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A new method for the numerical analysis of thermoluminescence glow curve

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Abstract

A new method to analyze the thermoluminescence (TL) glow curve has been presented. It has been shown that this method is efficient and fast in generating the TL glow curves and can be adopted in a numerical curve fitting for obtaining the relevant TL parameters of a given TL glow curve data. This new method is based on a general approximation (GA) which assumes only that the concentration of the electrons in the conduction band is negligible when compared with the concentration of the electrons in the traps. The GA method has been tested against the reference glow curve data which was generated by the full iteration method without any prior approximation in the one-trap-one-recombination-centre model. By finding the best fit between the reference data and the curves generated by the GA method, the values of the kinetics parameters have been determined. Also, the general order kinetics (GOK) and the peak shape method have been examined. The fitted values of the activation energy and the initial concentration of electron by the GA method match reasonably well with the original value.

Keywords: Numerical analysis; Thermoluminescence glow

1. Introduction

Thermoluminescence (TL) is the thermally stimulated emission of light following the previous absorption of energy from radiation (McKeever, 1985). This thermally stimulated light contains information about the trap structure of the TL material and its previous exposure to the ionizing radiations. Usually the glow curve, the intensity of light as a function of time or temperature is measured and analyzed. The typical glow curve contains one or more glow peaks. Each peak gives information about each trap level and its occupation state, etc in the TL material. Traditionally the glow peak is analyzed by an empirical method in which a parameter called the order of kinetics is introduced. When the trapped electrons jump up to the conduction band by the thermal energy, they have two kinds of chances to jump down. One is the retrapping process returning to the same kind of traps and another is the recombination with the hole accompanied by the emission of TL light. When the probability of being retrapped is negligible, the glow curve has a narrow peak shape by a rapid recombination process (Randall and Wilkins, 1945). Instead, if the retrapping dominates, the recombination with the holes is suppressed and the curve has a wide peak (Garlick and Gibson, 1948). These two descriptions are called the first order kinetics (1OK) and the second order kinetics (2OK) phenomena, respectively. Between these two types, the general order kinetics (GOK) is introduced for providing a proper analytic continuation from the discrete two types of kinetics (May and Partridge, 1964).

Halperin and Braner (1960) introduced a set of coupled differential equations in which the coefficients of recombination and retrapping could have different values. These equations describe the flow of the charges between the various energy levels and bands during a trap emptying by thermal heating. On the other hand, by applying several physical assumptions to the three flow equations introduced by Halperin and Braner (1960) makes it possible to analyze them systematically. One of these assumptions is that the free carrier concentration in the conduction band (n_c) is very much less than the trapped carrier concentration (n). Another one is that the rate of change of n_c is also much less than the rate of change of n. The TL light

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intensity is expressed as

$$I(t) = -\alpha\frac{\mathrm{d}n}{\mathrm{d}t} = \alpha\frac{n^2 p}{n + R(N-n)}, \tag{1}$$

where R is the ratio of the retrap and recombination coefficient, N is the concentration of the available electron traps of depth E below the conduction band and α is a scaling factor of the light detecting system. Here, $p = s\,\exp(-E/kT)$ is defined as the probability per unit time of the release of an electron from the trap where s is the frequency factor for the escape from the traps to the conduction band. Eq. (1) is firstly introduced by Levy (1985) who undertook the semi-physical treatment for the luminescence mechanism. In the case of the linear temperature increase, (1) is called the general one trap (GOT) equation.

In this paper, a new method to analyze the TL curve is described. It is shown that this method is efficient and fast in generating TL glow peaks and can be adopted in to a numerical curve fitting. This new method is based on (1). Although this method is based on the GOT model, there is no restriction in the temperature profile. We call this model the 'general approximation' (GA).

2. The model and analysis

In the case of $R(N-n) \ll n$ and $R(N-n) \gg n$ (or $R = 1$), Eq. (1) could be solved exactly by including the term $\int p(t)\,\mathrm{d}t$ and the two solutions are related to the first and second order kinetics, respectively. When these two extreme cases do not hold, it is difficult to display $I(t)$ or $n(t)$ as an explicit function form. Sunta et al. (1997) treated the above model and have calculated the glow curve for typical values of R and n_0/N, where n_0 is the concentration of the electron introduced by ionizing radiation. They employed the Runge–Kutta technique (Gerald and Wheatley, 1994) to solve the flow equations. Even if all the kinds of the flow equations could be solved by a stereotype numerical analysis, it needs a lot of computer arithmetical run time for determining various parameters with optimization algorithm. We found that $n(t)$ could be expressed with an inverse function and there is an easy and fast way to calculate the function by a computer using the following procedure. Eq. (1) is rewritten as

$$(R-1)\ln\frac{n(t)}{n_0} - RN\frac{n(t)-n_0}{n_0 n} = \int_0^t p(t)\,\mathrm{d}t. \tag{2}$$

Define two functions:

$$G_{R,N,n_0}(n) \equiv (R-1)\ln\frac{n(t)}{n_0} - RN\frac{n(t)-n_0}{n_0 n}, \tag{3}$$

$$F_{E,s}(t) \equiv s\int_0^t \exp\left(-\frac{E}{kT(t)}\right)\mathrm{d}t. \tag{4}$$

Then (2) can be solved generally as

$$G_{R,N,n_0}(n) = F_{E,s}(t) \quad \text{or} \quad n(t) = G^{-1}[F(t)]. \tag{5}$$

In the stage of a numerical analysis, the first problem we meet is calculating the function $F_{E,s}(t)$. Especially the linear temperature dependence leads to a very simple interpretation of it. In this case, temperature and time are related by the expression $T = T_0 + \beta t$ or $\mathrm{d}T = \beta\,\mathrm{d}t$, where β is the heating rate in degrees per unit time. So

$$F(t) = \frac{s}{\beta}\frac{E}{k}\left[C\left(\frac{kT(t)}{E}\right) - C\left(\frac{kT_0}{E}\right)\right], \tag{6}$$

where the function $C(\tau)$ is related to the exponential integral function $E_i(z)$, one of special function, as

$$C(\tau) = \int \mathrm{e}^{-1/\tau}\,\mathrm{d}\tau = \mathrm{e}^{-1/\tau}\tau + E_i\left(-\frac{1}{\tau}\right). \tag{7}$$

In spite of this, $E_i(x)$ is not adopted as an internal function in an ordinary program language, but it is possible to define $E_i(x)$ as an efficient external function by the introduction of the lookup table and interpolation method.

When the temperature dependency is nonlinear, i.e. is hyperbolic or extremely arbitrary, the function $F(t)$ is considered as a function of both t and E. More computing time and more memory is needed to calculate the value of $F(t)$ for a given t and E. But we also developed efficient techniques to overcome such difficulties with a two-dimensional interpolation method.

The residual problem we meet is to calculate the inverse function of $G(n)$. Because the function $G(n)$ shows a monotonously decreasing behaviour and its second derivative is positive, the inverse function $G^{-1}(a)$ can be evaluated quickly by Newton's method (Gerald and Wheatley, 1994) which is the most widely used technique for finding the roots of functions.

As shown at Fig. 1, for a given t, firstly $F(t)$ is calculated. Then for this function value, $n(t)$ is evaluated from $G^{-1}(a)$. Once $n(t)$ is calculated as a function of t, the intensity of the TL light, i.e., glow curve I is calculated as a function of t by applying this result to (1). The above treatment does not have any divergent problem and does not need much CPU time.

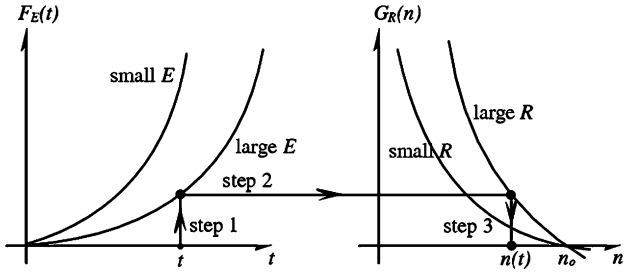

Fig. 1. The procedure to find out $n(t)$ when t is given.

3. Computational results and discussion

The numerical analysis based on (1) requires the assumption of the values of four parameters—E, s, N, R and one initial value—n_0 to solve the TL glow peak with one trap. Usually, the glow curve is not measured with the absolute intensity, so the coefficient α of (1) is also an unknown parameter. The curve fitting technique requires a comparison of the computed curve with the experimental or reference data. If the fitting result is

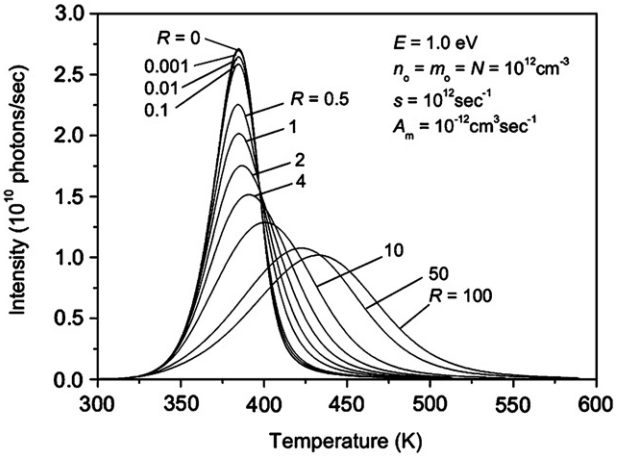

Fig. 2. The glow curves generated by the FI method using the reference data show the R dependence. Here, the intensity axis is the rate of decreasing n^0.

Table 1
Values of the parameters found by the GA curve fitting method for the glow curves of Fig. 2

R	E_{fit} (eV)	s_{fit} (10^{12} s^{-1})	$n_{0\ \text{fit}}$ (10^{12} cm^{-3})	R_{fit}	N_{fit} (10^{12} cm^{-3})	CV (%)
0	1.014	1.71	0.976	0.045	3.72	3.3
10^{-3}	1.014	1.71	0.976	0.048	3.44	3.3
0.01	1.015	1.54	0.976	0.153	1.03	3.3
0.05	1.015	1.63	0.975	0.157	1.29	3.4
0.1	1.015	1.60	0.975	0.234	1.03	3.4
0.5	1.015	2.01	0.975	0.527	1.52	3.4
1	1.002	1.83	0.976	1.14	1.61	3.2
2	0.966	0.049	0.980	3.19	1.59	2.7
4	0.936	0.215	0.984	4.49	1.18	1.9
10	0.967	0.565	0.983	13.8	1.05	1.9
50	0.988	0.384	0.983	27.3	0.97	1.8
100	0.991	0.510	0.983	65.9	0.98	1.6

The first column shows the input value of R and the other input values are the same as those in Fig. 2.

not satisfied with a set of six parameters, a different set must be chosen and the procedure must be repeated until the best fit is obtained. If there are completely independent p traps, the number of unknown parameters is $5p+1$. In determining six or more parameters with the TL glow curve, we adopted two curve fitting algorithms. One is the Hessian method, and the other is the simplex method (Avriel, 1976). If all the parameters are to be represented as the components of a vector $B=(b_1, b_2, \ldots, b_K)$, the problem is to find vector B_o such that the sum of the squares of the residuals $G(B) = \Sigma_I[I_i^m - I^c(B; t_i)]^2$ is a minimum, where I_i^m are the measured data and I^c are the corresponding TL intensities computed using (1). Among these two curve fitting techniques, the simplex method is more efficient than the Hessian method. So the simplex method was adopted in the first stage of the iteration. When the result is not so good, the more accurate result was required, the Hessian method was introduced. But in a case having many peaks in a TL glow curve, the dimension of the parameter space is $5p + 1$, so a lot of CPU time is required by the Hessian method. We could obtain satisfactory results up to five peaks within reasonable computing time.

In order to test our algorithm, reference glow curve data is generated by using a fully numerical iteration of the three linear simultaneous equations introduced by Halperin and Braner (1960). This full iteration (FI) method requires too much computing time for adopting it as a usual glow curve deconvolution. In using the FI method, the Runge–Kutta technique (Gerald and Wheatley, 1994) is employed and the curves are calculated for various values of R and for a given set of $E=1.0$ eV, $n_0=m_0=N=10^{12}$ cm^{-3}, $n_{c0}=0$, $s=10^{12}$ s^{-1} and $A_m=10^{-12}$ cm^3 s^{-1} which are shown in Fig. 2. Where the parameters m_0 and n_{c0} are the initial values of the concentration of the holes in the recombination centres and the electrons in the conduction band, respectively, and A_m is the recombination transition coefficient for the electrons in the conduction band with the holes in the centres, these three parameters disappeared at the stage of introducing the model explained here (GA).

As the value of R increases, the recombination is delayed in a thermal process, so the peak shifts to a higher temperature and the curve becomes wider. In this case, the initial rising temperature does not shift much. Changing the other six parameters also affects the glow curve such as the peak shape and/or peak, rising and falling temperatures. Among all the eight parameters of the FI model, E, n_0, R or (b) and s which are also involved in the GOK model, are the most crucial in circumstances of proper TL phenomena. N which is involved in the GA model also affects the glow curve slightly. There are some comments on the remaining m_0 and n_{c0}. The initial hole concentration m_0 is generally set at the same value of n_0+n_{c0}, so it is not really an unknown parameter. While in the other models which accept the thermally disconnected traps (Chen et al., 1981), m_0 is really one of the initial conditions of the TL material and should be determined by a curve fitting. The initial concentration of the electron in the conduction band, n_{c0} is usually supposed to be negligible.

Each single peak of the GA method and the GOK model was fitted to the reference data generated by the FI method.

Table 1 shows the best GA-fitted values of E, s, n_0, R and N together with the coefficient of variation (CV). The fitted values of E and n_0 match reasonably well with their original value used in the FI calculations within 4% in the most physical region ($R<4$). But the other values, s, R and N reveal slightly different values from their original values. To compare our strategy with the ordinary GOK, the GOK-fitted values of the parameters are shown in Table 2.

The parameter R might be related with the order of kinetics b which is also related with the shape factor δ/ω. As given in Table 2, the values of the trap energy E are less agreeable to those of GA.

The best fitting curves for GOK and GA are illustrated in Fig. 3. The exaggerated fitting error curves in Fig. 3 demonstrate that the fitting using the GA method must be much better than that using the GOK. This is also supported by the comparison of the relative deviations in Table 1. It should be noted

Table 2
Values of the parameters found by the GOK curve fitting method for the glow curves of Fig. 2

R	E_{fit}(eV)	$s_{\mathrm{fit}}(10^{12}\,\mathrm{s}^{-1})$	$n_{0\ \mathrm{fit}}$ $(10^{12}\,\mathrm{cm}^{-3})$	b_{fit}	CV(%)
0	1.095	19.4	0.959	1.40	7.8
10^{-3}	1.095	19.5	0.959	1.40	7.8
0.01	1.097	20.5	0.959	1.41	7.8
0.05	1.102	24.3	0.959	1.48	7.8
0.1	1.106	27.7	0.959	1.55	7.6
0.5	1.087	14.8	0.970	1.93	4.9
1	1.028	2.21	0.981	2.13	2.2
2	0.921	0.066	0.993	2.22	2.4
4	0.786	7.35×10^{-4}	1.001	2.13	4.8
10	0.634	4.06×10^{-6}	1.003	1.87	5.3
50	0.513	4.21×10^{-8}	0.993	1.56	2.8
100	0.496	1.79×10^{-8}	0.989	1.51	2.0

The first column shows the input value of R and the other input values are the same as those in Fig. 2.

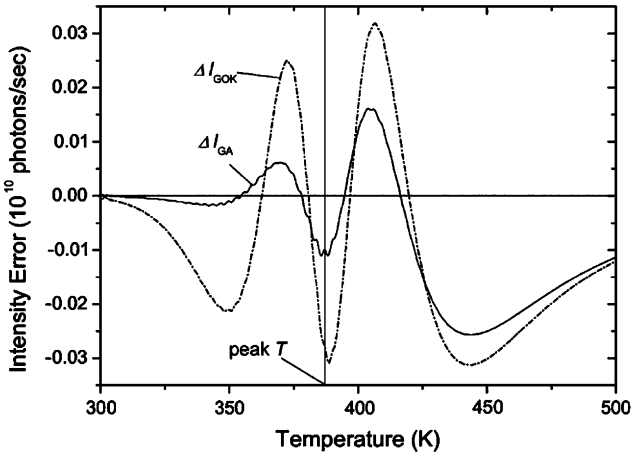

Fig. 3. The fitting error of the glow intensity as a function of the temperature. The reference TL data to fit is generated in the condition of Fig. 2 with $R = 0.5$. The curve denoted as ΔI_{GA} (solid line) is fitted by the method explained here; ΔI_{GOK} (dashed line) is fitted by the GOK method.

that the maximal error is encountered in the tail side of the GA-curve. As mentioned above, the GA treatment that assumes the condition $|n_c| \ll |n|$ is fulfilled for the entire region of the temperature, but it is explicit that the trap density n fades out in the falling or tail stage of the TL, so the condition is not satisfied. It is confirmed from the fact that a good agreement is achieved in the rising stage of the TL.

Using the GA method, a quick and efficient computer program was developed in order to resolve many peaks from a TL glow curve (Chung et al., 2005). The program was designed to be used easily on a MS windows based computer with a graphic user interface. In the program, the traditional methods such as the 1OK, the 2OK, GOK and FI were also adopted with GA.

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