

INFLUENCE OF ANNEALING TEMPERATURE ON PHOTOPHYSICAL PROPERTIES OF NANOSTRUCTURED TiO₂ FILMS

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The spectral and kinetic characteristics of the photoluminescence of titanium dioxide films were studied. At ultraviolet excitation of films the luminescence spectrum characteristic of the anatase structure is observed. Heat treatment of the samples at temperature of 1273 K leads to a long-wavelength shift of the photoluminescence band with a maximum wavelength of 850 nm that indicates the formation of the rutile crystal structure. The current-voltage characteristics of titanium dioxide films were measured. It is found that the films with the anatase structure have a higher photocurrent than the films with the rutile structure. The photocatalytic properties of titanium dioxide films were studied. It is shown that titanium dioxide films with anatase structure have the highest photocatalytic activity.

Keywords: titanium dioxide, anatase, rutile, luminescence, current-voltage characteristics, photocatalysis

Introduction

In recent years the interest in the nanomaterials based on titanium dioxide was steadily growing due to their unique physical and chemical properties. This is due to the widespread use of TiO₂ in a variety of practical problems. Thus, nanomaterials based on titanium dioxide are used in photocatalysis, solar energy, water and air purification from organic impurities, as well as for destruction of bacteria [1, 2].

Electronic structure and the structure of energy bands of crystalline TiO₂ are studied in detail and results were shown in several papers [3, 4]. Titanium dioxide has a wide band gap and its photocatalytic properties begin to appear during irradiation in the ultraviolet region of the spectrum. It is known that powder particles of TiO₂ (P25, Hombikat UV-100) have the highest catalytic activity. It is believed that its high activity is due to an effective separation of charge carriers at the interface of two semiconductors [5]. Despite the fact that the powder particles are highly efficient and inexpensive photocatalysts the work on producing TiO₂ with improved photocatalytic properties is continuing [6]. Therefore, at the present time for expansion of the application of these catalysts the main focus is on creating of thin films based on TiO₂, as in this form it is easier to use TiO₂ for conducting photocatalysis in a variety of conditions.

This paper presents the results of a study of luminescent, electrophysical and photocatalytic properties of nanostructured films of titanium dioxide.

2. Preparation of samples and experimental technique

For obtaining TiO₂ film the solution containing powder of colloidal TiO₂ (Sigma Aldrich) was prepared. The solution was prepared in the following way: colloidal TiO₂ powder was ground in a porcelain mortar with a small amount of deionized water and acetone, taken in a volume ratio of 10:1. Acetone was added to prevent clumping of the particles. After the formation of a homogeneous viscous paste the solution of titanium dioxide nanoparticles was deposited on the surface of the substrate by the method of doctor-blading. Then, the resulting films were subjected to heat treatment at a temperature of 773 and 1273 K during 2 hours.

The microstructure and the thickness of the films were studied on the cleaved samples on a scanning electron microscope (SEM) TESCAN Mira 3. The measurements of spectral and kinetic characteristics of TiO₂ films were performed on an automated spectral and kinetic installation with the registration in photon counting mode. Stimulation was performed by a nitrogen laser AIL 3 ($\lambda_{\text{gen}}=337$ nm, $E=30$ mJ, $\tau_{\text{imp}}=10$ ns).

Measurement of CVC films formed by NPs and NTs titanium dioxide with the anatase structure and rutile was performed using a potentiostat (ELINS, Russia) in a standard three-electrode cell. The nanostructures of titanium dioxide were used as a working electrode, they were deposited on the surface of the glass substrate with a conductive layer of FTO. The opposite electrode was platinum foil and as a comparison AgCl electrode was used. Measurements were carried out in an electrolyte of 0.1 M NaOH in a quartz cuvette at room temperature. When registering photocurrent titanium dioxide films were irradiated with light from a xenon lamp of 80 W. The long-wavelength part of the spectrum was cut off light filter UFS-6.

Electrical and transport properties of titanium dioxide films were investigated by measurement of the photocurrent and impedance of the electrochemical cell. Measurements by the method of electrochemical impedance spectroscopy were carried out under standard simulated solar radiation (Air Mass (AM) 1.5) at impedancometry Z-500PRO (Elins, Russia). The amplitude of the applied sinusoidal signal was 20 mV and the frequency was varied from 1 MHz to 100 MHz. The absorption spectra of dye of methylene blue films were prepared by a dual-beam spectrophotometer Cary 300 UV-Vis.

3. Results and discussion

The morphology of surface and cross cleavage of TiO₂ films obtained at an annealing temperature of 773 and 1273 K are shown in Figure 1. The figure shows that the surface of the film has a granular structure. Also it is evident that the film annealed at 1273 K (Figure 1 b) has less granular structure than the film that was subjected to thermal annealing at a temperature of 773 K (Figure 1 a). This is probably due to the fact that under the influence of heat some of the particles sintered. From the cross cleavage of samples it is evident that the thickness of the films was 7-8 microns.

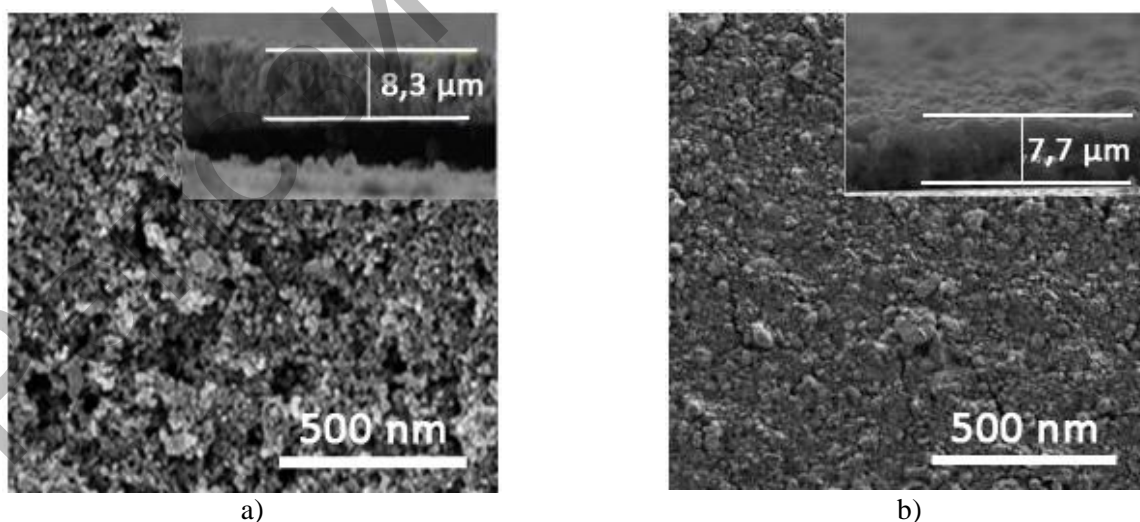


Fig.1. SEM images of TiO₂ films.

It is known that before heat treatment the TiO₂ structure is amorphous. Crystallization of the structure occurs during thermal annealing of the sample starting with the temperature of 553K. At a

temperature of 773 K the amorphous phase transforms to the anatase structure. At further annealing to 1273 K anatase structure is completely transformed into the rutile phase [7].

Figure 2 shows the luminescence spectra of TiO₂ films annealed at 773 K. The measurements were performed in an optical cryostat which can cool the sample to the boiling point of liquid nitrogen. Before the measurements the sample was placed in the cryostat, it was pre-evacuated to residual pressure $P=5 \cdot 10^{-4}$ mbar. When photoexcitation of TiO₂ samples with anatase form of the crystal cell at room temperature luminescence was not observed. After cooling the samples to $T=200$ K the luminescence with a maximum spectrum at a wavelength of 525 nm is observed. By lowering the temperature of the sample to 80 K the luminescence intensity increases.

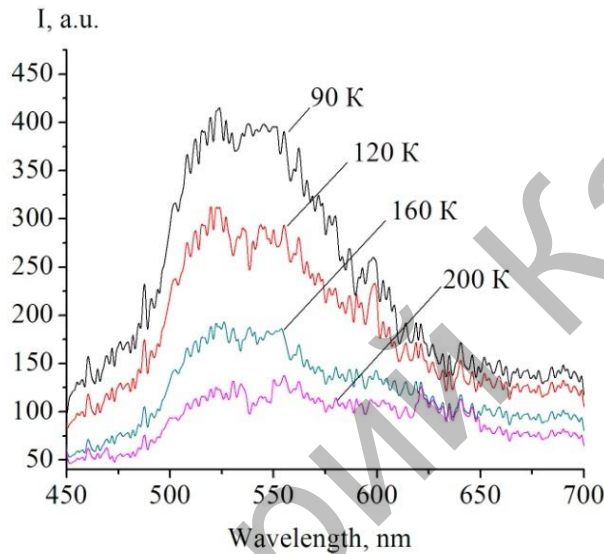


Fig.2. The luminescence spectra of TiO₂ films with anatase structure

Measurements of the kinetics of the luminescence were carried out on the wavelength of 530 nm in the temperature range of 90-200 K. The kinetic curve is generally non-exponential. Lifetimes of excited states, calculated from the exponential part of the decay curves are shown in Table 1.

Table 1. The effect of temperature on the luminescent properties of TiO₂ films with anatase structure.

T, K	I_{\max}^{lum} , a.u.	λ_{\max}^{lum} , nm	$\Delta\lambda_{1/2}^{lum}$, nm	τ , ms
90	419	525	114	3.19
120	322	525	120	2.77
160	266	525	133	1.26
200	197	525	237	1.18

Figure 3 shows the luminescence spectra of TiO₂ films annealed at 1273 K. It can be seen that the photoluminescence spectra contain a broad band in the region of 750-950 nm that indicates the presence of multiple emission centers. As a result of thermal effects on the films a phase transition of the crystalline cell from anatase to rutile takes place. This leads to the fact that the emission band with a maximum 525 nm disappears, at the same time in the emission spectrum a new band with a maximum 850 nm appears. According to the paper [8] such behavior of TiO₂ luminescence

spectrum is due to the formation of additional emission centers associated with oxygen vacancies in different charge states.

Lifetimes of the excited states calculated from the exponential curves of the TiO₂ damping films are presented in Table 2.

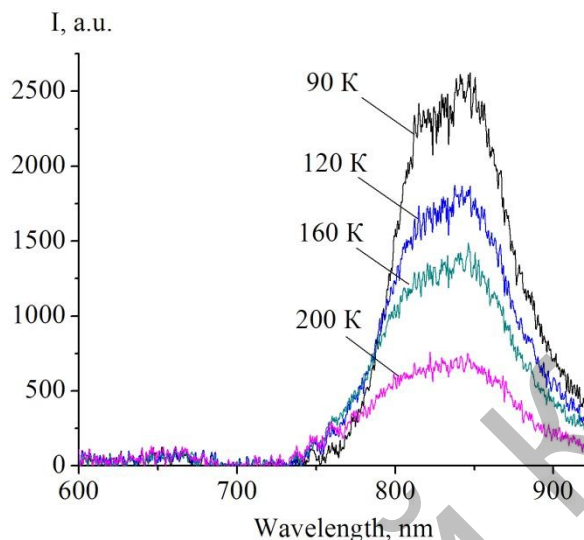


Fig.3. The luminescence spectra of TiO₂ films with rutile structure

Table 2. The effect of temperature on the luminescent properties of TiO₂ films with rutile structure.

	T, K	I_{\max}^{lum} , a.u.	λ_{\max}^{lum} , nm	$\Delta\lambda_{1/2}^{lum}$, nm	τ , ms
1	90	2653	850	78	7.5
2	120	1886	850	87	3.9
3	160	1509	850	88	2.3
4	200	762	850	96	1.7

The current-voltage characteristics of pure TiO₂ films with anatase and rutile structure are presented in Figure 4. The figure shows that for TiO₂ films the value of the photocurrent for anatase is 4 times higher than that for rutile.

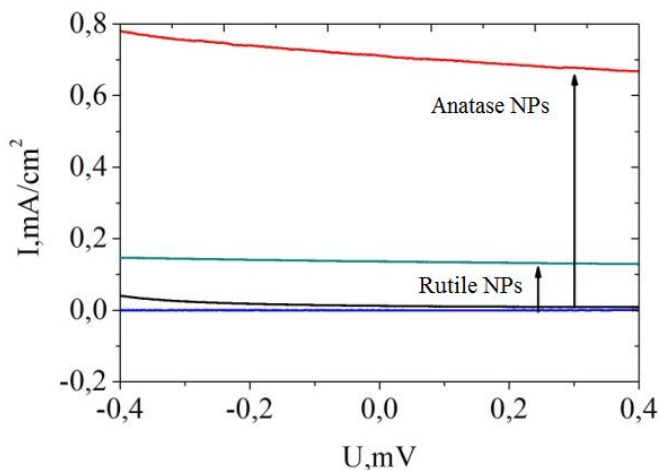


Fig.4. The current-voltage characteristics of TiO₂ films

The studies of electrical and transport properties of TiO₂ films were carried out by measuring the electrical impedance. Figure 5 shows hodographs of impedance in Nyquist coordinates for TiO₂ films with anatase and rutile structure.

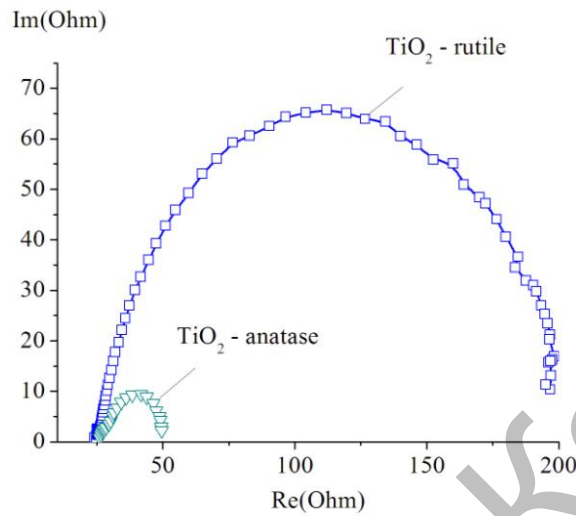


Fig.5. Impedance spectra of TiO₂ films with anatase and rutile structure

From the presented data it is evident that the impedance spectrum is composed of multiple circles. Using the method described in [9, 10] from a central arc of impedance spectra effective diffusion coefficient of electrons D_{eff} , the effective speed of recombination k_{eff} , effective lifetime of electron τ_{eff} , resistance of electron transport in the film of titanium dioxide R_w , charge transfer resistance R_k associated with the recombination of the electron were calculated. The results are shown in Table 3.

Table 3. Electrical and transport options of TiO₂ films

Films	D_{eff}	$k_{eff}, (s^{-1})$	$\tau_{eff}, (s)$	$R_k, (Ohm)$	$R_w, (Ohm)$
TiO ₂ (anatase)	$9.9 \cdot 10^{-5}$	14.0	0.07	22.0	26
TiO ₂ (rutile)	$4.7 \cdot 10^{-5}$	57.0	0.02	175.0	26

From the tabulated data it is evident that the electron transport resistance in TiO₂ (R_w) for films of anatase and rutile structures does not change. At the same time the rate of recombination (k_{eff}) in films with anatase structure is less than k_{eff} films of TiO₂ with rutile structure. The magnitude of the recombination resistance shown in Table 3 indicates a high rate of recombination of charges in films with rutile structure. This is also evidenced by the low efficiency of the electron lifetime in films with rutile structure.

In accordance with the formula $k_{eff} = 2N_s k_r$ (N_s - density of electrons at the defect levels of energy (cm^{-3}), k_r - recombination rate constant ($cm^3 s^{-1}$) into electrolyte of electrons from TiO₂ defective levels [10]) it can be concluded that in the rutile films the concentration of defects through which the recombination processes take place is higher than in anatase.

Photocatalytic activity of TiO₂ films with anatase and rutile structures was measured in the model reaction of decomposition of the methylene blue dye under irradiation of UV light from a xenon lamp (Figure 6). Obtained data indicate that TiO₂ films with rutile structure have a sufficiently high catalytic activity in the oxidation reaction of methylene blue. At the same time, when excited by ultraviolet radiation activity is lower than the activity of TiO₂ films with anatase

structure. This may be due to the fact that TiO_2 contains the defects which can serve as traps and recombination centers of charge carriers.

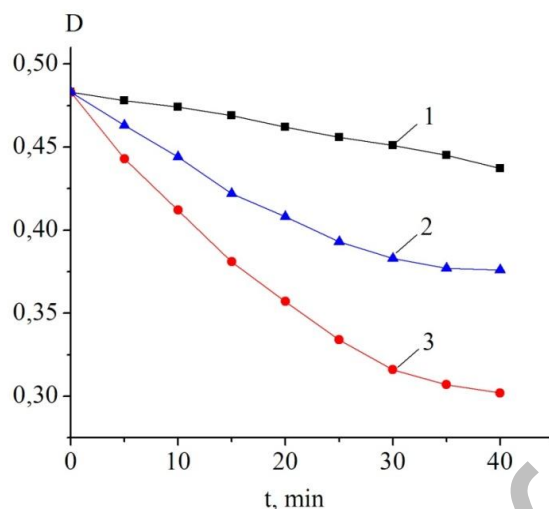


Fig.6. Photocatalytic activity of the samples in the oxidation reaction of methylene blue: 1 - alcoholic solution of methylene blue; 2 - TiO_2 film with rutile structure; 3 - TiO_2 film with anatase structure.

Conclusion

In the paper the luminescence and photovoltaic properties of TiO_2 films were examined. For samples annealed at $T=773$ K, when excited by a nitrogen laser luminescence is observed with a spectrum characteristic of the anatase structure.

Annealing of the samples at $T=1273$ K leads to a long-wavelength shift of the photoluminescence band with maximum at 850 nm wavelength which corresponds to the rutile structure. For the anatase the duration of films luminescence of NPs was 3 ms. The lifetime of photoluminescence of rutile films is higher than the lifetime of luminescence of anatase structure.

The current-voltage characteristics of TiO_2 films of different structures were measured from which it follows that the films of anatase structure have a higher photocurrent than films with rutile structure. It is found that the films of anatase structure have higher photocatalytic activity than the films of rutile structure.

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