PERGAMON

Radiation Physics and Chemistry 61 (2001) 421–423

Radiation Physics and Chemistry

www.elsevier.com/locate/radphyschem

Determination of thermoluminescence kinetic parameters of terbium-doped zirconium oxide

T. Rivera[a], J. Azorín[a,b,*], C. Falcony[c], E. Martínez[d], M. García[d]

[a] *Departamento de Fisica Universidad Autónoma Metropolitana-Iztapalapa 09340 México, D.F., Mexico*
[b] *Centro de Investigación en Ciencia Aplicada y Tecnología Avanzada-IPN 11500 México, D.F., Mexico*
[c] *Centro de Investigación y Estudios Avanzados-IPN 07000 México, D.F., Mexico*
[d] *Instituto de Investigaciones en Materiales-UNAM 04510 México, D.F., Mexico*

Abstract

In recent years considerable importance has been attached to zirconium oxide doped with rare earth (ZrO_2 : RE) thin films due to their desirable characteristics for use in UV dosimetry. In our laboratories we have developed a method to prepare ZrO_2 : RE thin films. Dosimetric characteristics of these materials have been reported previously (Azorin et al., Radiat. Meas. 29 (1998) 315; Radiat. Prot. Dosim. 85 (1999) 317) and results of these have stimulated continued development and analysis of the thermoluminescence mechanism. Two important parameters to be determined in TL studies are the activation energy (E) and the frequency factor (s). This paper presents the results of determining kinetic parameters of terbium-doped zirconium oxide (ZrO_2 : Tb) thin films, exposed to 260 nm UV light, using the Lushchik (Sov. Phys. JETF 3 (1956) 390) and Chen (J. Appl. Phys. 40 (1969) 570; J. Electrochem. Soc. 166 (1969) 1254) methods. Kinetic analysis of the glow curve shows second order kinetics for both the first and second glow peaks. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Thermoluminescence; Kinetics; Zirconium oxide

1. Introduction

In the structure of the most insulating solids there exist point defects, naturally occurring or artificially created, which induce electronic states in the forbidden band. These defects have great importance on understanding the thermoluminescence (TL) phenomenon. Several models exist, which explain the basic principles of the TL process using charge carrier traps induced by impurities called dopants. These models provide diagnostic tools that can be employed to evaluate the TL kinetic parameters using processes based on electronic transitions of the charge carriers.

Crystalline TL materials exhibit a glow curve with one or more peaks when the charge carriers are released. This glow curve is a graphical representation of the luminescence intensity as a function of time or temperature, providing information about parameters corresponding to each peak, such as activation energy, frequency factor and the order of the kinetics (Azorín, 1986).

The aim of this work is to determine the kinetic parameters of the two peaks exhibited by the glow curve of ZrO_2 : Tb thin films, by applying standard methods of analysis. The glow curve shape methods applied were those of Lushchik (1956) and Chen (1969a,b).

2. Materials and methods

Materials used in this study were 0.005 mm thick ZrO_2 : Tb films coated on glass substrates of $5 \times 5 \times 1\,mm^3$. These films were prepared in our laboratory using the technique described in previous work (Azorín et al., 1998, 1999). Samples of the

*Corresponding author. Departamento de Fisica Universidad Autónoma Metropolitana-Iztapalapa 09340 México, D.F., Mexico. Tel.: +52-5-804-4620; fax: +52-5-804-4611.

E-mail address: azorin@xanum.uam.mx (J. Azorín).

PII: S0969-806X(01)00286-9

deposited film were investigated with an X-ray diffractometer to determine their crystalline structure both undoped and terbium-doped. To determine the concentration of impurities, samples were analysed using neutron activation and X-ray fluorescence analysis.

Prior to the exposure of the samples to UV light, they were annealed for 30 min at 300°C to erase all existing information. To determine the kinetic parameters, samples were individually exposed to UV light, selecting different wavelengths between 200 and 900 nm.

The TL measurements were made using a Harshaw 4000 TL analyser connected to a PC for recording and processing the data. The TL signal was integrated from room temperature up to 300°C using a heating rate of 10°C/s. All TL measurements were made in a nitrogen atmosphere.

The methods used to determine the kinetic parameters are commonly known as "peak shape methods". These extract information from a glow peak utilising the temperature peak T_m and two temperatures (T_1 and T_2) on either side of T_m, cading to the half peak intensity, the half width parameters and the symmetry properties.

Fig. 1 shows a peak of a typical glow curve, analysis cading to peak parameters such as $\omega = T_2 - T_1$, the total half intensity width, $\delta = T_2 - T_m$, the high temperature half width and $\tau = T_m - T_1$, the low temperature half width.

The Lushchik method uses the descending part of the glow peak, it being assumed that the area of the half peak equals the area of the triangle having identical height and half width. E is found by means of the following expressions:

$$E = \frac{kT_m^2}{\delta} \quad \text{first order,}$$

$$E = \frac{2kT_m^2}{\delta} \quad \text{second order,}$$

$$s = \left(\frac{\beta}{\delta}\right) \exp\left(\frac{T_m}{\delta}\right),$$

where $\beta = dT/dt$ is the heating rate.

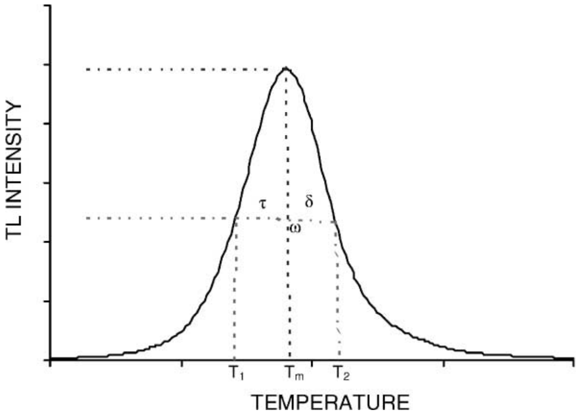

Fig. 1. Typical glow curve peak showing the geometrical parameters used to determine E and s values by methods based on the glow curve shape.

The Chen method makes use of the following equations:

$$E_\tau = 1.51 + 3.0(\mu_g - 0.42)\frac{kT_m^2}{\tau}$$

$$- 1.58 + 4.2(\mu_g - 0.42)2kT_m$$

$$E_\delta = 0.97 + 7.3(\mu_g - 0.42)\frac{kT_m^2}{\delta}$$

$$E_\omega = 2.52 + 10.2(\mu_g - 0.42)\frac{kT_m^2}{\omega} - 2kT_m$$

where $\mu_g = \delta/\omega$ is the symmetry factor that determines the order of the kinetics (if $\mu_g = 0.42$, we have first order and if $\mu_g = 0.52$ second order).

The frequency factor can be evaluated using the equation

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

where b is the order of the kinetics.

Table 1
Kinetic parameters of ZrO_2 : Tb exposed to 260 nm UV light

Method		Peak 1		Peak 2	
		E (eV)	s (s^{-1})	E (eV)	s (s^{-1})
Lushchick		0.88 ± 0.01	$1.97 \pm 0.01 \times 10^8$	1.41 ± 0.01	$4.46 \pm 0.01 \times 10^{14}$
	τ	0.64 ± 0.01	$3.53 \pm 0.01 \times 10^9$	1.39 ± 0.01	$5.85 \pm 0.01 \times 10^{11}$
Chen	δ	0.68 ± 0.01	$5.15 \pm 0.01 \times 10^8$	1.30 ± 0.01	$3.73 \pm 0.01 \times 10^{12}$
	ω	0.66 ± 0.01	$2.74 \pm 0.01 \times 10_8$	1.54 ± 0.01	$1.23 \pm 0.01 \times 10^{14}$

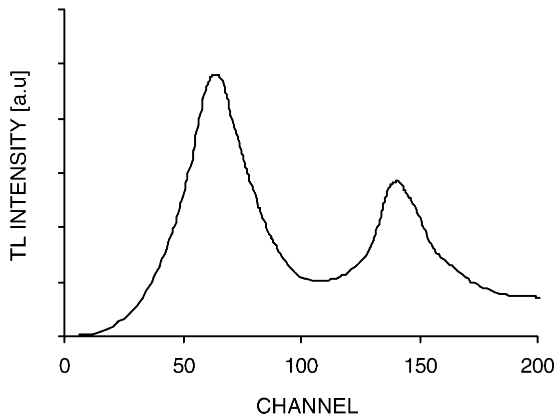

Fig. 2. Glow curve of ZrO_2:Tb thin films exposed to 260 nm UV light.

3. Results

Fig. 2 shows the glow curve of ZrO_2:Tb thin films exposed to 260 nm UV light. This glow curve exhibits two peaks, at 112°C and 220°C, respectively. The order of the kinetics obtained was second order for both peaks. The average E and s values obtained by applying these methods are shown in Table 1.

4. Conclusion

Analysis of experimental results for estimating the order of the kinetics involved, yields similar values applying both methods. Given the order of the kinetics, a good estimation of the activation energy and frequency factor can be made by using the Lushchik and/or the Chen method. It can be concluded that the kinetic parameters of ZrO_2:Tb determined applying these methods are in agreement within 30% of each other.

Acknowledgements

This work was supported under the CONACYT Project No. 400200-5-32564-E.

References

Azorín, J., 1986. Determination of thermoluminescence parameters from glow curves I. A Review. Int. J. Radiat. Instrum. Part. D. Nucl. Tracks 11 (3), 159–166.

Azorín, J., Rivera, T., Martínez, E., García, M., 1998. Thermoluminescence of Eu-doped ZrO_2 thin films exposed to ultraviolet and visible light. Radiat. Meas. 29, 315–317.

Azorín, J., Rivera, T., Falcony, C., Martínez, E., García, M., 1999. Ultraviolet thermoluminescent dosimetry using terbium-doped zirconium oxide thin films. Radiat. Prot. Dosim. 85, 317–319.

Chen, R., 1969a. On the calculation of activation energies and frequency factors from glow curves. J. Appl. Phys. 40, 570–585.

Chen, R., 1969b. Glow curves with general order kinetics. J. Electrochem. Soc. 166, 1254–1257.

Lushchik, C.B., 1956. The investigation of trapping centers in crystals by the method of thermal bleaching. Sov. Phys. JETF 3, 390–399.