

Properties of TiO₂ films with gold nanoparticles

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Abstract. The physicochemical and optical properties of titanium dioxide films, made by gel technology and doped with gold nanoparticles, were investigated. The structures of the titanium dioxide films synthesized by different techniques have been compared. Using methods of high-resolution microscopy and the results of X-ray diffraction analysis it was shown, that the developed gel technology allows getting almost 100% nanostructured anatase phase. Titanium dioxide was modified by nanoparticles of gold with different concentration and transmittance spectra of the samples were studied.

1. Introduction

Nowadays, nanocrystalline titanium dioxide (TiO₂) is the subject of active research due to several unique properties of this compound [1-3]. TiO₂ films are photosensitive, possess chemical and mechanical stability, good optical properties. Particular interest in titanium dioxide is caused by its photocatalytic properties, which makes it a promising material to solve many environmental problems, including the creation of highly efficient solar cells. In addition, the titanium dioxide films have good optical properties, which can be used to create photonic devices.

Titanium dioxide is an effective photocatalyst for a variety of chemical reactions [4-5]. Its photocatalytic properties are caused by the formation on the surface during the illumination of a number of radicals or paramagnetic centers (PC), which are capable of entering into the secondary reaction. This TiO₂ property is widely used to create a filter for water and air treatment from toxic organic impurities. Free radicals, such as O²⁻ and OH⁻ [6], formed on the surface of TiO₂ under the oxygen and water influence, can destroy environmental pollutants, because they are strong oxidants. Nano-titanium dioxide in anatase form structure has increased specific surface area, which allows to increase the yield of photo oxidation reaction by several orders.

Large specific surface area of titanium dioxide in the anatase form structure makes it a promising material for the creation of efficient solar cells, since the absorption capability of the material is increased by nanostructuring. Currently, there appeared studies where nanoparticle net was replaced by single crystals of titanium dioxide having pores with diameter of about 10 nm. Solar cells with such a structure have a record rate of conversion of light energy into electrical energy (7.4%) [7]. Moreover, since titanium dioxide is a porous material, it can be activated using dye molecules such as rhodamine 6G. The development of the injection type solar cells is possible [8], because energy position of the conduction band of TiO₂ coincides with the energy of excitation of many dyes. The perspective of improving device characteristics on the base of titanium dioxide is associated with increasing catalytic activity and widening its absorption spectrum.



Recently, new technologies for the synthesis of titanium dioxide are being actively developed, allowing to obtain samples with enhanced photoactivity which is associated with an increase in the content of TiO₂ films proportion of fine-grained structure in the form of anatase.

Titanium dioxide is doped with nanoparticles of metals [9], in order to expand the spectral absorption band and raise the amplitude of the absorption of the material, for increasing photocatalytic activity. Moreover, the injection of such particles into a composite film leads to an appearance of qualitatively new physical properties [10-12]. The substance that is in a nanoscale modification differs significantly by many features from the volume materials. For example, gold nanoparticles display ferromagnetic and catalytic properties, specific optical properties which consist in the appearance of absorption bands in the visible spectrum, caused by resonance events on plasmons. The intensity of the resonance absorption and spectral position depends on the amount of metal nanoparticles included in the dielectric matrix. Titanium dioxide can be used as the matrix. Such templates can be used to improve sensitivity of the spectral methods for the analysis of substances composition, to create a variety of sensors and new metamaterials, superlattices synthesis, including photonic crystals, and others. Of special interest are optical and nonlinear optical properties of such structures.

The present study investigates the properties of titanium dioxide films, synthesized using a new method – gel method [13]. The results are compared with the research results obtained for films produced by sol-gel technology. In addition, the influence of modification by gold nanoparticles on the characteristics of the TiO₂ gel-films is investigated.

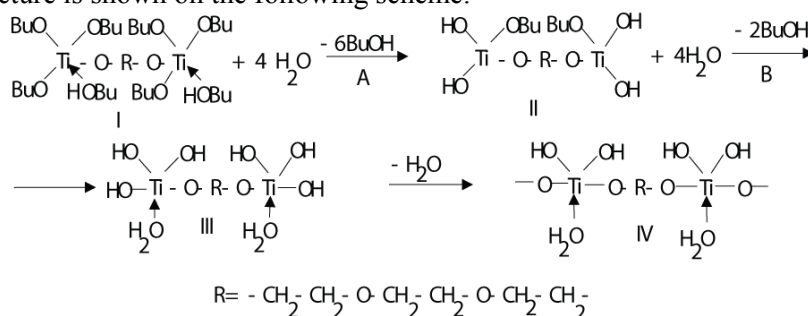
2. Formation of titanium dioxide films by gel method and modifying by gold nanoparticles

Sol-gel method is most often used for the production of titanium dioxide. It is known that titanium dioxide can exist in three configurations: amorphous, nanocrystalline (anatase) and rutile forms. As for the above applications large specific surface area is of importance, the most interesting is the highly structured anatase modification. In practice, a mixture of these crystal modifications is usually used. Relative content of structural modifications depends on the synthesis method and on the temperature of heat treatment conditions.

Amorphous TiO₂ is transformed into anatase at a temperature greater than 300°C. Furthermore, the anatase content of the amorphous film depends on the film thickness. Films of thickness 100-200 nm are strictly amorphous, and at the thickness of 500 nm and more they contain anatase [14]. This is due to the fact that the initial degree of crystallization decreases with decreasing film thickness.

Manufacturing films by the sol-gel method leads to the formation of titanium hydroxide TiO₂ × H₂O, which, depending on the deposition conditions may contain a variable number of OH groups connected to titanium. During annealing of titanium dioxide in the amorphous state, first anatase is formed (thus OH-groups are partially removed), and then – rutile. Complete removal of water occurs at temperature above 600°C.

In the present work, TiO₂ films were obtained not only by the sol-gel method described in [15], but also by the gel method [16], which allows to get nearly 100% of anatase form of titanium dioxide. Unlike the sol-gel method, in this case gelation takes place in the true solutions. Film formation occurs from the solution of gel, which is the result of reaction of titanium tetrabutoxide (TBT) compounding with triethylene glycol (TEG), in butanol-1 in the air and subsequent transformation during annealing. The chemical structure is shown on the following scheme:



Unlike the sol-gel process, in this case, sol-formation does not occur, films are drawn directly from solution, rather than from the suspension, and there is no direct hydrolysis reaction. Hydrolysis takes place without the addition of water to the solution, water condenses out of the atmosphere, moreover the OH groups for hydrolysis split out while removing the alcohol from the solution.

The process of making gel films samples of the titanium dioxide was similar to manufacturing process of sol-gel films described in [15]. It consisted of several phases: preparing a solution, applying it to the prepared substrate, drying and subsequent annealing. As a basic material for producing titanium dioxide films the titanium tetrabutoxide $\text{Ti}(\text{OCH}_2\text{C}_3\text{H}_7)_4$ was used, which was mixed in the appropriate proportions with triethylene glycol $\text{C}_6\text{H}_{14}\text{O}_4$, then butanol $\text{C}_4\text{H}_{10}\text{O}$ was added to the predetermined volume and stirred again.

Substrate layers with applied titanium dioxide were dried at $\sim 100^\circ\text{C}$ for 10-20 min. Porous film-frame was formed on a substrate due to the evaporation of the solvent. Subsequent annealing at temperature $\sim 300\text{-}800^\circ\text{C}$ led to the formation of a continuous film, where the porosity does not exceed 10-15%. Some samples were doped with gold.

A series of titanium dioxide films samples was produced by the described technology (table 1), the parameters of which, namely the refractive index and thickness, were varied by changing the ratio of the solution components, the drawing speed of the substrate from the solution, the solution temperature and annealing time and temperature. Several samples were modified by gold nanoparticles with different concentration.

Table 1. The ratio of components of the solution, annealing temperature and relative content of gold in the samples.

TEG:TBT		1:2	1:1	2:1	1:1 (Au:TiO ₂ = 1:100)	1:1 (Au:TiO ₂ = 1:50)
Annealing	450°C	K1	K2	K3	KZ1	KZ2
temperature	700°C	K4	K5	K6	KZ3	KZ4

Experimental samples were studied by integrated optics methods, optical spectrophotometry and EPR spectroscopy, thermal analysis, high-resolution microscopy and Raman scattering.

3. Experimental studies

3.1. Study of dependence of the gel films refractive index on the parameters of technological regime and the introduction of gold nanoparticles

The thickness and refractive index of the manufactured samples were determined using the method of integrated optics based on the waveguide propagation of radiation through the film [17].

Calculations of the refractive index and film thickness were carried out using the dispersion equations for the optical waveguide composed of the studied film deposited on quartz substrate. Dispersion equations determine the relationship between the effective refractive index (ERI) for the modes propagating in the optical waveguide, the film thickness, the refractive indices of the film and the substrate, and the wavelength of the radiation injected into the film. For determining the thickness and refractive index of the material of the film using the dispersion equations, ERI of two modes (TE_1 and TM_1) were measured at wavelength of light injected into the waveguide. The film thickness in this case must exceed the critical thickness h_{cr} for each mode, which has been calculated for the given waveguide. The refractive index of the quartz substrate was equal to 1.4585, and the wavelength of the radiation – 632.8 nm.

The He-Ne laser radiation was injected into the waveguide through the prism at certain resonant angles. After measuring angles of the excitation of the waveguide, the ERI were determined using the relationship between the angles of the excitation, ERI and the refractive index of the input prism.

Table 2. The results of calculation for the samples of titanium dioxide films produced with different ratios of the components of stock solutions, and different values of the annealing temperatures.

Sample	γ_{TE}	γ_{TM}	h_{crTE} , nm	h_{crTM} , nm	h , nm	n_2
K1	2.0339	1.6424	24	64	120	2.48
K2	1.9419	1.5064	24	64	89	2.54
KZ1	1.8494	1.5769	32	71	130	2.24
KZ4	1.7911	1.4817	28	69	91	2.35

The table 2 shows that the refractive index of the films of titanium dioxide, synthesized by gel method, has a rather high value of ~ 2.4 , which is much higher than the refractive index of the sol-gel films [15], and is almost independent of the ratio of stock solution components and annealing temperature.

The introduction of gold nanoparticles decreases the refractive index, and the higher is the concentration of gold, the smaller is the refractive index.

3.2. Determining of the phase transition temperature and study of the films morphology

In order to choose the proper annealing temperature for the films, the thermal analysis was conducted, which resulted in finding the temperatures of phase transitions for gel material.

Determination of the phase transitions temperatures was carried out by the thermal analysis on SDTQ600. By simultaneous thermal analysis, thermogravimetric analysis (TGA) (figure 1) of samples was performed.

As seen in figure 1 the addition of gold does not change the phase transition temperature.

The morphology of the manufactured films was investigated using Raman spectroscopy (figures 2, 3).

Raman spectra were obtained at the facility NTegra Spectra. In the Raman spectrum of the sample annealed at the temperature 450°C, 4 peaks were observed, which correspond to the position of anatase [18], and at the temperature 700°C peaks characteristic for rutile appeared. It was found that increasing the proportion of TEG in the stock solution, as well as adding the gold in the solution, both lead to the rise of the temperature of phase transition anatase-rutile. Raman spectra of the commercial film fabricated by company “Aldrich” and of sample (solution 1) annealed at 450°C confirm the presence of the anatase only.

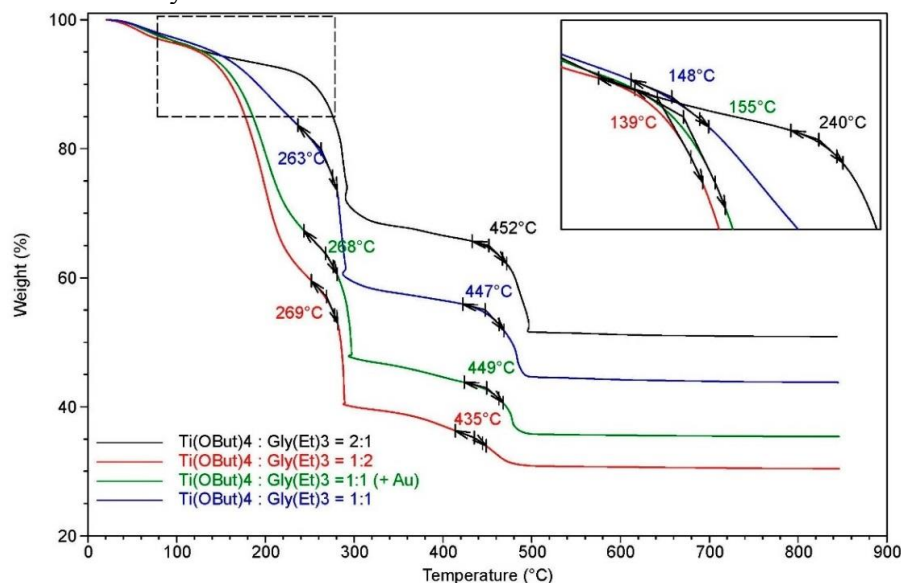


Figure 1. TGA of samples.

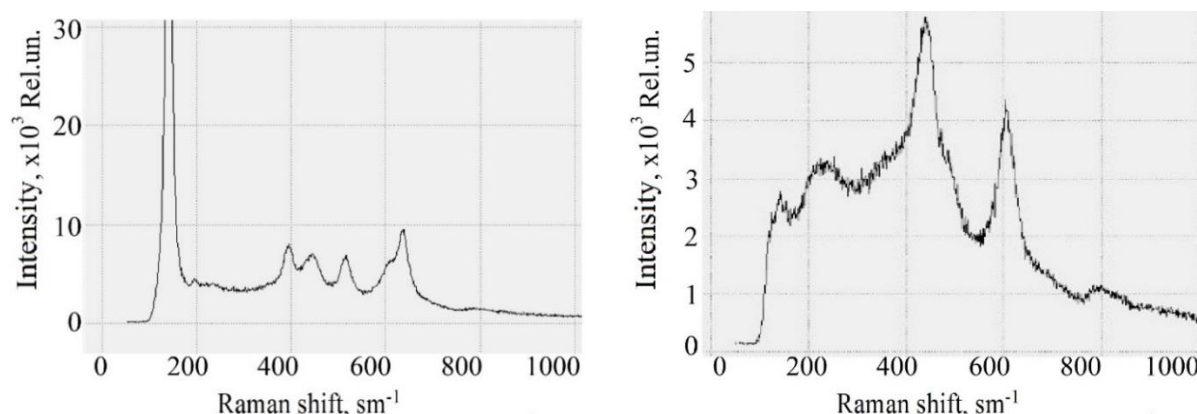


Figure 2. Raman spectra of the films confirm the presence of the anatase only (left – solution 2, 450°C) or of mixed (anatase + rutile) phase (right – solution 3, 700°C).

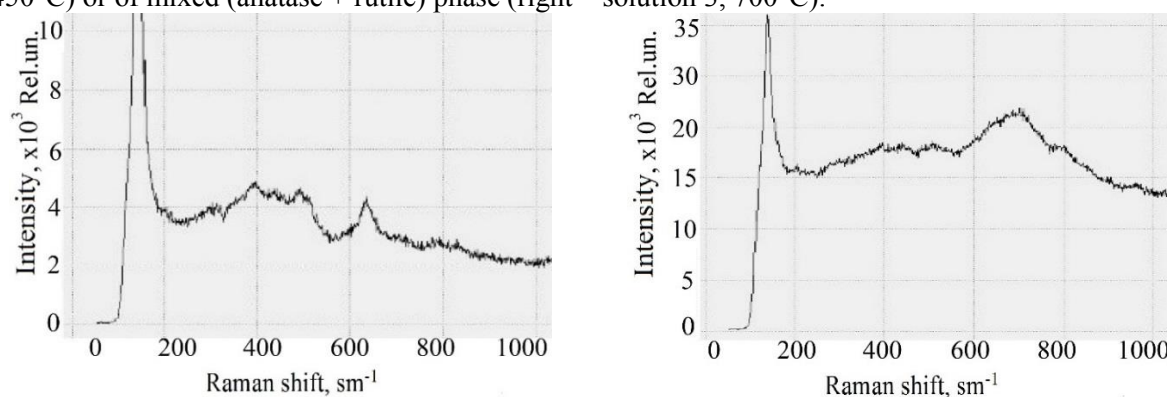


Figure 3. Raman spectra of the films of TiO₂ with Au (TiO₂:Au = 50:1) annealed at 450°C (left) and at 700°C (right).

Studies of the optical properties of TiO₂ films were carried out at room temperature using a monochromator-spectrograph MS 3504I and photometric lamp SIRSH 6-100, grating 1200 grooves/mm, the measurement step 1 nm, lamp color temperature 2840 K. The data show changes of photosensitivity depending on changing the parameters of the technological regime, the ratio of components of solutions, as well as the addition of the gold nanoparticles.

3.3. Study of optical characteristics of gel films with gold nanoparticles

Analysis of transmission spectra of samples without the addition of gold (K1, K2, K3) with the annealing temperature of 450°C (figure 4a) showed that the absorption edge corresponds to $\lambda = 330$ nm. The maximum absorption of K1 sample was observed at $\lambda = 500$ nm with an amplitude of about 40% and about 150 nm wide. For sample K2 absorption peak (50%) shifted 50 nm to the shorter wavelengths $\lambda = 450$ nm with width of 80 nm. Transmittance was 97% at a wavelength of 600 nm, and at $\lambda = 850$ nm a second absorption peak appeared with width ~ 200 nm and amplitude of about 30%. The long-wavelength peak was similar to the peak of K1.

The edge of the absorption band shifted to 350 nm for all samples (figure 4b) by increasing annealing temperature (700°C). Absorption maximum of sample K4 corresponded to $\lambda = 450$ nm (60% amplitude, width 80 nm). For sample K5 slow growth of absorption intensity was observed in the range from 470 nm to 870 nm and the maximum absorption was 50%.

Samples K3 and K6 had a greater scattering associated with the ratio of solution components. Custom solution contained a large amount of solvent and alcohol, which prevented the formation of a strong structural frame of components, and as a result the fabricated film cracked during annealing and was not optically homogeneous. That is why K3 and K6 samples had about the same ~ 40 -60% transmittance in the wavelength range from 500 nm to 870 nm.

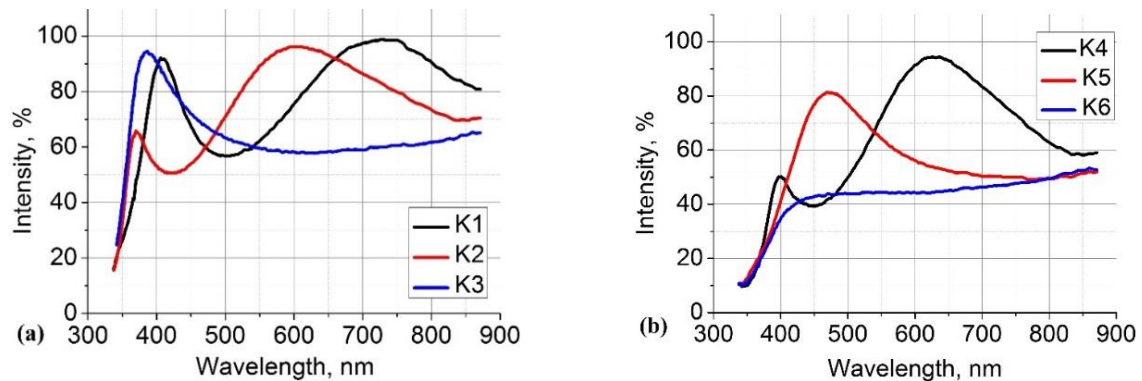


Figure 4. Transmission spectra of samples without gold after annealing at temperature of 450°C (a) and 700°C (b).

Analysis of the results allows to conclude that the transmission spectra is changed, after modifying film with gold nanoparticles (figure 5a). Introduction of nanoparticles changes the intensity of the absorption bands and their spectral position. A visual representation of spectra changes can be seen on the figure 5b, which is a difference spectrum obtained by subtracting the spectra of the sample with and without gold. Introduction of gold increases the absorption over the entire spectral range. As shown in figure 5b with annealing temperature of 450°C there is characteristic peak at the wavelength of 600 nm. Increasing the annealing temperature changes the spectral peak position by sliding it into the short-wavelength region by 130 nm. The shift of the absorption peak is associated with the change in nanoparticle size [19]. Similarly to silver nanoparticles, gold absorbs at different wavelengths depending on the diameter, which can be varied by changing the parameters of manufacturing process, specifically, the annealing temperature.

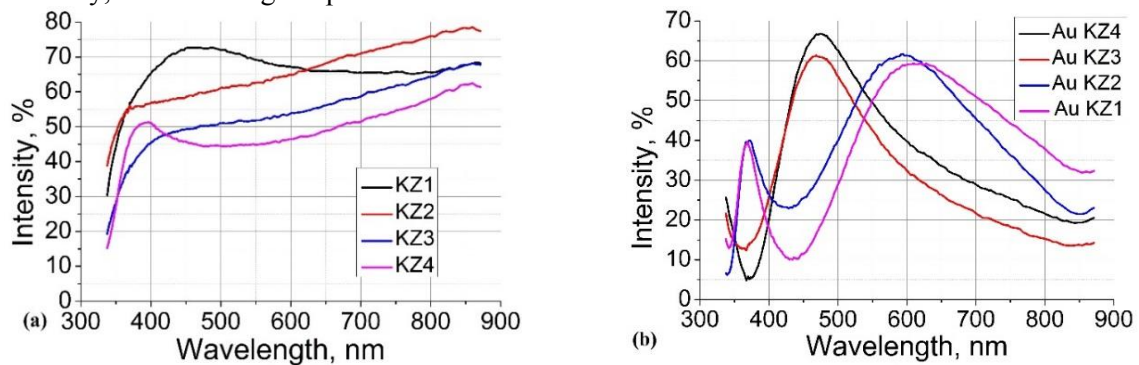


Figure 5. The transmittance spectra of samples with gold (a) and difference spectra of Au absorption in the films (b).

Table 3. The short-wavelength absorption edge λ of the samples in visible range and the corresponding band gap are presented.

Sample	Temperature	λ , nm	E, eV
K1	450°C	505	2.456
K2		421	2.947
K4	700°C	452	2.744
K5		342	3.627
Au KZ1	450°C	369/619	3.362/2
Au KZ2		372/593	3.335/2.092
Au KZ3	700°C	468	2.651
Au KZ4		475	2.612

3.4. Research of photosensitivity of titanium dioxide films by ESR spectroscopy

TiO₂ photoactivity is based on the semiconducting properties of the material, the electronic structure of which is due to the existence of defects on the surface of the crystalline structure. The absorption of a photon of light causes the transfer of an electron from the valence band to the conduction band of the semiconductor to form an electron and a hole, which leads to the formation of the paramagnetic centers (PC). The quantum yield of the process is largely determined by the size and geometry of the material owing to the exclusively superficial phenomena. Increasing the specific surface area can increase the degree of material photoactivity. Therefore, anatase, which has high specific surface area, exhibits a higher photocatalytic activity than the rutile. Increasing of photoactivity is explained, in particular, by a higher position of the Fermi level in anatase (3.3-3.4 eV), compared with rutile (3.1-3.2 eV) [19].

The intensity of the absorption of photons and the efficiency of photocatalysis are determined by the form of its electronic spectrum in the band gap. The band gap of titanium dioxide varies within 3.2-3.6 eV, depending on the method of synthesis. The band gap of the investigated material made by gel method, was estimated to be 2.456-3.362 eV. The photosensitivity of titanium dioxide films was investigated by electron paramagnetic resonance spectroscopy (ESR), which allows registering the paramagnetic centers, such as free radicals, ion radicals and other formations, possessing an unpaired electron. The study of paramagnetic centers was conducted on the spectrometer "SENS ESR 70-03 XD/2" [20] whose operation is controlled by a personal computer. The sample was placed inside the cavity, the sample irradiation was carried out through the cavity transparent window.

A high-pressure mercury lamp was used as a source of UV radiation. Spectrum of lamp (PRK-4) contained a number of intense lines. The most intense lines are at wavelengths of 315 nm, 367 nm and 407 nm, which correspond to radiation energies of 3.936 eV, 3.397 eV and 3.024 eV, respectively.

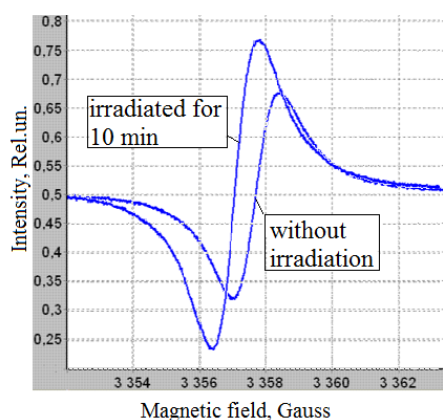


Figure 6. ESR spectra of the sample TEG:TBT = 1:2 annealed at 450°C irradiated with a mercury lamp.

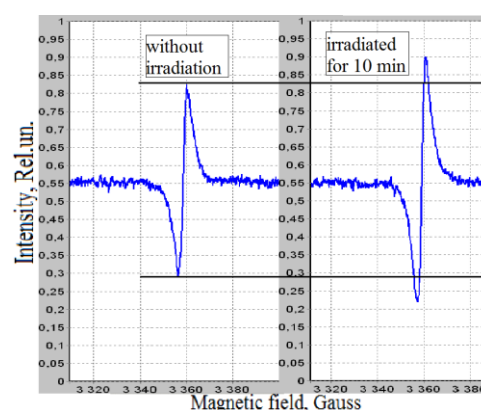


Figure 7. ESR spectra of the sample TEG:TBT = 1:1 annealed at 450°C and irradiated with a mercury lamp.

We can trace the dynamics of change in intensity of the lines after irradiation according to these graphs (figures 6, 7). Total relaxation was 2.5 hours. The difference in the ESR spectra of samples, apparently is due to the different ratios of the components of stock solutions.

Irradiation by UV light of the films annealed at 450°C showed increasing the number of paramagnetic centers.

4. Conclusion

Films samples, with TiO₂ in anatase form, were prepared using the developed gel technology. The mass fraction of anatase is close to 100%, this was confirmed by high-resolution microscopy techniques and the results of X-ray diffraction analysis. The physicochemical properties of titanium dioxide films were studied. The presented results of topography and morphology studies of the obtained film samples also confirmed the existence of anatase phase of material in films.

It is found that the refractive index of the film of titanium dioxide, synthesized by the gel method, has a quite high value of about ~ 2.4 , which is much higher than the refractive index of the sol-gel films and almost independent of the ratio of stock solution components, and the annealing temperature. The modification by gold nanoparticles decreases the refractive index and the higher the concentration of gold, the smaller the refractive index.

The photoactivity research of the synthesized films by ESR spectroscopy showed an increase of films photoactivity under UV irradiation from mercury lamp. It is revealed that films of titanium dioxide in anatase form demonstrate greater photoactivity than the rutile and mixed modifications, while free radicals are not generated on the surface of titanium dioxide in the amorphous phase during the irradiation and the films do not demonstrate photosensitivity in UV range.

Transmission spectra research has shown their dependence on the ratio of the solution components while manufacturing the gel film, and the annealing temperature during their formation.

Raman spectra showed that for the sample annealed at the temperature 450°C , four peaks were observed, which correspond to the position of anatase [18], and at the temperature 700°C there appeared peaks characteristic of rutile. It can be concluded that with increasing the proportion of TEG in the stock solution increases the temperature of phase transition anatase-rutile.

In addition, the absorption spectra are significantly dependent on the parameters of the technological regime. Research of the absorption spectra of titanium dioxide films, containing gold nanoparticles, showed significant changes in the spectra, specifically, additional absorption peaks of various intensity and the shift of the absorption band edge were observed. These spectra features are caused, presumably, by changes in the film structure, specifically, by changes of the size and shape of the particles, while changing the parameters of the technological regime. An important role is played by the aggregation of gold nanoparticles, i.e., occurrence of agglomerates, resulting in an increase of absorption over the entire spectral range. The research of the absorption spectra of titanium dioxide films, modified with other elements such as cobalt and carbon, is of interest.

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