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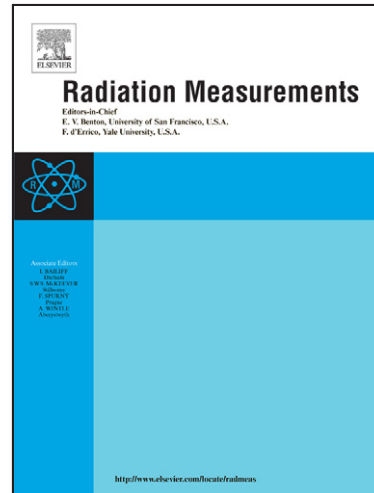
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A quantitative kinetic model for Al$_2$O$_3$:C: TL response to UV-illumination

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Abstract

This paper presents a quantitative kinetic model applicable to the important dosimetric material Al$_2$O$_3$:C. The model describes successfully the thermoluminescence (TL) response of the material to UV illumination (206 nm). The energy levels in this model consist of the main dosimetric trap, two competing deep hole and deep electron traps, and the luminescence center. The model also describes successfully the experimental variation of the optical absorption coefficient K with UV fluence. The values of the kinetic parameters are not arbitrary, but are obtained either from published experimental data, or by using reasonable physical assumptions. A correction factor is applied to the calculated UV-fluence to account for the fact that the samples used in the experiments were several optical lengths thick. By using this correction factor, the experimental data can be shown on the same graph as the calculated curves of TL vs. UV-fluence and K vs. UV-fluence, with the UV fluences given in photons/cm^2 and not in some arbitrary units.

1. Introduction/Scope

The study of the thermoluminescence (TL) response of Al$_2$O$_3$:C to ionizing radiation and to UV radiation is of great practical importance in dosimetric applications. There have been several previous attempts to produce theoretical models to describe various aspects of the TL response of this material to ionizing radiation (see for example Agersnap Larsen, 1999; Pagonis et al., 2006, 2007, and references therein).

Recently we have presented a quantitative model (Lawless et al., 2005; Chen et al., 2006; Pagonis et al., 2006, 2007) for the TL and OSL response of Al$_2$O$_3$:C to ionizing radiation. The model provided a mathematical description for several experimental results: the TL vs. beta dose behavior, the variation of the absorption coefficient K with the beta dose and the nonmonotonic behavior of TL and OSL at high doses.

Yukihara et al. (2003) carried out a comprehensive experimental study of the effect of deep traps on the thermoluminescence (TL) of Al$_2$O$_3$:C by using both beta irradiation and UV-illumination. The concentration of F and F$^+$-centers in the samples were monitored by optical absorption

measurements, and competing deep holes and deep electron traps were identified.

In this paper it is shown that the same model can also describe the corresponding experiments with UV-illumination instead of beta irradiation. The study of Yukihara et al. (2003) involved three samples from different batches labeled D320, Chip101 and B1040. Their data showed that the maximum height of the TL peak at 450 K increased monotonically as a function of the UV illumination period. The UV data showed no decrease of the TL signal at high UV-fluences, in contrast to the drop in the corresponding TL signal observed at high beta doses. The value of the TL signal reached a saturation value for samples D320 and Chip 101, while for sample B1040 the saturation point was not reached even at the highest value of the UV-fluence used in the experiments.

In a second series of experiments, these authors studied the variation of the absorption coefficient K of the samples with the UV illumination period. The value of K increased monotonically with the UV irradiation time, up to different saturation values for all 3 samples used. The authors noted that sensitization occurred after either beta or UV irradiation, and associated these sensitization phenomena with the filling of the

deep electron traps. On the other hand, the fact that UV illumination does not cause desensitization while beta irradiation does so, led the authors to associate desensitization with the filling of deep hole traps. Both sensitization and desensitization phenomena were found to be reversible by annealing to 800-875 K for the deep hole effects, and up to 1100-1200 K for the deep electron trap effects.

The purpose of this paper is to extend our previous modeling work to provide a mathematical description of the UV-illumination experiments of Yukihara et al. (2003). The results presented in this paper show that the same kinetic parameters can also describe the TL vs. UV-fluence, as well as the K vs. UV-fluence behavior.

Estimates of the values of the kinetic parameters in the model are obtained either from published experimental data, or by using reasonable physical assumptions (Chen et al., 2006 and Pagonis et al. 2006, 2007). A correction factor is applied to the calculated UV-fluences to account for the fact that the samples used in the experiments were four optical lengths thick. By using this correction factor, the experimental data can be shown on the same graph as the calculated curves, with the UV fluences in these graphs given in photons/cm^2 and not in some arbitrary units, as is commonly the practice in published kinetic models.

THE MODEL

Several previous studies of the UV-response of Al$_2$O$_3$:C showed that irradiation with UV (206 nm) excites electrons from the F-centers to the conduction band according to the process $F + h\nu\,(206\,nm) \rightarrow F^+ + e^-$ (Yukihara et al., 2003, and references therein). This process produces free electrons that can be captured by electron traps only, at the same time causing a conversion of the F centers into F$^+$ centers. The present kinetic model consists of the dosimetric trap, competing deep hole and deep electron traps, and of the luminescence center. The electron and hole transitions involved in the kinetic model and the detailed arguments leading to an estimate of the kinetic parameters were discussed in detail previously (Chen et al., 2006 and Pagonis et al. 2006, 2007). Since no free holes are created during the UV experiments we can set $dn_v/dt = n_v = 0$ and the set of simultaneous differential equations governing the UV- excitation and heating stages of the simulation becomes:

$$\frac{dm_1}{dt} = R\sigma(M_1 - m_1) - A_{m1}m_1 n_c, \quad (1)$$

$$\frac{dm_2}{dt} = -A_{m2}m_2 n_c, \quad (2)$$

$$\frac{dn_1}{dt} = -s_1 n_1 \exp(-E_1/kT) + A_{n1}(N_1 - n_1)n_c, \quad (3)$$

$$\frac{dn_2}{dt} = A_{n2}(N_2 - n_2)n_c, \quad (4)$$

$$\frac{dn_c}{dt} = \frac{dm_1}{dt} + \frac{dm_2}{dt} - \frac{dn_1}{dt} + \frac{dn_2}{dt}, \quad (5)$$

$$\frac{dn_v}{dt} = 0. \quad (6)$$

In equation (1) R represents the photon flux in photons per cm^2 per second (photons·cm^{-2}s^{-1}), and σ is the absorption cross-section in cm^2. The term $(M_1 - m_1)$ expresses the number of available F-centers (which the UV turns into F$^+$ centers), m_1

(cm^{-3}) is the instantaneous concentration of F$^+$ centers and M_1 (cm^{-3}) is the total concentration of these radiative hole centers in the material. The product $R\sigma(M_1 - m_1)$ represents the rate of creation of the F$^+$ luminescence centers in the material by UV-illumination. The units of the product $R\sigma(M_1 - m_1)$ in equation (1) are holes per cm^3 per sec, in agreement with the rest of the equations.

An estimate of the value of σ in equation (1) can be obtained from the experimental data of Yukihara et al. (2003) as follows. Their Figure 8 shows that the value of the F-center absorption coefficient for sample Chip101 is equal to 45 cm^{-1}. The samples used are 0.09 cm thick, which corresponds to four optical absorption lengths. This introduces a spatial non-uniformity in the UV-illumination of the samples, with the UV-fluence received by the front surface being much larger than the one received by the back-surface. By using the definition of the absorption cross-section $\sigma = K/M_1$ and the value of $M_1 = 10^{17}$ cm^{-3} given by Yukihara et al., we obtain an approximate value of $\sigma = (45\,cm^{-1})/(10^{17}\,cm^{-3}) \sim 4.5 \times 10^{-16}$ cm^2.

The rest of the parameters are as follows: M_2 (cm^{-3}) is the concentration of non-radiative hole centers with instantaneous occupancy of m_2 (cm^{-3}), N_1 (cm^{-3}) is the concentration of the electron dosimetric trapping state with instantaneous occupancy of n_1 (cm^{-3}), and N_2 (cm^{-3}) is the concentration of the deep electron trapping state with instantaneous occupancy of n_2 (cm^{-3}). n_c and n_v are the concentrations (cm^{-3}) of electrons and holes in the conduction and valence bands respectively. B_1 and B_2 (cm^{3}s^{-1}) are the trapping coefficients of free holes in centers 1 and 2 respectively. A_{m1} and A_{m2} (cm^{3}s^{-1}) are the recombination coefficients for free electrons with holes in centers 1 and 2 and A_{n1} (cm^{3}s^{-1}) is the retrapping coefficient of free electrons into the dosimetric trapping state N_1. A_{n2} (cm^{3}s^{-1}) is the retrapping coefficient of free electrons into the competing trapping state N_2.

The simulation contains the irradiation stage for time t_D, a relaxation time of 1 sec, and the heating stage with a constant linear heating rate $\beta = 1$ K·s^{-1}. If the time of excitation is t_D, then $D = R \cdot t_D$ represents the total UV-fluence in photons per cm^2. The photon flux in equation (1) is taken equal to some arbitrary value of $R = 1.1 \times 10^{16}$ (photons·cm^{2}s^{-1}) and the irradiation time t_D is varied from 0.005 sec to 1 sec in steps of 0.05 sec. This results in a range of calculated UV-fluences between 5.5×10^{13} and 1.1×10^{16} photons/cm^2.

The set of equations (1) through (6) are valid for both the irradiation and the heating stages of the simulation. During irradiation at room temperature sets the term $-s_1 n_1 \exp(-E_1/kT)$ is negligible. During the heating stage one sets $R = 0$ in equation (1).

The TL intensity I(T) is associated with the electron-hole recombination in the recombination center m_1, and is given by

$$I(T) = A_{m1}m_1 n_c \eta(T) \quad .(7)$$

The temperature-dependent factor $\eta(T)$ describes the thermal quenching of the TL intensity and is given by

$$\eta(T) = \frac{1}{1 + C_1 \exp(-W_1/kT)} \quad .(8)$$

The thermal quenching constants $W_1 = 1.1$ eV and $C_1 = 10^{11}$ are known from previous experimental studies of thermal

quenching effects in this material (see for example Agersnap Larsen, 1999, and references therein).

The values of the parameters in equations (1)-(6) are the same as used previously to simulate the TL and OSL response of the sample Chip101 to beta irradiation (Pagonis et al. 2007, their Table 1). These parameters are: $E_1=1.3$ eV; $s_1=10^{13}$ s^{-1}; $M_1=10^{17}$ cm^{-3}; $B_1=10^{-8}$ cm^3/s; $A_{m1}=4\times10^{-8}$ cm^3/s; $M_2=2.4\times10^{16}$ cm^{-3}; $B_2=4\times10^{-9}$ cm^3/s; $A_{m2}=5\times10^{-11}$ cm^3/s; $N_1=2\times10^{15}$ cm^{-3}; $A_{n1}=2\times10^{-8}$ cm^3/s; $N_2=2\times10^{15}$ cm^{-3}; $A_{n2}=2\times10^{-9}$ cm^3/s; $C_1=10^{11}$; $W_1=1.1$ eV; $m_{10}=9.4\times10^{15}$ cm^{-3}; $n_{10}=n_{20}=m_{20}=n_{c0}=n_{v0}=0$.
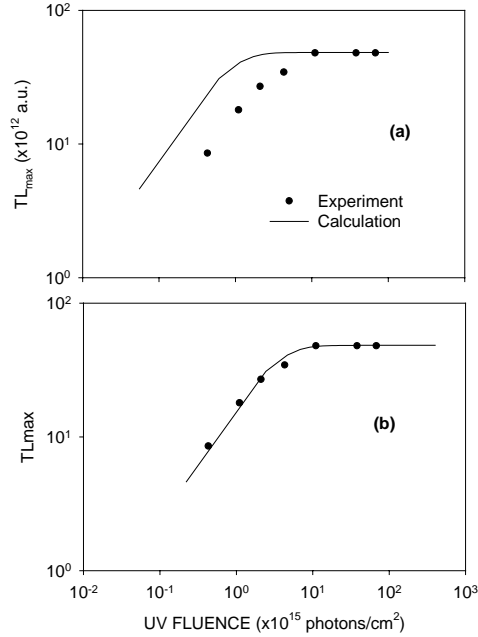

Fig 1. (a) The solid points are the experimental data of TL vs. UV-fluence for sample Chip101 by Yukihara et al. (2003). The solid curve indicates the calculated values using the kinetic parameters in the text. (b) The same data as in (a), with the x-axis for the experimental data divided by a correction factor of 0.243, to account for the thickness of the sample.

Numerical Results

Figures 1 and 2 show the results of running the simulation with the parameters given in the previous section. The solid lines in Figures 1a and 1b show the calculated dependence of the TL signal on the UV-fluence. The TL signal is defined here and in the Yukihara et al. (2003) paper as the maximum TL intensity. The experimental data of Yukihara et al. (2003) are also shown in Figures 1a and 1b as solid circles. The y-axis of the experimental data has been multiplied by a scaling factor for comparison purposes, while no scaling has been applied to the dose axis in Figure 1a. Figure 1b shows the same calculations as Figure 1a, with the x-axis for the experimental data divided by the correction factor of 0.243, which is derived in the next paragraph. The corrected data in Figures 1b show close agreement between theory and experiment.

The value of the correction factor used in Figures 1 and 2 was estimated as follows. The samples are four optical lengths thick (L=0.09 cm and K=45 cm^{-1}). If F_o represents the nominal UV fluence incident on the sample during the experiment and F_{eff} represents the reduced effective UV fluence due to the four optical lengths of the sample, these two quantities must be related by:

$$F_{obs} = F_o \frac{\int_{x=0}^{x=L} e^{-Kx} dx}{L} = F_o \frac{e^{-Kx}}{-KL}\Big|_0^L$$

$$= F_o \frac{e^{-KL}-1}{-KL} = F_o \frac{e^{-(45)(0.09)}-1}{-(45)(0.09)} = 0.243 F_o \quad (9)$$

Equation (9) gives the correction factor of 0.243 by which the nominal UV-fluences must be divided in order to account for the thickness of the samples, in agreement with the results shown in Figures 1 and 2.

Figure 2 shows the variation of the concentration of holes in the luminescence center (m_1) as a function of the UV-fluence for sample Chip101. The value of m_1 is proportional to the absorption coefficient K of the material, and can be directly compared with the experimental data given in Figure 9a of Yukihara et al. (2003). The experimental data are also shown as solid circles in Figure 2. The x-axis of the calculated UV-fluence in Figure 2 has also been corrected using the same correction factor of 0.243. The agreement between theory and experiment is seen to be reasonably good, especially considering that only 7 experimental data points are available over more than 2 orders of magnitude of the UV fluence.

Figure 3 shows the detailed behavior of the concentrations of holes and electrons in the model at the end of the relaxation period for sample Chip101. The calculations in Figure 3 show that the dosimetric peak (n_1) reaches saturation at a UV-fluence of $\sim2\times10^{15}$ photons·cm^{-2}, while the competitor deep electron trap (n_2) continues to rise with UV-fluence. The F$^+$ center concentration (which is proportional to m_1) rises continuously for all fluences shown in Figure 4, while the deep hole traps (m_2) and the valence band do not participate in the UV-illumination process ($m_2=n_v=0$). The maximum of the TL peak (TL$_{max}$) rises to saturation at about the same UV-fluence as the dosimetric trap n_1.

It must also be noted that the simulated TL glow curves have the expected shape for first order kinetics, but they do not have the experimentally observed glow curve widths. The simulation shows an almost constant peak width of ~34 K, while the experimental data of Yukihara et al. (2003) show a widening of the TL glow curve with increasing UV-fluence. Another point of disagreement between theory and experiment is the predicted temperature of the maximum of the TL intensity (T$_{max}$). While theory predicts a constant T$_{max}\sim453$ K at all UV-fluences, the experiment shows a systematic shift of the T$_{max}$ with the UV-fluence, towards higher values of T$_{max}$. This disagreement between the experimental and the calculated TL glow curves was also observed during the previous simulation of the TL dose response graphs for this sample (Pagonis et al., 2007).

This discrepancy is easy to understand because previous experimental studies have shown that the dosimetric peak at 450 K has a composite structure. This structure has been interpreted as either involving two components corresponding to the release of both electrons and holes from the traps, or as a series of overlapping first order TL peaks (Agersnap Larsen et al., 1999; Colyott et al., 1996; Whitley and McKeever, 2000). This is obviously a feature not included in the current simplified model.

Discussion and Conclusions

The model presented in this paper was used previously to provide a mathematical description of the following

experiments: TL vs. beta dose behavior, variation of the absorption coefficient K with the beta dose and nonmonotonic behavior of TL and OSL at high doses. This paper showed that the same set of kinetic parameters in the model can also describe the experimental TL vs. UV-fluence behavior of Al_2O_3:C, as well as the closely related variation of the optical absorption coefficient K with UV-fluence. The values of the kinetic parameters in this model are based on reasonable physical assumptions and on available experimental data. A correction factor was applied to the calculated UV-fluences to account for the fact that the samples are 4 optical lengths thick. The experimental data are shown on the same graph as the calculated curves, with the UV-fluences given in photons/cm^2 and not in some arbitrary units, as is often the practice in TL kinetic models.

A more comprehensive model for this material must include: (a) the known shallow TL traps in this material, (b) thermal dissociation effects for the deep hole traps and deep electron traps at appropriate temperatures, and (c) localized transitions between F and F^+-centers and (d) the effect of finite thickness of the sample, especially at large doses.
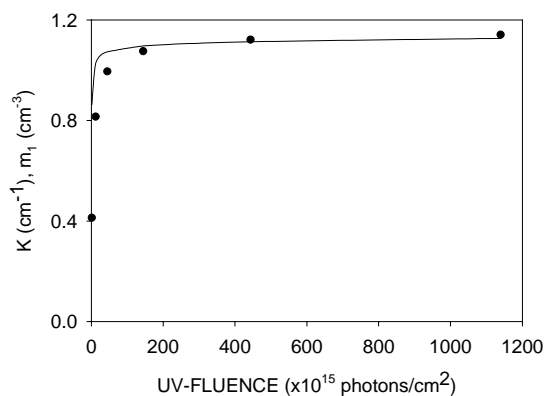

Fig 2. The solid points represent the experimental data of absorption coefficient K vs. UV-fluence for sample Chip101 by Yukihara et al. (2003). The solid curve indicates the calculated values using the kinetic parameters in the text. The x-axis for the experimental data has been divided by a correction factor derived in the text, to account for the finite thickness of the sample.
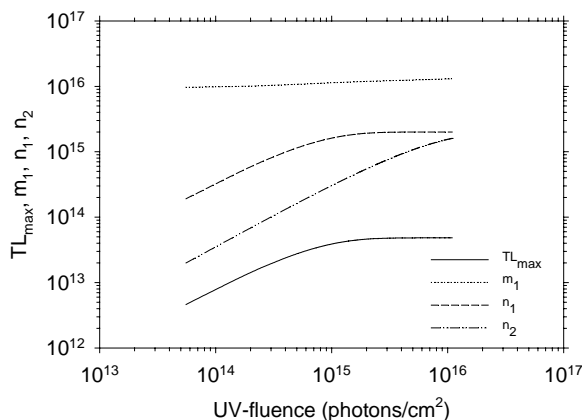

Fig 3. The electron and hole concentrations calculated from the model as a function of the UV-fluence, for sample Chip101.

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