Radiation Protection Dosimetry
Vol. 95, No. 3, pp. 225–229 (2001)
Nuclear Technology Publishing

FIT OF SECOND ORDER THERMOLUMINESCENCE GLOW PEAKS USING THE LOGISTIC DISTRIBUTION FUNCTION

V. Pagonis† and G. Kitis‡
†Physics Department, Western Maryland College
Westminster, MD 21158, USA
‡Aristotle University of Thessaloniki, Nuclear Physics Laboratory
540 06 Thessaloniki, Greece

Received March 7 2001, revised April 19 2001, accepted May 18 2001

Abstract — A new thermoluminescence glow curve deconvolution (GCD) function is introduced which accurately describes second order thermoluminescence (TL) curves. The logistic asymmetric (LA) statistical probability function is used with the function variables being the maximum peak intensity (I_m), the temperature of the maximum peak intensity (T_m) and the LA width parameter a_2. An analytical expression is derived from which the activation energy E can be calculated as a function of T_m and the LA width parameter a_2 with an accuracy of 2% or better. The accuracy of the fit was tested for E values ranging from 0.7 to 2.5 eV, for s values between 10^5 and 10^{25} s^{-1}, and for trap occupation numbers n_o/N between 1 and 10^{-6}. The goodness of fit of the logistic asymmetric function is described by the Figure of Merit (FOM) which is found to be of the order of 10^{-2}. Preliminary results show that the GCD described here can easily be extended to the description of general order TL glow curves by varying the asymmetry parameter of the logistic asymmetric function. It is concluded that the TL kinetic analysis of first, second and general order TL glow curves can be performed with high accuracy and speed by using commercially available statistical packages that incorporate the Weibull and logistic asymmetric functions.

INTRODUCTION

The deconvolution of thermoluminescence (TL) glow curves by computerised glow curve analysis has become very popular[1,2]. In a recent paper Pagonis *et al*[3] introduced a new thermoluminescence glow curve deconvolution (GCD) function that accurately describes first order thermoluminescence (TL) curves. The Weibull distribution function was found to describe accurately first order TL peaks with a wide variety of the values of the TL kinetic parameters E, s and with an accuracy of 2% in the energy values E.

The work presented here extends the results of Reference 3 to second order TL glow curves by using the 3-parameter logistic asymmetric (LA) distribution. The parameters of this function are the maximum peak intensity (I_m), the temperature of the maximum peak intensity (T_m) and the logistic width parameter a_2. An analytical expression is derived from which the activation energy E can be calculated as a function of T_m and the logistic width parameter a_2. The expression accurately reproduces the activation energy E within 2% of the reference values.

The LA distribution function described here has several similarities with the second order and general order TL glow curve deconvolution functions recently published by Kitis *et al*[4]. These authors introduced GCD functions that are based on two experimental parameters, namely the maximum peak intensity (I_m) and the corresponding temperature T_m. The variable parameter in their GCD functions is the activation energy E. The accuracy of the logistic fit was tested using the Figure of Merit (FOM) which is found to be of the order of 10^{-2}, of comparable accuracy to the GCD functions of Kitis *et al*[4].

The GCD described here can easily be extended to the description of general order TL glow curves by varying the asymmetry parameter of the logistic asymmetric function. Preliminary results show that GCD analysis of first, second and general order TL glow curves can be performed with high accuracy and speed by using commercially available statistical packages.

KINETIC EQUATIONS — THE LOGISTIC ASYMMETRIC PROBABILITY FUNCTION

The TL intensity for peaks exhibiting second order kinetics is given by the well known second order kinetics equation[5]:

$$I(T) = s\,\frac{n_o^2}{N}\exp(-E/kT)\left[1 + \frac{sn_o}{\beta N}\int_{T_o}^{T}\exp(-E/kT')\,dT'\right]^{-2} \quad (1)$$

where β is the heating rate assumed to be a linear function of time, T_o is the initial temperature, E is the activation energy for the TL process, k is the Boltzmann constant, n_o is the initial number of filled traps, the frequency factor s has the dimensions of s^{-1}, and the ratio n_o/N represents the trap occupancy factor. Recently Kitis *et al*[4] developed glow curve deconvolution

Contact author E-mail: vpagonis@wmdc.edu

(GCD) functions for second and general order kinetics which use the experimentally determined maximum intensity I_m and the corresponding temperature of maximum intensity T_m. The expressions derived for the TL intensity contain I_m,T_m and the kinetic parameters E and b. By comparing the GCD functions with synthetic TL glow curves, Kitis *et al*[4] showed that their GCD functions yield accurate values of the energy E , within 3% of the correct values. Their equation for TL peaks involving second order kinetics is:

$$I(T) = 4\ I_m \exp\left(\frac{E}{kT}\frac{T-T_m}{T_m}\right)\left\{1+\frac{2kT_m}{E} + \left(1-\frac{2kT}{E}\right)\left[\frac{T^2}{T_m^2}\exp\left(\frac{E}{kT}\frac{T-T_m}{T_m}\right)\right]\right\}^{-2} \quad (2)$$

Here I_m represents the maximum TL intensity and T_m is the corresponding temperature.

In this paper it is shown that a second order single TL peak is accurately described by the logistic asymmetric (LA) distribution function and the results are compared to the GCD function in Equation 2 as well as to the numerically integrated Equation 1. The *symmetric* 2-parameter logistic function is sometimes used instead of the normal distribution to describe scientific data[6]. In this paper the more general 4-parameter logistic *asymmetric* function is used which is given by the equation:

$$LA(T) = I_m\left(1+\exp\left[-\left(\frac{T-T_m}{a_2}+\ln(a_3)\right)\right]\right)^{-a_3-1} a_3^{-a_3}\ (a_3+1)^{a_3+1}\exp\left[-\left(\frac{T-T_m}{a_2}+\ln(a_3)\right)\right] \quad (3)$$

In the case of TL glow curves the parameter T represents the temperature in degrees K, while T_m represents the centre of the logistic asymmetric distribution. The parameter a_2 is known as the scale or width of the LA function and a_3 is called the asymmetry parameter of the distribution. The parameter I_m represents the maximum height of LA(T) at the centre point $T = T_m$. For second order TL peaks it is found by a least squares fitting procedure that the value of $a_3 = 1.4702$ gives the best fit for all second order TL peaks studied here, and therefore the value of $a_3 = 1.4702$ is fixed throughout the present work. By using $a_3 = 1.4702$ the logistic asymmetric equation above becomes

$$LA(T) = I_m 5.2973\left(1+\exp\left[-\left(\frac{T-T_m}{a_2}+0.38542\right)\right]\right)^{-2.4702}\exp\left[-\left(\frac{T-T_m}{a_2}+0.38542\right)\right] \quad (4)$$

An example of comparing the numerically integrated Equation 1 with the GCD functions 2 and with the logistic Equation 4 is shown in Figure 1 for the following values of the parameters: E = 1.0 eV, s = 10^{15} s^{-1}, $n_o/N = 1$, $\beta = 1$ K.s^{-1}. The corresponding parameters for the LA function 4 are: $I_m = 3.05$, $T_m = 315.6$ K, $a_2 = 9.08$. All three equations depicted in Figure 1 have been normalised to the same maximum intensity for comparison purposes.

Several other examples are shown in Table 1 for a wide range of values of E, s and the trap occupancy n_o/N. The results in Table 1 show that the logistic asymmetric function with $a_3 = 1.4702$ accurately describes second order TL glow peaks. The goodness of fit is expressed mathematically by the Figure of Merit FOM[2] which is defined by:

$$FOM = \sum_p \frac{|y_{experimental} - y_{fit}|}{Area_{fit}} \quad (5)$$

where $y_{experimental}$ and y_{fit} represent the experimental data and the values of the fitting function correspondingly. The summation extends over all the available points and $Area_{fit}$ represents the integral of the fitted glow curve. In the examples of Table 1, very good values of FOM of the order of 10^{-2} are obtained using the logistic equation 4. Slightly better fits are obtained by using the GCD function 2, and they are also shown in Table 1. It is also noted that the LA parameter T_m is very close to the temperature of maximum intensity obtained from Equation 1, with very small deviations of the order of 0.5 K, well within the accuracy of typical experimental data. Table 1 also shows that the accuracy of the logistic fits is not affected by the occupancy factor n_o/N.

The success of the logistic function in describing the second order TL peaks is explained in the next section, where the mathematical properties of Equations 2 and 4 are studied in more detail and analytical expressions for the activation energy E are derived using the logistic asymmetric parameters.

MATHEMATICAL PROPERTIES OF THE LOGISTIC ASYMMETRIC FUNCTION

The mathematical analysis presented in this section follows closely the previously published analysis for first order TL glow curves using the Weibull distribution function[3]. In this section the mathematical behaviour of the logistic asymmetric function is examined near the temperature of maximum intensity $T = T_m$ and an analytical relationship is derived between the activation energy E and the parameters a_2 and T_m. Finally an analytical linear relationship between the logistic width parameter a_2 and the full-width at half-maximum (FWHM) of the TL glow curve is derived, and the shape factor $\mu = \delta/\omega$ of the logistic distribution in Equation 4 is shown to be equal to that of a second order TL glow peak.

The relationship between the activation energy E and the logistic parameters T_m and a_2 can be found by a

Taylor expansion of Equation 4 near the temperature of maximum intensity T_m. The first three terms of the Taylor expansion of Equation 4 are easily found to be given by:

$$LA(T) = I_m \left(1 - \frac{(6.837)\, 10^{-7}}{a_2}(T - T_m) - \frac{0.29759}{a_2^2}(T - T_m)^2 + O(T^3)\right) \quad (6)$$

Next a Taylor series expansion of the GCD function 2 is performed around $T = T_m$. The first three terms of this Taylor series are found to be:

$$LA(T) = I_m \left(1 + \frac{6k}{E}(T - T_m) + \frac{-4E^3kT_m - E^4 + 24k^3T_m^3E + 108k^4T_m^4}{4k^2T_m^4E^2}(T - T_m)^2\right) + O(T^3) \quad (7)$$

At temperatures near the temperature of maximum intensity T_m, the second order TL glow peak is accurately described by the first three terms in both Taylor expansions. The linear terms in temperature can easily be shown to be negligible near $T = T_m$. By equating the quadratic terms of the two Taylor series 6 and 7 an analytical expression is obtained for the energy E as a function of the logistic width a_2 and of the temperature of maximum intensity T_m.

$$\frac{-0.2976}{a_2^2} = \frac{-4E^3kT_m - E^4 + 24k^3T_m^3\, E + 108k^4T_m^4}{4k^2T_m^4E^2} \quad (8)$$

It can be easily shown that the terms containing k^3 and k^4 are negligible compared with the rest of the terms

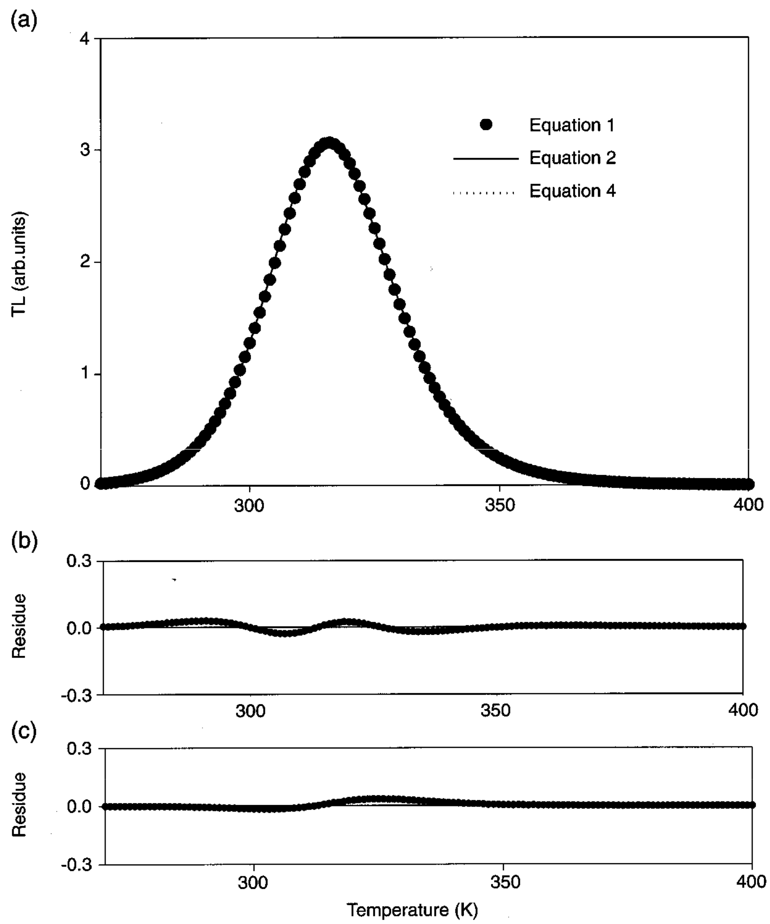

Figure 1. (a) Comparison of the TL glow curve obtained from Equation 1 with the logistic asymmetric Equation 4. Equation 2 is also shown. The parameters used are given in the text. (b) The deviations between Equations 1 and 4. (c) The deviations between Equations 1 and 2.

in the above equation, yielding a quadratic equation in the activation energy E:

$$\frac{-0.2976}{a_2^2} = \frac{-4E^3kT_m - E^4}{4k^2T_m^4E^2} \quad (9)$$

The solution of this quadratic yields the activation energy E as a function of the logistic parameters a_2 and T_m:

$$E = T_m k\left[-2 + \sqrt{\left(4 + 1.189\frac{T_m^2}{a_2^2}\right)}\right] \quad (10)$$

where k is the Boltzmann constant and the logistic constants T_m and a_2 are given in degrees Kelvin. The results of using Equation 10 to evaluate the activation energy E for a wide variety of the parameters E, s and n_o/N are shown in Table 1. The values of E calculated using equation 10 are seen to be very accurate, within 2% of the actual E values. The results of Table 1 indicate that the E values calculated using Equation 10 are systematically lower by 2% from the actual activation energies. It is then possible to improve the accuracy of Equation 10 by imposing a 2% correction, at least within the range of the parameters studied in this paper.

A relationship can be derived between the logistic parameter a_2 and its full-width at half-maximum (FWHM) as follows. The low temperature $T_1 < T_m$ and the high temperature $T_2 > T_m$ for which the height of the logistic is equal to the half-maximum intensity $I_m/2$ are calculated as follows. By equating Equation 4 with $I_m/2$ the equation below is obtained:

$$0.5I_m = I_m\,5.2973\left(1 + \exp\left[-\left(\frac{T-T_m}{a_2} + 0.38542\right)\right]\right)^{-2.4702} \exp\left[-\left(\frac{T-T_m}{a_2} + 0.38542\right)\right] \quad (11)$$

This equation can be solved numerically and yields the two values

$$\frac{T_1 - T_m}{a_2} = -1.52414 \text{ and } \frac{T_2 - T_m}{a_2} = 1.68024 \quad (12)$$

It is concluded that the FWHM of the logistic is equal to

Table 1. Accuracy of the logistic asymmetric analysis for second order TL glow curves.

Logistic parameters			Frequency factor s (s^{-1})	Calculated activation energy (Equation 4) $E_{Logistic}$ (eV)	Actual activation energy E_{actual} (eV)	% accuracy in E Logistic Equation 4	FOM Equation 4	FOM Equation 2
T_{max} (K)	a_2 (K)	n_o/N						
315.6	9.082	1	10^{15}	0.978	1.0	−2.2	0.015	0.011
413.1	15.329	10^{-4}		0.977		−2.3	0.012	0.004
487.3	21.087	10^{-6}		0.977		−2.3	0.012	0.010
447.2	17.874	1	10^{10}	0.977	1.0	−2.3	0.012	0.006
487.3	21.104	10^{-1}		0.977		−2.3	0.012	0.010
534.9	25.219	10^{-2}		0.978		−2.2	0.013	0.016
592.2	30.648	10^{-3}		0.978		−2.2	0.018	0.023
662.5	37.940	10^{-4}		0.979		−2.1	0.022	0.032
468.5	13.351	1	10^{15}	1.466	1.5	−2.3	0.015	0.012
530.8	17.022	10^{-2}		1.466		−2.3	0.012	0.007
611.4	22.404	10^{-4}		1.466		−2.3	0.011	0.004
719.6	30.682	10^{-6}		1.467		−2.2	0.010	0.009
479.3	10.596	1	10^{20}	1.956	2.0	−2.2	0.020	0.019
585.9	15.704	10^{-4}		1.955		−2.3	0.016	0.014
596.5	13.130		10^{20}	2.445	2.5	−2.2	0.020	0.020
656.0	15.825			2.445		−2.2	0.018	0.017
293.8	5.342	1	10^{25}	1.468	1.5	2.1	0.024	0.024
317.7	6.233	10^{-2}		1.467		−2.2	0.023	0.022
378.9	8.812	10^{-6}		1.467		−2.2	0.019	0.018
485.6	8.763	1	10^{25}	2.446	2.5	−2.2	0.025	0.024
570.5	12.031	10^{-4}		2.445		−2.2	0.021	0.021
624.9	14.385	10^{-6}		2.445		−2.2	0.019	0.018
536.4	35.0046	1	10^{7}	0.684	0.7	−2.3	0.020	0.024

The parameters $\beta = 1$ K.s^{-1} $a_3 = 1.47023$ for all entries.

$$\mathrm{FWHM} = \omega = T_2 - T_1 = (1.52414 + 1.68024)\,a_2 = 3.204\,a_2 \text{ or } a_2 = 0.3121\,\omega \qquad (13)$$

The shape factor for the logistic distribution is then equal to

$$\mu = \frac{\delta}{\omega} = \frac{1.68024}{3.204} = 0.524 \qquad (14)$$

Hence it is shown that the logistic distribution has the correct shape factor for a second order TL glow peak[5]. By combining Equations 10 and 13 an equation is derived which gives the activation energy E as a function of the temperature T_m and the FWHM ω of the logistic distribution. By inserting the value of $a_2 = 0.3121\,\omega$ from Equation 13 into Equation 10 it is found after some simple algebra that:

$$(E + 2kT_m)^2 = 4(k^2T_m^2) + 12.213k^2\frac{T_m^4}{\omega^2} \qquad (15)$$

The term $4k^2T_m{}^2$ is easily shown to be negligible compared with the second term, so it can be omitted and the above equation becomes:

$$E = \frac{3.495kT_m^2}{\omega} - 2kT_m \qquad (16)$$

It is noted that Equation 16 is almost identical with the commonly used approximation derived by Chen[5]:

$$E = \frac{3.54kT_m^2}{\omega} - 2kT_m \qquad (17)$$

The values of E obtained using Equation 16 are within 1% of the values of E obtained using Chen's Equation 17.

DISCUSSION AND CONCLUSION

Several researchers have attempted previously to use analytical equations to fit first order TL glow curves and the results have been summarised in the intercomparison papers of Bos *et al*[1,2]. The logistic asymmetric function introduced in this paper gives fittings for second order glow curves that are very accurate, with FOM values of the order of 10^{-2}. Moreover an expression for E is deduced which is close to that derived from the kinetics models and with an accuracy of 2% in the E values. Two of the parameters I_m, T_m in the logistic function are the same as in the recently published GCD functions of Kitis *et al*[4], and can be determined experimentally. The third parameter represents the width a_2 of the logistic distribution and is found to be proportional to the FWHM of the second order TL glow curve, as given in Equation 13.

Another important advantage of the logistic asymmetric function is that it can be easily extended to describe general order kinetics with values of b between 1 and 2. This is easily accomplished by introducing a variable asymmetry factor a_3 in Equation 3. Preliminary results show that by using an asymmetry factor a_3 between the values of 0.556 and 1.164, the logistic asymmetric function describes accurately general kinetics TL glow curves with b values between 1.2 and 1.8 correspondingly. The FOM values in all cases were found to be of the order of 10^{-2}.

In practical terms, the good fits obtained in this paper and in Reference 3 mean that first, second and general order glow curves can be analysed accurately and quickly using commercially available software packages that incorporate the Weibull and logistic asymmetric functions. The authors implemented these functions rather easily on the statistical package PEAKFIT[7] and obtained very good fits for single TL glow curves of any order b, and with FOM values of the order of 10^{-2}.

REFERENCES

1. Bos, A. J. J., Piters, T. M., Gomez-Ros, J. M. and Delgado, A. *An Intercomparison of Glow Curve Analysis Computer Programs: I. Synthetic Glow Curves*. Radiat. Prot. Dosim. **47**, 473–477 (1993).
2. Bos, A. J. J., Piters, T. M., Gomez-Ros, J. M. and Delgado, A. *An Intercomparison of Glow Curve Analysis Computer Programs: II. Measured Glow Curves*. Radiat. Prot. Dosim. **51**, 257–264 (1994).
3. Pagonis, V., Mian, S. M. and Kitis, G. *Fit of First Order Thermoluminescence Glow Peaks using the Weibull Distribution Function*. Radiat. Prot. Dosim. **93**, 11–17 (2001).
4. Kitis, G., Gomez-Ros, J. M. and Tuyn, J. W. N. J. *Thermoluminescence Glow Curve Deconvolution Functions for First, Second and General Order Kinetics*. J. Phys. D: Appl. Phys. **31**, 2636–2641 (1998).
5. Chen, R. and McKeever, S. W. S. *Theory of Thermoluminescence and Related Phenomena* (Singapore: World Scientific Publishing) Chapters 2–3 (1997).
6. Weisstein, E. W. (Ed.) *CRC Concise Encyclopedia of Mathematics* (Boca Raton: CRC) p. 1100 (1999).
7. *The commercial statistical packages PEAKFIT and SIGMAPLOT*. Available from SPSS SCIENCE (http://www.spss.com/software/science/).