GENERALIZATION OF A METHOD FOR CALCULATING
ACTIVATION ENERGIES OF GLOW CURVES

R. CHEN

Department of Physics and Astronomy, Tel-Aviv University,
Tel-Aviv, Israel

A known method for calculating activation energies of certain thermally stimulated conductivity glow curves is slightly modified and is thus shown to apply to other thermally stimulated conductivity curves and to various thermoluminescence curves as well.

Various methods for calculating activation energies from the geometrical shape of thermoluminescence (TL) glow curves have been developed [1–3]. Thermally stimulated conductivity (TSC) curves have been investigated for some time, assuming that they obey the same laws, namely, assuming that formulae developed for calculating TL activation energies can be used for TSC curves as well. Dussel and Bube [4] and Land [5] have shown that TSC curves may substantially differ from TL curves. Following Saunders [6], Chen has investigated [7] the case of TSC curves corresponding to second order TL peaks when the lifetime of free carriers is not necessarily assumed to be constant. A similar treatment was given by Chen [8] for TSC peaks corresponding to first order TL peaks when constant lifetime is not necessarily assumed. The shape of the curve is given in eq. (7) of ref. [8]. In this case, an empirical formula for calculating the activation energy was found to be

$$E_c = 3\mu_g kT_m^2/\tau ,　　　　　　　(1)$$

where E_c is the calculated activation energy, μ_g is the form factor given by $\mu_g = \delta/\omega$ where $\delta = T_2 - T_m$ and $\omega = T_2 - T_1$ and where T_m is the temperature of the maximum and T_1 and T_2 are the low and high temperatures at half intensity, respectively, k is the Boltzmann constant and $\tau = T_m - T_1$. Variations of the parameter $\alpha = c/n_0$, namely, the ratio of concentrations of inactive traps to the initial concentration of active

traps, were investigated. Values of μ_g between 0.42 and 0.44 were found for $\alpha > 1$, which is also characteristic to the corresponding TL peaks [3]. The values of μ_g decreased substantially for $\alpha \ll 1$, and for $\alpha < 10^{-3}$ values of $\mu_g < 0.3$ where found. For all these cases, E_c given in eq. (1) was reported to be correct to 15% or better, with values more often above the correct ones than below.

The above mentioned TSC curves for $\alpha < 1$ are thus characterized by a fast decrease at the high temperature side of the maximum as compared to the first order TL peaks where $0.415 < \mu_g < 0.440$. On the other hand, second order kinetics TL peaks are characterized by almost symmetric curves [3], namely with $\mu_g \approx 0.52$. TSC curves corresponding to second order glow curves are found to decrease more slowly at the high temperature range [6,7]. The shape of these curves is given by eq. (4) in ref. [7] and the derived values of μ_g are as high as 0.78 to 0.85. In view of the different nature of the function at the above mentioned extreme cases of TSC curves, it was quite surprising to discover that eq. (1) is a good approximation for the latter case as well. In both cases the calculated values were on the higher side so that it seemed reasonable to slightly decrease the empirical value of 3 in eq. (1). A value of 2.8 was found to be better.

Apart from this, it seems valuable to introduce a new parameter $\theta = \tau/\mu_g = \tau\omega/\delta$ which is also given in

Table 1
Calculated parameters of non-constant lifetime TSC peaks
corresponding to first order TL

E (eV)	α	T_m (°K)	μ_g	E_c (eV)
0.1	10^2	86.8	0.436	0.097
0.1	10^1	87.0	0.434	0.098
0.1	10^0	88.3	0.419	0.100
0.1	10^{-1}	91.7	0.379	0.105
0.1	10^{-2}	95.3	0.335	0.107
0.1	10^{-3}	98.2	0.297	0.104
0.1	10^{-4}	100.5	0.267	0.098

Table 2
Calculated parameters of non-constant lifetime TSC peaks
corresponding to second order TL

E (eV)	s (sec^{-1})	T_m (°K)	τ (°K)	μ_g	E_c (eV)
0.1	10^{13}	41.1	3.9	0.836	0.088
0.4	10^{13}	157.3	75.6	0.840	0.347
1.6	10^{13}	603.3	53.9	0.843	1.373
0.1	10^9	57.9	6.8	0.812	0.096
0.4	10^9	218.4	24.9	0.816	0.377
1.6	10^9	826.0	90.7	0.820	1.493
0.1	10^5	94.8	15.2	0.788	0.113
0.4	10^5	347.2	52.8	0.788	0.434
1.6	10^5	1278.5	184.9	0.792	1.693

°K. Eq. (1) is thus transformed into

$$E_c = 2.8\, kT_m^2/\theta .\qquad(2)$$

Tables 1 and 2 give some representative parameters calculated for non-constant lifetime TSC peaks corresponding to first and second order TL peaks respectively. The data were taken from the tables in refs. [8] and [7] respectively and E_c was calculated by the use of eq. (2).

TL glow curves, not necessarily of first or second order were investigated [9,10] assuming the following equation

$$I = -dn/dt = s'n^l \exp(-E/kT) ,\qquad(3)$$

where I is the TL intensity, n the concentration of trapped carriers, s' a constant and l a number representing the order of the kinetics. Thus, first order peaks are found for $l = 1$ and second order for $l = 2$. The general solution of eq. (3) is given in ref. [10] to be

$$I = sn_0 \exp(-E/kT)$$

$$\times\ [\{(l-1)s/\beta\} \int_{T_0}^{T} \exp(-E/kT')dT'+1]^{-l/(l-1)} ,\qquad(4)$$

where $s = s'n_0^{l-1}$ and β is the (constant) heating rate. Values of l between 0.7 and 2.5 were investigated as shown in ref. [10].

It is even more surprising than before that eq. (2) gives activation energies correct up to 15% for this broad variety of TL peaks as well. Table 3 gives some representative parameters of glow curves of this sort, the data are taken from table 2 in ref. [10]. First and second order TL peaks were separately checked with data taken from ref. [3], the results being again in the range of ±15%.

A method for calculating glow curves' activation energies based on the shape of the peak which is more general than any other shape method has thus been found. This method is limited in that the accuracy of the method is only up to 15% whereas the methods given before [3,7,10] are correct to 3—4%. This limitation is not too severe as in many cases, the experimental errors due to uncleaned peaks, noise and other inaccuracies, are of the same order.

The fact that this method is usable for such extreme cases both of TL and TSC glow curves, encourages us to use eq. (2) for many other glow peaks for which the kinetics is not precisely known. An experimental comparison of the results with those of the rather general initial rise method [11] should be carried out when it is possible, namely, when the initial rise range is broad enough to perform the measurement.

As shown in ref. [3], equations for calculating activation energies should be modified by subtracting akT in cases where the frequency factor s depends on temperature as $s = s''T^a$ where s'' is a constant and $-2 \leqslant a \leqslant 2$. Eq. (2) should now become

$$E_c = 2.8kT_m^2/\theta - akT ,\qquad(5)$$

which should be used when a is known separately. If a is not known, eq. (2) should be used, and an additional inaccuracy of up to ±10% may thus be introduced.

It is to be noted that the present treatment involves only the case where a single trapping level contributed

Table 3
Calculated parameters of general order TL peaks

E (eV)	s (sec^{-1})	l	T_m ($^{\circ}$K)	τ ($^{\circ}$K)	μ_g	E_c (eV)
1.6	10^{13}	2.5	554.1	28.1	0.548	1.445
0.1	10^5	2.5	82.1	8.8	0.566	0.105
1.6	10^{13}	1.9	554.6	26.4	0.509	1.431
0.4	10^{13}	1.9	144.3	7.1	0.510	0.361
0.1	10^{13}	1.9	37.6	1.9	0.511	0.092
1.6	10^5	1.9	1124.3	100.2	0.524	1.595
0.4	10^5	1.9	303.6	28.9	0.526	0.405
0.1	10^5	1.9	82.5	8.4	0.529	0.103
1.6	10^{13}	1.5	554.9	25.0	0.476	1.415
0.4	10^{13}	1.5	144.4	6.7	0.476	0.357
0.1	10^{13}	1.5	37.6	1.8	0.477	0.090
1.6	10^5	1.5	1126.6	95.9	0.490	1.564
0.4	10^5	1.5	304.3	27.7	0.492	0.397
0.1	10^5	1.5	82.7	8.1	0.495	0.101
1.6	10^{13}	1.1	555.2	23.3	0.431	1.375
0.4	10^{13}	1.1	144.5	6.3	0.431	0.345
0.1	10^{13}	1.1	37.6	1.7	0.432	0.087
1.6	10^5	1.1	1129.1	90.4	0.445	1.514
0.4	10^5	1.1	305.1	26.1	0.447	0.385
0.1	10^5	1.1	82.9	7.6	0.449	0.098
1.6	10^5	0.7	1131.6	82.6	0.376	1.410
0.1	10^8	0.7	57.6	3.5	0.372	0.085

to the thermally stimulated process. The case of quasi-continuous or continuous trap distribution had previously been investigated [12,13], mostly for the relatively simple case of the phosphorescence decay. As for the general case of a thermally stimulated curve, it seems that in cases where one has a narrow distribution (e.g. narrow gaussian distribution), the methods for calculating the activation energy, including the present one, would give the value of the center of the distribution curve to a good accuracy. When the distribution curve is much broader, the only applicable method for finding the traps' spectrum seems to be the repeated heating and cooling of the sample after one irradiation and using the initial rise method for each partial curve thus observed [14].

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