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Resolving the limitation of the peak fitting and peak shape methods in the determination of the activation energy of thermoluminescence glow peaks

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ABSTRACT

An overview of the successes and failure of the computerized glow curve deconvolution (CGCD) and the peak shape methods in describing the glow peaks generated from the fundamental one trap-one recombination center (OTOR) model was discussed. Also, the existing method, and a new developed one, to test the applicability of the existing thermoluminescence (TL) expressions to describe the glow peaks were discussed. The new TL expressions deduced by Kitis and Vlachos ([17] G. Kitis, N.D. Vlachos, Radiat. Meas. 48 (2013) 47–54) were tested in the cases in which the other existing TL expressions failed. The results showed that the error in the calculated activation energy (E) using the existing expressions may reach up, in some cases, to 50%. While, using the new TL expressions, the error in the calculated E did not exceed 0.5%.

1. Introduction

The clear knowledge of the kinetics parameters of the thermoluminescence (TL) material is essential for many applications in TL dosimetry [1–4]. Thus, several methods were developed to determine the kinetics parameters of a single glow peak e.g., the peak shape methods and the glow peak fitting method. These methods are based on the well-known model for explaining a single TL glow peak, the one trap-one recombination center (OTOR) [5,6]. This model consists of an electron trapping state, the conduction band and hole center. Unfortunately, the differential equations describing this model cannot be solved analytically. Thus, using simplifying assumptions, the OTOR model is reduced to either first- or second-order kinetics expressions but not to intermediate kinetics orders. For the intermediate cases, the general-order kinetics (GOK) expression was developed [7] which is an empirical expression. Application of GOK has been most commonly practiced in this connection for over two decades. However, recently the mixed-order kinetics (MOK) [8] has getting substantial attention due to the fact that the MOK has a physical basis [9,10].

The success and failure of the general- and mixed- order kinetics analytical expressions to fit numerically generated TL glow peaks based on the OTOR model, as well as more complicated models, have also been investigated [9,11–16]. The general conclusion from these attempts is that both the general- and mixed-order kinetics fit numerically generated glow peaks well in terms of the limits of the first- and the second-order kinetics but deviate in the intermediate kinetic orders. Furthermore, all analytical peak model expressions fail to describe the glow peak in the cases in which the re-trapping probability becomes greater than the recombination one ($A_n \gg A_m$), and the sample dose is in the saturation range ($N = n_o$).

Recently, Kitis and Vlachos [17] have developed new general semi-analytical expressions for TL glow peak based on the OTOR level model using the Lambert *W* function. The aim of this study is to use these new developed expressions to attempt to resolve the limitation of the existing TL expression in describing the OTOR glow peaks.

2. OTOR level model

The process of TL consists of the transition of electrons released thermally from the electron traps into the conduction band from which they may either recombine with holes in the center or re-trap, namely fall back into the traps. Halperin and Braner [6] wrote the set of three simultaneous differential equations governing the

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TL process for the OTOR case as follows:

$$-\frac{dm}{dt} = A_m n_c m \tag{1}$$

$$-\frac{dn}{dt} = S\, n \exp\left(-\frac{E}{kT}\right) - A_n n_c (N-n) \tag{2}$$

$$\frac{dm}{dt} = \frac{dn}{dt} + \frac{dn_c}{dt} \tag{3}$$

where N (cm^{-3}) is the total concentration of trapping states and n_o is the initial number of trapped electrons, m (cm^{-3}) is the instantaneous concentration of holes in centers, n_c (cm^{-3}) is the instantaneous concentration of electrons in the conduction band. A_n ($cm^{-3}\,s^{-1}$) and A_m ($cm^{-3}\,s^{-1}$) are the re-trapping and recombination probability coefficients, respectively. E (eV) is the activation energy and S (s^{-1}) is the frequency factor.

In fact, the complete OTOR model consists of two stages;

i. the irradiation (excitation) stage and
ii. the heating (recombination) stage.

For consistency, one has to solve the equations of irradiation stage prior to the simulation of the heating stage in order to use the final concentrations of the irradiation stage as the initial values of the recombination stage. In the present work, however, only the recombination stage is used, for two reasons. (a) The major part of the present work requires fixed values of the concentration of traps and luminescence centers. (b) In case this concentration varies, the variation is allowed in a very broad region, so that in fact it includes any possible concentration that had to be arisen running the irradiation stage.

In fact, the set of nonlinear differential equations Eqs. (1)–(3) cannot be solved analytically, and in order to get a simpler expression, Halperin and Braner [6] assumed that $dn_c/dt = 0$, which is more or less, the quasi-equilibrium (QE) assumption [18]. Obviously, this condition cannot be fulfilled strictly since the concentration of electrons in the conduction band varies during heating, and later the QE condition has been stated as

$$\left|\frac{dn_c}{dt}\right| \ll \left|\frac{dm}{dt}\right|, \left|\frac{dn}{dt}\right| \tag{4}$$

The QE assumption requires that the free electron concentration in the conduction band is quasi-stationary [19]. With these assumptions, one can obtain

$$I = -\frac{dn}{dt} = p(t)\frac{n^2}{(N-n)R+n} \tag{5}$$

where $R = A_n/A_m$ and $p = S\exp(-E/kT)$

If the probability of trapping is negligible compared with the probability of recombination, i.e. $nA_m \gg (N-n)A_n$, then Eq. (5) reduces to

$$-\frac{dn}{dt} = np \tag{6}$$

Processes based on Eq. (6) are said to follow *first-order kinetics*. For linear heating rate β, the shape of the TL glow peak derived from this equation is given by [20]

$$I = n_o\, S\, \exp\left(-\frac{E}{KT}\right) \exp\left(-\frac{S}{\beta}\int_{T_o}^{T} \exp\left(-\frac{E}{kT}\right) dT\right) \tag{7}$$

where n_o is the initial number of trapped electrons. If the trapping process dominates, i.e. $nA_m \ll (N-n)A_n$, the rate equation yields [21]

$$I = -\frac{dn}{dt} = \left(\frac{S}{N}\right) n^2 \exp\left(-\frac{E}{kT}\right) \tag{8}$$

Processes based on Eq. (8) are said to follow *second-order kinetics*. The shape of the TL glow peak generated by this equation is given by [22]

$$I = S' n_o^2 \exp\left(-\frac{E}{kT}\right)\left\{1 + \left(\frac{S'}{\beta}\right) n_o \int_{T_o}^{T} \exp\left(-\frac{E}{kT}\right) dT\right\}^{-2} \tag{9}$$

Along with the Eqs. (6) and (8), which yield first- and second-order kinetics, respectively, a *general order* equation has been proposed [7]

$$I = \frac{n_o S' \exp\left(-\frac{E}{kT}\right)}{\left\{1 + \frac{(b-1)S'}{\beta}\int_{T_o}^{T} \exp\left(-\frac{E}{kT}\right) dT\right\}^{\frac{b}{b-1}}} \tag{10}$$

where $S' = S(n_o/N)^{b-1}$ is the pre-exponential frequency, and b is the kinetics order, which can take values between 1 and 2 but sometimes may exceed this range [23].

We note the integral appearing in Eqs. (7),(9) and (10). The solution of this integral is given by [24]

$$\int_{T_o}^{T} \exp\left(-\frac{E}{kT} dT\right) = T\exp\left(-\frac{E}{kT}\right) + \frac{E}{k} E_i\left[-\frac{E}{kT}\right] \tag{11}$$

where E_i is the exponential integral function and it is a MATLAB built-in function. Thus, there is no need to use its usual asymptotic approximation [25,26].

Recently, Kitis and Vlachos [17] have deduced new TL expressions based on the OTOR model using the Lambert W function as follows:

$$For\ A_n < A_m, \qquad I = \frac{N\,R\,S\exp(-\frac{E}{kT})}{(1-R)^2\, W\left[e^{z1}\right] + W[e^{z1}]^2} \tag{12}$$

$$For\ A_n > A_m, \quad I = \frac{NRS\ exp(-(E/kT)}{(1-R)^2 W\left[-1, -e^{-z2}\right]^2 + W[-1, -e^{-z2}]} \tag{13}$$

where

$$z1 = \frac{1}{c} - \ln(c) + \frac{S}{(1-R)\beta}\int_{T_o}^{T} exp\left(-\frac{E}{kT}\right) dT \tag{14}$$

$$z2 = \frac{1}{|c|} + ln(|c|) + \frac{S}{(1-R)\beta}\int_{T_o}^{T} exp\left(-\frac{E}{kT}\right) dT \tag{15}$$

and

$$c = \frac{n_o(1-R)}{NR} \tag{16}$$

$W\left[\boldsymbol{e}^{z1}\right]$ and $W\left[-1, e^{-z2}\right]$ are the principal and the second branches of the Lambert W function, respectively. Due to the importance of the Lambert W function, it has been implemented in various software packages as a built-in function. In MATLAB software, the Lambert function is implemented as *lambertw*. Therefore, with the implementation of the Lambert W function, the deduced expressions of Kitis and Vlachos [17] can be now considered as a fully analytical expressions.

The quality of the fitting is tested by the figure of merit (FOM) [27]:

$$FOM = \sum_{j_i}^{j_f} \frac{|y_i - y(x_i)|}{A} \times 100 \tag{17}$$

where FOM is the figure of merit (%), j_i is the first channel in the region of interest, j_f is the last channel in the region of interest, y_i is the information content of channel j, $y(x_i)$ is the value of the fitting function in channel j, and A is the integral of the fitted glow peak in the region of interest.