,12] — TL/TSC/TSEE (i.e. thermally stimulated exoelectron emission). In this paper a novel method is proposed on the assumption of QE conditions that allows an activation energy to be determined in a simple way, verifying also the applicability of the STM approximation.

THEORY

Properties of R(t) function

The ratio:

$$R(t) = J_{TL}/J_{TSC} \quad (2)$$

where J_{TL} and J_{TSC} are TL and TSC intensities, respectively, will be defined. It will be assumed that these intensities are corrected due to the temperature variation of charge carriers' mobility and the radiative efficiency. Therefore, these can be written:

$$J_{TL} = - \dot{m}/\chi_L \quad (3)$$

$$J_{TSC} = n_c/\chi_C \quad (4)$$

where χ_L and χ_c are constants. Using Equation 1b it is easy to show that

$$R(t) = \frac{\chi_c B}{\chi_L} m \quad (5)$$

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and $\dot{R}(t) \propto -J_{TL}$ (as was shown earlier by Gasiot and Fillard[8]), therefore in the framework of STM (1), R(t) must always be a decreasing function. An example of this kind for numerically generated TL and TSC curves is shown in Figure 1.

Quasi equilibrium conditions

An exact formula for the area under the TSC curve was derived by Mandowski and Świątek[9]:

$$S_{\infty} \equiv \int_0^{\infty} n_c(t')dt' = \frac{1}{B} \ln\left(1 + \frac{n_0}{M}\right) \tag{6}$$

where n_0 is the initial concentration of carriers in traps. By an analogy with a similar expression for limited heating cycles the same authors suggested the following approximation[13,14]:

$$S(t) \equiv \int_0^t n_c(t')dt' \approx \frac{1}{B} \ln\left[1 + \frac{n_0 - n(t)}{M + n(t)}\right] \tag{7}$$

which could be solved for n(t):

$$n(t) = (M + n_0) \exp[-BS(t)] - M \tag{8}$$

and differentiation with respect to t gives:

$$\dot{n}(t) = Bn_c(t)[n(t) + m] \tag{9}$$

As the solution of Equation 1b is: $m(t) = m_0 \exp[-BS(t)]$, using Equation 1c it is easy to prove that Equations 8 and 9 are equivalent to classical QE conditions, i.e. $n_c \ll n$ and $|\dot{n}_c| \ll |\dot{n}|$, respectively. The validity of QE conditions was tested numerically for a variety of trap parameters[13–16]. There was an agreement that QE most likely prevails in all common phosphors.
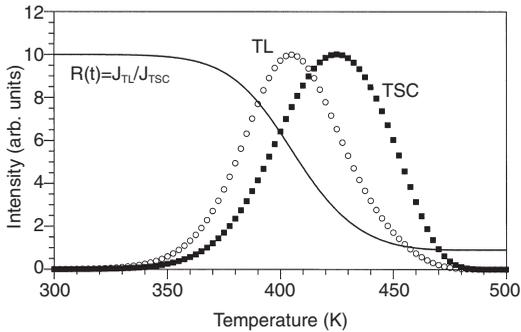

Figure 1. Typical TL/TSC curves and the ratio R(t) = J_{TL}/J_{TSC} calculated in the framework of the simple trap model defined by Equations 1. The spectra were calculated using the following parameters: E = 0.9, $\nu = 10^{10}$ s^{-1} and the heating rate β = 1 K.s^{-1}.

TL/TSC equation

Using approximations 7 and 8 it was possible to write equations for TL and TSC in the form of 'generalised initial rise' with a correction term added[13,14]. However, it was numerically verified that, for most cases, the validity of these approximations covered not only the 'initial rise' but the whole measurable part of TL and TSC peaks. Later, it was proved that using these equations it is possible to construct a very efficient algorithm that allows calculation of the whole TL or TSC curve even faster than by using some analytical approximations[4,17]. Unfortunately, the possibility of applying these formulae to the numerical fitting and deconvolution of glow curves is limited by a rather high number of unknown parameters. The 'generalised initial rise' TL equation is the following:

$$\frac{-E}{kT(t)} = \ln[\mathscr{L}(t)] + \ln\left\{\frac{1}{M + n_0 - \mathscr{U}(t)}\right.$$
$$\left.\left[\frac{1}{n_0 - \mathscr{U}(t)} + \frac{B - A}{AN + BM}\right]\right\}$$
$$+ \ln\left(\frac{AN + BM}{\nu B}\right) \tag{10}$$

The variables $\mathscr{L}(t)$ and $\mathscr{U}(t)$ are defined as follows:

$$\mathscr{L}(t) \equiv -\dot{m}(t) = \chi_L J_{TL} \tag{11}$$

$$\mathscr{U}(t) \equiv \int_0^t \mathscr{L}(t')dt' = m_0 - m(t) = n_0$$
$$+ M - \frac{\chi_L}{\chi_c B} R(t) \tag{12}$$

m_0 and n_0 relate to the initial values of the variables. The last Equation 12 was changed using the formula 5. Applying Equations 11 and 12 to Equation 10, after some algebra, finally we get the following equation:

$$\ln[J_{TSC}(t)] + \ln\left[\delta + \frac{1}{\frac{R(t)}{R_f} - 1}\right] = \frac{-E}{kT} - \ln(K) \tag{13}$$

where δ, R_f and K are constants:

$$\delta = \frac{1 - r}{1 + \frac{r}{\omega}} \tag{14}$$

$$R_f = \frac{BM\chi_c}{\chi_L} \tag{15}$$

$$K = \frac{B\chi_c}{\nu}\left(1 + \frac{r}{\omega}\right) \tag{16}$$

In the above equations $\omega = M/N$ denotes the relative concentration of deep traps and r = A/B is the retrapping coefficient. For arbitrary TL/TSC measurement data the

plot of the right-hand side of Equation 13 should give a straight line against (1/kT). As the measure of linearity one may choose the correlation coefficient, which in the case of Equation 13 depends only on two parameters: δ and R_f. Therefore, it is easy to fit the parameters to minimise the correlation coefficient r_c (which should be closest to -1). It should be noted that the equation coincides with a similar one derived by Bindi *et al*[18] for the second order kinetics. It holds in the case of $R(t) \gg R_f$ (which is evident for a low number of thermally disconnected traps $\omega \ll 1$) and $\delta \ll 1$ (which corresponds to $r \geq 1$).

Optimisation method

To fit experimental data to Equation 13 a number of methods could be applied. To find a global minimum within a physically allowed range of parameters a Monte Carlo method was applied. Details of the algorithm will be given in a separate paper, however the basic idea is very simple. One generates random pairs of the parameters (δ, R_f) for which the correlation coefficient r_c is calculated. In all the considered cases the number of 10^6 trials were found to be high enough to get accurate results. Each point (δ_i, R_{fi}) determines the value of the activation energy E_i which is calculated using a standard linear regression method. The final values of E, δ and R_f are estimated by averaging several 'best fit' results (i.e. points for which r_c is closest to -1).

APPLICATION TO α-ALUMINA SINGLE CRYSTALS

The proposed method was applied to the analysis of simultaneous TL/TSC measurements performed for α-alumina undoped single crystal synthesised by the Verneuil method and manufactured by Baikowski (France). The experimental conditions were described in detail in some earlier papers[18,19]. The measured TL/TSC curves are shown in Figure 2. Together with the data the R(t) function was calculated and plotted on the same diagram.

To analyse the data, initially, it is necessary to estimate the range of applicability of the STM (1) in which the 'one trap' approximation would be valid. The compulsory condition for this is for R(t) to be a decreasing function of time. In Figure 2 these important parts of R(t) are denoted as thick lines. These two ranges of temperature — i.e. 280–350 K and 500–590 K correspond to well known peaks B′ and D′ of α-alumina. The maximal allowed range does not mean necessarily the most appropriate one since the edges may be distorted by neighbouring peaks or the measurements errors that are particularly significant for low intensities. On the other hand the region of interest may not be too short as too low a number of data points (with statistical fluctuations) could not be properly handled by a fitting algorithm. Therefore the ranges chosen for calculations are the compromise between these two limitations. The activation energy obtained for B′ is $E_{B'} = 0.53 \pm 0.04$ eV which is in agreement with previous papers[18,19] and $\delta_{B'} = 0.07 \pm 0.10$. The second peak D′ is more problematic, because the determined values are more scattered. When analysed within a broad range from 500–510 K to 560–580 K it gives $E_{D'} = 0.95 \pm 0.04$ eV which is slightly smaller as compared with earlier results. The analysis performed inside the region — from 520–530 K to 550–560 K gives much higher
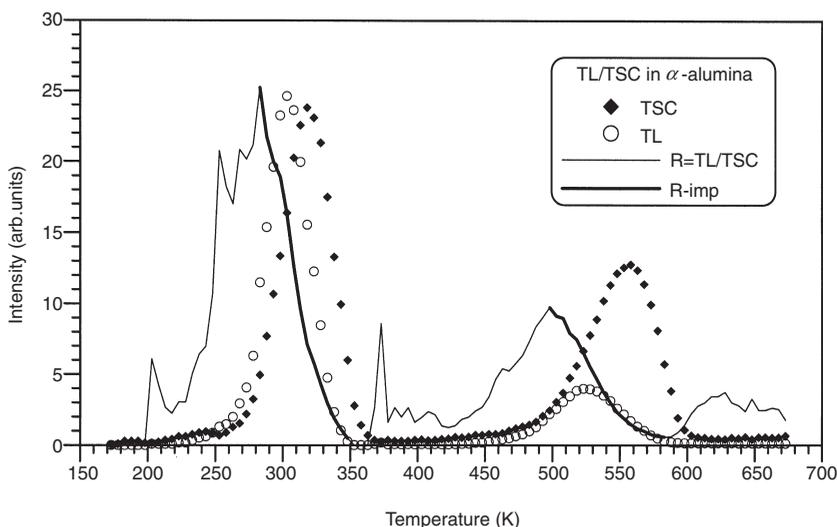

Figure 2. TL/TSC curves and the ratio R(t) measured for α-alumina single crystal. Thick line shows the regions when the function R(t) decreases.

values $E_{D'}$ = 1.3–2.4 eV. Even so these are less reliable due to a low number of fitted points used and probably higher influence of statistical fluctuations. Nevertheless the average values are also consistent with previous analyses. Considering all the data the value $E_{D'}$ = 1.3 ± 0.5 eV and $\delta_{D'}$ = 0.25 ± 0.23 is obtained. Rejecting the data with the number of points used less than 10, the values $E_{D'}$ = 1.13 ± 0.31 eV and $\delta_{D'}$ = 0.23 ± 0.16 are obtained.

CONCLUSIONS

A new method of analysis of simultaneous measurements TL/TSC has been presented. Plotting the R(t) function from experimental data allows the applicability of the basic STM to be checked. Using a new formula (13) that was derived under QE conditions one is able to find two physically important parameters — the activation energy E and δ. The method was successfully verified numerically and applied to the analysis of two peaks in α-alumina. The results obtained here are, in general, in agreement with previously published analyses. It is possible to get much more accurate estimations of E and δ by taking into account TL/TSC data obtained from several measurements to decrease statistical fluctuations.

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REFERENCES

1. Chen, R. and McKeever, S. W. S. *Theory of Thermoluminescence and Related Phenomena* (Singapore: World Scientific) ISBN 9810222955 (1997).

2. Opanowicz, A. *On the Kinetics Order of Thermoluminescence in Insulating Crystals*. Phys. Status Solidi a **116**, 343–348 (1989).

3. Sunta, C. M., Ferya Ayta, W. E., Kulkarni, R. N., Piters, T. M. and Watanabe, S. *Theoretical Models of Thermoluminescence and their Relevance in Experimental Work*. Radiat. Prot. Dosim. **84**(1–4), 25–28 (1999).

4. Mandowski, A. and Świątek, J. *New Fitting Algorithm for the Determination of Trap Parameters from TL Curves*. Radiat. Prot. Dosim. **84**(1–4), 123–126 (1999).

5. May, C. E. and Partridge, J. A. *Thermoluminescence Kinetics of Alpha-irradiated Halides*. J. Chem. Phys. **40**(5), 1401–1409 (1964).

6. Chen, R. *Glow Curves with General Order Kinetics*. J. Electrochem. Soc. **116**, 1254–1257 (1969).

7. Chen, R. *Simultaneous Measurement of Thermally Stimulated Conductivity and Thermoluminescence*. J. Appl. Phys. **42**(13), 5899–5901 (1971).

8. Gasiot, J. and Fillard, J. P. *Correlation in Simultaneous TSC and TSL Measurements*. J. Appl. Phys. **48**(7), 3171–3172 (1977).

9. Mandowski, A. and Świątek, J. *A Method for Determining the Density of Deep Traps by using the Simultaneous TL/TSC Measurement Technique*. J. Phys. D: Appl. Phys. **25**, 1829–1833 (1992).

10. Opanowicz, A. *Determination of the Kinetic Parameters by the Simultaneous Measurements of Thermally Stimulated Conductivity and Luminescence.* J. Appl. Phys. **86**(1), 6189–6195 (1999).

11. Guissi, S., Bindi, R., Iacconi, P., Jeambrun, D. and Lapraz, D. *Theoretical Model for Thermally Stimulated Luminescence, Conductivity and Exoelectronic Emission*. J. Phys. D: Appl. Phys. **31**, 137–145 (1998).

12. Guissi, S., Iacconi, P., Bindi, R. and Lapraz, D. *Characterization and Modelling of the 450 K TSL Peak of Alpha Alumina by the Simultaneous Analysis of TSL, TSC and TSEE*. Radiat. Prot. Dosim. **84**(1–4), 247–251 (1999).

13. Mandowski, A. and Świątek, J. *Determination of Trap Parameters from Generalised Initial Rise Equations*. Radiat. Prot. Dosim. **65**(1–4), 55–58 (1995).

14. Mandowski, A. and Świątek, J. *New Methods for Determining Trap Parameters in Semiconductors from TSC and TL Spectra*. Proc. SPIE **2373**, 225–230 (1995).

15. Opanowicz, A. and Przybyszewski, K. *Is the Quasi-equilibrium Approximation in Description of Thermally Stimulated Luminescence and Conductivity Valid?*, Proc. SPIE **2373**, 236–240 (1995).

16. Sunta, C. M., Ferya Ayta, W. E., Chubaci, J. F. D. and Watanabe, S. *Quasi-equilibrium Assumption in Analytical Models of Thermoluminescence and its Validity in Practical Cases*. Radiat. Prot. Dosim. **84**(1–4), 51–54 (1999).

17. Mandowski, A. and Świątek, J. *New Method for the Determination of Trap Parameters from TSC Curves*. In: Proc. ISE-10, Delphi, Greece. ISBN 07803503251, pp. 359–362 (1999).

18. Bindi, R., Lapraz, D., Iacconi, P. and Boutayeb, S. *Theoretical Analysis of the Simultaneous Detection Method of Thermally Stimulated Conductivity (TSC) and Luminescence (TSL); Application to an α-alumina Crystal*. J. Phys. D: Appl. Phys. **27**, 2395–2400 (1994).

19. Lapraz, D., Boutayeb, S., Iacconi, P., Bindi, R. and Rostaing, P. *Photoinduced Thermostimulated Electrical Conductivity of an Alpha Alumina Monocrystal*. Phys. Status Solidi a **136**, 497–507 (1993).