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Atomic Layer Deposition of the Titanium Dioxide Thin Film from Tetraethoxytitanium and Water

A. P. Alekhin, G. I. Lapushkin, A. M. Markeev, A. A. Sigarev, and V. F. Toknova

Moscow Physico-Technical Institute, Institutskii per. 9, Dolgoprudnyi Region, Moscow oblast, 141700 Russia
e-mail: amarkeev@mail.mipt.ru

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Abstract—Using the methods of Rutherford backscattering spectrometry, X-ray photoelectron spectroscopy, X-ray diffraction in the geometry of the grazing beam, and Fourier transform infrared spectroscopy, we studied the chemical composition and structure of thin films of titanium dioxide formed by atomic layer deposition from tetraethoxytitanium and water. It is shown that the films obtained are characterized by a high stoichiometry of composition and by amorphous or polycrystalline structure of the anatase modification, depending on the number of reaction cycles. Using a model of the process of atomic layer deposition that takes into account the size and number of ligands of the reacting molecules, we calculated the amount of titanium dioxide deposited in a single reaction cycle.

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Titanium dioxide films because of their attractive properties such as high refractive index, high dielectric constant, the ability to photocatalytic effects, and bioactivity, are of great interest for the application in optical coatings, electronic storage devices, solar cells, for the creation of new biomaterials, and in the photocatalytic coatings for self-cleaning surfaces.

The method of atomic layer deposition attracts attention of researchers [1–3], in particular, for obtaining the titanium dioxide thin films using titanium-containing reagents: titanium tetrachloride, titanium tetraiodide, and isopropoxytitanium [1]. Several less studied processes use tetraethoxytitanium as a titanium-containing reagent [4, 5]. The latter, like the isopropoxytitanium, is related to the group of alkoxides, but has a higher temperature of thermal decomposition, which in principle allows to realize the atomic layer deposition process in a wider temperature range. In the studies of the atomic layer deposition in the $Ti(OC_2H_5)_4$–H_2O system an insufficient attention has been paid to the integrated approach to the studying both the chemical composition and crystal structure of titanium dioxide formed depending on the number of reaction cycles, particularly in the early stages of the growth. Also in this system the problems of theoretical simulation of the process of the atomic layer deposition of TiO_2 were not adequately investigated [4].

Thus, the purpose of this study was the investigation of the chemical composition and structure of TiO_2 films using a wide range of techniques such as Rutherford ion backscattering, X-ray photoelectron spectroscopy, ellipsometry, X-ray diffraction, Fourier infrared spectroscopy (FT–IR), atomic force microscopy (AFM), as well as the theoretical calculation of TiO_2 growth per cycle at atomic layer deposition from the $Ti(OC_2H_5)_4$–H_2O system.

Investigations of the obtained titanium dioxide films by ellipsometry showed that their refractive index increases with increasing number of cycles from 2.3 (at $n < 400$) to 2.5 (at $n > 400$). The method of ellipsometry showed also that the obtained films are characterized by the relatively high thickness uniformity. The standard deviation of thickness over a 100 mm silicon wafer did not exceed 3%. These studies also showed that the amount of titanium dioxide deposited in one reaction cycle does not depend on the number of cycles and amounts to ~0.05 nm per cycle. Taking into account the fact that the $Ti(OC_2H_5)_2$ can decompose at a temperature of 250°C also to form TiO_2, in order to estimate the contribution of thermal decomposition of $Ti(OC_2H_5)_2$ in the atomic layer deposition process, an experiment on growing TiO_2 film was carried out at the feed of $Ti(OC_2H_5)_2$ to the reactor by 4000 pulses without

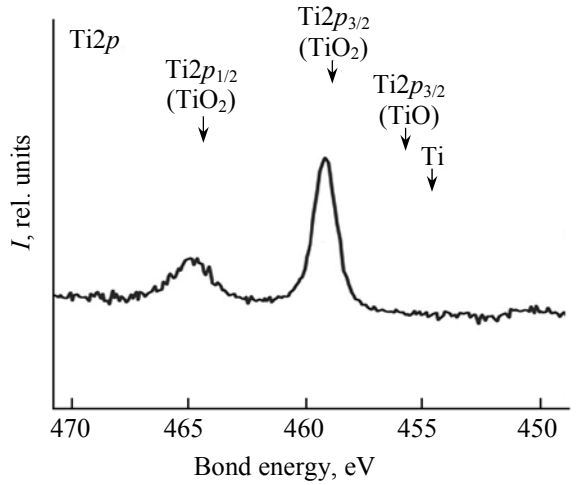

Fig. 1. X-ray photoelectron spectrum of the TiO_2 films on silicon wafer obtained for 1000 of reaction cycles.

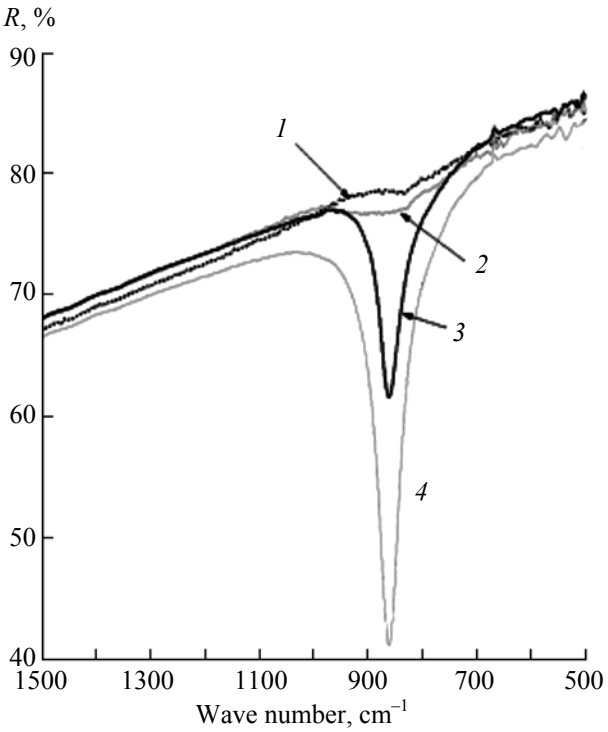

Fig. 2. FT–IR spectra measured in the geometry of reflection from the titanium substrate (*1*) before and after atomic layer deposition of TiO_2: (*2*) 200 cycles, (*3*) 400 cycles, and (*4*) 1200 cycles.

pulses of water. In this case the amount of titanium dioxide deposited in one cycle was 0.005 nm per cycle, that is, taking into account the contribution of the thermal decomposition of $Ti(OC_2H_5)_2$, the quantity of titanium dioxide Δh deposited in one reaction cycle by the atomic layer deposition mechanism (exchange of ligands between $Ti(OC_2H_5)_2$ and surface OH groups [1]) is ~0.045 nm per cycle.

Analysis of the films by the method of Rutherford ion backscattering showed that the ratio of the numbers of oxygen and titanium amounts to $N_O/N_{Ti} = 2\pm0.1$ in the entire range n of reaction cycles. The error of this method is ~5%, hence the stoichiometric composition of the films obtained by the atomic layer deposition is consistent with the titanium dioxide composition with a sufficiently high accuracy.

The chemical state of atoms in the films of titanium oxide was investigated by means of X-ray photoelectron spectroscopy. The analysis of the X-ray photoelectron spectroscopy data showed that in the spectra of the films obtained by the atomic layer deposition in the whole range of n the position of Ti2p peaks corresponded to the titanium degree of oxidation Ti^{4+}, and there are no peaks corresponding to intermediate degree of oxidation (Fig. 1). Thus, based on the data of Rutherford ion backscattering and X-ray photoelectron spectroscopy analysis, we can conclude that the titanium oxide film obtained by atomic layer deposition by the elemental composition and chemical state corresponds to titanium dioxide.

Study by Fourier transform infrared spectroscopy and X-ray diffraction showed that the structure of the obtained TiO_2 films depends on the number of reaction cycles n. Thus, Fig. 2 shows FT–IR spectra measured in the geometry of reflection from the titanium substrate before (curve *1*) and after (curves *2–4*) the TiO_2 atomic layer deposition. It is seen that in the spectra of the titanium substrate (curve *1*) and of TiO_2 deposited for 200 cycles (curve *2*) there is a broad band of absorption in the range 700–1000 cm^{-1} corresponding to amorphous titanium dioxide [5]. The increase in the number of cycles to a value of $n > 400$ leads to the appearance in the FT–IR spectra of a sharp absorption peak at 870 cm^{-1}, corresponding to the crystalline titanium dioxide with anatase structure [5] (curves *3, 4*). According to the data of FT–IR spectroscopy, similar transfer from an amorphous structure to polycrystalline anatase was observed at the increase in the number of cycles for the films obtained by atomic layer deposition on silicon substrates.

The appearance of the polycrystalline anatase structure in the deposited layer with an increase in the number of cycles is confirmed by the X-ray diffraction data (Fig. 3).

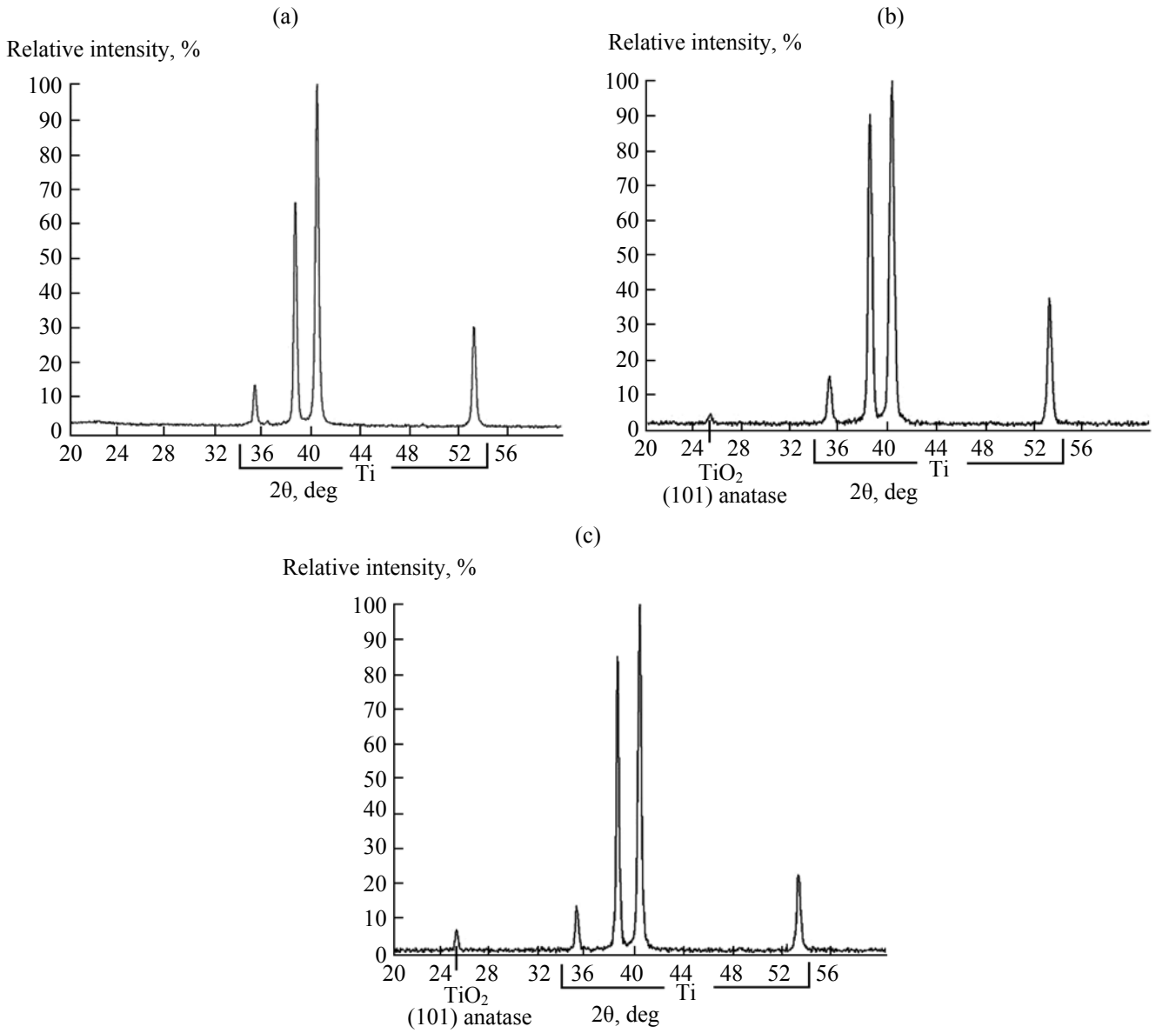

Fig. 3. X-ray diffractograms measured from the TiO_2 films on titanium substrate obtained by atomic layer deposition for (a) 200 cycles, (b) 600 cycles, and (c) 1200 cycles.

Polycrystalline films of titanium dioxide obtained by atomic layer deposition at $n > 400$ is seen also in their atomic force microscopy (AFM) images, in contrast to the films obtained by atomic layer deposition at $n < 400$ (Fig. 4). The size of the observed crystallites or their conglomerates in the horizontal plane increases with increasing film thickness, reaching ~0.5 μm at the 1000 cycles of deposition. Average roughness of the films also increases with the number of cycles, reaching 1.6 nm, 3.1 nm, and 9.3 nm at n = 500, 1000, and 2000 cycles, respectively.

Several models of the atomic layer deposition process were suggested in the literature, for example, a model based on the dense packing of the reacting source molecules [4, 6] and a model that takes into account the size and number of ligands in the reacting molecules [7].

The first model considers the actual atomic layer deposition process as physical sorption of the reacting molecules to form a monolayer. But actually in the atomic layer deposition process the chemosorbed

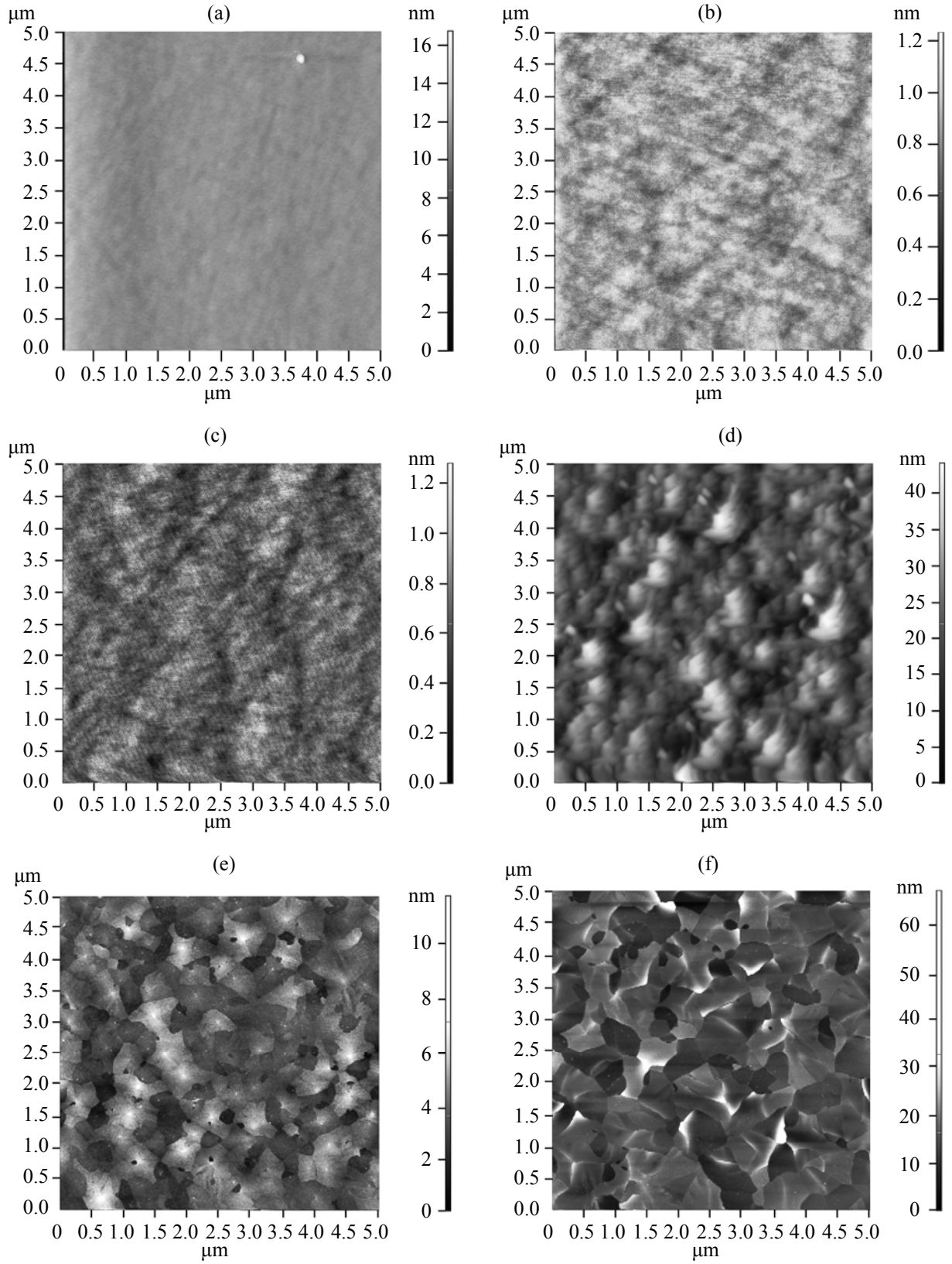

Fig. 4. Atomic force microscopy images of the initial silicon surface (a) before and after atomic layer deposition of TiO_2 films: (b) after 100 reaction cycles, (c) after 300 reaction cycles, (d) after 400 reaction cycles, (e) after 500 reaction cycles, (f) after 1000 reaction cycles.

molecules differ from the parent reacting molecules, and therefore this model can at best give only a rough estimate of the growth per cycle constant. Indeed, a calculation carried out with the first model [4] for the atomic layer deposition with the system $Ti(OC_2H_5)_2$–H_2O gave a value of Δh almost twice higher than the experimentally observed.

The second model takes into account such basic mechanisms of chemisorption as a ligand exchange reaction between $Ti(OC_2H_5)_2$ and surface OH groups and the dissociation and association of $Ti(OC_2H_5)_2$, in view of the law of mass conservation, and it leads to the following expression [7]:

$$\Delta h = (M/\rho N_A m)\,(\varphi \Delta C_L^{maxthr} + fC_A), \quad (1)$$

where M is the molar mass of substance (g mol^{-1}); ρ is the density of the substance (g nm^{-3}); N_A is Avogadro's number (1 mol^{-1}); m is the number of ligands; φ is the actual percentage of coverage of the surface by ligands; ΔC_L^{maxthr} is theoretical maximum number of chemisorbed ligands (nm^{-2}); f is the fraction of reacted OH groups of the surface; C_A is the number of OH groups before the reaction (nm^{-2}).

For spherical ligands with a radius r_L, the theoretical maximum number of chemisorbed ligands ΔC_L^{maxthr} can be calculated under the assumption of their dense packing in the monolayer [7]:

$$\Delta C_L^{maxthr} = 1/(2\sqrt{3r_L^2}). \quad (2)$$

Taking into account the non-spherical shape of ethoxy group its effective size for estimation of C_L^{maxthr} was determined by subtracting the titanium covalent radius (0.13 nm) from the radius of the $Ti(OC_2H_5)_2$ molecule (0.39 nm) [4]; the value obtained is 0.26 nm.

According to [8], for the typical atomic layer deposition conditions are $\varphi = 0.7$, and $f = 1$. According to [9], for the substrate temperature ~250°C the value of C_A is ~2.9 nm^{-2}. Based on the above, the calculation with Eq. (1) gives the Δh value 0.05 nm per cycle for the atomic layer deposition conditions used in this work. Thus, the calculated value of Δh 0.05 nm per cycle differs from the experimentally observed (0.045 nm/cycle) by about 10%, which is comparable with the error of experimental measurements of the thickness of the grown layer.

Thus, in this work we investigated involving various techniques both chemical composition and structure of the titanium dioxide thin films obtained from $Ti(OC_2H_5)_2$ and H_2O. It is shown that the method of atomic layer deposition with the use $Ti(OC_2H_5)_2$ and H_2O as reagents allows to obtain titanium dioxide films homogeneous across the film thickness and with high stoichiometry of the composition.

By the methods of X-ray diffraction and Fourier transform infrared spectroscopy it is shown that the structure of the TiO_2 films obtained by atomic layer deposition for the system of reagents $Ti(OC_2H_5)_2$ and H_2O depends on the number of reaction cycles n, and varies from amorphous at $n < 400$ to polycrystalline anatase at $n > 400$.

The calculation of the gain in titanium dioxide layer thickness in one reaction cycle Δh demonstrated the correctness of application the model of atomic layer deposition accounting for the number and size of the ligands of reacting molecules in the $Ti(OC_2H_5)_4$ and H_2O system of reagents.

EXPERIMENTAL

For obtaining the titanium dioxide thin films we used a vertical type atomic layer deposition reactor operating in the mode of pumping nitrogen at a pressure of ~100 Pa. Due to the low vapor pressure of tetraethoxytitanium, it was fed to the reactor from a heated source at 150°C. The pulse duration of feeding $Ti(OC_2H_5)_4$ and H_2O was 0.1 and 0.2 s, respectively. The time of purging with nitrogen was 4 s after each pulse of feeding by the reagents. The number of cycles n varied between 100 and 3600. As the substrates were used silicon wafer (100) and polycrystalline titanium. For minimizing the effects of thermal decomposition of $Ti(OC_2H_5)_4$ the substrate temperature was 250°C.

The thickness and refractive index of the films obtained was studied by ellipsometry. The wavelength of the probe laser beam was 0.63 μm.

The elemental composition of the obtained titanium oxide films was studied by Rutherford backscattering of He^+ ions. The energy of the beam of ions He^+ was 2 MeV, scattering angle was 160°, the inclination of the beam was normal to the surface.

The chemical composition of the films was investigated by X-ray photoelectron spectroscopy. The energy of the probing X-ray was 1253.6 eV. X-ray photoelectron spectra were recorded at the angle of the photoelectrons collection 0° to the surface normal.

The crystal structure of titanium oxide films was investigated by X-ray diffraction. The measurements

were performed on a universal X-ray diffractometer Rigaku Ultima IV in the geometry of the parallel beam reflection. X-ray source was fixed in the position at a small angle relative to the substrate, Θ = 6°. The measurements were carried out with the scans at the varied detector angle.

The structure of titanium oxide films was also studied by the method of IR Fourier spectroscopy using a Perkin-Elmer Spectrum 100 IR Fourier spectrometer. The spectra were recorded in the range of wave numbers (ν) 7800–380 cm^{-1}. The spectral resolution was 4 cm^{-1}. The measurements were performed in the transmission geometry (for silicon substrates) and the reflection geometry (for titanium substrates). At the measurements was used a software option that compensates the IR absorption bands of water vapor and carbon dioxide in air.

The atomic force microscopy measurements were performed in tapping mode, on a Solver Pro-M atomic-force microscope of NT-MDT company. The maximum scan area was 11.5×11.5 μm.

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