Conference Paper

Optical Properties of Gel Titanium Dioxide Film, Modified By Metal Nanoparticles

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Abstract

The physic-chemical and optical properties of composite titanium dioxide films with gold, cobalt, copper, nickel and iron nanoparticles made using gel technology were studied in the work. The of titanium dioxide films structure synthesized according to different technologies is compared. The differential scanning calorimetry method was used to determine the temperatures of phase transitions of manufactured samples of various modifications of titanium dioxide. The transmission spectra of samples modified by metal nanoparticles with different concentrations were studied.

Keywords: sol-gel, gel method, titanium dioxide, modification, nanoparticles, gold, cobalt, copper, iron, nickel, spectroscopy.

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1. Introduction

Recently, nanocrystalline titanium dioxide (TiO2) has been the subject of active research due to a number of unique properties of this compound [1-3]. TiO_2 films have photosensitivity, chemical and mechanical strength, good optical properties. The special interest shown to titanium dioxide is due to its photocatalytic properties, which makes this material promising for solving many environmental problems, including the creation of highly efficient solar cells. In addition, titanium dioxide films, due to their good optical properties, can be used to create photonic devices and information optics.

Titanium dioxide is an effective photocatalyst for a number of chemical reactions [4-5]. Its photocatalytic properties are due to the formation of a number of radicals or paramagnetic centers (PCs) on the surface during illumination that are capable of entering secondary reactions. Nanostructured titanium dioxide in the structural form of anatase makes it possible to increase the yield of the photo-oxidation reaction by several orders of magnitude due to an increase in the specific surface area.

The large area of the specific surface area of titanium dioxide in the structural form of anatase makes it a promising material also for the creation of effective solar cells,

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since nanostructuring increases the absorbing capacity of the material. Now there are developments in which a network of nanoparticles was replaced by titanium dioxide monocrystals with pores of diameter about 10 nm. Solar photocells with a similar structure have a record conversion coefficient of light energy into electrical (7.4%) [6]. In addition, since titanium dioxide is a porous material, dye molecules, for example rhodamine 6 G, can activate it. This allowed the development of solar cells of injection type [7], since the energy position of the conduction band of TiO2 is consistent with the excitation energy of many dyes. The prospect of improving the characteristics of devices based on titanium dioxide is associated with an increase in catalytic activity and expansion of its absorption spectrum.

Recently, new technologies have been actively developed for the synthesis of titanium dioxide, which allow obtaining samples with increased photoactivity, which is associated with an increase in the content of fine crystalline structure in the form of anatase in TiO_2 films.

In order to expand the spectral absorption band and increase the absorption amplitude of the material, doping of titanium dioxide with metal nanoparticles is used to increase the photocatalytic activity [8]. In addition, the introduction of such particles into the composite film leads to the appearance of qualitatively new physical properties [9-11].

The substance present in the nanoscale modification differs significantly in many characteristics from bulk materials. For example, gold nanoparticles exhibit ferromagnetic and catalytic properties, special optical properties, which consist in the appearance of absorption bands in the visible spectral region caused by resonant phenomena on plasmons. The intensity of resonance absorption and its spectral position depends on the volume of metal nanoparticles included in the dielectric matrix. As a matrix, titanium dioxide can be used. Such matrices can be used to increase the sensitivity of spectral methods for analyzing the composition of substances, to create various sensors and new metamaterials, to synthesize superlattices, including photonic crystals, etc. Of particular interest are the optical and nonlinear optical properties of such structures.

In the present work, the optical and structural properties of titanium dioxide films synthesized using a new method-the gel method [12] and the results of the study are compared with the results obtained for films prepared by sol-gel technology. The influence of the introduction of nanoparticles of various metals on the characteristics of gel-films of titanium dioxide has also been investigated.

2. Materials and methods

2.1. Formation of titanium dioxide films by gel method and modification of metal nanoparticles

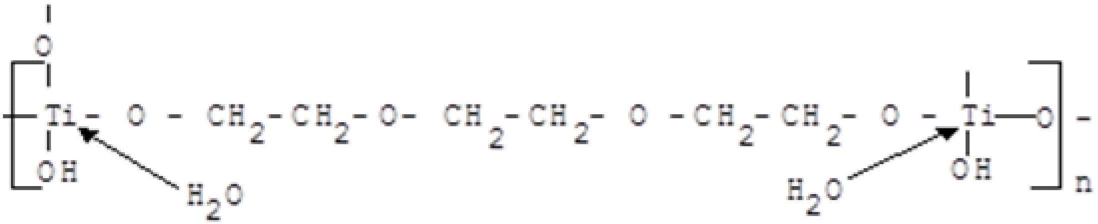
To obtain titanium dioxide, the sol-gel method is most often used. It is known that titanium dioxide can exist in three modifications: amorphous, nanocrystalline (anatase) and rutile forms. Since for the above applications a large specific surface area is important, the most interesting is the highly structured modification - anatase. In practice, as a rule, a mixture of these crystalline modifications is obtained. The relative content of structural modifications depends on both the method of synthesis and the temperature regime of heat treatment.

Amorphous TiO_2 passes into the anatase at a temperature greater than 300°C. In addition, the content of anatase in an amorphous film depends on the thickness of the film. Films 100-200 nm thick are strictly amorphous, and at a thickness of 500 nm and larger contain anatase [13]. This is due to the fact that the initial degree of crystallization decreases with decreasing film thickness.

In the production of films by the sol-gel method, titanium hydroxide $TiO_2 \times H_2O$ is formed, which, depending on its deposition conditions, may contain a variable number of titanium-bonded OH groups. When the titanium dioxide is annealed in an amorphous state, anatase is first formed (some OH groups are partially removed), and then rutile. Complete removal of water occurs at a temperature greater than 600°C.

In the present work, in addition to the sol-gel method described in [14], the gel method [12] was used to obtain TiO_2 films, which allows obtaining, as a result of synthesis, almost 100% of the anatase modification of titanium dioxide. Unlike the sol-gel method, gelling in this case occurs in true solutions.

Film formation occurs as a result of the reaction of titrabutoxide titanium (TBT) and its connection with triethylene glycol (TEG), gelation of the solution of the resulting TEG compound and TBT in butanol-1 in air and subsequent transformations during annealing. The chemical structure is shown in the diagram:



$$\left[-\underset{OH}{\overset{\overset{|}{O}}{Ti}}-O-CH_2-CH_2-O-CH_2-CH_2-O-CH_2-CH_2-O-\underset{OH}{\overset{|}{Ti}}-O\right]_n-$$

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In contrast to the sol-gel process, there is no ash formation in this case, the films are drawn directly from the solution and not from the suspension, nor is there a direct hydrolysis reaction, that is, hydrolysis occurs without the addition of water to the solution, the water condenses from the atmosphere, in addition, OH groups for hydrolysis are cleaved when the alcohol is removed from the solution.

The process of making samples of gel films of titanium dioxide was similar to the process of manufacturing sol-gel films described in [15]. It consisted of several stages: the preparation of the solution, applying it to the prepared substrate, drying and subsequent annealing. Titanium tetra-butoxide $Ti(OCH_2C_3H_7)_4$ was used as a base material for the preparation of titanium dioxide films, which was mixed in appropriate proportions with triethylene glycol $C_6H_{14}O_4$, then butanol $C_6H_{12}O_3$ was added to a predetermined volume and again mixed.

The resulting gel solution was applied to the quartz substrate by drawing it out of solution using an electromechanical device. The thickness of the layer was varied by changing the drawing speed and the viscosity of the solution. The voltage applied to the electromechanical device regulated the speed of the substrate movement, and in the experiments it was 0.14-0.25 mm /s. The viscosity of the solution could be changed either by changing the ratio of the components or by its temperature.

Substrates coated with titanium dioxide were dried at a temperature of $\sim$ 100°C for 10-20 minutes. Due to the evaporation of the solvent, a porous film, a skeleton, was formed on the substrate. Subsequent annealing at a temperature of $\sim$ 300-800°C led to the formation of a continuous film, the porosity of which did not exceed 10 -15%.

According to the described technology, a series of samples of titanium dioxide films was prepared (Table 1), the parameters of which, namely the thickness and the refractive index, were varied by changing the ratio of the solution components, the substrate drawing speed from solution, the solution temperature and the annealing temperature and time. A number of samples were modified with nanoparticles of metals with different concentrations. The modification occurred by the addition of gold salts AuCl3, nickel NiCl2, copper CuCl2, cobalt CoCl2 and iron FeCl3 to the solution [16]. The ratio of the solution components, the annealing temperature and the relative content of nanoparticles in the samples are shown in Table 1.

The experimental samples were investigated by optical spectrophotometry and thermal analysis.

Table 1

Ratio of TEG: TBT										
		1:2	1:1	2:1	1:1, TiO_2:Me = 1:50	1:1, TiO_2:Me = 1:100				
		TiO_2	TiO_2	TiO_2	Au	Au	Cu	Ni	Co	Fe
Annealing temperature	120°C	-	-	-	-	-	II	V	VII	IX
	450°C	K1	K3	K2/II	KZ2	Z1	IV	VI	VIII	X
	700°C	K4	K6	K5	KZ4	Z3	-	-	-	-

2.2. Determination of the temperature of phase transitions

For a purposeful choice of the annealing temperature of the films, a thermal analysis was carried out [17], as a result of which the temperatures of the phase transitions of the gel material were determined.

Determination of the temperature of the phase transitions was carried out using thermal analysis on the SDTQ600 thermal analyzer. A differential thermal analysis (DTA) (Fig. 1) of the samples was carried out by synchronous thermal analysis.

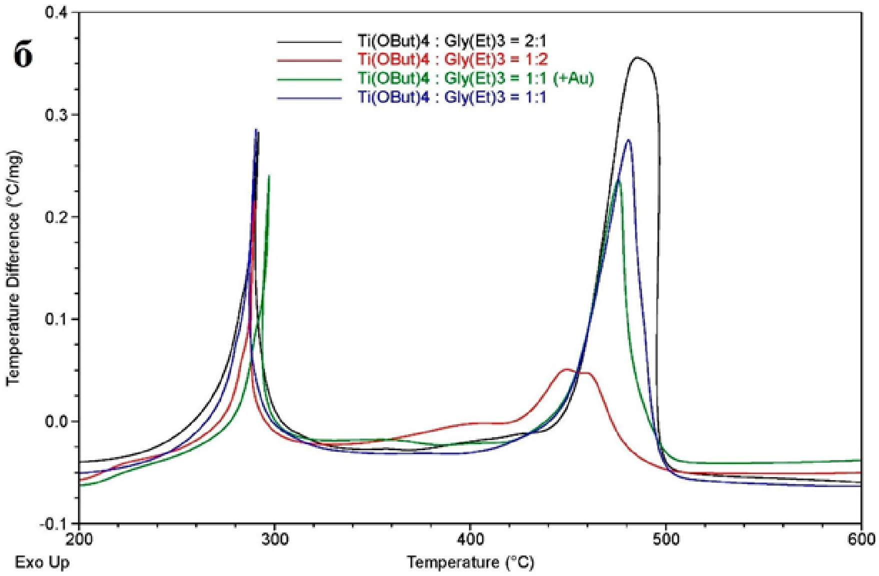

Figure 1: DTA of samples.

As can be seen in Fig. 1, the temperature of the phase transitions is not affected by the change in the ratio of the solution components and the introduction of metal nanoparticles. The transition temperature from the amorphous state to the anatase was 280°C, and the transition to the rutile modification was carried out at temperatures from 460°C to 480°C.

2.3. Investigation of absorption spectra

Investigations of the optical properties of TiO2 films were carried out at room temperature using a MS 3504I monochromator spectrograph and a SIRSCH band glow lamp of 6-100, a grating of 1200 pcs / mm, a measurement step of 1 nm, a color temperature of the lamp of 2840 K. The data obtained show a change in the photosensitivity as a function of from changes in the parameters of the technological regime, the ratio of the components of solutions, as well as the addition of gold nanoparticles.

In a work carried out earlier [18], spectra of samples prepared with different ratios of the solution components were obtained at annealing temperatures of 450°C and 700°C, and also with the addition of gold. It was shown that the change in the absorption band in all samples, the most optimal ratio of the components of solutions was 1:1. When gold nanoparticles with a lower concentration were added, an increase in the absorption intensity in the short-wave region of the spectrum occurred. In accordance with the obtained data, it was decided to add metal nanoparticles to a solution with a TiO_2: Me ratio of 1:100. Also, the samples were annealed at temperatures of 120°C and 450°C to obtain films in the amorphous and anatase phase.

Analysis of the absorption spectra of titanium dioxide films without nanoparticles (Fig. 2a) showed a significant increase in the absorption intensity in comparison with the amorphous modification. The absorption peak with a width of ~ 40 nm was observed in the violet range, at a wavelength of ~ 442 nm. When the nanoparticles were added (Fig. 2b, c, d, e), the absorption peaks moved to the shortwave region by ~ 10-15 nm. The addition of nickel and iron nanoparticles increased the absorption intensity in the long-wave range in samples with an amorphous modification of titanium dioxide, in comparison with anatase.

An analysis of the results obtained allows us to draw conclusions about the change in the absorption spectra when metal nanoparticles are introduced into the film (Fig. 3). Unlike gold, the main absorption peaks were in the violet range, while the absorption intensity decreased for samples annealed at 450°C. In samples prepared at an annealing temperature of 120°C with the addition of nanoparticles, the absorption line was higher in the long-wave range.

When gold is introduced, there is an increase in absorption over the entire spectral range. At an annealing temperature of 450°C, a characteristic peak at a wavelength of 600 nm was observed. An increase in the annealing temperature led to a change in the position of the spectral peak, shifting it to the short-wavelength region. The shift in the absorption peak is associated with a change in the size of the nanoparticles.

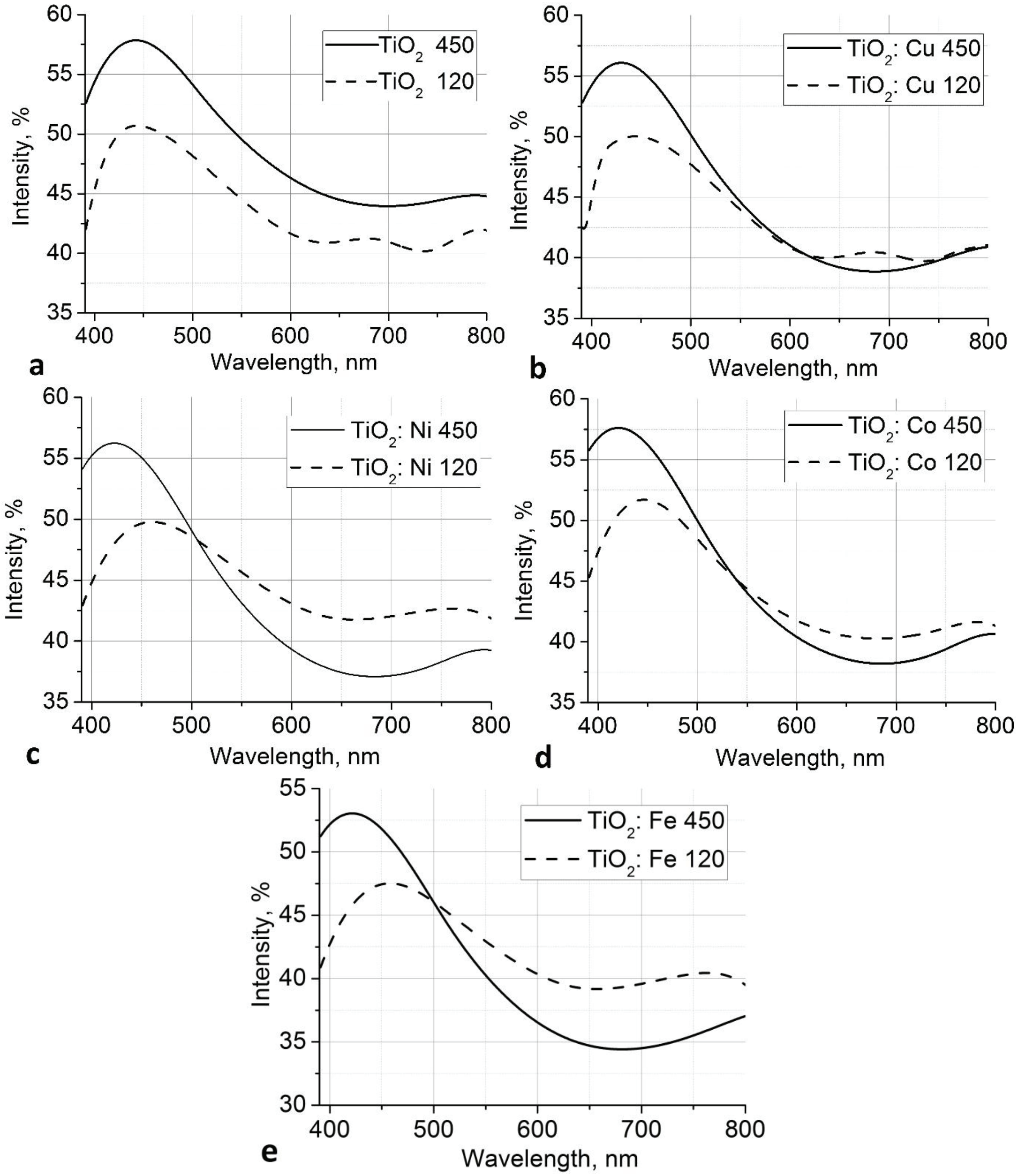

Figure 2: Absorption spectra of samples without nanoparticles (a) and with nanoparticles Cu (b), Ni (c), Co (d), Fe (e) made at annealing temperatures 120°C and 450°C.

A similar behavior of the absorption spectra was observed for silver nanoparticles in [19]. The spectral position of the absorption peaks depended on the diameter of the nanoparticles, the size of which could be varied by changing the annealing temperature and the concentration of the metal particles.

At the edge of the absorption spectrum of the samples, an estimate was made of the width of the forbidden band. The short-wave absorption edge λ of samples in the visible range and the corresponding estimate of the width of the band gap are presented in Table 2.

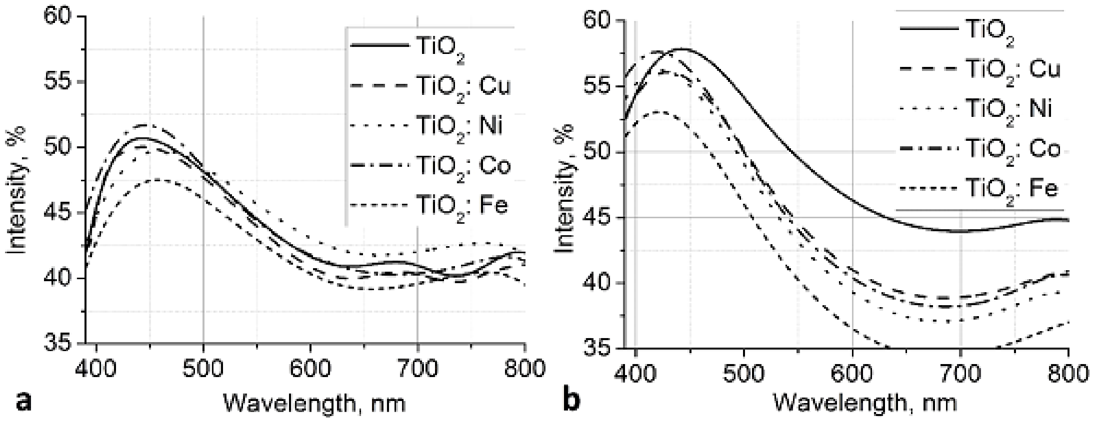

Figure 3: Comparative absorption spectra of samples prepared at annealing temperatures of 120°C (a) and 450°C (b).

Table 2

Sample	Temperature	λ, nm	E, eV
TiO_2	120 °C	444	2,794
	450 °C	442	2,807
TiO_2:Cu	120 °C	443	2,8
	450 °C	429	2,892
TiO_2:Ni	120 °C	461	2,691
	450 °C	423	2,933
TiO_2:Co	120 °C	446	2,781
	450 °C	421	2,947
TiO_2:Fe	120 °C	458	2,709
	450 °C	422	2,94
TiO_2:Au 1%	450 °C	369/619	3,362/2
TiO_2:Au 2%	450 °C	372/593	3,335/2,092

Table 2 shows that the introduction of metal particles into samples annealed at 120°C (amorphous phase of titanium dioxide) leads to a decrease in the width of the forbidden band. All samples of titanium dioxide having anatase phase (annealing temperature 450°C), modified by metals, had a larger bandgap width than samples without impurities.

3. Results

Studies have shown that the introduction of metallic impurities in titanium dioxide leads to a change in its spectral properties. It is shown that the phase structure of the material, determined by the annealing temperature, as well as the modifier type, is an important factor affecting the form of the spectral characteristics. An additional peak appeared in the spectral characteristics of amorphous films in the long-wave region of the spectrum when copper, nickel cobalt and iron were introduced. A similar peak in anatase films was absent.

When gold nanoparticles were introduced into the film, the intensity of the absorption bands and their spectral position changed. A characteristic peak at a wavelength of 600 nm was observed. The appearance of the peak is due, apparently, to the plasmon resonance. The increase in the annealing temperature changed the spectral position of the peak, shifting it into the short-wave region. The shift in the peak and the change in its width are apparently associated with the formation of agglomerates, a change in the size and shape of the particles.

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