

Study of photoinduced absorption by the method of modified laser photothermal radiometry

L.A. Skvortsov, E.M. Maksimov, A.A. Tuchkov

Abstract. The application of the method of modified laser photothermal radiometry for studying the photoinduced absorption in thin films is considered. The sensitivity of the method is estimated. The mechanism of induced near-IR absorption in titanium dioxide films is proposed and the nature of surface defects responsible for this process is explained. It is shown that kinetic equations describing monomolecular recombination are consistent with the experimental dependences for the thermal activation energy of defects equal to 0.17 ± 0.04 eV.

Keywords: photothermal radiometry, photoinduced absorption, photochromic effect, titanium dioxide.

1. Introduction

The spectral dependence of photoinduced absorption gives important information about defects of a material structure, which determine significantly its properties. Methods based on the photothermal effect developed recently are used for measuring photoinduced absorption in surface layers of materials and thin-film structures. They involve the modified method of photothermal radiometry [1, 2], deflection [3] and photoacoustic [4, 5] methods.

The aim of this paper is to demonstrate the possibilities of the modified method of photothermal radiometry for studying the photoinduced absorption in thin layers of a material and to estimate its sensitivity. In addition, an attempt was made to construct a model describing the experimental results for thin titanium dioxide films in the near-IR spectral region.

The basis of the employed method is the method of laser photothermal radiometry (PTR) [6–9]. The important difference of the PTR method from the method of passive radiometry is that this method detects the temperature derivative of the thermal radiation flux rather than the flux itself. Samples are irradiated by a train of laser pulses. Due to the partial absorption of laser radiation followed by the heat release, the surface temperature and detected

thermal signal are modulated at the laser pulse repetition rate. In this case, the detected thermal radiation signal depends on the quasi-periodic temperature fluctuation, which is linearly related to the absorption. Having a high sensitivity, the PTR method is used to measure weak absorptions both in the bulk of the materials and in thin films and surface layers of substances [8–10].

As a rule, the induced absorption is related to the population of acceptor levels (traps) by electrons excited by light to the conduction band from deep donor levels or from the valence band. Taking this into account, the PTR method was modified to measure the induced absorption in the following way [1, 2]. The sample under study was simultaneously irradiated by two radiation fluxes. One of them, short-wavelength radiation (pump wave) with the wavelength falling into the absorption band of the sample produces electron–hole pairs inside the sample and on its surface. The free electrons produced in the conduction band can be captured by traps before recombining. The other, long-wavelength radiation (probe wave) with the photon energy smaller than the energy gap leads to the depletion of the traps and heat release during the relaxation of electrons in the conduction band followed by their recombination. Thus, by measuring the variable component of the thermal flux at the pulse repetition rate of the long-wavelength radiation, one can determine induced absorption at this wavelength.

2. Experimental

We studied single-layer titanium dioxide coatings with a fine-crystalline structure, which were deposited on a fused quartz substrate by the method of electron-beam evaporation. The initial material for preparing films was TiO₂ pellets. The ~100-nm-thick films were deposited at the partial oxygen pressure $p_{O_2} = 1.1 \times 10^{-4}$ Torr at a rate of 0.45 nm s⁻¹. The substrate temperature was 200 °C.

Figure 1 presents the scheme of measurements by the modified PTR method. Probing was performed with a cw 1064-nm Nd³⁺:YAG laser with the average output power $P_{pr} = 20$ W, which was constant during the measurements. Repetitively pulsed IR laser radiation was obtained with the help of an acousto-optic modulator, which provided the pulse repetition rate from 1 Hz to 100 kHz. The acousto-optic modulator allows the use, along with an inertial detector of the thermal radiation, of fast and highly-sensitive devices based on InSb and HgCdTe compounds.

The sample was simultaneously irradiated by short-wavelength pulses from a 337-nm nitrogen laser (pump

L.A. Skvortsov, E.M. Maksimov, A.A. Tuchkov Institute of Cryptography, Communications and Informatics, Michurinsky prosp. 70, 117602 Moscow, Russia; e-mail: laserpolus@stream.ru

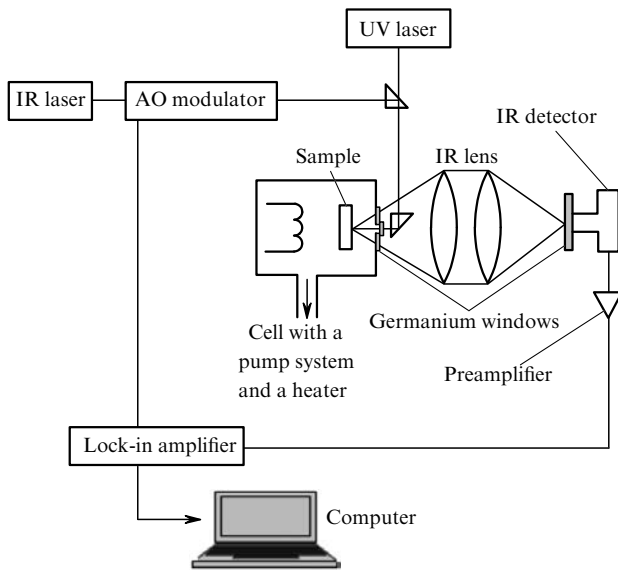


Figure 1. Scheme of the experimental setup.

wave) operating at a pulse repetition of 100 Hz. The maximum average power P_p and the laser pulse duration τ_p were 3 mW and 10^{-8} s, respectively. The average power of the nitrogen laser was varied by means of UV filters from a standard set of optical glasses. Radiation from both lasers was focused into a spot of diameter 1 mm on the sample. Measurements were performed both in air and vacuum. The samples were placed in a cell equipped with a heater and a germanium window with a small aperture at the centre to couple out thermal radiation. To transmit laser radiation into the cell, the aperture was sealed with a thin quartz plate. The cell was evacuated with a vacuum (zeolite) pump, which provided the oil-free evacuation down to the residual pressure of $\sim 10^{-2}$ Torr. The sample temperature was controlled with a chromel–alumel thermocouple. The heater provided the change in the substrate temperature within $\sim 290 - 500$ K by maintaining the specified value in this range with an accuracy of $\pm 1^\circ\text{C}$.

The variable component of the thermal flux was measured with a lithium tantalate photodetector. This provided the non-selectivity to the wavelengths of the detected signal and response only to variations in the surface temperature. The lower boundary of the spectral pass band of the photodetector was $\sim 2 \mu\text{m}$ and was determined by the material of the IR lens made of germanium. The threshold sensitivity Φ_{th} of the pyroelectric detector with the active region area $S_d \sim 1 \text{ mm}^2$ in the unit electric frequency band $\Delta\gamma = 1 \text{ Hz}$ for the modulation frequency of the detected signal $f = 20 \text{ Hz}$ did not exceed $1.4 \times 10^{-9} \text{ W}$. The output signal from the photodetector after a preamplifier was fed to the input of the UPI-2M pulse amplifier–converter with the time constant set equal to 1 s. The minimal absorption measured under these conditions in titanium dioxide thin films was $\sim 0.01\%$ [9]. Figure 2 presents the typical oscillogram of thermal radiation pulses obtained by using a highly sensitive cooled IR HgCdTe detector. The same figure shows the calculated dependence of the excess sample temperature $\Delta T(t)$ in the established irradiation regime.

Comparative measurements were also performed by using cw UV radiation emitted by a high-pressure DRS-250 mercury lamp. A UV filter separated emission

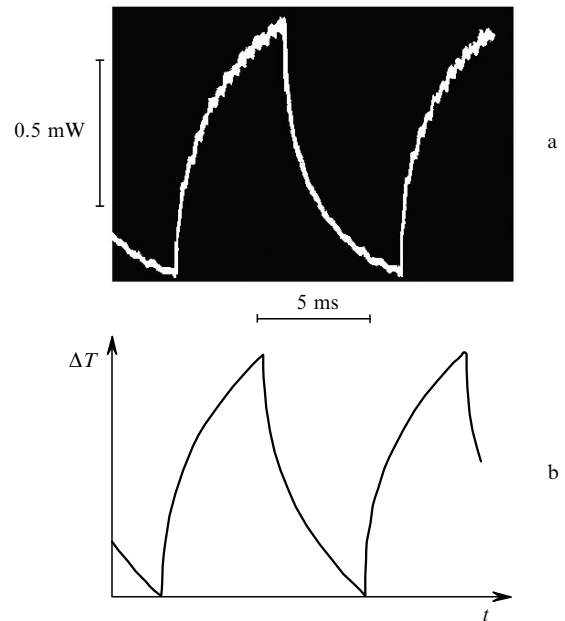


Figure 2. Oscillogram of thermal radiation pulses (HgCdTe photodetector) (a) and calculated dependence of the surface temperature change $\Delta T(t)$ in the established regime (b).

in the range from 320 to 390 nm (the most intense line at 365 nm). All the main experiments were performed by using the nitrogen laser.

It was found during the experiments that simultaneous irradiation of the sample by short-wavelength and probe radiations leads to a considerable increase in the near-IR absorption, i.e. to the appearance of photoinduced absorption at $\lambda_{pr} = 1064 \text{ nm}$. At the same time, when the sample was irradiated only by short-wavelength pulses in the selected intensity range, the signal was not observed. The measured value of the ‘dark’ absorption A at $\lambda_{pr} = 1064 \text{ nm}$ was 0.03%. The increase in the sample surface temperature ΔT did not exceed 1.5°C in this case [11].

Note the main features of the photoinduced near-IR absorption for the objects under study. First, the appearance of photoinduced absorption has a reversible nature. After switching off the UV pump beam, the near-IR absorption relaxes to its initial ‘dark’ value (Fig. 3). Note that in vacuum the characteristic relaxation time is approximately five times longer than in air. The relaxation time is taken as the time during which the induced

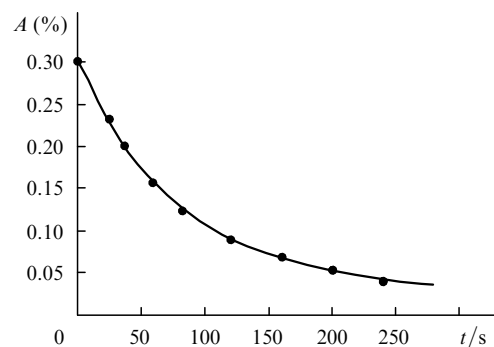


Figure 3. Time dependence of the photoinduced absorption after switching off pump radiation.

absorption decreased by a factor of e compared to its value right after switching off UV radiation. Second, photoinduced absorption depends on the short-wavelength radiation intensity and the ambient pressure (Fig. 4). In vacuum this absorption is significantly higher than that in air. In this case, an almost linear dependence of the absorption on the average UV radiation power density was observed. Finally, the temperature dependence of induced absorption (Fig. 5) is of special interest. One can see from Fig. 5 that when the sample is heated to $\sim 150^\circ\text{C}$, it decreases to the 'dark' value, which does not change in the entire temperature interval.

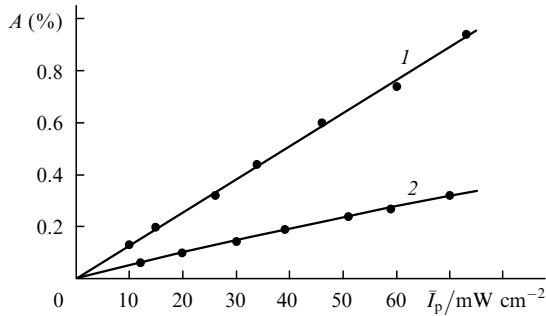


Figure 4. Dependences of the induced absorption on the average power density \bar{I}_p of the short-wavelength radiation in vacuum (1) and in air (2).

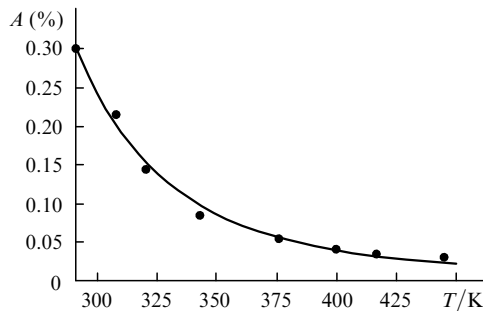


Figure 5. Temperature dependence of the induced absorption.

3. Estimate of the method sensitivity

We will estimate the possibilities of the method for titanium dioxide, the interest to which has been recently aroused due to its high photocatalytic activity [12–17]. In the stationary case, the minimal concentration N_{\min} of defects detectable by this method can be estimated from the expression

$$N_{\min} \leq A_{\min} \gamma \frac{\alpha_p}{\sigma_{pr}},$$

where A_{\min} are the minimum absorption losses detected by the PTR method; α_p is the absorption coefficient of the material at the pump radiation wavelength; σ_{pr} is the absorption cross section from the ground state of the defect to the conduction band of the material at the probe wavelength; $\gamma = N/(n + N)$ is the coefficient taking into account the degree of population of electron traps; n is the concentration of free charge carriers in the conduction band; N is the concentration of populated electron traps.

We will consider the moderate photoexcitation regime of a semiconductor, when $N \geq n$, i.e. $\gamma \sim 1$. The PTR method allows the measurement of absorption losses in thin films and on the surface layers of materials $A_{\min} \approx 10^{-6}$ [9]. Based on the measured absorption coefficient ($\sim 10 \text{ cm}^{-1}$) in films and typical concentration $N \sim 10^{18} \text{ cm}^{-3}$ of their structural defects [12], we will assume that the absorption cross section of the defect in the near-IR region is $\sigma_{pr} \approx 10^{-17} \text{ cm}^2$. Taking into account that $\alpha_p \approx 10^5 - 10^6 \text{ cm}^{-1}$, we will obtain the estimate $N_{\min} \leq 10^{15} \text{ cm}^{-3}$ for the minimal concentration of defects.

In turn, the power density of the pump wave required to populate electron traps through the conduction band can be estimated from the expression

$$I_p = \frac{E_{\min}}{\tau_p S} \geq N_{\min} L \frac{h\nu_p}{\tau},$$

where E_{\min} is the pump radiation energy; S is the sample area exposed to short-wavelength radiation; $L = (D\tau)^{1/2}$ is the diffusion length of electrons in the conduction band; D and τ are the diffusion coefficients and lifetime of electrons in this band, respectively.

Setting the radiation quantum energy of the pump wave equal to $h\nu_p = 6 \times 10^{-19} \text{ J}$ ($\lambda_p = 337 \text{ nm}$), $D \approx 0.01 \text{ cm}^2 \text{ s}^{-1}$ [13] and $\tau \approx 10^{-9} \text{ s}$ [14, 15], we estimate the required power density in the short-wavelength radiation pulse as $I_p \geq 10 \text{ W cm}^{-2}$. Note that during the lifetime in the conduction band, an electron shifts by the distance $L \approx 10^{-5} \text{ cm} = 100 \text{ nm} \sim l_x = \alpha_p^{-1}$ (l_x is the penetration depth of the pump-wave radiation).

4. Model of the near-IR induced absorption in titanium dioxide films.

Discussion of experimental results

The structure of thin-film titanium dioxide coatings is characterised by a high concentration of intrinsic defects caused by the nonstoichiometric composition. The most important of them are oxygen vacancies (Ti^{3+} ions) and defects located in interstitial sites ($\text{Ti}_{\text{irreg}}^{4+}$), which are treated as electron traps [12, 15–20]. It is also known that the most important adsorbents for the titanium dioxide are water molecules, oxygen and hydroxyl groups bound with titanium ions [15–20]. Among a variety of processes proceeding inside titanium dioxide and on its surface irradiated by light at the wavelength falling into the fundamental absorption band, in our opinion, the primary processes concerning the problem under study can be represented by the reaction [15–17]:

generation of electron–hole pairs



capture of charge carriers

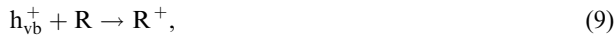


recombination of charge carriers





interphase charge transfer



where e_{cb}^- is an electron in the conduction band; e_t^- is an electron captured by a trap; h_{vb}^+ is a positively charged hole in the valence band; h_t^+ is a hole captured by the trap; T_{e^-} is an empty electron trap; T_{h^+} is an empty centre of hole trapping; R is the electron donor (deoxidiser); and O is the electron acceptor (oxidiser).

According to the experimental results and primary processes presented above, the mechanism of the near-IR photoinduced absorption, in particular at $\lambda_{pr} = 1064$ nm, can be described as follows. During the lifetime in the conduction band ($\tau \approx 10^{-9}$ s), an electron shifts by the distance $L \approx 100$ nm $\sim l_x$ and achieves the film surface, where it experiences trapping, recombination and participates in the interphase transfer. It is assumed at present that the trapped electron is localised on the surface Ti^{3+} ions [process (2)], whereas holes are trapped by hydroxyl groups adsorbed on the surface [process (3)] [12, 14–17]. The depth of energy levels related to the Ti^{3+} ions lies, according to different authors, in the region from 60–100 meV [17, 18, 21] to 400–600 meV [18, 19]. The increase in the induced absorption with increasing the average radiation power density is caused by processes (1) and (2) because the number of generated surface absorption centres is directly related to the production rate of electron–hole pairs.

The photoinduced absorption in vacuum, which is larger than that in air (Fig. 3), is probably related to a decrease in the amount of adsorbed oxygen. This reduces the efficiency of process (7). As a result, the quantum yield of process (2) increases. In turn the slow relaxation of absorption can be caused by the attachment of an electron in the conduction band or localised in the trap to the acceptor molecule of the same oxygen interacting with the titanium dioxide surface [processes (7), (8)]. In this case, the relaxation of photoinduced absorption in vacuum should proceed for longer time, which is observed in the experiment. Recall that the main channel of trapping positively charged holes by hydroxyl groups adsorbed on the titanium dioxide surface is represented by process (3). If it is the case, the elimination of this channel should lead to an increase in the intensity of processes (4) and (6), i.e. to the depletion of electron traps and decrease in the concentration of current carriers in the conduction band. Accordingly, the induced absorption should also decrease.

To verify this assumption, we studied samples subjected to special thermal treatment. By heating coatings up to 400 °C and then cooling them down to room temperature in dehydrated atmosphere, it is possible to obtain samples with a hydrophobic surface on which hydroxyl groups are

absent [22]. These samples do not have photoinduced absorption in the near-IR region. At the same time, ‘dark’ absorption at $\lambda_{pr} = 1064$ nm remains virtually invariable. This is also confirmed by the results of paper [23], where it was shown that photoconduction of the titanium dioxide surface considerably decreased when hydroxyl groups were removed.

Note that the UV pulse duration ($\tau_p = 10$ ns) is much longer than the time of trapping electrons from the conduction band ($\tau_{tr} \leq 0.1$ ns) and exceeds the recombination time of photoexcited carriers both in the bulk and on the surface ($\tau_{rec} \sim 1$ ns) [14]. This suggests that the generation of surface defects was established within the laser pulse. The pump pulse repetition rate is comparable with the characteristic duration time of process (8) [15], which causes the dependence of the photoinduced absorption on the average radiation power during the interaction times under study. This explains the satisfactory coincidence of the results (within $\sim 20\%$) obtained during the cw irradiation of the sample by the mercury lamp and during the irradiation by laser pulses with the same average power density.

An almost linear dependence of the photoinduced absorption on the average pump power (Fig. 4) suggests that the moderate irradiation regime was obtained at which $n_0 \leq N_0$ (n_0 and N_0 are initial concentrations of free carriers and electron trapping centres). Indeed, knowing the pump wave intensity, the pump photon energy, the laser beam diameter, and the absorption and reflection coefficients for UV radiation, we can estimate the initial charge density n_0 in the conduction band, which varied from 10^{17} cm $^{-3}$ ($I_p = 3 \times 10^3$ W cm $^{-2}$) to 10^{18} cm $^{-3}$ ($I_p = 3 \times 10^4$ W cm $^{-2}$). It was assumed in this case that the generation of long-lived electrons by UV radiation [process (2)] is characterised by the quantum yield, which does not exceed $\sim 1\%$ [24].

In turn, the moderate photoexcitation level of samples under study and the exponential drop in the induced absorption allows the application of the monomolecular recombination model to describe the process under study. In this case, kinetic equations taking into account the presence of one trapping centre can be written in the form:

$$\frac{dn}{dt} = k_1 I_p + k_2 N I_p + k_3 N I_{pr} - r_1 n - r_2 n + r_3 N, \quad (11)$$

$$\frac{dN}{dt} = r_2 n - r_3 N - k_2 N I_p - k_3 N I_{pr}, \quad (12)$$

where I_{pr} is the probe wave intensity; k_1 is the probability of the electron appearance in the conduction band due to absorption of a pump-wave photon; k_2 and k_3 are the cross sections for the defect photoionisation at pump and probe wavelengths; r_1 is the probability of the direct electron–hole recombination; r_2 is the probability of trapping an electron; $r_3 = C \exp[-\Delta/(kT)]$ is the probability of the thermal ionisation of a defect; Δ is the energy of the defect thermal activation; k is the Boltzmann constant.

In the stationary state of the system, $dn/dt = 0$ and $dN/dt = 0$. Then, for the induced absorption we have

$$A_{ind} = \sigma_{pr} N_0 l = \frac{r_2 k_1 \sigma_{pr} I_p l}{r_1 k_1 I_p + r_1 k_3 I_{pr} + r_3 (r_1 + r_2)}, \quad (13)$$

where l is the optical coating thickness.

Taking into account the experimental temperature dependence of the induced absorption presented in Fig. 5, expression (13) allows the selection of the approximating function (solid curve in Fig. 5). In this case, the best coincidence is achieved for the activation energy of the trapping centre $\Delta = 0.17 \pm 0.04$ eV.

Of special interest is the study of the photoinduced absorption relaxation after switching off the pump radiation, i.e. for $I_p = 0$. In this case, the system of equations (11) and (12) allows one to find, in the general form, the time dependence of the concentration of populated traps $N(t)$ from the differential equation

$$\frac{d^2N}{dt^2} + (r_1 + r_2 + r_3 + k_3 I_{pr}) \frac{dN}{dt} + (r_1 r_3 + r_2 r_3 + r_1 k_3 I_{pr}) N = 0, \quad (14)$$

whose solution has the form

$$N(t) = C_1 \exp(\lambda_1 t) + C_2 \exp(\lambda_2 t), \quad (15)$$

where λ_1 and λ_2 are the roots of the corresponding characteristic equation.

By setting $N(0) = N_0$ and $n(0) = 0$ or, in other words, $n \ll N$, which is valid for the moderate irradiation regime, we finally obtain

$$N(t) = \frac{N_0}{2} \left\{ \left(\frac{r_3 + k_3 I_{pr} + s_2 - s_1}{s_2} \right) \exp[-(s_1 + s_2)t] + \left(\frac{r_3 + k_3 I_{pr} - s_1 - s_2}{s_2} \right) \exp[-(s_1 - s_2)t] \right\}, \quad (16)$$

where

$$s_1 = \frac{r_1 + r_2 + r_3 + k_3 I_{pr}}{2};$$

$$s_2 = \frac{1}{2} (r_1^2 + r_2^2 + r_3^2 + 2r_1 r_3 - 2r_1 r_2 - 2r_2 r_3 + 2r_2 k_3 I_{pr} + 2r_3 k_3 I_{pr} - 2r_1 k_3 I_{pr} + k_3^2 I_{pr}^2)^{1/2}.$$

Based on the type of the obtained dependence $N(t)$, we can assume that there exist 'fast' and 'slow' segments of the decay curve. The fast decay, obviously, takes place at the initial stage due to the recombination processes, when the number of free charge carriers substantially exceeds the number of carriers trapped by surface defects. At the same time, the observed slow decay depends on the environment and is most likely related to the adsorption of oxygen molecules, which is accompanied by the depletion of electron traps [process (8)]. Figure 3 shows the experimental time dependence of the induced absorption after switching off the pump radiation. The same figure presents the approximating dependence obtained by fitting the parameters entering expression (16). One can see that the experimental results are in satisfactorily agreement with

the conclusions of the model under study. Note also that the results of paper [4] confirm our mechanism of the photoinduced absorption in titanium dioxide films based on the first-order kinetics of the electron–hole recombination.

5. Conclusions

The modified method of laser photothermal radiometry can be used for studying surface layers of dielectrics and semiconductors, including thin-film coatings. The method has a high sensitivity and, when properly calibrated, allows one to determine the concentration of surface defects much faster than the existing methods, which is very important for studying the photocatalysis and its applications [5]. The possible mechanism of the photoinduced near-IR absorption (1064 nm) in polycrystalline titanium dioxide films has been proposed. The key role of the surface levels related to the Ti^{3+} ions has been pointed out. The model of the process based on the monomolecular recombination approximation is in good agreement with the experimental data. In particular, it follows from this model that the thermal activation energy of such defects is $\Delta = 0.17 \pm 0.04$ eV and the photoinduced absorption decay curved consists of the 'fast' and 'slow' regions with different lifetimes of the charge carriers. The described modified method of the laser photometry has, in our opinion, a number of important advantages compared to the photoacoustic method such as the absence of an acoustically sealed cell, the higher sensitivity and faster response in contactless measurements [11, 25].

References

1. Sidoryuk O.E., Skvortsov L.A. *Zh. Prikl. Spektrosk.*, **53** (4), 641 (1990).
2. Sidoryuk O.E., Skvortsov L.A. *Poverkhost'*, No. 11, 91 (1996).
3. Chen Y.F., Dai Y.T., Choy H.P., Chang I.M. *Chin. J. Phys.*, **31** (6), 767 (1993).
4. Highfield J.G., Grätzel M. *J. Phys. Chem.*, **92**, 464 (1988).
5. Murakami N., Omar O., Mahaney P., Torimoto T., Ohtani B. *Chem. Phys. Lett.*, **426** (1-3), 204 (2006).
6. Nordal P.E., Kanstad S.O. *Phys. Scr.*, **20**, 659 (1979).
7. Zverev G.M., Skvortsov L.A. *Izv. Acad. Nauk SSSR. Ser. Fiz.*, **45**, 644 (1981).
8. Santos R., Miranda L.C.M. *J. Appl. Phys.*, **52**, 4194 (1981).
9. Lopatkin V.N., Sidoryuk O.E., Skvortsov L.A. *Kvantovaya Elektron.*, **12**, 339 (1985) [*Sov. J. Quantum Electron.*, **15**, 216 (1985)].
10. Kolodnyi G.Ya., Levchuk E.A., Novopashin V.A., Mosievsky V.A., Poletaev V.N., Skvortsov L.A. *Elektron. Tekhn. Ser. 6. Mater.*, No. 4, 100 (1988).
11. Skvortsov L.A., Kirillov V.M. *Kvantovaya Elektron.*, **33**, 1113 (2003) [*Quantum Electron.*, **33**, 1113 (2003)].
12. Emeline A., Salinaro A., Ryabchuk V., Serpone N. *Int. J. Photoenergy*, **3**, 1 (2001).
13. Kavan L., Grätzel M., Gilbert S., Klemenz C., Scheel H. *J. Am. Chem. Soc.*, **118**, 6716 (1996).
14. Kapinus E., Khalyavka T., Shimanovskaya V., Viktorova T., Strelko V. *Int. J. Photoenergy*, **5**, 159 (2003).
15. Hoffmann M., Martin S., Choi W., Bahnemann D. *Chem. Rev.*, **95**, 69 (1995).
16. Martin S., Herrmann H., Hoffmann M. *J. Chem. Faraday Trans.*, **90** (21), 3323 (1994).
17. Martin S., Herrmann H., Choi W., Hoffmann M. *J. Chem. Faraday Trans.*, **90** (21), 3315 (1994).
18. Shkrob I., Sauer M.C. Jr. *J. Phys. Chem. B*, **4**, 1 (2004).
19. Szczepankiewicz S., Colussi A., Hoffmann M. *J. Phys. Chem. B*, **104**, 9842 (2000).

20. Sathyamoorthy R., Sudhagar P., Chandramohan S., Vijayakumar K. *Cryst. Res. Technol.*, **42** (5), 498 (2007).
21. Schindler K.M., Kunst M. *J. Phys. Chem.*, **94**, 8222 (1990).
22. Zverev G.M., Sidoryuk O.E., Skvortsov L.A. *Kvantovaya Elektron.*, **8**, 2274 (1981) [*Sov. J. Quantum Electron.*, **11**, 1393 (1981)].
23. Chin J., Scierka S., Kim T., Forster A. *Proc. 81st Annuall Meeteng of FSCCT* (Orlando, FL, USA, 2003).
24. Castellano F., Stipkala J., Friedman L., Meyer G. *Chem. Mater.*, **6**, 2123 (1994).
25. Zharov V.P., Letokhov V.S. *Lazernaya optiko-akusticheskaya spektroskopiya* (Laser Acoustooptic Spectroscopy) (Moscow: Nauka, 1984).