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Low Temperature Deposition of Nanocrystalline Titanium Dioxide from Titanium Tetraisopropoxide

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Abstract—Effect of ozone and water vapor on the chemical deposition of TiO_2 from the gas phase in the system of titanium tetraisopropylate–oxygen was examined. Introduction of ozone in the reaction medium was shown to result in the precipitation of smooth TiO_2 layers at 240°C, and the addition of water vapor leads to the formation with higher rate of unconsolidated layers. Adding ozone to the reaction medium with low moisture content (up to 0.65 Pa) allows obtaining at temperatures 250–350°C with high rate of growth the TiO_2 layers with the anatase nanocrystals of high photocatalytic activity.

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Thin films of titanium dioxide are widely used as active layers in gas sensors, photocatalytic coatings, dielectric films of different functionality, in the products of microelectronics and engineering microsystems. The process of chemical vapor deposition from gas phase is the most widely used for obtaining the high quality TiO_2 layers. The use of organometallic reagents, including titanium tetraisopropylate, allows the preparation of nanocrystalline film of TiO_2 at relatively low temperatures (400ºC) [1]. Nevertheless, the problem of further reducing the temperature of the layers deposition is relevant as its decision can provide a significant extension of the spectrum of heat-sensitive materials suitable for use as substrates, and, above all, the polymeric materials.

In addition to the requirements of low temperature, the technological processes of producing titanium dioxide films must provide the formation of layers with a definite structure, characterized by a predominance of the crystalline phase over amorphous. Just such layers are of most interest for applications in microelectronic devices, creation of the dielectric films with high dielectric premeability constant [2], and for solving ecological tasks, in particular, the creation of photocatalytic coatings that provide an effective decomposition of organic contaminants.

The available published data [3] and the results of the experimental studies performed in our laboratory [4] indicate a possibility of deposition of the titanium dioxide films with inclusions of a crystalline phase from the system titanium tetraisopropylate–O_2–Ar, with a rate higher than 1.5 nm min^{-1} at temperatures above 400ºC. The low rate of chemical reaction, as well as its incompleteness leading to the capture by the growing film of hydrocarbon fragments and, consequently, the formation of low-quality unconsolidate layers, prevents further reducing the temperature of the titanium dioxide deposition from the titanium tetraisopropylate–O_2–Ar system.

In this connection it was interesting to elucidate a possibility of reducing the deposition temperature through application of more efficient oxidant of titanium tetraisopropylate. The most attractive from the practical viewpoint is water vapor–ozone mixture. The published information on the preparation of the titanium dioxide films from the titanium tetraisopropylate–H_2O system is only fragmentary [5, 6], and the use of ozone as an oxidant for titanium tetraisopropylate in the deposition of TiO_2 layer has not practically been studied. On the other hand, there are numerous publications on its effective application for the formation of silicon dioxide layers from silicon compounds [7].

The aim of this work was obtaining on the basis of experimental study the data on the effect of ozone and water vapor additives on the chemical deposition of the titanium dioxide films from the gas phase in the system titanium tetraisopropylate–oxygen.

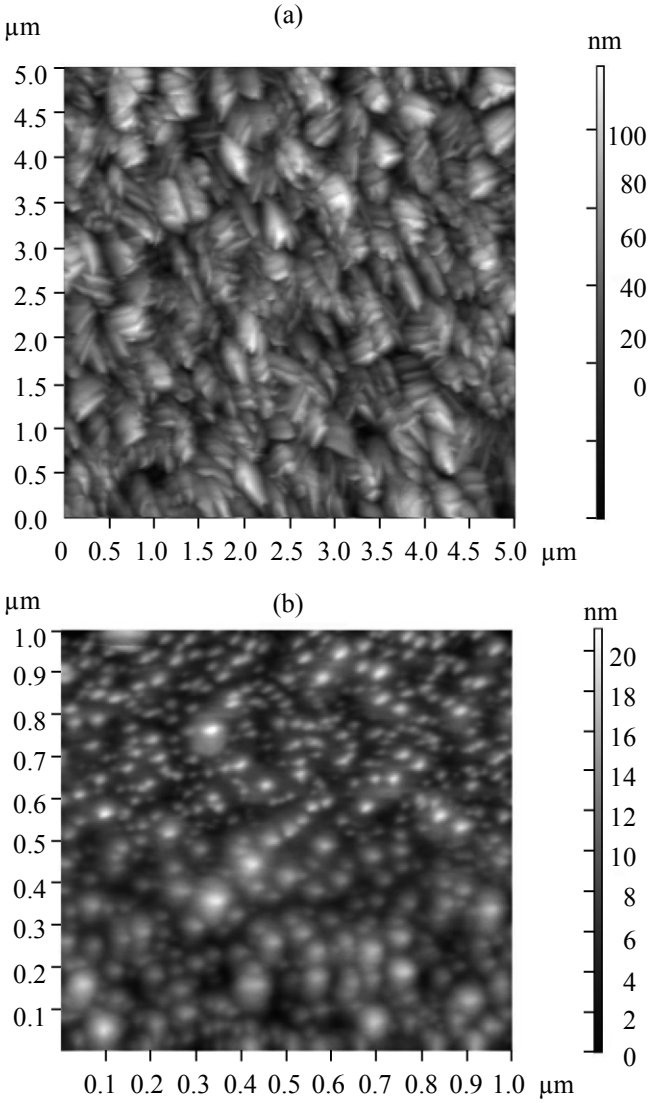

Fig. 1. The resulting AFM image of the surface of films deposited at 320°C in the systems: (a) titanium tetraisopropylate–H_2O–O_2–Ar [$P(H_2O)$ = 6 Pa], (b) titanium tetraisopropylate–O_3–O_2–Ar [$P(O_3)$ = 5.7 Pa].

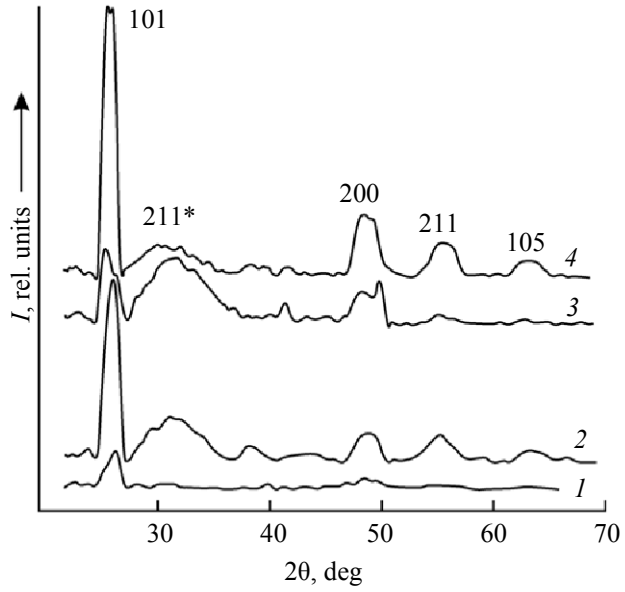

Fig. 2. X-ray films obtained in the system of titanium tetraisopropylate–H_2O–O_2–Ar at a temperature of 320°C, $P(H_2O)$ = 0.65 Pa, $P(O_3)$ = 5.7 Pa with ozone (plot *1*) and without ozone (plot *2*) and in the system of titanium tetraisopropylate–O_3–O_2–Ar at 400°C with $P(O_3)$ = 23 (plot *3*) and without ozone (plot *4*). The figures show Miller indices for anatase, figures with asterisk, for brookite.

The results of experiments with the introduction of water vapor in the amount of 0.65–6 Pa and varying the deposition temperature in the range 220–350ºC at a partial pressure of oxygen and titanium tetraisopropylate 6 kPa and 1.7 Pa showed a sharp increase in the deposition rate. At forming the layers of titanium dioxide in a dry atmosphere at 320ºC the rate of film deposition was of a value of 0.25 nm min^{-1}, and the introduction of even a relatively small amount of water vapor [$P(H_2O)$ = 6 Pa] led to an increase in the deposition rate up to 6 nm min^{-1}. As shown by AFM (Fig. 1a), the layers of titanium dioxide obtained in a humid atmosphere has a columnar structure. The results of X-ray diffraction analysis, presented in Fig. 2 (X-ray 2) indicate the formation of crystals of titanium dioxide primarily with the structure of anatase. The average size of crystals is 5 nm.

The titanium dioxide films obtained in the system of titanium tetraisopropylate–H_2O–O_2 –Ar in the range of technological parameters [at $P(H_2O)$ = 0.65 Pa and deposition temperature 320°C, the surface roughness was 60 nm] were loose and had poor adhesion to silicon substrate, and therefore, were not of the practical interest.

The results of experimental studies on the introduction of ozone into the reaction gas environment showed that the gradual increase in the partial pressure to 40 Pa led to a steady increase in the rate of deposition (Fig. 3, curve *1*). At 320ºC the deposition rate of the titanium dioxide films in the system of titanium tetraisopropylate–O_3–O_2–Ar is about five times higher than the value characteristic of the process based on the oxidation of titanium tetraisopropylate with oxygen. The layers formed at these conditions (Fig. 1) are characterized by smooth

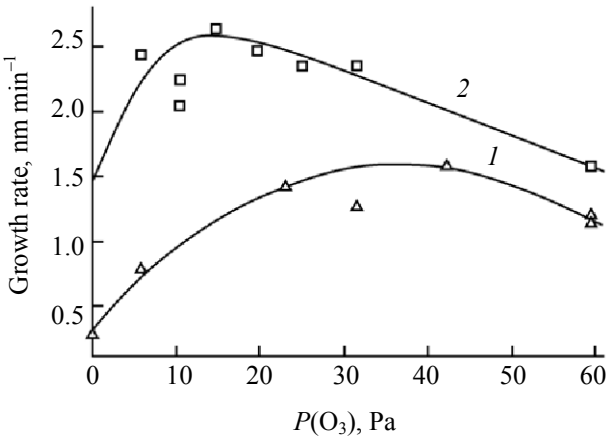

Fig. 3. The dependence of growth rate on the partial pressure of ozone in the systems of (*1*) titanium tetraisopropylate–O_3–O_2–Ar and (*2*) titanium tetraisopropylate–H_2O–O_3–O_2–Ar. Deposition temperature 320ºC, partial pressure of water vapor 0.65 Pa.

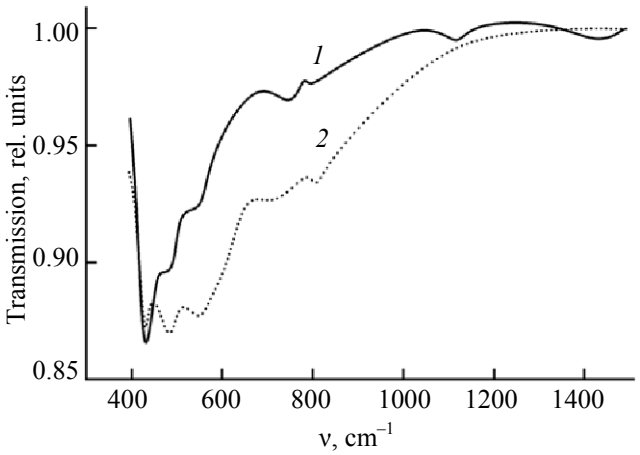

Fig. 4. IR transmission spectra of the films obtained in the system titanium tetraisopropylate–O_3–O_2–Ar at a substrate temperature of 320°C and partial pressure of ozone in the reactor of (*1*) 5.7 and (*2*) 60 Pa.

surface (the roughness was 5 nm) and had good adhesion to the substrate.

Further increase in the partial pressure of ozone up to 60 Pa led to a decrease in the rate of growth, originating from the decrease in content of titanium tetraisopropylate in the reaction gas phase as a result of parallel homogeneous reactions leading to formation of powdered products deposited on the cold walls of the reactor. The role of depletion of gas phase of titanium tetraisopropylate is seen also in the increase of uneven distribution of the film thickness over the substrate area. This change in the film thickness along the surface of the substrate was 5% at $P(O_3)$ = 30 Pa (under conditions of insignificant formation of homogeneous powder) and 50% at $P(O_3)$ = 60 Pa.

The results of examination of the films obtained by means of transmission Fourier infrared spectroscopy showed a change in their structure upon increase in the partial pressure of ozone (Fig. 4). IR spectra of the films deposited at low $P(O_3)$ had pronounced absorption band with a maximum at 435 cm^{-1}, caused, as evidenced by the results of numerous studies [2, 8, 9], by the vibrations of atomic fragments in the anatase nanocrystals. The broad absorption bands in the regions 400–700 cm^{-1} and 700–1000 cm^{-1} are characteristic of amorphous titanium dioxide [9], and, as follows from the data obtained, their intensity grew significantly with an increase in the partial pressure of ozone up to 60 Pa (Fig. 4). Regularities in the change of the intensities of these bands indicate that the films deposited at high concentrations of ozone include large amorphous component. This is confirmed by the results of X-ray diffraction analysis (Fig. 2, cf. plots *3* and *4*). It is interesting to note that there is a correlation between the beginning of intensive amorphization of the deposited layers and the beginning of the mentioned homogeneous formation of an amorphous powder. This relationship probably reflects the changes in the chemical features of the process, consisting in the formation in the gas phase of highly reactive intermediates at higher partial pressures of ozone, characterized by a short "lifetime" and therefore not able to participate in the surface processes of the crystalline phase formation.

The temperature dependence of the titanium dioxide deposition in the system titanium tetraisopropylate–O_3–O_2–Ar (ozone partial pressure 23 Pa) is nonmonotonic (Fig. 5). In the temperature range 230–350ºC the deposition rate increases exponentially (the apparent activation energy is 5.7 kJ mol^{-1}), and then decreases with increase in the deposition temperature. Earlier studies [10] showed that in a flow system ozone suffers a noticeable decomposition at the temperatures above 150ºC, and is completely decomposed at 300ºC. Despite the use of a reactor with cold walls, near the surface of the substrate there is a thermal boundary layer, in which the temperature of the gas phase changes from the temperature of the substrate to room temperature, and where the decomposition of ozone occurs. Decomposition of ozone is accompanied by the formation of highly reactive atomic oxygen, which, apparently, reacts

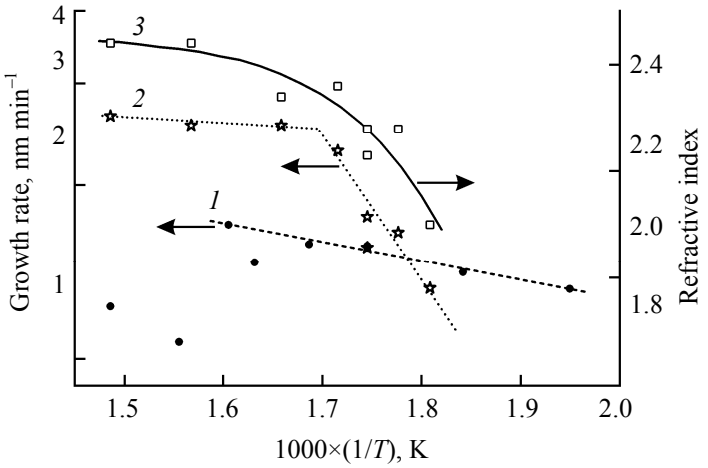

Fig. 5. The dependence on the substrate temperature: (*1*) of growth rate of layers deposited in the titanium tetraisopropylate–O_3–O_2–Ar; (*2*) of growth rate, and (*3*) of refractive index of layers deposited in the titanium tetraisopropylate–H_2O–O_3–O_2–Ar system.

rapidly with titanium tetraisopropylate that leads to the formation of homogeneous powdered products, as well as to the marked uniformity in the thickness of the deposited film over the area of the substrate at the temperatures above 350ºC.

The results of transmission Fourier infrared spectroscopy showed an increase in the contribution of anatase crystalline phase, resulting in an increased intensity of the absorption band with the maximum at 435 cm^{-1} when temperature of titanium dioxide deposition increases.

It is important, that these results demonstrate a possibility of obtaining at a temperature 320ºC the titanium dioxide films with a growth rate 1.4–1.6 nm min^{-1} (approximately 5 times higher compared with the titanium tetraisopropylate–O_2–Ar system at 320ºC) with good adhesion to the substrate.

In connection with the fact that the layers obtained at low temperatures in the system of titanium tetraisopropylate–O_2–Ar with ozone have an amorphous structure, and that the introduction of water vapor in the system initiates intensive formation of the anatase crystalline phase, it was of interest to study the influence of simultaneous addition of ozone and water vapor on the process of titanium dioxide deposition. Taking into account the results obtained in the system of titanium tetraisopropylate–H_2O–O_2–Ar, we performed respective experiments at a sufficiently low partial pressure of water vapor, 0.65 Pa.

Figures 2, 3 show the dependence of the titanium dioxide deposition in the titanium tetraisopropylate–O_3–H_2O–O_2–Ar system on the ozone partial pressure. The comparison of these results with the data for the system of titanium tetraisopropylate–O_3–O_2–Ar shows that the introduction of water vapor has no significant effect on the nature of the process, the graph also is represented by a curve with a peak, but approximately 2.5-fold increase in the deposition rate occurs.

According to X-ray diffraction analysis (Fig. 2) and IR spectroscopy, the change in the structure of films with the concentration of ozone is also similar in the examined systems. In the presence of water vapor, addition of ozone in the reaction gas phase leads to a decrease in the fraction of nanocrystalline anatase.

The results of X-ray photoelectron spectroscopy of the films obtained in this series of experiments showed that their compositions correspond to stoichiometric titanium dioxide within the error of analysis. No changes were detected in the chemical state of titanium atoms and oxygen at varying the partial pressure of ozone. The composition stability is evidenced indirectly also the constancy of the refractive index of the deposited layers, falling in the range of 2.3–2.35.

The results of the temperature dependence of film growth rates in the system of titanium tetraisopropylate–O_3–H_2O–O_2–Ar [for $P(O_3)$ = 5.7 Pa] built in the Arrhenius coordinates, showed the presence of a fracture at 320°C, separating the two areas characterized by different values of the apparent activation energy, 50 and 2.3 kJ mol^{-1} (Fig. 5).

As shown by transmission infrared spectroscopy, in the transmission spectra of the films obtained at

temperatures below 330°C an absorption band is present characteristic of amorphous phase and of nanocrystalline anatase. In the spectra of films deposited at temperatures above 360°C, more substantial intensity had only the absorption band with a peak at 435 cm^{-1} belonging to the anatase nanocrystals. Thus, the detected inflection on the temperature dependence graph corresponds to the temperature range in which there is a significant change in the relative amounts of amorphous and nanocrystalline phases formed in the titanium dioxide layer. Regularities in the change of the film structure with the deposition temperature is confirmed by a simultaneous increase in the refractive index of the films (Fig. 5) from the value 2.1 (at 280°C) to 2.45 (for 365 and 400°C), that is close to the value characteristic of anatase, 2.49 [E||c] and 2.56 [E$\perp$c] [11].

The results of the investigations carried out with the titanium tetraisopropylate–O_3–H_2O–O_2–Ar system showed that small additions of water vapor allow to obtain dense smooth titanium dioxide film having good adhesion to silicon substrate, with a deposition rate approximately 2.5 times greater than in the system of titanium tetraisopropylate–O_3–O_2–Ar. Significant increase in the proportion of nanocrystalline anatase phase in the material does not occur.

For some of deposited samples their photocatalytic activity was evaluated. Measurements showed that the degree of crystallinity is not the sole factor determining the effectiveness of the catalyst. For example, the rate of removal of the glycerol film by ultraviolet radiation from the surface of titanium dioxide layer consisting mainly of amorphous phase was 0.9 nm min^{-1}, while that of the layer composed mainly of nanocrystalline anatase phase was 0.65 nm min^{-1}. Obviously, the photocatalytic activity is determined also by the value of specific surface and the structure of pores of the titanium dioxide layer. The obtained values of the rate of removal of organic contamination from the surface indicate a high catalytic activity of titanium dioxide films deposited in the investigated reaction systems.

The results of performed experimental studies showed that the introduction of water vapor and ozone in the reaction system of titanium tetraisopropylate–O_2–Ar leads to a significant increase in the rate of titanium dioxide deposition. The presence of ozone in the reacting medium allows the preparation of smooth layers of titanium dioxide even at 240°C, and the addition of water vapor leads to the formation with higher rates of loose polycrystalline layers easily removable mechanically from the substrate surface. It is found that the addition of ozone into the reaction medium containing a small amount of water vapor (up to 0.65 Pa) allows to obtain at temperatures 280–350°C with relatively high rate of growth the titanium dioxide layers containing inclusion of nanocrystalline anatase phase, having low roughness, good adhesion to the substrate, and high photocatalytic activity.

EXPERIMENTAL

The deposition was carried out at atmospheric pressure in flow-type vertical quartz reactor with cold walls (diameter 84 mm, height 330 mm). The silicon substrates [KEF 4.5 (111)] were placed perpendicular to the flow on a resistively heated pedestal of 50 mm diameter located 45 mm from the point of mixing of reagents. The total gas mixture expenditure was 2.5 l min^{-1}. Argon (dew point –110°C) was used as carrier gas and diluent for the titanium tetraisopropylate vapor. The partial pressure of oxygen (dew point –52°C) in all experiments was 6 kPa, of titanium tetraisopropylate 1.7 Pa. The partial pressure of ozone, synthesized from oxygen in an ozonator operating through the dielectric barrier discharge, was varied in the range of 0–60 Pa. The partial pressure of water vapor was varied in the range of 0.65–6 Pa. The partial pressure of water vapor in the experiments in which it was not specifically indicated did not exceed 0.25 Pa, which corresponded to the residual amount of moisture in specially dried technological gases. Deposition temperature ranged from 40 to 400°C. Deposition time ranged from 30 min to 2 h.

The X-ray phase analysis of the film obtained was performed on a Bruker D8 Advance X-ray diffractometer (detector LynxEye, radiation CuK_α). The size of coherent scattering areas (in this case the nanocrystal size) was calculated by the Scherrer model with a profile analysis of the whole diffraction pattern, and refinement of the crystal structure was performed with the Rietveld method, using the program DIFFRACplus TOPAS. The film composition was determined using X-ray photoelectron spectroscopy (analytical processing unit NANFAB-25, "NT-MDT"), as well as using transmission Fourier infrared spectroscopy (FSM 1201, "Monitoring" company). In addition, atomic force microscopy (AFM) (Solver-PRO, "NT-MDT") was used to study the surface topology of layers and the thickness and refractive indices of the films was determined by ellipsometry

(LEF-752, λ = 632.8 nm). Photocatalytic activity of the deposited films was estimated from the rate of oxidation of a glycerol film of about 40 nm thickness, applied on the silicon substrate with a preliminary deposited titanium dioxide film. To activate the process was used an ultraviolet lamp DDS-30 (continuum of 195–385 nm, power 30 W). The distance between the working window of the lamp and the sample was 7 mm. The rate of degradation of the glycerol layer was determined using infrared absorption spectroscopy by measuring the change in the intensity of the absorption band with a peak at 3370 cm^{-1}.

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