

Real-Time *in-situ* Monitoring of Optical Absorption Changes in Visible-Light-Active TiO₂ under Light Irradiation and Temperature-Programmed Annealing

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Supplementary Information

Chen's half-width method¹ for calculating activation energies, E_a , and pre-exponential (frequency) factors, ν , from thermoluminescence peak uses the maximum temperature, T_m , and the total half width $\omega = T_2 - T_1$, where T_1 and T_2 are the half-intensity temperatures on the low- and high-temperature side of the peak, respectively.

For the first-order peak with a pre-exponential factor independent of temperature, the activation energy is given by

$$E_a = 2 \kappa T_m (1.26 T_m / \omega - 1)$$

where κ is Boltzmann's constant. The pre-exponential factor is found for this case to be given by

$$\nu = [\beta (1.26 T_m / \omega - 1) / (3.7 T_m)] \exp (2.52 T_m / \omega)$$

where β is the heating rate. For the peak at 468 K in Figure 4b T_m , T_1 , T_2 and ω are equal to 467, 437.4, 492.6 and 55.2, respectively, For the peak in Figure 5b T_m , T_1 , T_2 and ω are equal to 469, 440.8, 495 and 54.2. Calculated values $E_a = 0.80$ and 0.78 eV and $\nu = 0.84 \times 10^7$ and 0.50×10^7 s⁻¹ agree very well with those obtained by analysis of the low-temperature side of the peaks and the numerical simulation of the peak's shape.

Solution of the system of differential eqns 3–9 gives the dependences on time for concentrations of h -traps, $p_1(t) - p_3(t)$, concentration of holes in the VB, $p_{VB}(t)$, and concentrations of e -traps, $n_1(t) - n_3(t)$. These dependences obtained for heating at a constant rate after irradiation and minor dark pause

are plotted *versus* T in Figures S1 and S2. Figure S3 displays the sum of three dependences $n_i(t)$ (curve 2) and the derivative of this sum (curve 2a). The latter is the temperature dependence of the rate of disappearance of e -traps, i.e. the TPAA spectrum. Note that the shape of the TPAA spectrum is determined by the shape of the hole detrapping spectrum (curve 1a in Figure 3).

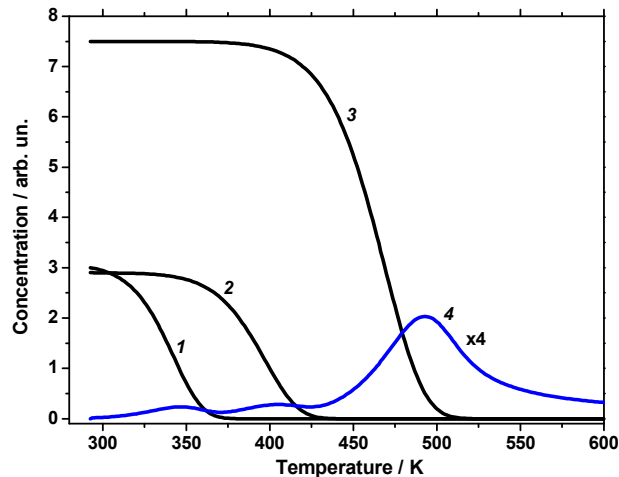


Figure S1. Change in the concentration of the three h -traps p_1 (curve 1), p_2 (curve 2) and p_3 (curve 3), and the concentration of holes in the valence band (VB), p_{VB} , (curve 4) during heating at a constant rate of 0.5 K s^{-1} .

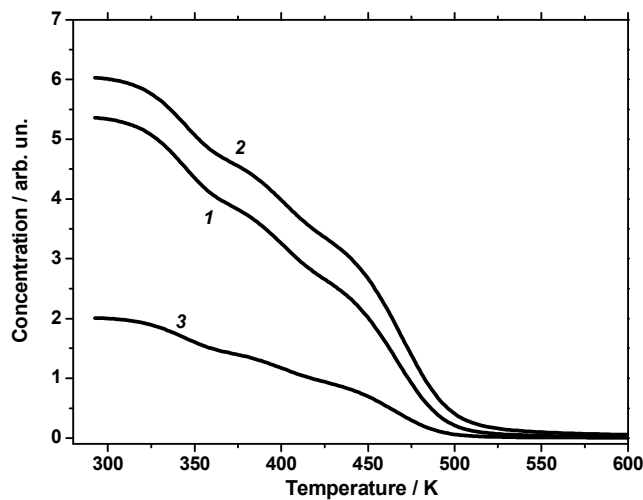


Figure S2. Decrease of the concentration of three e -traps n_1 (curve 1), n_2 (curve 2) and n_3 (curve 3) during heating at a constant rate of 0.5 K s^{-1} .

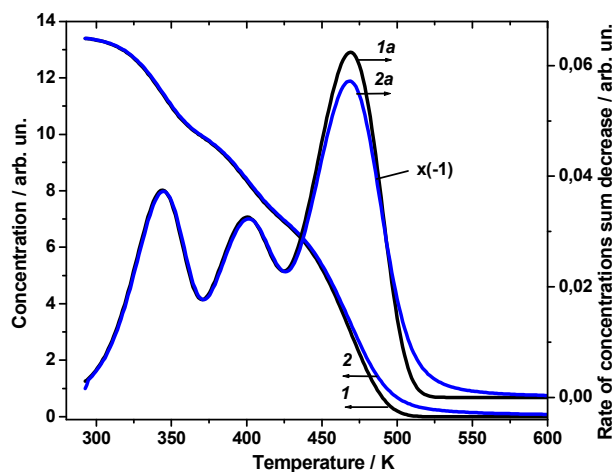


Figure S3. Decrease of the sum of concentrations (curves **1** and **2**) and the rate of decrease (curves **1a** and **2a**) of *h*-traps (curves **1**, **1a**) and *e*-traps (curves **2**, **2a**) during heating at a constant rate of 0.5 K s^{-1} . Curve **2a** exhibits the model TPAA spectrum.

Reference

(1) Chen, R. On the Calculation of Activation Energies and Frequency Factors from Glow Curves. *J. Appl. Phys.* **1969**, *40*, 570–585.