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DETERMINATION OF ZrO_2 THERMOLUMINESCENCE KINETIC PARAMETERS AFTER UV IRRADIATION USING PEAK SHAPE METHODS

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Abstract

Various experimental methods are currently employed for the determination of the trap parameters. Methods based on the glow curve shape extract information from a glow peak utilizing the temperature at the maximum emission, T_M, the temperature on the ascending part of the peak ,T_1, which corresponding to half peak intensity and the temperature on the descending part of the peak, T_2, also corresponding to the half peak intensity; as well as, the half width parameters and the symmetry properties. In order to obtain the kinetic order b and the trap parameters, ZrO_2 samples were exposed to 260 nm ultraviolet radiation (UVR). The trapping kinetics parameters of the ZrO_2 dosimetric peak using the shape of the glow curve were then determined. The order of kinetics followed by the main peak was also determined using the same method. The values of activation energy E and frequency factor ,s, for the main peak of ZrO_2 obtained by the above mentioned methods, showed a good agreement among them.

1. INTRODUCTION

Thermoluminescence (TL) technique is a method based on the measurement of the amount of light emitted, by previously irradiated crystals, during readout. The light intensity is a measure for the total absorbed dose of radiation to which the crystal was exposed in a radiation field. Due to ionizing radiation, electrons are detached from their parent atoms in the valence band and excited to meta-stable states near the conduction band into the crystal. These meta-stable states are called traps and are characterized by the energy, E, that an electron must acquire to be released from the trap to the conduction band, moving through the crystal and then recombine. Thus, energy emitted from the crystal during the heating as light in the form of a glow curve which can present one or more peaks. Position and intensity of the glow peak are related to various parameters at the trapping states responsible for the TL emission. The must important parameters to be determined are the trap depth, E, which is the thermal energy required to liberate the trapped electrons or holes, and the frequency factor ,s, which is the parametric amount correlated to the crystal vibracional energy when an electron interacts n times with the crystal lattice of the solid.

2. THEORETICAL ASPECTS

Various experimental methods are currently employed for determining the trap parameters. The first method for estimating the activation energy from TL glow curves was proposed by Urbach (Urbach 1930) who empirically found a reasonable estimate for the trap depth, E, in eV, by means of the equation $E= T_M /500$ where T_M is given in K.

The next method consisting of peak isolation, by means of suitable thermal treatments, is that proposed by Hoogenstraaten (Hoogenstraaten 1958). The first theoretical treatment for a well isolated glow peak was given by Randall and Wilkins (Randall δ Wilkins 1945), whose working assumption was a non-retrapping of freed charge carriers.

A general technique to determine E and s is that based on the isothermal decay, which was proposed by Towsend (Towsend 1967). Another revolutionary method is based on the different heating rates, this method was proposed by Booth (Booth 1954) and by Bohun (Bohun 1954).

Methods based on the glow curve shape, extract information from a glow peak, utilizing the temperature at the maximum emission, T_M, the temperature on the ascending part of the peak , T_1, corresponding to the half peak intensity and the temperature on the descending part of the peak, T_2, also corresponding to the half peak intensity, as well as the half width parameters and the symmetry properties.

Figure 1 depicts a schematic glow peak with the relevant parameters where $\omega=T_2-T_1$ is the total half peak intensity width, $\delta=T_2-T_M$ is the high temperature half width and $\tau=T_M-T_1$ is the low temperature half width.

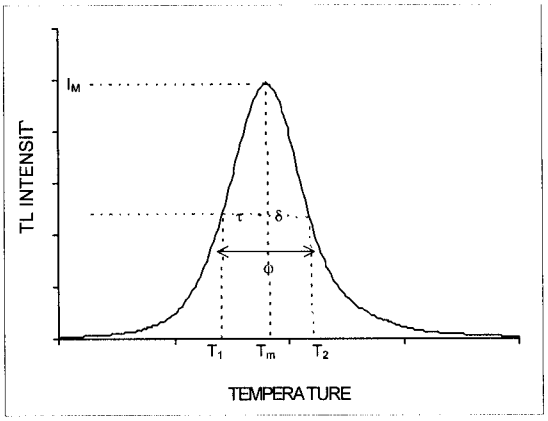

Fig. 1. Typical isolated dosimetric peak showing , in schematic form, the glow curve shape parameters

3. MATERIALS AND METHODS

Materials used in this study were sintered ZrO_2+PTFE discs of 5 mm diameter and 0.8 mm thickness, obtained by the method described in previous woks (Azorin 1999, Rivera 2002). Before exposure of the samples to the UVR they were annealed at 300°C for 10 min in order to erase all remaining information. Samples were irradiated with 260 nm ultraviolet radiation from a Xe lamp which was coupled to a monochromator to select the wavelength desired. The emission lamp was normalized to a reference light by to manufacturer (Azorin 1999).

Thermoluminescent readings were carried out in a TL analyzer Harshaw model 4000 connected to a PC in order to store and to analyze the glow curves, digitizing both TL and temperature signals by means of two channels of an RS232C interface. All TL measurements were made in nitrogen atmosphere in order to reduce the thermal noise from the heating planchet of the TL reader and chemiluminescence effects.

The methods applied in this work to determine the TL parameters were those based on the shape of the glow curve which require the knowledge of the kinetics order.

3.1 Determination of the kinetic order

The kinetics order, b, for the main glow peak of ZrO_2 phosphor can be determined by means of Chen's plot (Chen 1969), which allows the evaluation of b as a function of the measured value of the geometrical factor $\mu_g=\frac{\delta}{\omega}$. The geometrical factor assumes the value of 0.42 for a first kinetics order process and 0.52 for the second order process. Table 1 lists the numerical values of T_1, T_M, T_2, μ_g and b obtained by means of the experimental glow curve of ZrO_2, which corresponding to the previous defined quantities, for the main peak of ZrO_2.

Parameters	Values
T_1	426.5 K
T_M	447.5 K
T_2	473 K
τ	21 K
δ	25.5 K
ω	46.5 K
μ_g	0.54
b	2

Table 1. Geometrical parameters of the main peak of ZrO_2 glow curve obtained after UV irradiation, using a constant heating rate of 10°C/s

3.2 Determination of the trap parameters

The methods currently used for determining the trap parameters are based on a simple model for TL which assumes that irradiation produces free electrons, which were trapped in energy levels within the forbidden band.

3.3 Peak shape method

The peak shape methods used in this study were proposed by Grossweiner [Grossweiner 1953], Lushchik [Lushchik 1956], Halperin and Braner [Halperin and Braner 1960], Balarin [Balarin 1979a,1979b], Chen [Chen 1969a, 1969b, 1970] and Chen modified equation [Chen 1981, 1984]. According to the value of the kinetic order previously obtained. Only the expressions for a second order process are reported here. To obtain the trap parameters the following expressions were used:

Grossweiner $(E_G)_\tau = 1.68k\frac{T_1 T_M}{\tau}$

Lushchik $(E_L)_\delta = 1.706k\frac{T_M^2}{\delta}$

Halperin and Braner $(E_{HB})_\tau = 1.813\frac{kT_M^2}{\tau} - 4kT_M$

Balarin $(E_B)_\omega = \frac{T_M^2}{\omega.3542}$

Chen $(E_C)_\omega = 2kT_M\left(1.756\frac{T_M}{\omega} - 1\right)$

Chen suggested a modified structure form of the equations applied by the mentioned authors (Chen 1970, 1972, 1981).
Equations corrected by Chen (Chen 1981, 1984, Furetta 2002) can be summed up as

$$E_\alpha = c_\alpha\left(\frac{kT_M^2}{\alpha}\right) - b_\alpha(2kT_M)$$

Where α is τ, δ or ω. The values of c_α and b_α are summarized as following:

$c_\tau = 1.51+3.0(\mu-0.42)$; $b_\tau = 1.58+4.2(\mu-0.42)$

$c_\delta = 0.976+7.3(\mu-0.42)$; $b_\delta = 0$

$c_\omega = 2.52+10.2(\mu-0.42)$; $b_\omega = 1$

$$\mu_g = \frac{\delta}{\omega} = \frac{T_2 - T_M}{T_2 - T_1}$$

3.4 Determination of the frequency factor

The frequency factor value of ZrO_2 was obtained by means of the following equation that corresponds to a second order kinetics.

$$s = \frac{\beta E \exp\left(\frac{E}{kT_M}\right)}{kT_M^2}\left[1+\frac{2kT_M}{E}\right]^{-1}$$

4 RESULTS AND DISCUSSION

Figure 2 shows a typical glow curve of ZrO_2 obtained after irradiation with 260 nm ultraviolet radiation (UVR), using a linear heating rate of 10K/s. The TL signal was integrated from 323K to 623K obtaining a glow curve exhibiting a well resolved peak centered at 447.5±2K.

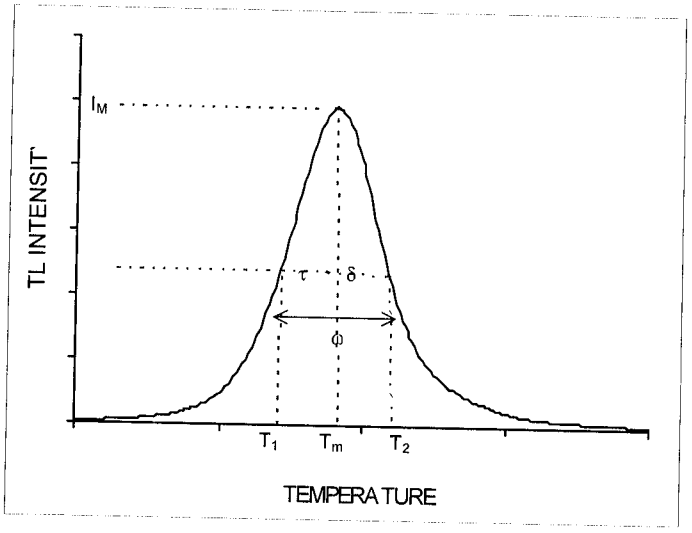

Fig. 2. Typical glow curve of ZrO_2 obtained after exposure to 260 nm ultraviolet radiation.

The geometrical factor was determined by means of Chen's plot and the parametric points schematized in figure 1. It was found that the symmetry factor, μ_g, of the main peak of ZrO_2 glow curve was 0.54±0.08. It is obvious that this value gives an indication that the peak follows a second order kinetics.

Table 2 summarizes the results obtained applying the various methods discussed in this work to determine E and s. All the values obtained have good agreement among the different methods.

Method	**E(eV)**	**S(s^{-1})**
Grossweiner	1.38±0.06	43.09±0.02E+15
Lushchik	1.25±0.25	6.38±0.15E+12
Halperin and Braner	1.33±0.04	8.13±0.08E+14
Balarin	1.21±0.16	3.27±0.09E+13
Chen	1.22±0.03	4.28±0.08E+13
Chen modified		
τ	1.24±0.08	7.73±0.01E+13
δ	1.29±0.05	2.71±0.09E+14
ω	1.12±0.18	2.92±0.19E+12

Table 2. E and s values obtained for ZrO_2 using different glow shape methods.

5. CONCLUSIONS

The very simple glow curve structure, presenting one very well resolved peak, allows to use the peak shape methods for determining the activation energy E of the trapping centers corresponding to the 447.5K peak. The calculated kinetic parameters values for the main peak of ZrO_2 exhibit good agreement among them.

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