Thermally stimulated current curves with non-constant recombination lifetime

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Abstract. Thermally stimulated current peaks, corresponding to second-order thermo-luminescence when the recombination lifetime is a rapid function of temperature, are investigated. By numerical calculation, values of the maximum and the half intensity temperatures are calculated. A method for calculating the activation energy by use of the maximum and half intensity temperatures is found empirically in analogy with similar first- and second-order methods.

The initial-rise method for calculating the activation energy is also shown to hold true in this case. The value of the parameter μ_g characterizing the geometrical shape of the peak is found to be around 0·8 for various values of the activation energy and the frequency factor. This, in comparison with the value of about 0·4 for first-order and 0·5 for second-order peaks, indicates very slow decay of this phenomenon at high temperatures.

1. Introduction

It was usually considered true that thermally stimulated current (TSC) peaks behave in the same way as thermoluminescence (TL) peaks (Nicholas and Woods 1964, Wright and Allen 1966). Thus, the theories for first-order kinetics TL peaks (Randall and Wilkins 1945) and of second-order TL peaks (Garlick and Gibson 1948) were applied to TSC peaks.

According to Keating (1961) we have

$$\sigma = -e\mu\bar{\tau}(\mathrm{d}h/\mathrm{d}t) \tag{1}$$

or

$$\sigma = e\mu\bar{\tau}I \tag{1a}$$

where σ is the conductivity, μ the mobility, e the electronic charge, h the number of carriers in the centres, $\bar{\tau}$ the average lifetime of carriers in the band, I the TL intensity and t the time. The similarity between the TL peak and the corresponding TSC one results from the assumption that the lifetime is constant during the heating process.

Garlick and Gibson investigated the case in which the number of free carriers is much smaller than the number of filled centres, the initial number of carriers in a trap is equal to the initial number of opposite charge carriers in the recombination centres and the pro-babilities for recombination and retrapping are equal. The differential equation governing this case (the second-order process) is

$$I = -\mathrm{d}h/\mathrm{d}t = (\nu/H)\,h^2 \exp\left(-E/kT\right) \tag{2}$$

where H is the total number of traps having the activation energy E (out of which h are occupied), T is the temperature, ν the frequency factor and k the Boltzmann constant. By assuming a linear heating rate β and introducing a new frequency factor $\nu' = h_0\nu/H$, where h_0 is the initial concentration of carriers, the solution of equation (2) is

$$I(T) = \nu'h_0 \exp\left(-E/kT\right) \left\{1 + (\nu'/\beta) \int_{T_0}^{T} \exp\left(-E/kT'\right) \mathrm{d}T'\right\}^{-2} \tag{3}$$

where T_0 is the initial temperature. ν usually has values of 10^9 to 10^{13} s^{-1} or smaller. ν' will have the same values for cases of saturation ($H = h_0$) and smaller ones for other cases.

By use of equation (3) an expression for $\sigma(T)$ is found by multiplying by $e\mu\bar{\tau}$. By assuming that $\bar{\tau}$ is constant, the curve for the TSC peak seems to have the same shape as the corresponding TL one.

Saunders (1967) has shown that the assumptions of Garlick and Gibson (1948) imply that $\bar{\tau}$ is inversely proportional to h. By multiplying the expression in (3) by $e\mu\bar{\tau}$ and inserting $N/h\nu$ instead of $\bar{\tau}$, where h is the solution of (2), we have

$$\sigma(T)=(\nu'/\nu)\,\mu eN \exp\left(-E/kT\right) \left\{1+(\nu'/\beta) \int_{T_0}^{T} \exp\left(-E/kT'\right) dT'\right\}^{-1} \tag{4}$$

where N is the density of states in the conduction band.

For these assumptions Saunders (1967) shows that, for given trap parameters, the maximum of the function in (3) has to appear at a lower temperature than the maximum in (4). This may account for the shifts between TSC and TL peaks, which result apparently from the same trap (Broser and Broser-Warminsky 1955).

The aim of the present work is to investigate further the properties of such a TSC peak (equation (4)). This is done by calculating several parameters of these peaks (with an IBM 360 computer) for various activation energies E and frequency factors ν'. The method is similar to the one given by Chen (1969) for first- and second-order peaks. A method for calculating the activation energy by use of the temperatures at the maximum and at half intensity is given and tested for these peaks.

2. Calculational procedure and results

In order to deal with expressions as given in (4), it is necessary to calculate

$$\int_{T_0}^{T} \exp\left(-E/kT'\right) dT'$$

numerically. This can be done easily and to a very good approximation by taking a certain number of terms in the following asymptotic expansion (Haake 1957):

$$\int_{T_0}^{T} \exp\left(-E/kT'\right) dT' = T \exp\left(-E/kT\right) \sum_{n=1}^{J} (kT/E)^n (-1)^{n-1} n! \tag{5}$$

For most real cases it was found (see below) that $kT/E \leqslant 0.08$ and for these cases it was found useful to take $J=14$ terms in the expansion. The possible error in these cases did not exceed 0.05% of the value of the integral. The figure gives (on an arbitrary unit scale for σ) a typical peak of the form given in (4) calculated by the use of (5) with the IBM 360
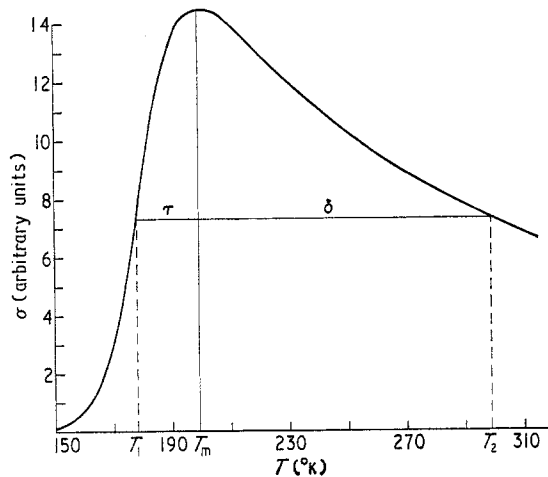
Saunders-type TSC peak for the parameters $E=0.4$ ev, $\nu'=10^{10}$ s^{-1} and $\beta=0.5$ degK s^{-1}.

computer. The parameters for this peak are $\nu' = 10^{10}$ s^{-1}, $\beta = 0.5$ degK s^{-1} and $E = 0.4$ ev. The striking difference between this peak and first- and second-order ones with corresponding parameters (apart from the shift in the maximum of the peak mentioned by Saunders) is the very slow fall off of the intensity at temperatures higher than the maximum. While the first half of the peak is quite similar to the low-temperature half peaks of first- and second-order kinetics (which are quite similar to one another; see figure 1 of Nicholas and Woods 1964), the second halves differ substantially. In this case the high-temperature half width $\delta = T_2 - T_m$ (where T_m is the temperature at the maximum and T_2 the higher temperature of half intensity) is much larger than the low-temperature half width $\tau = T_m - T_1$ (where T_1 is the lower temperature of half intensity). Halperin and Braner (1960) gave a simple geometrical criterion for distinguishing between first- and second-order peaks by introducing the factor $\mu_g = \delta/\omega$ where $\omega = T_2 - T_1$. Values of μ_g around 0.43 indicate first-order kinetics, whereas values around 0.52 are typical of second order. The value of μ_g in the case shown in the figure is 0.826, a value which will be shown to be typical of these TSC peaks.

In order to find the general properties of peaks of the form (4), T_1, T_m, T_2 and other parameters have been found for values of the parameters E and ν' varying in broad ranges (i.e. for values of E between 0.1 and 1.6 ev and values of ν' between 10^5 and 10^{13} s^{-1}). This has been done in a way similar to what had been done for the first- and second-order cases (Chen 1969). By differentiation of equation (4), and equating the derivative to zero, a condition for the maximum is given by

$$1 + (\nu'/\beta) \int_{T_0}^{T_m} \exp(-E/kT)\, \mathrm{d}T = (\nu' k T_m^2/\beta E) \exp(-E/kT_m). \tag{6}$$

This is very similar to the equation for the maximum of a second-order peak, except for a factor of 2 which is now missing on the right-hand side. For given values of ν', E and β this can be solved for T_m by reducing numerically (by use of the Newton–Raphson method) the value of the function

$$f(T_m) = 1 + (\nu'/\beta) \int_{T_0}^{T_m} \exp(-E/kT)\, \mathrm{d}T - (\nu' k T_m^2/\beta E) \exp(-E/kT_m) \tag{6a}$$

down to the point in which the correction in the temperature is smaller than 10^{-3} degK. As a first approximation it was found useful to take $T_m = 800 \times E$. The approximation (5) for the value of the integral was used throughout the iterations (14 terms in the series). Once the value of T_m is known, the value of $\sigma(T_m)$, the intensity at the maximum, is easily found by inserting T_m into the expression in (4). Now the values T_1 and T_2, the temperatures at half intensity, are to be found by finding T in $\sigma(T) = \frac{1}{2}\sigma(T_m)$. This again is done by reducing iteratively the value of $f(T) = \sigma(T) - \frac{1}{2}\sigma(T_m)$ where the expression for $\sigma(T)$ is given by (4). As a first approximation for T_1 we take $0.9T_m$. For T_2 we take as a first approximation $1.6T_m$, because of the expected occurrence of a very broad fall-off part of the peak.

The table gives results of these calculations for various given parameters. Column 1 shows the given energy values changing from 0.1 to 1.6 ev. Column 2 gives the values of ν' varying from 10^{13} down to 10^5 s^{-1}. Column 3 gives the calculated T_m values and columns 4, 5 and 6 give the values of τ, δ and ω respectively, calculated by the aid of the computed T_1 and T_2 values. Column 7 gives the value of $\Delta = 2kT_m/E$. It is important to remember that the accuracy of the numerical method depends on the smallness of the value of Δ, where the relative error in the calculated value of the integral is about $(\frac{1}{2}\Delta)^{n-1}n!$

Some useful method for calculating activation energies for first- and second-order glow peaks were summarized (Chen 1969) in the form

$$E = AkT_m^2/\alpha - B(2kT_m) \tag{7}$$

where α represents either τ, δ or ω and A and B are constants depending on whether α is

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Calculated parameters of non-constant recombination lifetime TSC peaks for given E and ν values

1	2	3	4	5	6	7	8	9	10	11	12
E	ν'	T_m	τ	δ	ω	Δ	μ_g	X_τ	X_τ'	E_σ	C
(ev)	(s^{-1})	(°K)	(°K)	(°K)	(°K)					(ev)	
0·1	10^{13}	41·1	3·9	19·9	23·7	0·071	0·836	2·673	3·808	0·101	0·9732
0·2	10^{13}	80·4	7·5	38·7	46·2	0·069	0·838	2·692	3·811	0·201	0·9733
0·4	10^{13}	157·3	14·5	75·6	90·0	0·068	0·840	2·712	3·815	0·401	0·9735
0·8	10^{13}	308·0	27·9	147·6	175·5	0·066	0·841	2·731	3·818	0·801	0·9736
1·6	10^{13}	603·3	53·9	288·3	342·2	0·065	0·843	2·750	3·822	1·599	0·9737
0·1	10^{11}	48·1	5·1	23·8	28·9	0·083	0·825	2·532	3·792	0·101	0·9725
0·2	10^{11}	93·9	9·7	46·3	56·0	0·081	0·827	2·554	3·793	0·202	0·9726
0·4	10^{11}	183·1	18·6	90·0	108·6	0·079	0·829	2·576	3·795	0·404	0·9727
0·8	10^{11}	357·4	35·7	175·0	210·7	0·077	0·830	2·597	3·797	0·807	0·9728
1·6	10^{11}	698·1	68·7	340·5	409·2	0·075	0·832	2·618	3·800	1·612	0·9729
0·1	10^{9}	57·9	6·8	29·6	36·5	0·100	0·812	2·370	3·790	0·101	0·9719
0·2	10^{9}	112·4	13·0	57·2	70·2	0·097	0·814	2·396	3·789	0·203	0·9720
0·4	10^{9}	218·4	24·9	110·5	135·3	0·094	0·816	2·421	3·788	0·405	0·9720
0·8	10^{9}	424·6	47·5	213·7	261·2	0·092	0·818	2·446	3·788	0·811	0·9721
1·6	10^{9}	826·0	90·7	413·8	504·5	0·089	0·820	2·470	3·788	1·621	0·9722
0·1	10^{7}	72·2	9·8	38·8	48·6	0·125	0·798	2·184	3·815	0·100	0·9717
0·2	10^{7}	139·3	18·5	74·1	92·6	0·120	0·800	2·214	3·808	0·201	0·9717
0·4	10^{7}	269·1	35·0	141·9	176·9	0·116	0·802	2·243	3·803	0·403	0·9717
0·8	10^{7}	520·2	66·2	272·3	338·5	0·112	0·804	2·272	3·799	0·807	0·9717
1·6	10^{7}	1006·7	125·5	523·2	648·6	0·108	0·807	2·299	3·795	1·617	0·9717
0·1	10^{5}	94·8	15·2	56·4	71·6	0·163	0·788	1·952	3·884	0·097	0·9726
0·2	10^{5}	181·3	28·3	104·8	133·1	0·156	0·787	1·998	3·870	0·195	0·9723
0·4	10^{5}	347·2	52·8	196·6	249·4	0·149	0·788	2·033	3·857	0·393	0·9721
0·8	10^{5}	665·8	98·7	371·1	469·8	0·143	0·790	2·070	3·846	0·790	0·9720
1·6	10^{5}	1278·5	184·9	703·5	888·4	0·138	0·792	2·096	3·836	1·588	0·9718

τ, δ or ω and on the order (first or second) of the process. We have tried to find a similar equation which will be suitable for the peaks discussed here (by finding the corresponding A and B values). Equation (7) can be written in the form

$$A = \alpha E / kT_m^2 + 2B\alpha / T_m. \tag{8}$$

Values of the first term on the right, where α is replaced by τ, namely values of

$$X_\tau = \tau E / kT_m^2$$

are given in column 9 of the table. By trial and error, multiples of τ/T_m were added so as to make the right-hand side of equation (8) as close to a constant value as possible. It was found that the best results are obtained for $2B = 12$. The values of $X_\tau' = \tau E / kT_m^2 + 12\tau/T_m$ are given in column 10, having an average value of about 3·82. Thus equation (7) can be written for this case as

$$E_\sigma = 3\cdot82 kT_m^2 / \tau - 12kT_m. \tag{9}$$

The calculated values of activation energies by (9) are given in column 11 of the table. The deviation from the given values of E does not exceed 3%. It is interesting to note that the methods for the first- and second-order peaks, represented here by the general form of equation (7), were proved by assuming a constant ratio between the areas of the first half, the second half and the total areas of the glow peak to triangles having the same height and the same half width (Lushchik 1955, Halperin and Braner 1960, Chen 1969). The fact that we could find (empirically) equation (9) seems to be connected to the fact that the ratio between these areas for the first half of the presently discussed peaks

$$C = \sigma_m \tau / (1/\beta) \int_{T_0}^{T_m} \sigma(T)\, dT \tag{10}$$

is a constant to very good accuracy ($0.9727 \pm 0.1\%$; see column 12 in the table). We cannot, however, prove this connection on purely theoretical grounds. A similar trial and error method for finding an equation for the activation energy by use of δ or ω has failed.

3. Conclusions

The case of TSC peaks, corresponding to second-order TL peaks when the lifetime is inversely proportional to the number of trapped carriers, introduced by Saunders (1967), is further investigated here. Values of the temperature of the maximum as well as the total half width and the low-temperature and high-temperature half width are calculated numerically for values of activation energy and the frequency factor v' varying in broad ranges. A method for finding the activation energy by use of the maximum temperature and the low-temperature half width is found empirically and checked. The accuracy in obtaining the activation energy in this way is shown to be better than 3% for the entire investigated range of the parameters E and v' (which seems to cover most of the experimentally possible cases). It should be noted here that the method of initial rise (Garlick and Gibson 1948), namely finding the activation energy from the slope of $\ln \sigma$ as a function of $1/T$ in the initial-rise portion, which is used both for first- and second-order TL peaks, should be useful here as well. In the initial-rise range

$$(v'/\beta) \int_{T_0}^{T} \exp\left(-E/kT'\right) \mathrm{d}T'$$

is much smaller than unity, and according to equation (4) we have $\sigma \propto \exp\left(-E/kT\right)$. Thus, a plot of $\ln \sigma$ against $1/T$ yields a straight line in this region, whose slope is $-E/k$. This enables us to calculate directly the value of E, which can be used for verification of results found by the previously mentioned method.

The nature of the TSC peak investigated here can be characterized by the large magnitude of μ_g. First- and second-order peaks and these TSC peaks seem to be similar (for the same given parameters) to each other at the first half of the peak. On the other hand, the first-order peaks decrease very rapidly at temperatures higher than T_m, which is characterized by $\mu_g \simeq 0.42$. Second-order peaks decrease more slowly, with characteristic μ_g values around 0.53. The present peaks, of the form given by equation (4), were shown to have μ_g values around 0.82 for all the broad range of E and v' values discussed here, showing the very slow decrease of the intensity.

Acknowledgments

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