ISSN 1070-3632, Russian Journal of General Chemistry, 2013, Vol. 83, No. 8, pp. 1596–1600. © Pleiades Publishing, Ltd., 2013.
Original Russian Text © M.V. Baryshnikova, S.E. Aleksandrov, L.A. Filatov, A.B. Berberov, 2013, published in Zhurnal Obshchei Khimii, 2013, Vol. 83, No. 8, pp. 1367–1371.

FROM MATERIALS OF ALL-RUSSIAN CONFERENCE "CHEMISTRY OF SURFACE AND NANOTECHNOLOGY"

Kinetic Rules of Precipitation of Thin Films of Titanium Dioxide from the Gas Phase Containing Titanium Tetraisopropylate

M. V. Baryshnikova, S. E. Aleksandrov, L. A. Filatov, and A. B. Berberov

St. Petersburg State Polytechnical University, ul. Politekhnicheskaya 29, St. Petersburg, 195251 Russia
e-mail: BaryshnikovaMarin@gmail.com

Received December 27, 2012

Abstract—Precipitation of titanium dioxide layers from the gas phase in the reaction system containing titanium tetraisopropylate and oxygen at the total pressure 1 kPa is studied. It is shown that in the range of 300–500°C the precipitation proceeds in the kinetic regime and is accompanied by the formation of layers of monotonous thickness containing nanocrystalline phases of anatase and rutile. In the temperature range 300–350°C the activation energy value was 92.7 kJ mol^{-1}, and at higher temperatures (up to 500°C) it decreased to 17.5 kJ mol^{-1}. The increase in the precipitation temperature caused the increase in relative amount of rutile in the precipitated layers.

DOI: 10.1134/S1070363213080215

Wide interest to the preparation of thin films of titanium dioxide is connected with the possibility of their use as functional layers in the gas sensors, catalysts, MOP-transistors, and some other systems and devices [1–4].

Among various methods of formation of titanium dioxide layers a special interest presents chemical precipitation from the gas phase using organometallic reagents. It permits to obtain layers of high quality on the complex-form objects at comparatively low temperatures (below 400°C [5]).

Results of our previous studies of chemical precipitation of titanium dioxide layers from the gas phase carried out at atmospheric pressure and based on the reaction of titanium isopropylate with oxygen and ozone [6] showed that thickness of the layers formed on the substrate surface is not monotonous. Besides in all temperature range under investigation proceeding of the gas phase homogenic reactions leading to precipitation of powder on the walls of the reactor was observed.

As known, performing of the process at reduced pressures in some cases, especially when the process may occur in the kinetic regime, permits achieving a high evenness of thickness on the surface of the substrate. Besides, the decrease in the partial pressure of reagents permits to decrease significantly the rate of homogenic side reactions.

The aim of this work is the investigation of rules of chemical precipitation of titanium dioxide layers from the gas phase in titanium isopropylate–O_2–Ar system carried out at reduced pressure.

Results of experimental studies of precipitation of thin TiO_2 layers showed that at total pressure 1kPa the coatings of monotonous thickness on the substrate are formed. Variation of thickness of layers on the substrate with the diameter of 30 mm was no more that 10%. The noticeable precipitation begins at 300°C, and at the temperature rise to 350°C the rate of growth of the titanium dioxide layers increases exponentially from 0.15 nm min^{-1} to 1.2 nm min^{-1} (Fig. 1). The value of the apparent activation energy is 92.7 kJ mol^{-1}. In the temperature range 360–500°C the rate of

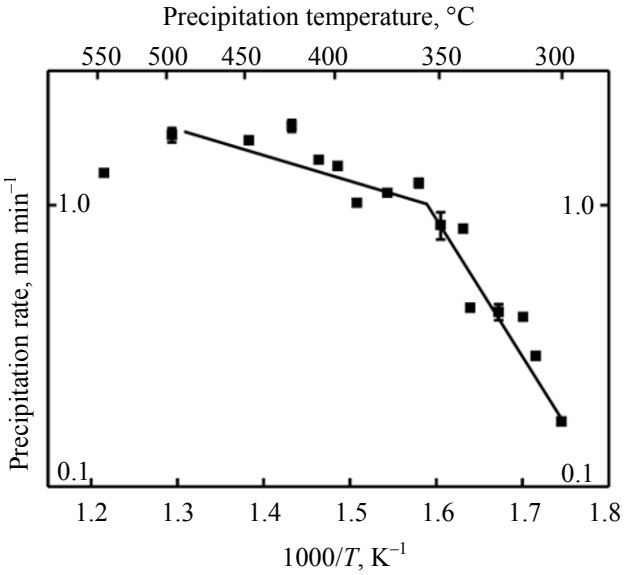

Fig. 1. Temperature dependence of precipitation rate of thin films of titanium dioxide in the system titanium tetraisopropylate–O_2–Ar at the total pressure 1 kPa.

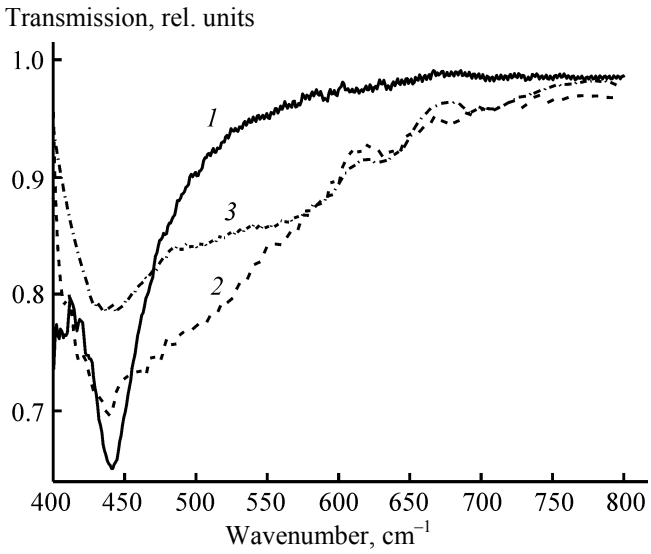

Fig. 2. IR absorption spectra of titanium dioxide films obtained at, °C: (*1*) 315, (*2*) 450, and (*3*) 500.

precipitation also increases according to the rule close to exponential to 1.8 nm min^{-1}, and the corresponding value of the apparent activation energy is 17.5 kJ mol^{-1}.

The precipitation on the substrate of silicon, gallium arsenide, glass, and ceramic showed that in all temperature range under study the mass rate of growth of layers depended on the material of substrate having the same roughness (see the table). The established differences exceeded the error of evaluation of precipitation rate (no more than 10%) indicating the kinetic character of the process at all temperatures studied.

The data of the absorption IR spectroscopy demonstrate the variation of the phase composition of precipitated layers with temperature (Fig. 2). The spectra of films obtained in all temperature range under study contain the intense absorption band at 435 cm^{-1}. On the basis of comparison of X-ray diffraction data and the IR absorption spectra of specially prepared nanostructured titanium dioxide films having anatase structure [7] it was shown that the appearance of such absorption band is characteristic of only nanocrystalline phase of anatase. In the spectra of titanium dioxide layers obtained at the temperatures above 350°C the increase of absorption in the range 450–600 cm^{-1} took place. It was probably caused by the vibration of groups consisting of the titanium and oxygen in the rutile structure [7, 8] (Fig. 2, curves *2, 3*). The intensity of the absorption band with the maximum at 435 cm^{-1} decreased with the increase in the precipitation temperature while the absorption in the range 500–600 cm^{-1} increased.

Results of the IR spectroscopy data of layers show that they consist mainly of the nanocrystalline anatase phase. Its relative amount decreases with the increase in the precipitation temperature, and beginning from the temperatures about 350°C when the break on the plot of the precipitation rate is observed, a gradual increase in the amount of titanium dioxide having the rutile structure takes place. Considering the fact that precipitation in all temperature range under study proceeds in kinetic regime, it can be suggested that the break on the plot of the temperature dependence of the precipitation rate of layers (Fig. 1) and the corresponding change in the apparent activation energy are caused probably by the change in the phase composition of layers.

Mass rate of precipitation of TiO_2 (μg cm^{-2} min^{-1}) on the substrates of different materials

T, °C	Silicon	Gallium arsenide	Glass	Ceramics
320	0.23	0.29	0.16	0.27
350	0.29	0.30	0.25	0.36
400	0.35	0.37	0.28	0.32
450	0.41	0.51	0.39	0.54

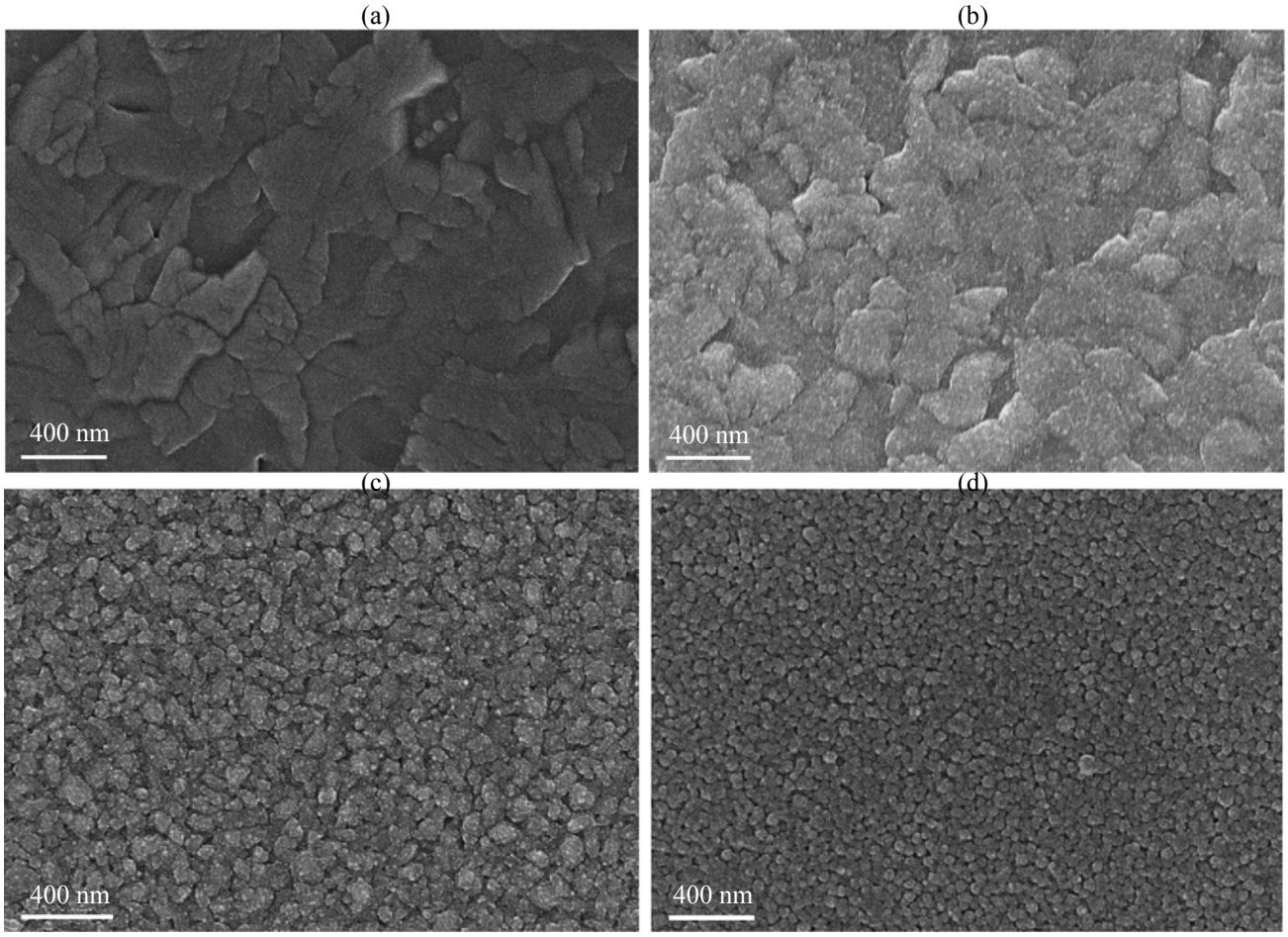

Fig. 3. Zebra-stripe electron microphotographs of thin layers of titanium dioxide obtained in the titanium tetraisopropylate–O_2–Ar system at, °C: (a) 315, (b) 350, (c) 400, and (d) 500.

Results of investigation of surface morphology of the layers obtained also confirm the presence of the significant changes in the structure of layers at the increase in the precipitation temperature above 350°C . The samples obtained in the temperature range 315–350°C are large-block agglomerates (Figs. 3a, 3b) characterized by linear dimensions 300–600 nm which are formed from smaller particles with the dimensions about 30 nm. Layers of titanium dioxide precipitated at higher temperatures consisted from tightly packed grains (Figs. 3c, 3d) with the characteristic dimensions of several tens of nanometers (e.g. 40 nm in the case of precipitation at 500°C). They also consisted of smaller nanoparticles with the dimensions up to 10 nm.

With the purpose of more detailed investigation of the rules of formation of titanium dioxide layers in the initial stages we studied the effect of duration of precipitation on the rate of precipitation and the morphology of obtained product. In Fig. 4 the dependence of specific mass of precipitating substance at 315°C on the duration of the process is shown. From the presented data it follows that the rate of precipitation in the range 20-140 min is a stationary value.

The investigation of the morphology of surface of the titanium dioxide layers by the atomic force microscopy showed that just after 20 min of precipitation separate grains with the dimensions about 60 nm were formed. Their amount gradually increased, and after 45 min their density reached 1.2–1.5 μm^{-2}. Separate grains acquired “faces” (Fig. 5a) and later formed the pyramid-like structures (Fig. 5b). A detailed consideration of these structures showed that they consisted of separate particles having 20 nm in diameter. At the increase in the duration of the process the growth in height and breadth was observed, but the amount of seeds increased insignificantly. Beginning

from the 90 min of duration joining of the grown pyramid-like formations is observed, and the growth proceeds only in the direction normal to the substrate (Fig. 5c). Basing on the obtained data (Fig. 4) it may be suggested that the process is characterized by incubation period (about 20 min) necessary for the appearance of titanium dioxide seeds. For checking this assumption the surface of the silicon substrate after performing the process in the course of 10–15 min were studied.

Results of the atomic force microscopy of the surface of the samples obtained in the course of 10 min showed that it contained two-dimensional clusters with the up to 1 nm height with the vacancies between them (Fig. 5d). Dimensions of clusters increased in time while the area of vacancies decreased. About 20 min of duration of the process joining of clusters was observed (Fig. 5e). Results of the IR absorption spectroscopy of samples showed that anatase, rutile, and probably the amorphous phase were present in the films. The obtained data show that the formation of titanium dioxide layers at low precipitation temperatures proceeds according to the Stranski–Krastanow mechanism [9] when in the initial stage the formation of superthin monotonous two-dimensional layer takes place. After covering all the surface of substrate with this layer the above-described growth

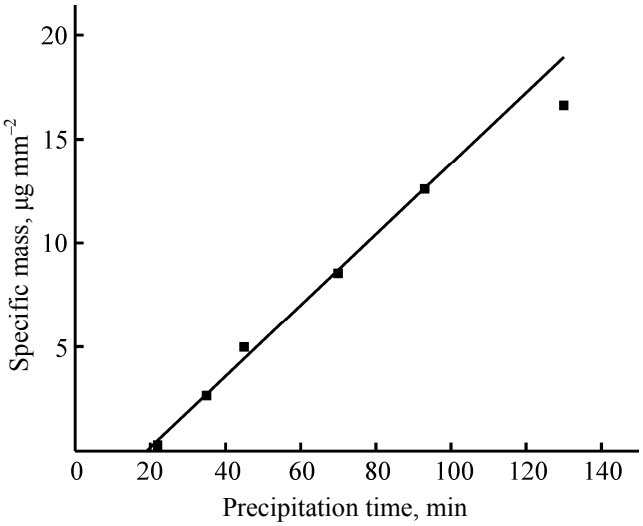

Fig. 4. Dependence of mass of the precipitated titanium dioxide on the precipitation time in the titanium tetraisopropylate–O_2–Ar system.

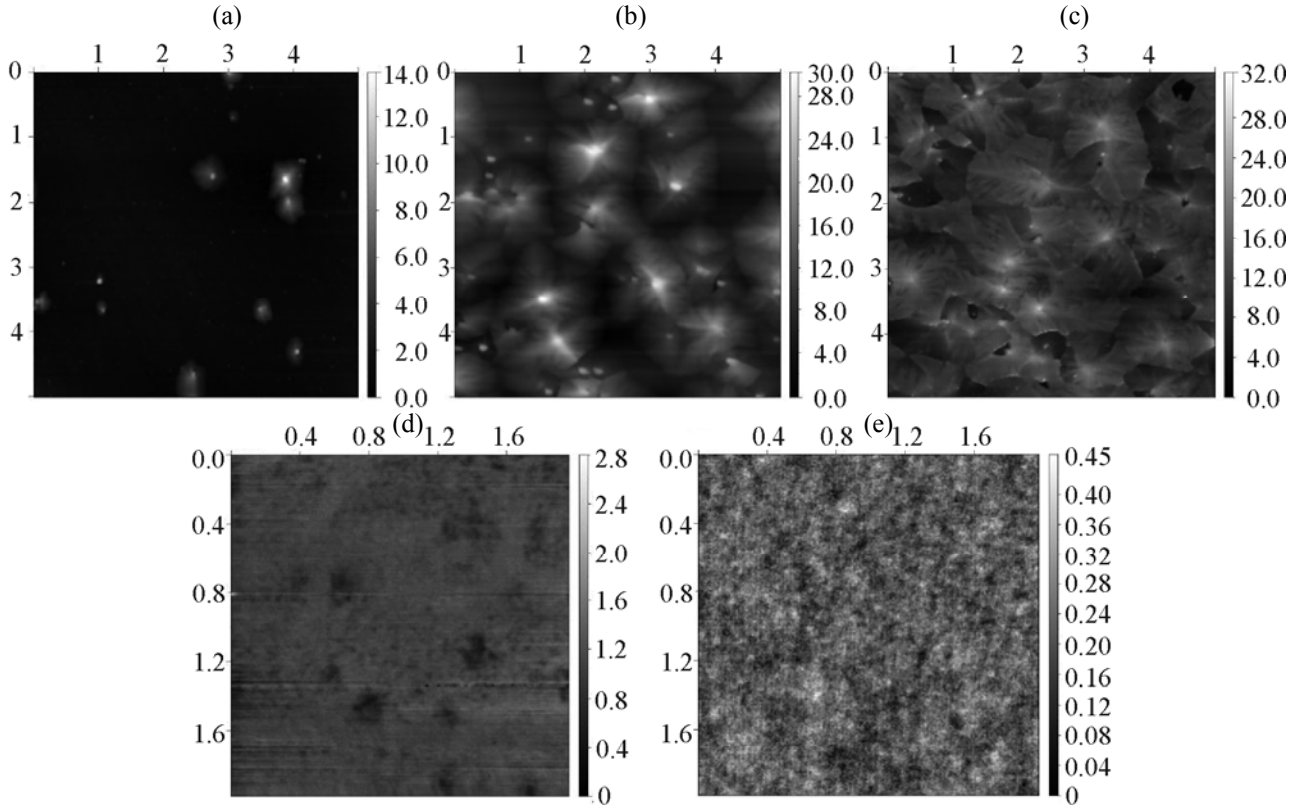

Fig. 5. Images of surface of growing film of titanium dioxide at the precipitation temperature 315°C [(a) 45 min, (b) 60 min, (c) 90 min, (d) 10 min, and (e) 22 min] obtained by means of atomic force microscopy.

from separate voluminous grains begins (Fig. 5a). Results of the performed studies showed that in titanium tetraisopropylate–oxygen system at 1 kPa total pressure beginning from 300°C monotonous layers of titanium dioxide containing nanocrystalline phases of anatase and rutile were formed. In the temperature range 300–350°C the value of activation energy was 92.7 kJ mol^{-1}. The increase in the precipitation temperature to 500°C caused the decrease in the activation energy to 17.5 kJ mol^{-1} and the increase in relative amount of rutile.

Studies of the initial stages of formation of titanium dioxide films at precipitation temperature 315°C showed that the formation of films proceeds according to the Stranski–Krastanow mechanism. In the course of first 20 min the formation of superfine two-dimensional layer with smooth surface takes place. After covering of all surface of the substrate with this layer the growth of titanium dioxide from the separate bulky grains begins. In the course of time they form the pyramid-like structures. In the duration interval 20–140 min the precipitation rate of TiO_2 is a constant value.

EXPERIMENTAL

Precipitation was carried out at 1 kPa in the vertical flow-type quartz reactor with cold walls (diameter 84 mm, 330 mm height). Substrates of silicon of KEF4.5 grade (100), of gallium arsenide (100), of glass and ceramics were placed perpendicularly to the flow on the resistively heated steel pedestal of the diameter of 50 mm. The reagents were fed separately and mixed at a distance of 30 mm above the substrate. Argon was used as diluent and the carrier gas. Total flow of gas mixture in all experiments was 500 ml min^{-1}. The partial pressure of titanium tetraisopropylate was maintained constant, 0.04 Pa, the pressure of oxygen 300 Pa. The precipitation was carried out in the range of substrate temperature 300–500°C.

The structure and composition of films was studied by the absorption Fourier IR spectroscopy (FSM 1201, OOO "Monitoring"). The thickness and refraction index of films were evaluated by ellipsometry (LEF-752, λ 632.8 nm). For the evaluation of mass of the precipitated material a procedure was used basing on the measurement of the intensity of the characteristic line of titanium in the X-ray fluorescence spectrum (Spectroscan MAKS-GV spectrometer, OOO NPO "Spektron"). The morphology of the surface of the obtained films was analyzed by means of zebra-stripe electron microscopy on a Supra 55 VP instrument and the atomic force microscopy on a Solver-PRO "NT-MTD" installation.

ACKNOWLEDGMENTS

The work was carried out within the frames of the Federal Targeted Program "Scientific and scientific-pedagogical stuff of innovation Russia" (2009–2013) with the financial support of Ministry of Education and Science of the Russian Federation (contract 14.B36.21.2062, theme "Obtaining of nanodisperse powders, foliated nanomaterial, ferrite films of different composition, investigation of properties of the materials obtained").

REFERENCES

1. Depero, L.E., Ferroni, M., Giudi, V., Marca, G., Martinelli, G., Nelli, P., Sangaletti, L., and Sberveglieri, G., *Sensors and Actuatirs, B.,* 1996, nos. 35–36, p. 381.
2. Pore, V., Rahtu, A., Leskela, M., Ritala, M., Sajavaara, T., and Keinonen, J., *Chem. Vap. Deposition*, 2004, vol. 10, no. 3, p. 143.
3. Xie, Q., Deduytsche, D., Schaekers, M., Caymax, M., Delabie, A., Qu, X.-P., and Detavernier, C., *Appl. Polym. Lett*., 2010, no. 97, p. 112905.
4. Gratzel, M., *J. So–-Gel Sci. Technol*., 2001, no. 22, p. 7.
5. Taylor, C.J., Gilmer, D.C., Colombo, D.G., Wilk, G.D., Campbell, S.A., Roberts, J., and Gladfelter, W.L., *J. Am. Chem. Soc*., 1999, vol. 121, p. 5220.
6. Aleksandrov, S.E., Filatov, L.A., Baryshnikova, M.V., and Andreeva, V.D., *Zh. Obshch. Khim*., 2010, vol. 80, no. 6, p. 1015.
7. Jogi, I., Pars, M., Aarik, J., Aidla, A., Laan, M., Sundqvist, J., Oberbeek, L., Heitmann, J., and Kukli, K., *Thin Solid Films*, 2008, vol. 516, p. 4855.
8. Busani, T. and Devine, R.A.B., *Semicond. Sci. Technol*., 2005, vol. 20. p. 870.
9. Stranski, I., Krastanow Von, L., *Akad. Wiss. Lit. Mainz Math.-Natur. Kl. IIb*, 1939, vol. 146, p. 797.